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Dissolved organic carbon in a eutrophic lake; dynamics, biodegradability and origin

Takehiko Fukushima[1,2], Je-chul Park[3], Akio Imai[1] and Kazuo Matsushige[1]

[1] National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305, Japan
[2] The present address: Department of Civil and Environmental Engineering, Hiroshima University, Higashihiroshima, Hiroshima 739, Japan
[3] Tokyo University of Fisheries, 4-5-7, Konan, Minato-ku, Tokyo 108, Japan

Key words: Dissolved organic carbon, bio-degradation test, pedogenic (allochthonous), authochthonous, UV-absorbance.

ABSTRACT

The seasonal and spatial changes in dissolved organic carbon (DOC) in Lake Kasumigaura, a shallow, eutrophic lake, were analyzed and the lability of DOC was tested by long-term incubations. There was a nearly 1 mgC l^{-1} downstream increase in refractory DOC in the lake; at the center it fluctuated little seasonally. The characteristic UV-absorbance: DOC ratios were determined for samples from the influent rivers (pedogenic: used interchangeably with "allochthonous") and outdoor experimental ponds (autochthonous) during incubations. These ratios were then used to calculate the proportion of total measured lake water DOC in each of four components: pedogenic-refractory (PR), pedogenic-labile (PL), autochthonous-refractory (AR) and autochthonous-labile (AL). PR was uniform (around 1.5 mgC l^{-1}) or diminished very slightly over time. AR increased from nearly zero at the station closest to an influent river to 1 mgC l^{-1} at the lake center. PL declined downstream from 0.3 mgC l^{-1} to zero. AL was virtually constant at 0.8 mgC l^{-1} except at the station closest to the influent river. The constancy of the UV-absorbance: DOC ratio during the biodegradation process was confirmed for Lake Kasumigaura; hence a two-component model (pedogenic-autochthonous) could be applied here without consideration of DOC lability. However, this assumption is not always met for other water bodies, and therefore it should be checked before applying a two-component model elsewhere.

Introduction

Much attention has been paid to dissolved organic matter and dissolved organic carbon (DOC), as its representative index, in natural aquatic systems, basically as a source of organic pollution, and further 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 some components, e.g. phytoplankton, bacteria (Salonen et al., 1992). Two different types of DOC are distinguished according to their origin. Autochthonous DOC is mainly composed of photosynthetic inputs of the littoral and pelagic flora through secretion and autolysis of cellular con-

tents, DOC excreted by zoolankton and higher animals, bacterial chemosynthesis of organic matter with subsequent release of DOC, etc. (Wetzel, 1983). On the other hand, allochthonous DOC, which is of terrestrial origin, consists mainly of humic substances synthesized biologically and chemically from the degradation products of terrestrial plants, animals and microorganisms, nonhumic substances discharged through human activities, etc. In order to avoid confusion about the abbreviations, we use "pedogenic" as synonymous with "allochthonous" in the present paper. The loss of DOC from the lake is accounted for by advection into an effluent river, uptake by microbes, abiotic decomposition, coprecipitation with $CaCO_3$, etc. (Otsuki and Wetzel, 1973; Buffle and Deladoey, 1982; Wetzel, 1983).

In several lakes, chemical fractionation methods have been applied to analyze and record temporal changes in DOC (Tatsumoto et al., 1991; Munster and Albrecht, 1994). However, the dynamics of DOC could not be quantitatively explained by these data alone. There are a very few lakes for which the DOC budget has been estimated (Wetzel, 1983).

If we could analyze the dynamics of both pedogenic and autochthonous DOC separately, we would gain insights useful for the efficient management of natural water bodies to reduce organic pollution and eutrophication. Zumstein and Buffle (1989) reported a method which partitions DOC into pedogenic and autochthonous components and applied this method to Lake Bret to analyze DOC dynamics. There are, however, several problems when applying this method to other lakes. Among these problems are the assumption that pedogenic organic matter is always refractory, lack of consideration of the spatial changes in DOC, etc. Whereas water color measured with a Hellige color comparator was used to distinguish pedogenic from autochthonous dissolved organic matter in 18 Swedish forest lakes covering a wide range of dystrophy (Meili, 1992), application of this method to low dystrophic lakes would be impossible.

