

$$\log K'_{\text{FeNN}_3} = -1.04 \log(\text{salinity}) + 30.12 \quad (10)$$

Here, a value for salinity of 2.9 was used (equivalent to 50mM NaCl which was added to the sample, see above). Salinity derived from the original sample was negligible against the salinity derived from added NaCl because the salinity of the original sample was 0.16 practical salinity units (psu) and in addition to that, the sample was diluted ten times. Equation 10 was obtained for seawater at pH 6.9 but can be applied to cases at pH 8.1, such as in our experiment, because the conditional stability constant of $\text{Fe}(\text{NN})_3$ for seawater at pH 8.1 is the same as for seawater at pH 6.9 (van den Berg 1995).

The free metal ion concentration $[\text{Fe}^{3+}]$ originally present in the sample was calculated from the following equation (Boye et al. 2001):

$$[\text{Fe}^{3+}]^2 \alpha'_{\text{Fe}} K'_{\text{FeL}} + [\text{Fe}^{3+}] (\alpha'_{\text{Fe}} + K'_{\text{FeL}} C_L - K'_{\text{FeL}} C_{\text{Fe}}) - C_{\text{Fe}} = 0 \quad (11)$$

The concentration of inorganic iron $[\text{Fe}']$ originally present in the sample was calculated from $[\text{Fe}'] = \alpha'_{\text{Fe}} [\text{Fe}^{3+}]$, and $p\text{Fe}'$ is defined as $-\log[\text{Fe}']$. The fraction of iron occurring as organic species was calculated as $\{(C_{\text{Fe}} - [\text{Fe}'])/C_{\text{Fe}}\} \times 100$.

Results and discussion

Method development

A standard addition voltammetric scan showed that the iron peak appeared at -0.5V and that the peak heights increased linearly with increasing iron concentration until at least 40nM (Fig. 1). The increase in the peak height became nonlinear and flattened out at iron concentrations higher than 40nM because of saturation of the mercury drop electrode. Therefore, most of the freshwater samples needed to be diluted prior to analysis.

We used the differential pulse stripping mode for voltammetric scans and 50mM of NaCl as electrolyte. Square-wave voltammetry is often used for trace metal analysis in seawater but is prone to contamination because this scan mode requires high concentrations of electrolyte. For this reason, square-wave voltammetry is suitable for seawater samples but not for freshwater samples.

We determined the optimum conditions of sample pre-treatment for analysis of total dissolved iron. We examined the efficiency of our irradiation system for the UV digestion of typical lake water acidified to pH 2.5 with HCl. Figure 2 shows the effect of UV irradiation time on dissolved organic carbon (DOC) and absorbance at 260nm of water from Lake Kasumigaura. The DOC decreased more slowly than the absorbance with irradiation time, and the organic compounds were completely digested within 60min [Yokoi et al. (1999) reported that, with our irradiation system, all tested compounds having complexing ability or surface activity were 80% decomposed within 25min]. An irradiation

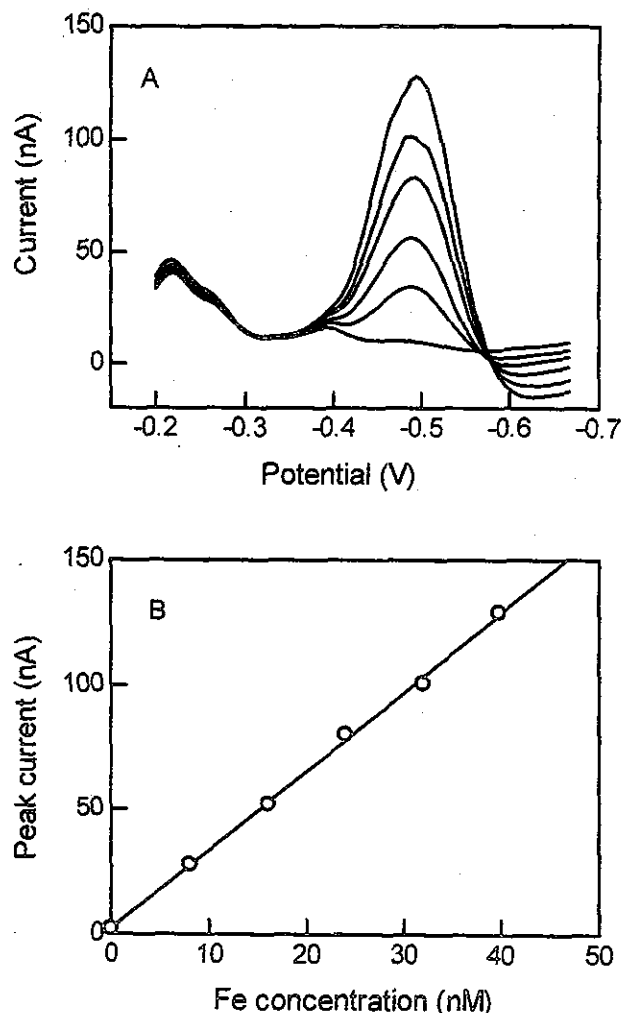


Fig. 1. Cathodic stripping voltammetry scans for 0, 8.5, 16.9, 25.3, 33.7, and 42.0nM iron in Milli-Q water (A) and peak heights as a function of iron concentration (B)

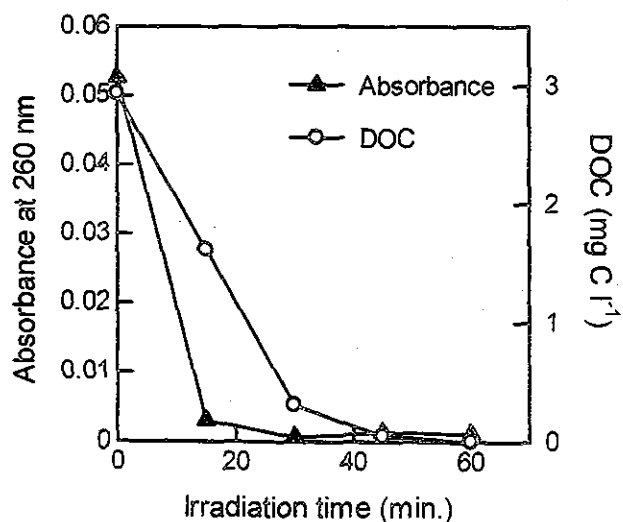


Fig. 2. Effect of ultraviolet (UV) irradiation time on absorbance at 260nm and dissolved organic carbon (DOC) levels. Absorbance was measured with a Shimadzu UV-2500 UV/VIS spectrometer (Kyoto, Japan) and DOC was measured with a Shimadzu TOC 5000 total organic carbon analyzer

time of 60 min was used for all analyses. Samples were acidified to pH 2.5 with HCl before UV irradiation to prevent iron precipitation. HCl rather than HNO₃ was used for acidification because, during UV irradiation, nitrate ions are reduced to nitrite ions, which greatly interfere with the voltammetric scan. When samples were acidified to pH < 2.5, more time was needed for complete UV digestion because chloride ions derived from HCl decreased the digestion efficiency significantly (data not shown). Therefore we concluded that the optimum pH for UV digestion was 2.5, which minimizes the risk of precipitation and sample evaporation.

In the speciation experiment, the problem of measurement instability caused by interfering organic compounds was overcome by using a high NN concentration (50 μM), dilution of the samples, and a well-conditioned voltammetric cell. Although seawater has been successfully analyzed by using NN concentrations of 2–13.6 μM, our attempts to analyze lake water using such NN concentrations were not successful. Surface active materials reduce the available surface area of the electrode and therefore reduce the linear range of the CSV response for iron. However, the linear range was extended by using a high NN concentration. Wu and Luther (1995) also reported a nonlinear signal response for iron concentrations greater than 4 nM when using NN at concentrations less than 6.8 μM. Dilution of the samples prevents saturation of the iron peak and reduces the concentration of dissolved organic matter. Conditioning the voltammetric cell improves the stability of the iron peak (van den Berg 1995; Wu and Luther 1995).

Total dissolved iron

We estimated the detection limit of our voltammetric method from experiments using blank solutions. MQ was filtered through a 0.2-μm Nuclepore filter and then stored in a high-density polyethylene bottle after acidification to pH 2.5. The iron concentration was determined five times after UV irradiation. A detection limit of 1.8 nM was found (3 × the standard deviation of the measurement).

We verified the accuracy of our method by analyzing two standard river waters for which the iron concentration was certified (123.5 ± 9.0 nM for JAC 0031 and 1020.6 ± 35.8 nM for JAC 0032; standard samples obtained from The Japan Society for Analytical Chemistry). The iron concentration range between the two standards is in the normal range for freshwater, but the standards are not appropriate for our CSV method because they are acidified to pH < 1.2 with nitric acid. To reduce the effect of nitrite ion produced from nitrate ions, we diluted the standards with MQ 20 times (for JAC 0031) and 50 times (for JAC 0032). The analytical parameters were the same as those for lake water samples, except that potassium bromate was added (final concentration 20 mM) to the JAC 0031 standard to increase sensitivity. The iron concentrations determined for JAC 0031 and JAC 0032 were 118 ± 5 nM (*n* = 4) and 1037 ± 56 nM (*n* = 5), respectively. These values are not significantly different from the certified values (verified by *t* test,

$\alpha = 0.05$). These results show the validity of our method for determining the total dissolved iron in freshwater.

The iron concentration in the water samples from Lake Kasumigaura was determined to be 47.8 ± 4.4 nM (*n* = 3). This level of iron is difficult to determine accurately by either graphite furnace atomic absorption spectrometry or inductively coupled plasma (ICP) emission spectrometry without preconcentration. We tried to determine the total dissolved iron concentration in the samples from Lake Kasumigaura by these spectrometric methods, but the iron concentration was too low. We also tried to determine the iron concentration by ICP mass spectrometry, but iron could not be detected because of interference from other elements. Therefore, our CSV method should be quite useful for the determination of total dissolved iron in lake water.

Iron speciation

Iron titrations were carried out for a filtrate sample and a UV-digested sample (UV irradiated for 60 min at natural pH). For the filtrate sample, the CSV peak height was suppressed at low iron concentrations, indicating the presence of excess iron complexing ligands (Fig. 3A). A linear relationship between the peak height and the iron concentration was obtained for the UV-digested sample, indicating that the complexing ligands had been successfully destroyed by UV irradiation and that they were organic in nature. Moreover, the slopes of the two titration curves at high iron concentrations were identical, indicating that all natural ligands were saturated with the added iron at high iron concentrations and that the titration range we used was appropriate. The effect of surface-active materials appeared to be small.

The ligand concentration and conditional stability constants for the lake water samples were determined from linear plots of [Fe labile]/[FeL] versus [Fe labile] (Fig. 3B). The ligand concentration was 80.0 ± 19.6 nM and the conditional stability constant was 10^{25.9±0.4} M⁻¹ (*n* = 3). A pFe' value of 13.4 was calculated, and the fraction of iron occurring as organic species was greater than 99.9%. These results indicate that virtually all dissolved iron in Lake Kasumigaura exists as organic complexes due to the very high conditional stability constants of the organic ligands in the lake water.

It should be noted that the pFe' value (13.4) is only valid at pH 8.1. The pH of seawater is nearly constant at 8, whereas the pH in Lake Kasumigaura varies between 7 and 10 (Center for Global Environmental Research 2001). α'_{Fe} and K'_{FeL} are functions of pH, and thus pFe' values should be greatly affected by pH. We did not evaluate changes in the K'_{FeL} value as a function of pH. Moreover, we did not determine the redox speciation of iron in this study. We calculated the iron speciation on the assumption that all iron in the sample exists as iron(III), because iron(II) is immediately oxidized to iron(III) in oxic water. However, there are a few studies reporting the existence of iron(II) in lake water despite the presence of oxygen (Aldrich et al. 2001; Sivan et al. 1998). This may be a result of photochemi-

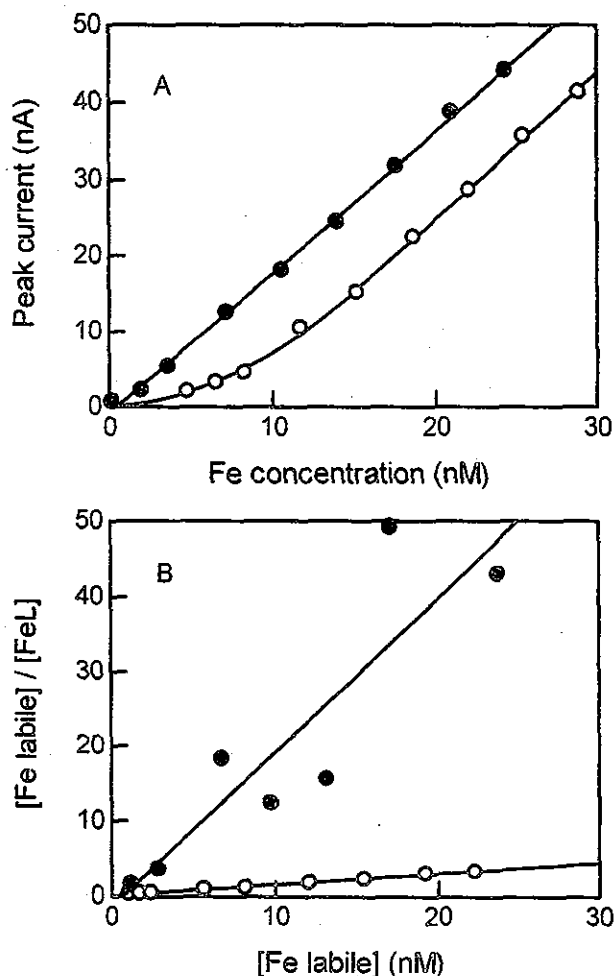


Fig. 3. Iron titrations of filtrate sample (O) and UV-digested sample (●) from Lake Kasumigaura: A, titration curves; B, linear plots. The UV digestion was performed without adjustment of pH to compare the two titration curves. As a result, iron was precipitated and lost in the UV-digested sample

cal reduction and biological activity (Emmenegger et al. 2001; Shaked et al. 2002). There is some possibility of changing the bioavailability of iron as a result of the production of iron(II). In this study, if iron(II) exists, the total iron concentration could contain both iron(III) and iron(II) species. In the iron speciation experiments, any iron(II) species in the samples could be oxidized to iron(III) during the equilibration period (van den Berg 1995).

In our analytical technique, it is important that appropriate ligand competition between natural ligands and NN occur: no iron is detected if the complexes with the natural ligands are much more stable than the complex with NN, whereas no complexation is detected if the complexes with natural ligands are much less stable (van den Berg 1995; Wu and Luther 1995). The degree of ligand competition could be estimated by comparing the α -coefficient values α'_{FeNN} and α'_{FeL} (calculated from $K'_{\text{FeNN}}[\text{NN}]^3$ and $K'_{\text{FeL}}C_L$, respectively). The values were $10^{16.7}$ and $10^{17.8}$ (in the sample diluted ten times), respectively, indicating that the natural complexes were more stable than the complex with NN under the conditions of this study. Gledhill and van den Berg (1994) mentioned that the detection window is one order of magni-

tude either side of α'_{FeNN} ($10^{15.7}$ – $10^{17.7}$ under our conditions) and that high values of α'_{FeL} that are outside the detection window result in a great error in the determination of $\log K'_{\text{FeL}}$ (± 2). The α'_{FeL} value we obtained ($10^{17.8}$) was slightly outside the detection window, indicating that a higher NN concentration should have been used from the viewpoint of the detection window. Nevertheless, we used an NN concentration of $50 \mu\text{M}$ in our study because we did not obtain a great error in the value of $\log K'_{\text{FeL}}$ (± 0.4), and using a higher concentration of NN carries a risk of iron contamination.

According to van den Berg and Donat (1992), several complexing ligands or sites can be detected by several detection windows. Using modeled CSV responses of a hypothetical seawater containing four iron complexing ligands, van den Berg (1995) suggested that a single titration experiment is insufficient to resolve the presence of several complexing ligands. In contrast, Rue and Bruland (1995) suggested that two ligands could be resolved from a single set of titration data by using the Scatchard transformation method to obtain C_L and K'_{FeL} . The Scatchard transformation method involves plotting the ratio $[\text{FeL}]/[\text{Fe labile}]$ against $[\text{FeL}]$. For a single class of iron complexing ligands, the y-axis intercept of the resulting linear plot equals $K'_{\text{FeL}}C_L$ and the x-axis intercept equals C_L . If two classes of iron complexing ligands (a strong ligand and a weak ligand) exist, the linearized plots should yield a nonlinear curve. For such a case, Rue and Bruland (1995) suggested that two linear regions should be easy to separate using the Scatchard transformation rather than the Langmuir transformation. Langmuir and Scatchard plots of our titration data are compared in Fig. 4. Only one linear region was evident in the both plots. The total C_L and K'_{FeL} (single class of ligand) values were calculated from the linear plots. The Langmuir transformation gave a C_L value of $80.0 \pm 19.6 \text{ nM}$ and a K'_{FeL} value of $10^{25.9 \pm 0.4} \text{ M}^{-1}$, whereas the Scatchard transformation gave a C_L value of $84.9 \pm 18.9 \text{ nM}$ and a K'_{FeL} value of $10^{25.6 \pm 0.2} \text{ M}^{-1}$. Although the values of C_L and K'_{FeL} obtained from the Langmuir and Scatchard plots were not significantly different, the correlation coefficient for the Scatchard plot (average value 0.921) was lower than that for the Langmuir plot (average value 0.997). Therefore, we believe that the Langmuir transformation is more appropriate for the determination of total ligand concentration.

Field study

It is surprising that the value of the conditional stability constant for iron ligands (K'_{FeL}) in water from Lake Kasumigaura determined in this study was greater than any reported K'_{FeL} value for seawater (Table 1). These very strong ligands could be detected because a high NN concentration (equivalent to a high detection window) was used. Rue and Bruland (1997) and Boye et al. (2001) suggested that strong iron ligands ($\log K'_{\text{FeL}} = 22$ – 23 M^{-1}) in seawater might be siderophores. Imai et al. (1999) calculated a conditional stability constant of greater than 10^{25} M^{-1} for Fe^{3+} complexed with fulvic acid isolated from Lake Kasumigaura. It can therefore be hypothesized that the iron ligands in Lake Kasumigaura are fulvic acid. Imai et al.

Table 1. Conditional stability constants (K'_{FeL}) of iron ligands and inorganic iron levels as determined by cathodic stripping voltammetry

Area	$\log K'_{FeL} (M^{-1})$	pFe' ^a	Reference
Lake Kasumigaura	25.9	13.4	This study
North Atlantic	18.8–19.7	10.6–12.0	Gledhill and van den Berg (1994)
Western Mediterranean	19.4–22.5	11.3–12.1	van den Berg (1995)
Northern North Sea	20.7–21.7	9.3–13.9	Gledhill et al. (1998)
Southern Ocean	21.0–23.0	11.5–13.2	Boye et al. (2001)
North Pacific	23.1	13.1–14	Rue and Bruland (1995)
Equatorial Pacific	22.7	14	Rue and Bruland (1997)

^apFe' = $-\log[Fe']$, where [Fe'] is the concentration of inorganic iron

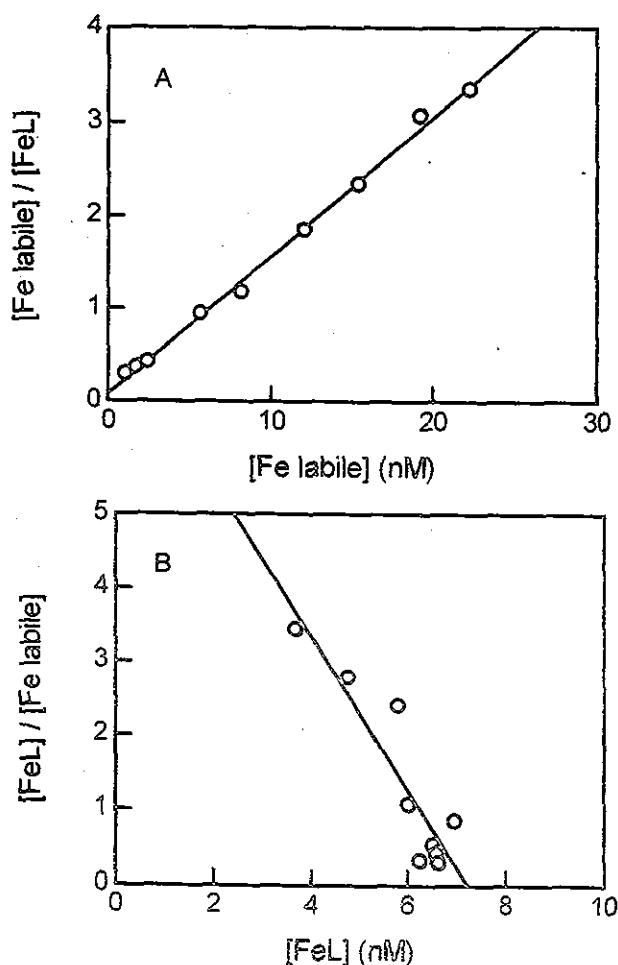


Fig. 4. Comparison of Langmuir transformation (A) and Scatchard transformation (B) when calculating ligand concentrations and conditional stability constants

(1999) also reported that the average concentration of fulvic acid in Lake Kasumigaura was $2.5 \mu M$, which is about 30 times higher than the ligand concentration we measured (80 nM). However, fulvic acid is a nonspecific ligand, and thus if the iron ligand we detected is fulvic acid, the ligand concentration could be underestimated because of competitive interference from other trace metals or major divalent cations (Ca^{2+} and Mg^{2+}).

Whereas the stability constants of bivalent metal (such as copper) cation–fulvic acid complexes are well studied (e.g., Mantoura et al. 1978), there are only a few studies on stabil-

ity constants of iron–fulvic acids complexes. Langford and Khan (1975) reported that conditional stability constants of iron–fulvic acid complexes were $10^{4.2}$ – $10^{4.4}$ at pH 1.0–2.5. Pandeya also determined stability constants of iron–fulvic acid complexes using ligand exchange (Pandeya 1993), spectrophotometry (Pandeya and Singh 1997), and potentiometry (Pandeya and Singh 2000) and the values found were $10^{12.0}$ – $10^{13.3}$, $10^{6.0}$ – $10^{6.9}$, and $10^{5.6}$ – $10^{7.6}$, respectively. However, they used fulvic acids extracted from soil, sludge, and manure. There are significant differences in physicochemical characteristics among fulvic acids of different origin. Therefore, these results cannot be simply compared with our result. Investigation of the interaction of iron with extracted fulvic acids using our CSV method is a subject for further study.

Comparison of the pFe' values (representative of inorganic iron) in Table 1 reveals that the pFe' value for Lake Kasumigaura water is similar to that found in the open ocean. Because the concentration of total dissolved iron in the open ocean is subnanomolar, the concentration in Lake Kasumigaura is 10–100 times higher. However, the bioavailability of iron in Lake Kasumigaura is very low, and thus the iron competition between phytoplankton that takes place in the open ocean may have occurred in the lake. Imai et al. (1999) reported the effect of iron limitation on the growth of *M. aeruginosa* in defined growth media. According to that study, *M. aeruginosa* could grow at a pFe' of higher than 12.9 but not at a pFe' of 13.9. Therefore, the pFe' value we obtained (13.4) was borderline for the growth of *M. aeruginosa*. Consequently, our result supports the hypothesis that the shift of the dominant species of phytoplankton in Lake Kasumigaura from *Microcystis* to *Oscillatoria* was caused by iron limitation.

Conclusion

We have presented a methodology for determining dissolved iron, its organic complexation, and its bioavailability in freshwater. We applied this method to lake water containing a large amount of interfering organic compounds and successfully determined the concentration of total dissolved iron and iron(III)–organic ligand complexation. We found that the level of inorganic iron in Lake Kasumigaura was similar to that in the open ocean. It is therefore possible that iron is a dominant selective factor in algal species suc-

cession and diversity in Lake Kasumigaura. We are currently using the methodology developed in this preliminary study to analyze additional freshwater samples and are investigating the following: (1) temporal and spatial changes of iron speciation in Lake Kasumigaura; (2) the effect of iron speciation on cyanobacterial blooms in a eutrophic lake; and (3) characterization of the iron ligand (i.e., fulvic acid or not).

Acknowledgment Sampling was supported by the GEMS/Water Monitoring Project at Lake Kasumigaura. We thank the members of the project for their cooperation.

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CHARACTERIZATION OF DISSOLVED ORGANIC MATTER IN SHALLOW EUTROPHIC LAKE KASUMIGAURA

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SUMMARY – Dissolved organic matter (DOM) in water samples from the shallow eutrophic Lake Kasumigaura, the second largest lake in Japan, and its inflowing rivers was fractionated and characterized by using resin adsorbents into 5 classes: aquatic humic substances (AHS), hydrophobic neutrals (HoN), hydrophilic acids (HiA), bases (BaS) and hydrophilic neutrals (HiN). DOM-fraction distribution patterns were significantly different depending on the origin of the sample. AHS and HiA were found to be the dominant fractions in DOM in all samples studied. HiA prevailed over AHS in the lake water, whereas AHS were slightly more abundant than HiA in the river waters. AHS were in the great majority in forest streams and plowed-field percolates. HiA abounded in paddy-field outflow, domestic sewage, and sewage-treatment-plant effluent. Only domestic sewage contained a significant amount of HoN.

Furthermore, the trihalomethane formation potential (THMFP) and molecular size distribution of the lake-water DOM, AHS and hydrophilic fractions (HiF = HiA + BaS + HiN) were examined. The THMFP of HiF, normalized on a DOC basis, was found to be comparable to that of AHS (0.176 vs. 0.195 $\mu\text{mol THM mg}\cdot\text{C}^{-1}$, respectively). Molecular size distributions all exhibited a narrow size range and relatively low molecular weights. The weight-averaged molecular weights of DOM, AHS and HiF were 780, 957 and 606 $\text{g}\cdot\text{mol}^{-1}$, respectively.

1. INTRODUCTION

A steady increase in dissolved organic matter (DOM) has been observed in several lakes in Japan, even though extensive measures have been implemented to reduce organic pollutant loadings from their catchment areas. For instance, in Lake Biwa, the largest lake in Japan, the chemical oxygen demand (COD), an index for total organic matter, has been gradually increasing in the surface water since 1984. On the other hand, the biochemical oxygen demand (BOD), a parameter for easily biodegradable organic matter, has remained virtually constant. Since the concentration of chlorophyll-*a* does not exhibit any pattern of increase, phytoplankton activity is unlikely to relate directly to the COD increase. The dissolved fraction accounted for most of the COD. It is likely that some recalcitrant DOM has been accumulating in the water of Lake Biwa. This phenomenon is apparently new and has not been given any previous consideration.

The accumulation of recalcitrant DOM in lake water certainly influences the way in which lake environmental protection should be managed, because DOM is regarded as a source of organic pollution and, further, as an energy source for microbe-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 increase in DOM also presents a serious challenge for drinking-water management because recalcitrant DOM can be a major precursor to carcinogenic trihalomethanes produced during chlorination in water treatment plants. Therefore, evaluation of the characteristics

of DOM in lake water is urgently needed.

Nevertheless, DOM in natural waters is a heterogeneous mixture of organic compounds, and its physico-chemical characteristics are not clearly understood. In such a situation, the rational first step toward that understanding should be the evaluation of the characteristics of DOM in waters. An appropriate approach to this end is to separate DOM into well-defined macro-fractions and to examine their distribution and physico-chemical characteristics.

Aquatic humic substances (AHS), which are typical naturally occurring recalcitrant DOM, constitute 30% to 80% of DOM as dissolved organic carbon (DOC), and they constitute the largest fraction of natural organic matter in waters (Thurman, 1985). They are straw-colored, polar, hydrophobic organic acids derived from soil humus, terrestrial and aquatic plants, and plankton. For our purpose of evaluating the characteristics of DOM in waters, DOM fractionation methods based on the separation of AHS, namely, hydrophobic - hydrophilic and acidic-basic breaks, appear reasonable.

In this study, modifying the DOM fractionation method developed by Leenheer (1981) and Imai et al. (1998), we fractionated DOM 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 were to (1) apply the DOM fractionation method to the waters of shallow eutrophic Lake Kasumigaura and its inflowing

ivers as well as to several DOM sources in its watershed, such as sewage-treatment-plant effluent, and so on, and to evaluate their DOM-fraction distributions, and (2) to determine the comparative significance of AHS and hydrophilic fractions of the lake-water DOM as trihalomethane precursors by measuring their trihalomethane formation potential (THMFP) and then to examine the relationships between their THMFP and physico-chemical characteristics.

2. METHODS AND MATERIALS

2.1 Collection of water samples

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 (Fig. 1). More than 900,000 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% other. The lake basin 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 its extremely high loads of organic matter and nutrients, this lake is well known for eutrophication.

The Koise and Sakura rivers are the main rivers influent to Takahamairi and Tsuchiurairi, respectively. Water flows through the lake largely from the northwest parts of Takahamairi and Tsuchiurairi southeast to the Hitachitone River. The average time needed for water to flow through the two bays to the center of lake may be around three months. In addition, Lake Kasumigaura is so shallow that vertical stratification is easily destroyed by a moderately strong wind.

Water samples were collected in a 1-liter glass bottle with a 2-m column sampler from the center of the lake monthly from May 1994 to February 1996. Samples for the determination of trihalomethane formation potential and molecular size distribution were collected from January 1997 to December 1997. The samples were immediately cooled in an ice cooler and brought back to our 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 filtrate was usually kept at 3 °C in a precombusted glass bottle until analysis.

Four large rivers, arranged in order of drainage-area size, were chosen for this study: the Koise, Sakura, Hanamuro, and Ono rivers. River-water samples were obtained in May, August, and November 1994 and in February 1995 at downstream stations on these four influent rivers (Fig. 1). Distinctive DOM sources chosen in the watershed were domestic sewage

(DS), sewage treatment plant effluent (STPE), paddy-field inflow (PFI) and outflow (PFO), plowed-field percolate (PFP) and upland-forest stream (FS) (Fig. 1). PFI and PFO samples were collected only in May and August. Otherwise, samples were collected in May, August, and November 1995, and in February 1996. The samples of river water and other DOM sources were collected in HCl-washed polycarbonate containers and treated in the same manner as the lake-water samples.

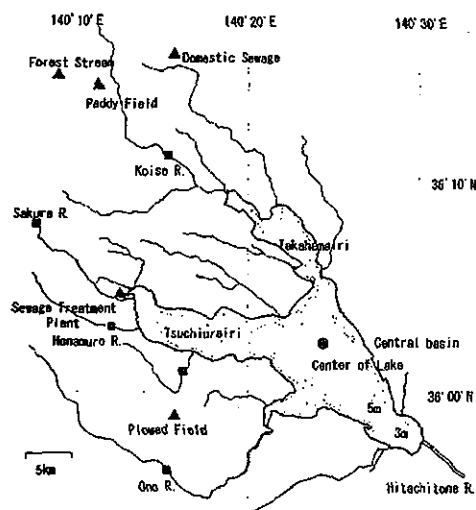


Fig.1. Sampling sites in Lake Kasumigaura, its inflowing rivers and other DOM sources in the lake catchment area.

2.2 DOM fractionation

Sample filtrates were fractionated into 5 fractions: aquatic humic substances (AHS), hydrophobic neutrals (HoN), hydrophilic acids (HiA), bases (BaS), and hydrophilic neutrals (HiN), based on their adsorption on a series of macroporous resin adsorbents. Nonionic Amberlite XAD-8 resin (20–60 mesh, Sigma Chemical Co., St. Louis, USA), strong cation-exchange resin (Bio-Rad AG-MP-50, 50–100 mesh, Nippon Bio-Rad Lab. KK, Tokyo, Japan), and strong anion-exchange resin (Bio-Rad AG-MP-1, 50–100 mesh) were used.

The XAD-resin was cleaned and conditioned as described by Thurman and Malcolm (1981). Three milliliters (wet volume) of the XAD-8 resin was packed into a glass column and rinsed 3 times, alternating 0.1 M NaOH with 0.1 M HCl each time, just before application of the sample. A blank sample was collected from the final rinse with 0.1 M HCl (B1). Both the AG-MP-50 (hydrogen form) and AG-MP-1 (chloride form) were Soxhlet-extracted with methanol for 24 h. AG-MP-1 was then converted into its free-base form with 1 M NaOH and rinsed with Milli-Q water (Milli-Q SP.TOC, Nihon Millipore Ltd.,

Tokyo, Japan). 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 through the resins. Blank samples were collected from each column after pumping 1–2 bed volumes of 0.01 M HCl solution just before and after application of the samples.

A flow schematic of the DOM fractionation procedure is shown in Fig. 2. Details of the DOM fractionation procedure can be found elsewhere (Imai et al., 2001). DOM fractionation was done in duplicate for each sample. After fractionation, dissolved organic carbon (DOC) was measured for DOM fractions 1 to 5 and for the blank samples. Each DOM fraction was calculated as follows:

$$\begin{aligned} \text{AHS} &= \text{DOM2} \times (\text{elutant volume}) / (\text{sample volume}) & (1) \\ \text{HoN} &= \text{DOM1} - \text{AHS} - (\text{DOM3} - \text{B1}) & (2) \\ \text{BaS} &= (\text{DOM3} - \text{B1}) - (\text{DOM4} - \text{B2}) & (3) \\ \text{HiA} &= (\text{DOM4} - \text{B2}) - (\text{DOM5} - \text{B3}) & (4) \\ \text{HiN} &= \text{DOC5} - \text{B3} & (5) \end{aligned}$$

The blank DOC from the XAD-8 column during 0.1 M NaOH elution contained less than 0.7 mg·C l⁻¹; its contribution to AHS would have been no more than 0.03 mg C·l⁻¹. Thus, the blank DOC contribution to AHS was neglected. The relative errors of the duplicated measurements for AHS, HoN, HiA, BaS, and HiN in the DOM fractionation were 4–8%, 20–53%, 4–35%, 20–48%, and 22–38%, respectively.

DOC measurements were conducted as non-purgeable DOC with a Shimadzu TOC-5000 total-organic-carbon analyzer (Shimadzu Co., Kyoto, Japan). At least 3 measurements were made for each sample, and analytical precision was typically less than ± 2%. Potassium hydrogen phthalate was used a standard.

2.3 Trihalomethane formation potential

Sample filtrates, AHS and the hydrophilic fractions (HiF, equivalent to DOM3 in Fig. 2) were diluted with Milli-Q water to produce a DOC concentration of 1 mg·C·l⁻¹ before chlorination. Freeze-dried AHS samples were reconstructed in Milli-Q water. The HiF samples, the pH of which remained at 2 after the DOM fractionation, were adjusted to about pH 7 with NaOH.

Trihalomethane formation potential (THMFP) was measured according to the Standard Methods for the Examination of Drinking Water (JWSA 1993). Samples were adjusted to pH 7 with phosphate buffer. Double-distilled sodium hypochlorite solution was added at a dose that produced a free chlorine concentration of 1 to 2

mg·l⁻¹ as Cl₂ after a reaction time of 24 h at 20 °C. Reactions were performed in headspace-free containers and in the absence of light. Following the 24-h reaction period, free chlorine concentrations were determined by the *o*-trizine method. Excess chlorine was quenched with anhydrous sodium sulfite, and then concentrations of trihalomethanes were determined by the headspace method using gas-chromatography/mass-spectrometry equipped with a headspace autosampler. Analytical precision was typically less than ± 2%.

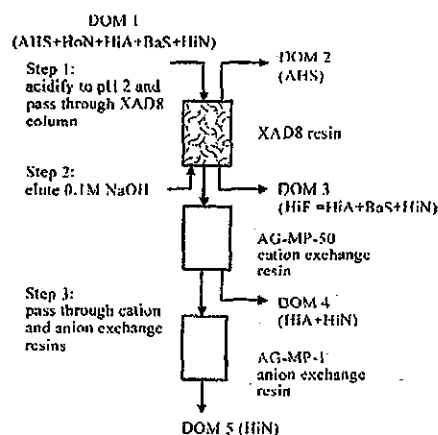


Fig. 2. Schematic diagram of the procedure for DOM fractionation. DOM fractions are AHS, aquatic humic substances; HoN, hydrophobic neutrals; HiA, hydrophilic acids; BaS, bases; HiN, hydrophilic neutrals.

2.4 Molecular size determination

High-pressure size exclusion chromatography (HPSEC) was performed at room temperature with a Hitachi L-6200 pump (Hitachi Ltd., Tokyo, Japan), a Hitachi L-4000 UV detector operating at 260 nm, a Hitachi D-2500 data integrator, and a Rheodyne rotary injection valve equipped with a 100- μ l sample loop. A Waters Protein-Pak 125 modified silica column (Waters Co., Milford, USA) was used for this study (Chin et al. 1994). Mobile phases were composed of Milli-Q water buffered with phosphate to a pH of 6.8 and sodium chloride to yield an ionic strength of 0.1 M. Molecular weight standards were composed of sodium polystyrene sulfonates (35, 18, 8, 5.4, and 1.8 K) and acetone. The calibration curves were semi-log linear over the range defined by our standards, showing an excellent correlation ($R^2 = 0.99$), and were used to determine both number- and weight-averaged molecular weights. Sample filtrates were adjusted to an ionic strength of 0.1 M with the appropriate addition of 4 M NaCl, and to a pH of 6.8 with additions of phosphate buffer and HCl. AHS samples were prepared by dissolving the freeze-dried samples into the mobile phase solution. HiF samples were adjusted to an ionic strength of 0.1 M and a pH of 6.8 with additions of phosphate buffer, NaOH and NaCl.

Typical precision for the determination of averaged molecular weights was $\pm 3\%$.

3. RESULTS AND DISCUSSION

3.1 DOM fractionation distribution of lake and river waters

DOC concentrations at the center of Lake Kasumigaura ranged from 2.97 to 4.80 $\text{mgC}\cdot\text{l}^{-1}$ and averaged 4.08 $\text{mgC}\cdot\text{l}^{-1}$ during the sampling period (Table 1). The lake-water DOC exhibited a tendency to increase from spring to fall and then to decline gradually. DOC concentrations in the four rivers were found to vary from 1.45 to 3.28 $\text{mgC}\cdot\text{l}^{-1}$ with an average value of 2.76 $\text{mgC}\cdot\text{l}^{-1}$. DOC concentrations in all rivers exhibited the greatest values in May, decreased in August, and reached their lowest in November and February. The highest riverine DOC concentrations observed in May are likely to result from massive usage of river water to fill paddy fields with water in preparation for transplanting young rice plants.

Table 1. Average concentrations of dissolved organic carbon (DOC) in Lake Kasumigaura, its inflowing rivers, and other DOM sources in the lake catchment area

Sample name	DOC [$\text{mgC}\cdot\text{l}^{-1}$]	N
Lake water	4.08 (0.49)*	22
River water	2.76 (0.57)	16
Forest stream (FS)	0.47 (0.07)	4
Paddy field inflow (PFI)	3.12	2
Paddy field outflow (PFO)	7.26	2
Plowed field percolate (PFP)	0.28 (0.07)	4
Domestic sewage (DS)	16.62 (5.53)	4
Sewage treatment plant effluent (STPE)	4.93 (0.85)	4

*Standard deviation.

In Lake Kasumigaura, AHS and HiA dominated, collectively accounting for more than 70% of the DOM as DOC (Fig. 3). Thus, the lake-water DOM is predominantly acidic. HiA was dominant over AHS, amounting to 43% of the DOM against AHS being 32%. The HoN fraction was around 9%, indicating that hydrocarbons, pesticides, carbonyl compounds, and linear alkylbenzene sulfonate (LAS) do not contribute significantly to DOM in the lake. The average percentage of BaS and HiN was 10% and 4% of total DOM, respectively. Protein-like and carbohydrate-like DOMs are unlikely to be present in significant quantities as their free forms in lake water.

The DOM-fraction distribution pattern in the river waters was significantly different from the pattern in the lake water (Fig. 3). As in the lake water, AHS and HiA dominated in riverine DOM, accounting for more than 70%. However, the percentage of AHS was only slightly greater, 39% vs. 37%. The HoN, BaS, and HiN fractions accounted for 9%, 11%, and 6%, respectively. Riverine DOM appears to be more hydrophobic than lake DOM. Two-sample *t*-tests comparing

the mean percentages of the DOM fractions revealed that only AHS and HiA were significantly different with respect to DOM-fraction distribution between the lake and river waters ($p < 0.0001$ for AHS, $p < 0.001$ for HiA). As far as DOM composition is concerned, the percentages of AHS and HiA were of importance in distinguishing between the DOM in Lake Kasumigaura and its inflowing rivers.

Thurman (1985) reported that AHS and HiA generally account for 40% and 41%, respectively, of DOM as DOC in lakes. He also states that AHS is the major component of DOM in rivers, accounting for about 50% of DOC, with HiA being about 25%. McKnight et al. (1994), studying lakes where DOM is mostly derived from phytoplankton, found that AHS accounts for 13% - 20% of DOM. These results suggest that (1) river waters are rich in AHS but poor in HiA, since most DOM in rivers is allochthonous and (2) lake waters contain more HiA compared with AHS since autochthonous DOM sources outweigh allochthonous ones in lakes. Our results for the waters of Lake Kasumigaura and its inflowing rivers are consistent with these reported findings. It appears, however, that in Lake Kasumigaura DOM is more likely to be algal derived than is typical, but its inflowing rivers may have less allochthonous or pedogenic DOM.

3.1 DOM-fraction distribution in DOM sources

DOM-fraction distributions in the other DOM sources also showed an interesting feature. AHS and HiA also dominated in all the other DOM sources as they did in the river and lake DOM (Fig. 3). Nevertheless, their distribution exhibited more widely different patterns, depending on the

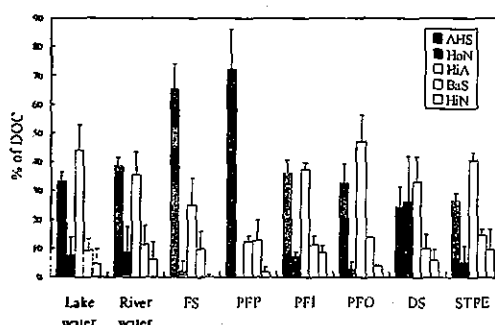


Fig. 3. DOM-fraction distributions of water samples from the center of Lake Kasumigaura, its inflowing rivers and other DOM sources in the lake catchment area. DOM fractions are AHS, aquatic humic substances; HoN, hydrophobic neutrals; HiA, hydrophilic acids; BaS, bases; HiN, hydrophilic neutrals. DOM sources are FS, forest stream; PFP, plowed-field percolate; PFI, paddy-field inflow; PFO, paddy-field outflow; DS, domestic sewage; STPE, sewage treatment plant effluent. Error bars represent ± 1 standard deviation of the mean except for PFI and PFO. Bars for PFI and PFO represent relative deviation from the mean.

origin of the sample. Compared with the lake and

river waters, FS and PFP were by far dominated by AHS, which accounted for more than 60% and 70% of DOM, respectively. Both FS and PFP have only allochthonous DOM; thus, such high percentages of AHS are understandable. The DOM-fraction distribution of PFI was similar to that of the river waters, as expected. PFO was very different from PFI and exhibited the greatest percentage of HiA among the samples. The muddy sediment in paddy fields is likely to diffuse DOM containing much more HiA than AHS.

The DOM-fraction distribution of DS was noticeably different from that of the lake water. DS, like the lake water, had a considerably greater proportion of HiA than of AHS; however, its HoN fraction was distinctively greater, accounting for 25% of the DOM. Since DS samples were foamy when they were collected, DS should contain a large amount of synthetic detergent such as LAS, which is categorized as a HoN.

STPE contained more HiA (45%) than AHS (27%), like the lake water. DOM in STPE is considered to be mostly of microbial origin and should be refractory to bacterial degradation since it is what remains after extensive biodegradation. This finding suggests that not only AHS but also HiA may accumulate as recalcitrant DOM when STPE is discharged into a lake either directly or indirectly.

3.2 Molecular size distribution

All HPSEC chromatograms of DOM, AHS and HiF showed broad, monomodal size distributions with subtle shoulders and small sub-peaks. Typical HPSEC chromatograms of DOM, AHS, and HiF are shown in Fig. 4. The weight-averaged to number-averaged molecular weight ratio (i.e., the analyte's polydispersity) was less than 2 in all cases, indicating that the DOM, AHS, and HiF molecules all occupy a relatively narrow size range and do not possess molecular weights that vary by orders of magnitude. The weight-averaged molecular weights of DOM were relatively low, having an average of $780 \text{ g}\cdot\text{mol}^{-1}$. AHS had a greater weight-averaged molecular weight than HiF, exhibiting an average value of $957 \text{ g}\cdot\text{mol}^{-1}$, compared with $606 \text{ g}\cdot\text{mol}^{-1}$ for HiF. AHS and HiF appeared to contribute mainly to the high- and low-molecular-weight fractions, respectively, of the DOM in Lake Kasumigaura. Seasonal variations in the weight-averaged molecular weights of DOM, AHS and HiF were not very pronounced, varying within $\pm 13\%$, $\pm 11\%$ and $\pm 24\%$ of the monthly average values of DOM, AHS and HiF, respectively.

The weight-averaged molecular weights of DOM, AHS and HiF in Lake Kasumigaura were found to be small, showing the average values of 780, 957

and $606 \text{ g}\cdot\text{mol}^{-1}$, respectively. Thurman et al. (1982) measured the molecular weight of AHS from various environments and concluded that an average molecular weight for humic substances from surface water was 1000 to $2000 \text{ g}\cdot\text{mol}^{-1}$. The molecular weights of AHS determined in this study were around the lowest end of that range. The molecular weight of HiF has not been reported before as far as we know; thus, the measured values cannot be compared with those in the literature. Nevertheless, it can be suggested that the molecular size of DOM belonging to HiF is very small.

3.3 Trihalomethane formation potential

When normalized on a DOC basis, the specific THMFP (STHMFP) of AHS in Lake Kasumigaura was found to be slightly greater than that of HiF. The average STHMFP of the AHS samples was $0.195 \mu\text{mol THM mg}\cdot\text{C}^{-1}$, while the average HiF STHMFP was comparable at $0.176 \mu\text{mol THM mg}\cdot\text{C}^{-1}$ (Fig. 5). The paired *t*-test on the comparison of STHMFP between AHS and HiF showed a significant difference at $P < 0.05$ ($n = 12$); however, when we excluded one pair of data observed in July, which showed the largest difference, the *t*-test did not give a significant result. The DOM samples exhibited STHMFP values somewhere between those of HiF and AHS ($0.188 \mu\text{mol THM mg}\cdot\text{C}^{-1}$).

The STHMFP of the non-humic fraction, namely HiF, was found to be comparable to that of AHS. This finding appears to be somewhat contrary to the conventional belief that AHS behave as the principal THM precursor material. Nevertheless, this result is consistent with those reported by Owen et al. (1995). They showed in studying THMFP of different waters from a reservoir, river and groundwater that the non-humic fraction reacted with chlorine and produced THM per unit DOC at an extent comparable to the humic fraction.

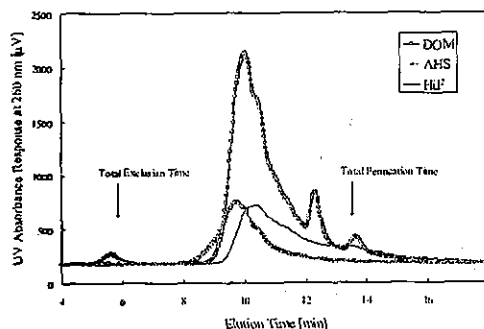


Fig. 4. Typical high-pressure size exclusion chromatograms of DOM, AHS and HiF in water from Lake Kasumigaura. The water sample was collected on September 10, 1997 at a point near the intake of a water treatment plant located on the shore of the lake.

The importance of HiF over AHS as THM

precursors becomes more pronounced when THM formation is evaluated in terms of concentration, that is, when THMFP is assessed in $\mu\text{mol}\cdot\text{l}^{-1}$. The THMFP of HiF is much greater than that of AHS: the average values for HiF and AHS are 0.374 and 0.229 $\mu\text{mol THM}\cdot\text{l}^{-1}$, respectively. This comparison reveals that HiF account for, on average, 57% of the THMFP of DOM, while AHS account for 35%. Therefore, we concluded that when waters from eutrophic lakes such as Lake Kasumigaura are used as sources of drinking water, lower-molecular-weight hydrophilic DOM, in particular HiA, should be of more concern as a THM precursor than AHS, from the viewpoint of water treatment practices.

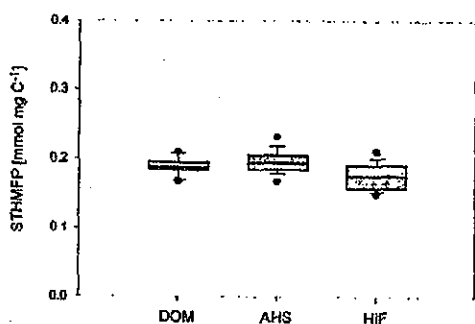


Fig. 5. Comparison of specific trihalomethane formation potential (STHMFP) between DOM, AHS and HiF in water samples taken from Lake Kasumigaura 1997. The lower boundary of each box indicates the 25th percentile, a line within the box marks the mean, and the upper boundary of the box indicates the 75th percentile. Whiskers indicate the 90th and 10th percentiles, and solid dots indicate outlying points. Abbreviations are explained in the text.

4. SUMMARY

DOM in water samples from Lake Kasumigaura, its inflowing rivers and several other DOM sources in the lake watershed was fractionated into five classes: AHS, HoN, HiA, BaS, and HiN. DOM-fraction distribution was found to be very useful parameters for evaluating the characteristics of DOM in waters.

DOM-fraction distribution patterns were significantly different depending on the origin of the sample. AHS and HiA were found dominantly in both the lake and the rivers. HiA prevailed over AHS in the lake water, while AHS was present in a slightly greater percentage in the river water. AHS and HiA were also dominant in all other DOM sources. AHS was the most abundant fraction in FS and PFP. HiA abounded in PFO, DS, and STPE. Only DS contained a significant amount of HoN, indicating the presence of LAS-like DOM.

The THMFP of HiF normalized on a DOC basis was found to be comparable to that of AHS

(0.176 vs. 0.195 $\mu\text{mol THM mg}\cdot\text{C}^{-1}$, respectively). When THMFP is evaluated in terms of concentration (i.e., $\mu\text{mol THM}\cdot\text{l}^{-1}$), the THMFP of HiF was by far greater than that of AHS (mean 0.374 vs. 0.229 $\mu\text{mol}\cdot\text{l}^{-1}$, respectively).

Molecular size distributions of lake-water DOM, AHS and HiF were found to exhibit a narrow size range and relatively low molecular weight. The weight-averaged molecular weights of DOM, AHS and HiF in the waters of Lake Kasumigaura were, on average, 780, 957, and 606 g mol^{-1} , respectively.

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5. ACKNOWLEDGEMENTS

This work was supported by a Grant-in-Aid (H14-Kenka-026) from the Scientific Research Fund from the Health-Science Research Fund of the Ministry of Health, Labour and Welfare, Japan.

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河川水中の溶存有機物分画データと流域特性の関係

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Relationships between Fractionation Data in River Water and Watershed Characteristics

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Abstract

In the basin of Lake Biwa and Lake Kasumigaura, relationships between fractionation data of dissolved organic matter (DOM) and in inflowing river water and watershed characteristics were investigated by regression analysis and specific unit modeling. Most hydrophobic neutrals were found to originate from domestic sewage. Domestic wastewater treatment plant effluent was found to significantly contribute to the load of hydrophilic acids in river water. Specific unit modeling based on the load of DOM fraction and the ratio of land use contribution in watershed enabled source identification for each DOM fraction including refractory dissolved organic matter. In the north basin of Lake Biwa, forest outflow significantly contributed to the load of aquatic humic substances and refractory fractions. The loads of other DOM fractions were found to be dominated mainly by urban drainage.

Key words: dissolved organic matter, fractionations, watershed characteristics, regression analysis, specific unit modeling

1. はじめに

溶存有機物に関する調査研究については、地球規模の炭素循環における海洋の溶存有機物の役割の重要性や水域の物質代謝過程でのバクテリアの役割と溶存有機物の関係に関する知見¹⁾などにより近年注目を集めている。湖沼における溶存有機物の問題が指摘されるようになってきたのは、1980年代後半から琵琶湖北湖においてBOD濃度が減少しているにもかかわらずCOD濃度が上昇するという「水質乖離現象²⁾」が観測されるようになってからである。

この乖離現象の原因としては、湖内のCOD成分の大部分が溶存有機物であることから溶存有機物に何らかの変化が起こっていると考えるのが一般的である。琵琶湖表層では特に春季と冬期にCODの増加が目立ち、深層では季節によらずCODの増加が報告されている³⁾。植物プランクトンの指標であるクロロフィルaには一定の増加傾向がみられないことから、内部生産の増大によるCODの増加は考え難く^{4,5)}、BODが易分解性有機物の代表的指標であることから、BODには反映されないがCODに反映される難分解性溶存有機物が蓄積しているのではないかという推測^{6,7)}も説得力を持っている。

本研究では、湖沼流域における河川由来の有機汚濁負荷の量的な変化や質的な変化がどのような土地利用に起因するのかを解明することを目的として、日本の代表的湖沼である琵琶湖と霞ヶ浦に流入する河川水中の溶存有機物分画データと流域特性の関係を解析する。具体的には、難分解性溶存有機物と流域発生源の関係を整理することで、有機汚濁発生源の総合的な管理に資する基礎情報の提示を目指す。主たる解析方法は、一般的な回帰分析と土地利用形態別汚濁負荷発生原単位解析である。

まず、溶存有機物分画データと流域特性の単相関を考察した上で、変数増減法による重回帰分析を試みる。さらに、土地利用データと溶存有機物分画に基づいた比負荷量データを用いて、土地利用形態別流出原単位の推定を行う。最後に、琵琶湖と霞ヶ浦に流入する河川データから推定された土地利用形態別流出原単位により発生源ごとの溶存有機物中の各分画成分の存在比を考察するとともに、難分解性有機物の蓄積が懸念されている琵琶湖北湖流域の溶存有機物の流入負荷発生原単位寄与率を分画別に推定する。

2. 溶存有機物分画データ

本研究で使用する溶存有機物分画データは、1994年度か

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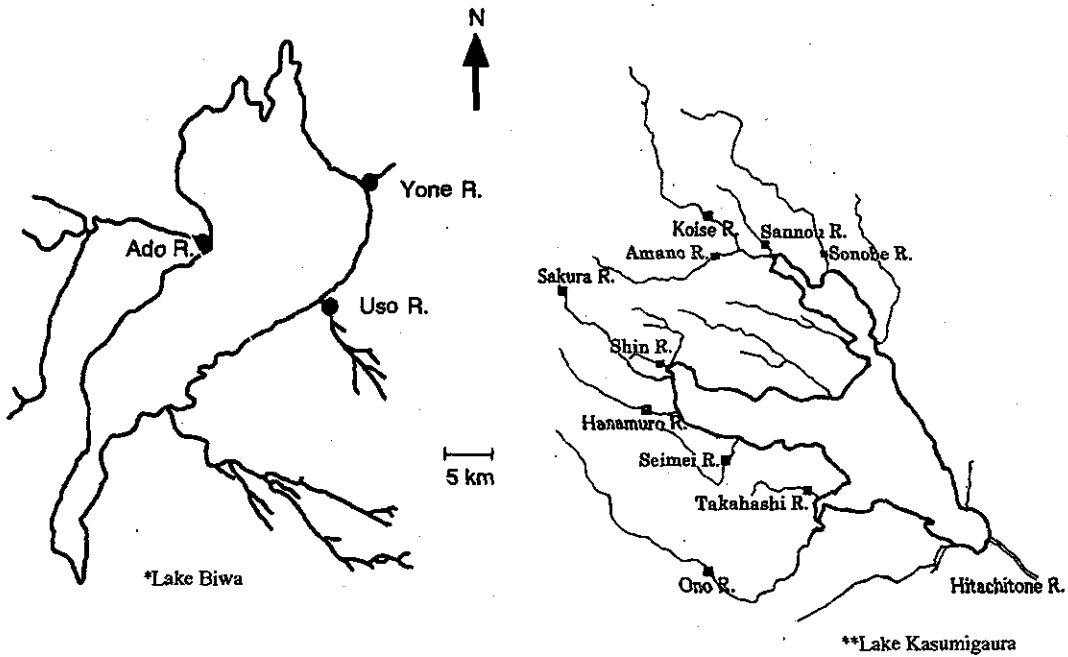


Fig.1 Location of sampling sites in Lake Biwa and Lake Kasumigaura** basin

ら1996年度にかけて琵琶湖^{3,10}と霞ヶ浦^{1,11}において測定されたものである。Fig. 1に測定地点を示す。琵琶湖流入河川では、宇曾川、米川、安曇川の3河川において1995年度と1996年度に各年度4回測定された溶存有機物分画データ(易分解性-難分解性の分画¹¹)については1995年度のみを用いた。同時期に日野川でも分画データを測定してあるが、流量データが無く比負荷量が算定できなかったため、本研究の対象にはしていない。霞ヶ浦流入河川については、園部川、山王川、天野川、恋瀬川、桜川、新川、花室川、清明川、小野川、高橋川の10河川で1994年度に年4回の頻度で測定された溶存有機物分画データを用いた。

有機物分画分析手法の詳細については既報^{1,5,11}を参照されたいが、XAD樹脂・イオン交換樹脂によるフミン質の分離に基づいて、溶存有機物をフミン物質(AHS)、疎水性中性物質(HoN)、親水性酸(HiA)、塩基物質(BaS)、親水性中性物質(HiN)の5つに分画したものである。ま

Table 1 Acronyms of Organic Solutes for Dissolved Organic Matter

acronym	Fraction
DOC	Dissolved Organic Carbon
—AHS	Hydrophobic Acids
—HoN	Hydrophobic Neutrals
—HiA	Hydrophilic Acids
—BaS	Bases
—HiN	Hydrophilic Neutrals
R-DOC	Recalcitrant Dissolved Organic Carbon
—R-AHS	Recalcitrant Hydrophobic Acids
—R-HoN	Recalcitrant Hydrophobic Neutrals
—R-HiA	Recalcitrant Hydrophilic Acids
—R-BaS	Recalcitrant Bases
—R-HiN	Recalcitrant Hydrophilic Neutrals

た、難分解性分画は、100日間生分解性試験^{1,11}による難分解-易分解性の分離に基づいている。本報告における有機物分画データの略称はTable 1に示す通りであるが、各々の分画データはDOCの内訳となり、難分解性分画(略称先頭にRを付加)はDOCを始め各分画成分合計に含まれる。

3. 流域諸特性と溶存有機物分画データの関係について

3.1 使用するデータの概要

ここでは、河川流域における土地利用面積比率(市街地、田、畑、山林)および排水処理形態別人口密度(公共下水道、農村下水道、合併浄化槽、単独浄化槽、尿尿処理)と河川水中の溶存有機物分画データの比負荷量年度平均値(各年度とも、4回の測定日に直近の流量データ公表値を濃度データに乗じた負荷量の算術平均値)の関係を考察する。一般的に、流域発生源と河川水質あるいは負荷量の間を関係を検討する際には、発生源から採水地点までの自浄作用等を考慮しなければならない。本研究では、特に難分解性の溶存有機物の主要な起源に着目しているため、流下過程における生分解や懸濁態の沈降による水質変化は副次的な要因として扱い、流域特性と分画データの直接的な関係に焦点を当てながら、気象条件による季節変化が大きい濃度データよりも年間代表値的な扱いが妥当と考えられる比負荷量データを中心に流域諸特性と関連付けた。

対象河川流域は、流量データおよび流域単位の土地利用面積比率と排水処理形態別人口密度の両方が各種統計資料^{3,10}より引用可能な琵琶湖流域3河川(宇曾川、米川、安曇川)と霞ヶ浦流域3河川(新川、花室川、清明川)である。琵琶湖流域3河川の土地利用面積比率と排水処理形態別人口密度は1995年度および1996年度の各々の年度単位の集計されているため、これら3河川の溶存有機物分画データの比負荷量については年度別の算術平均値を採用

した。土壌や植生など自然条件のバックグラウンドが異なる流域の河川データを同一母集団として統計解析することに関しては、既存報告の極めて少ない実河川における溶存有機物分画データのフィールド特性を考察する主旨で重要と考えた。対象河川における有機物分画濃度の平均値と標準偏差をTable 2に示す。

3.2 単相関分析による考察

溶存有機物分画データの比負荷量年間平均値と単位面

積あたりの流域特性値との間の相関係数をTable 3に示す。DOC, HoN, HiA, HiNなど項目において、合併浄化処理人口、単独浄化処理人口との相関が高い。特に、HiAと単独浄化処理人口および合併浄化処理人口の間の相関係数が0.9以上という高い値を示している。下水処理水中ではHiAの占める比率が大きく生活雑排水ではHiAに加えて合成洗剤成分由来のHoNの存在比が高いという報告⁹⁾もあり、合併浄化槽や単独浄化槽の処理水において親水性酸 (HiA) や疎

Table 2 Mean values (standard deviations) of DOMfractions in the objected rivers

mg/L	DOC	AHS	HoN	HiA	BaS	HiN	R-DOC	R-AHS	R-HoN	R-HiA	R-BaS	R-HiN
Uso R. 1995	1.60 (0.59)	0.54 (0.12)	0.25 (0.29)	0.30 (0.04)	0.21 (0.08)	0.32 (0.37)	0.83 (0.24)	0.40 (0.12)	0.07 (0.06)	0.25 (0.09)	0.04 (0.04)	0.06 (0.04)
Uso R. 1996	1.33 (0.49)	0.49 (0.14)	0.23 (0.21)	0.52 (0.17)	0.06 (0.03)	0.04 (0.03)						
Ado R. 1995	0.38 (0.05)	0.24 (0.06)	0.00 (0.00)	0.06 (0.04)	0.04 (0.03)	0.04 (0.03)	0.30 (0.06)	0.20 (0.02)	0.01 (0.02)	0.07 (0.02)	0.00 (0.01)	0.01 (0.01)
Ado R. 1996	0.37 (0.02)	0.17 (0.04)	0.07 (0.07)	0.05 (0.03)	0.01 (0.02)	0.06 (0.04)						
Yone R. 1995	1.63 (0.52)	0.52 (0.06)	0.23 (0.20)	0.38 (0.10)	0.23 (0.17)	0.26 (0.28)	0.83 (0.10)	0.36 (0.14)	0.09 (0.12)	0.26 (0.05)	0.04 (0.04)	0.09 (0.06)
Yone R. 1996	1.23 (0.36)	0.37 (0.10)	0.29 (0.25)	0.39 (0.18)	0.04 (0.04)	0.15 (0.20)						
Shin R. 1994	4.84 (1.09)	1.57 (0.24)	0.73 (0.48)	1.97 (0.41)	0.43 (0.06)	0.13 (0.09)	3.23 (0.75)	1.13 (0.15)	0.39 (0.46)	1.34 (0.34)	0.36 (0.19)	N.D.
Hanamuro R. 1994	3.07 (0.19)	1.14 (0.06)	0.13 (0.11)	1.32 (0.28)	0.35 (0.19)	0.12 (0.09)	2.32 (0.55)	0.96 (0.19)	0.13 (0.15)	0.81 (0.41)	0.27 (0.18)	0.15 (0.12)
Seimei R. 1994	3.09 (1.04)	1.24 (0.27)	0.17 (0.25)	1.28 (0.51)	0.16 (0.12)	0.24 (0.16)	2.43 (0.79)	0.96 (0.23)	0.31 (0.42)	0.91 (0.32)	0.12 (0.14)	0.13 (0.10)

Table 3 Correlation coefficients between DOMfraction load in river and watershed characteristics

	DOC	AHS	HoN	HiA	BaS	HiN
urban sewer system	0.01	-0.14	0.10	0.22	0.02	-0.05
rural sewer system	-0.40	-0.44	-0.34	-0.41	-0.21	-0.34
domestic wastewater treatment	0.80 **	0.56	0.88 **	0.95 **	0.63	0.78 *
septic tank treatment	0.73 *	0.46	0.78 *	0.92 **	0.62	0.70 *
night soil collection	0.61	0.34	0.70 *	0.81 **	0.53	0.58
urban area	0.04	-0.17	0.12	0.31	0.08	-0.02
paddy field	0.46	0.22	0.59	0.53	0.42	0.50
field	-0.34	-0.41	-0.37	-0.14	-0.26	-0.38
forest	-0.23	0.10	-0.37	-0.51	-0.26	-0.20

*: p<0.05 **: p<0.01

Table 4 Correlation coefficients between refractory DOMfraction load in river and watershed characteristics

	R-DOC	R-AHS	R-HoN	R-HiA	R-BaS	R-HiN
urban sewer system	-0.19	-0.32	0.02	-0.02	0.41	-0.25
rural sewer system	-0.38	-0.36	-0.31	-0.44	-0.42	-0.10
domestic wastewater treatment	0.74	0.47	0.91 *	0.88 *	0.95 **	0.84 *
septic tank treatment	0.61	0.31	0.89 *	0.79	0.90 *	0.74
night soil collection	0.44	0.15	0.74	0.63	0.90 *	0.53
urban area	-0.18	-0.39	0.14	0.04	0.51	-0.18
paddy field	0.40	0.21	0.63	0.43	0.41	0.73
field	-0.43	-0.54	-0.09	-0.28	-0.14	-0.41
forest	0.04	0.37	-0.51	-0.21	-0.60	-0.20

*: p<0.05 **: p<0.01

Table 5 Partial correlation coefficients for multiple regressions between DOM fraction load in river and watershed characteristics

DOC (n=9)		AHS (n=9)		HoN (n=9)	
domestic wastewater treatment	1.26 **	domestic wastewater treatment	1.22 **	domestic wastewater treatment	1.21 **
forest	0.65 *	forest	0.95 *	forest	0.48 *
R ²	0.86	R ²	0.78	R ²	0.89
	p<0.05		p<0.05		p<0.01
HiA (n=9)		BaS (n=9)		HiN (n=9)	
forest	0.45 **	domestic wastewater treatment	0.63	domestic wastewater treatment	1.24 **
septic tank treatment	1.29 **			forest	0.66 *
field	-0.18 *				
R ²	0.98	R ²	0.40	R ²	0.83
	p<0.01				p<0.01
R-DOC (n=6)				R-HoN (n=6)	
domestic wastewater treatment	0.85			domestic wastewater treatment	0.91 *
forest	1.05 *				
night soil collection	0.68				
urban sewer system	-0.18				
R ²	1.00			R ²	0.83
	p<0.05				p<0.05
R-HiA (n=6)		R-BaS (n=6)		R-HiN (n=6)	
domestic wastewater treatment	1.43 **	domestic wastewater treatment	1.11 **	domestic wastewater treatment	1.08 **
forest	0.62 **	paddy field	-0.26	urban area	-1.29 *
paddy field	-0.22 **			urban sewer system	0.64 *
rural sewer system	0.07 *			forest	-0.15
R ²	1.00	R ²	0.95	R ²	1.00
	p<0.01		p<0.05		p<0.05

水性中性物質 (HoN) の存在割合が大きいことが改めて確認できた。

難分解性の画分についても同様に、比負荷量年間平均値と流域特性値との間の相関係数をTable 4に示す。R-DOCを含む全ての難分解性画分において合併浄化処理人口との相関係数0.7以上となっていることから、合併浄化処理水が河川の難分解性有機物負荷量に影響を与えている可能性を指摘することができる。また、R-HoNは総人口密度の間の相関も極めて強かった ($r=0.99$) ことから、各種化学物質由来と考えられる疎水性中性物質の中でも難分解性画分は人間活動全般に伴う負荷の影響を受けていると考えられる。

一方で、人間活動関連の流域特性との相関がさほど強くないAHSについては、人為的負荷よりも山林から流出する自然系負荷の影響が大きいと考えられる。この傾向は、森林渓流水や森林系河川の安曇川の河川水においてAHSの全溶存有機物中の存在比が非常に高いという既報の知見^{5,11)}と整合している。

3.3 重回帰分析による考察

溶存有機物分画データの比負荷量年間平均値を目的変数とする重回帰分析 (ステップワイズ変数増減法) を試みた結果をTable 5に示す。R-AHSについては、偏回帰係数が極端に小さい値となったため、解析対象から除いた。合併浄化処理人口密度がHiA, R-AHS以外の全て項目において説明変数として選択されており、標準偏回帰係数の値も相対的に大きい値となっていることが目立つ。これらの結果は、合併浄化槽で処理されない難分解性有機物が河川水中の溶存有機物負荷量に影響を与えていることによるものと

考えられる。また、山林面積が、DOC, AHS, HoN, R-DOC, HiAにおいて説明変数として選択されている。森林渓流水の溶存有機物はAHSの存在比が高い¹¹⁾ことから、AHSについては山林からの負荷の影響が明らかに大きいと言えよう。河川水中の溶存有機物は一般にAHSの存在比が高いことを考慮に入ると、DOCについてもAHSの影響により山林面積が比負荷量の説明変数として十分に機能している。

4. 溶存有機物分画データの流域内土地利用形態別流出負荷量原単位の解析

4.1 使用するデータの概要

ここでは、一般的な原単位モデルにより河川の比負荷量から溶存有機物分画成分の土地利用形態別流出負荷原単位を推定し、各分画成分の土地利用起源について考察する。対象河川は、流域単位の土地利用面積比率 (市街地、田、畑、山林) および河川流量データが各種統計資料¹⁻¹¹⁾より引用可能な琵琶湖流域3河川 (宇曾川、米川、安曇川) と震ヶ浦流域10河川 (園部川、山王川、天野川、恋瀬川、桜川、新川、花室川、清明川、小野川、高橋川) である。ただし、恋瀬川流域の土地利用面積比率は天野川と恋瀬川を併せて一つの流域として集計¹¹⁾してあったため、溶存有機物分画データについても天野川と恋瀬川の負荷量を足し合わせたものを恋瀬川の負荷量データとして解析に使用した。したがって、実質的な解析対象は合計12河川である。

4.2 溶存有機物分画データの土地利用形態別流出原単位の算出方法

各集水域から河川に流入する負荷量は、集水域の気象、

地質、地形、土地利用被覆状態や人間の社会経済活動など多くの環境条件により変動する¹¹⁾。しかしながら、個々の発生活濁負荷原単位や流達率などが時間的にも地域的にも異なることから、様々な流域を対象とした平均値として取り扱う場合には原単位や流達率の値そのものが問題視されることが多い¹³⁾。このような問題に対して、河川の土地利用形態比率を基に流達率や流出率を併せた形での各土地利用形態別の流出負荷量原単位の算定を試みる際には、①「生活排水は市街地負荷の一部として市街地面積に比例し、市街地面積比率の中に表現できる」、②「畜産排水はその大半が農地還元処分である場合、農耕地(田・畑)の面積比率で表現できる」といった仮定¹⁴⁾を設定することが提案されている。

これらに加えて、土地利用形態別原単位を算出する際に全ての土地利用形態別流出負荷原単位が正の値となるような制約条件の基に以下の(1)式で表す評価関数 E が最小になるような土地利用形態別流出負荷原単位 U を算出する方法¹¹⁾ が提案されている。

$$E = \sum_{i=1}^m \left(\frac{Li}{Ai} - \sum_{j=1}^n (U_j \cdot rij) \right)^2 \quad (1)$$

- Li : 各河川年間負荷量 (kg/year)
- Ai : 各河川流域面積 (km²)
- U_j : 土地利用形態別流出負荷原単位 (kg/km²/year)
- rij : 土地利用形態比率

ここで、 $i=1 \sim m$ は河川流域のサンプル数、 $j=1 \sim n$ は土地利用種別(例えば、市街地、田、畑、山林など)に対応している。本研究では、溶存有機物分画データを対象とした土地利用形態別流出負荷原単位の検討に際して、全ての原単位値が正の値となるような制約条件を重要視する主旨で、この(1)式による算定方法を基本として評価関数 E が最小になるような係数 U を各溶存有機物分画成分の原単位推定値として評価してみる。

4.3 溶存有機物分画データの土地利用形態別流出原単位の推定結果

まず、実測された溶存有機物分画濃度と流量を用いて各河川の平均比負荷量を求めた。ただし、琵琶湖流入河川における難分解性の画分は1995年度のみ測定であるため、琵琶湖流入河川では1995年度の年間比負荷量平均値を解析対象とした。算出した比負荷量が年間を通して一定であると仮定して求めた各河川の年間総流出比負荷量から、先の(1)式により土地利用形態別流出負荷原単位を算出した。なお、最初の計算ではR-BaS以外の全ての項目で畑の流出原単位がほぼゼロと算出されたため、畑面積比率を除外した上で再度計算を行った。

土地利用形態別流出負荷原単位の予測結果をFig. 2に、負荷量の予測値と実測値の間の相関係数をTable 6に示す。AHS, HoN, HiAについては比較的高い予測精度が得られたが、一般水質項目を対象とした既往の報告¹¹⁻¹⁴⁾と比較して全体的な精度は高いとは言えない。また、3.2でも述べたように、BaSの存在比率が平均で10%以下と低いことに加えて、HiNについても平均的な存在比率の低さから定量的な考察が困難となっている。市街地の原単位がどの画分につ

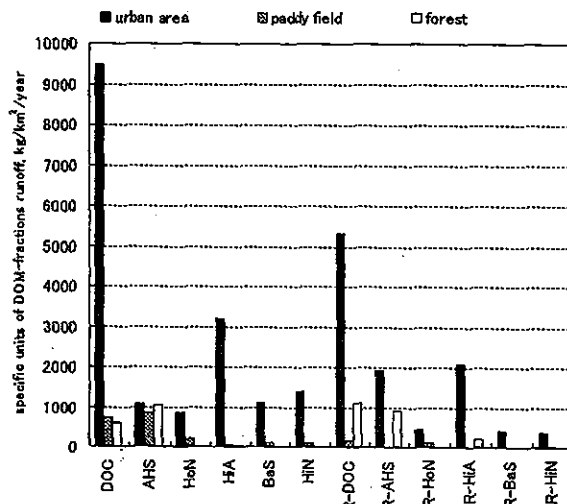


Fig. 2 Specific units of DOM-fractions runoff for three types of land use

Table 6 Correlation coefficients between observed load and estimated load of the specific unit modeling based on the load of DOM-fraction and the ratio of land use contribution in watershed

DOC	AHS	HoN	HiA	BaS	HiN
0.59 *	0.81 **	0.73 **	0.73 **	0.62 *	0.56
R-DOC	R-AHS	R-HoN	R-HiA	R-BaS	R-HiN
0.61 *	0.59 *	0.51	0.66 **	0.50	0.63 *

** : $p < 0.01$ * : $p < 0.05$

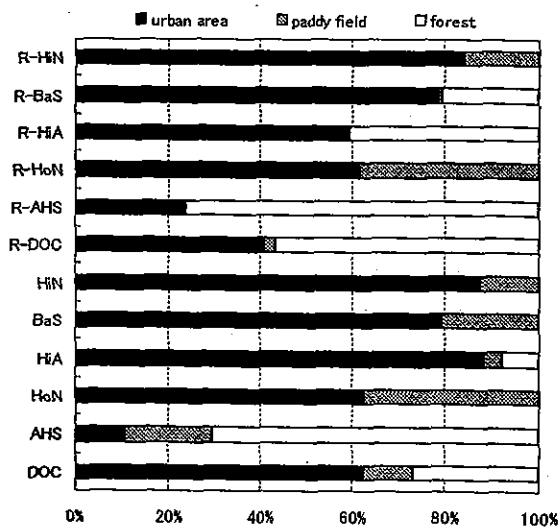


Fig. 3 Contributions of DOM-fractions runoff for three types of land use in the north basin of Lake Biwa

いても相対的に大きい値となっているが、特にDOC, HiA, R-DOC, R-HiAについて市街地の原単位が大きく、これらの画分は市街地という土地利用全般からの影響が大きいことを示している。また、AHSとR-AHSにおける山林の原単位が他の画分における山林の原単位より大きい結果につい

ては既報¹⁾と整合している。

しかし、DOCとAHSの田、山林の原単位については、全ての画分を合わせた溶存有機物であるはずのDOC原単位予測値がAHS原単位予測値より低い値をとっている。これは、原単位予測の基本とした(1)式が「DOCの原単位は各画分の原単位の合計となる」という制約条件を含んでいないためである。この制約条件を加えた上で原単位の再推計を試みたが、いずれの有機物画分においても負荷量の予測値と実測値の間の相関が低下したため、有機物組成としての全体性には若干の問題が残るが、溶存有機物の各画分原単位予測結果の特徴を考察する主旨で当初の予測結果 (Fig. 2) を基本に検討を行った。

これらの原単位予測値と琵琶湖北湖流域の土地利用形態別面積²⁾を用いて、琵琶湖北湖流域における溶存有機物各画分の発生源内訳 (市街地、田、山林) を予測した結果をFig. 3に示す。畑からの流出については、先に述べた通り(1)式における残差最小計算によりほとんどの画分で流出ゼロと算定されたため寄与率を無視してある。各画分の負荷流出内訳を見ると、AHS, R-DOC, R-AHS以外はどの画分も市街地から排出される負荷が最も大きく、AHS, R-DOC, R-AHSは山林からの負荷の割合が大きくなっている。AHSのほとんどが難分解性であり河川水ではAHSの存在比が大きいことを考えると、琵琶湖北湖流域における難分解性溶存有機物は山林から流出するAHSの負荷が大部分を占めていると言える。

5. まとめ

本研究では、今後いっそう重要視される有機物指標としての溶存有機物分画データと流域特性の関係を統計解析することにより、河川水中の難分解性画分を含む溶存有機物成分ごとの発生源について検討した。本研究で得られた主な知見は、以下の通りである。

1) 疎水性中性物質および親水性酸は、比負荷量として合併浄化槽の処理水の影響を強く受けている可能性が高い。

2) 人間活動関連の流域特性との相関がさほど強くないフミン物質については、人為的負荷よりも山林から流出する自然系負荷の影響が大きい。

3) 合併浄化槽で処理されない難分解性有機物が河川水中の溶存有機物負荷量に与える影響は無視できない。

4) 各河川流域における溶存有機物分画データと土地利用面積率を用いて、溶存有機物の各分画成分の土地利用形態別流出負荷原単位を推定し、発生源の傾向を詳細に考察することができた。

5) 琵琶湖北湖流域の溶存有機物の総流入負荷を推定した結果、フミン物質および溶存有機物の難分解性画分では山林からの寄与が最も大きく、それ以外の画分は市街地からの寄与が最も大きいことがわかった。

上記知見1)~3)については、既報^{1,2)}による各種発生源別の有機物分画データプロファイルに関する考察と整合するものであったが、実河川における比負荷量実測値と流域特性データによる相関分析や寄与率推定により現場のマクロな状況を裏付ける意義はあるものと考えられる。

今後の水質保全対策という観点では、河川水中の難分解

性溶存有機物負荷量は、下水処理水や合併浄化槽処理水などの市街地由来の晴天時負荷の影響を大きく受けると考えられるため、下水処理場や合併浄化槽における難分解性溶存有機物を考慮した処理機能の高度化が必要であると考えられる。特に、市街地からの難分解性溶存有機物負荷の大部分を占める親水性酸の削減が可能となるような高度処理技術の開発が望まれよう。

一方で、多くの河川や湖沼において年間負荷量に占める降雨時流出負荷の割合が大きいことを鑑みると、降雨時に流出する溶存有機物負荷についても分画データ情報が必要になるものと考えられる。土地利用形態別流出負荷原単位の算出に関しても、本研究で試みた土地利用面積比率による回帰分析型の原単位モデルを高い精度で検証するためには、各発生源から流出する溶存有機物について各分画成分の実測データの蓄積が求められる。溶存有機物成分の分画分析方法の簡易化に加えて、一般水質項目データによる難分解性有機物割合の推定方法なども実用的な流域環境管理において近々の課題となろう。

(原稿受付 2004年3月19日)

(原稿受理 2004年9月10日)

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