In the present paper, we report on spatial and seasonal changes in DOC, and its biodegradability and its chemical and spectrophotometric properties in a shallow, eutrophic lake. We use the dissolved organic matter obtained from the influent and outdoor experimental ponds as the representatives of pedogenic DOC and autochthonous DOC, respectively. We then propose and apply a method to distinguish DOC components by two criteria, i.e. pedogenic – autochthonous and refractory – labile (refractory: the remained components after 100-days of incubation; labile: the lost components, as explained below). Finally, we discuss the dynamics of each component.

Experimental

Lake Kasumigaura and sample collection method

Lake Kasumigaura, the second largest lake in Japan, is located in the eastern part of the Kanto Plain, 50 km north-east of Tokyo. The lake has two large bays, Takahamairi and Tsuchiurairi (Fig. 1). More than 600,000 people live in the lake's watershed (1,597 km^2). Land use in the watershed is 30% forest, 25% paddy field, 25% plowed field, 10% residential, and 10% others.

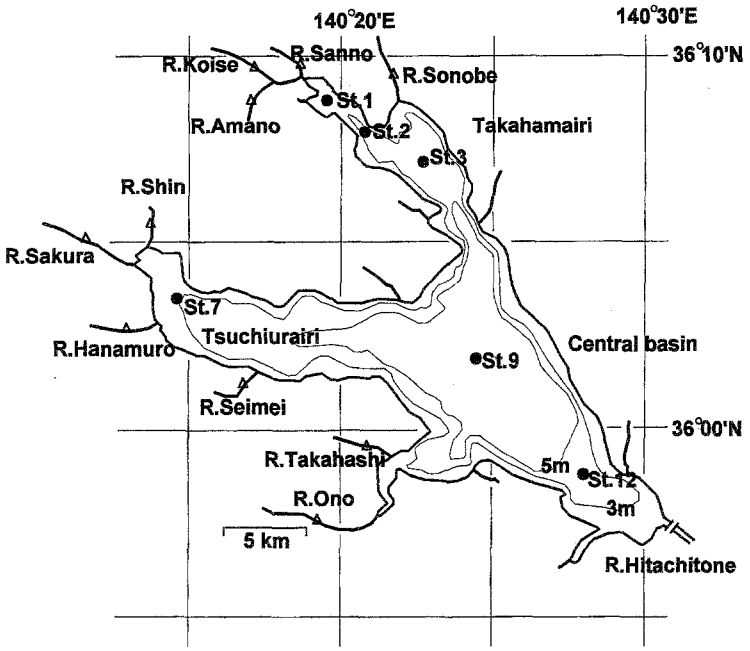

Figure 1. Sampling stations in Lake Kasumigaura (solid circles) and its influent rivers (open triangles) with depth contours (m)

The lake basin is smooth and shallow, with a surface area of 171 km^2, a mean depth of 4.0 m, and a maximum depth of 7.3 m. The elevation of the lake water surface is only 0.16 m above sea level. Because of extremely high loads of organic matter and nutrients, this lake is well known for eutrophication, with mean concentrations of chlorophyll-a, phosphorus, and nitrogen of 65 $\mu g\ l^{-1}$, 95 $\mu g\ l^{-1}$, and 1.15 $mg\ l^{-1}$, respectively at the lake center (Fig. 1, St. 9) for Aug. 1992–Mar. 1993.

There are more than 20 influent rivers but only one effluent river, the Hitachitone River. The Koise River and the Sakura River are the main rivers influent to Takahamairi and Tsuchiurairi, respectively. Water flows through the lake largely from the northwest parts of Takahamairi and Tsuchiurairi south-east to the Hitachitone River. Excluding the inflow from the Shintone River which enters the lake very close to the sole effluent river, the combined inflow from the 8 rivers influent to the bays comprised 77% of total lake inflow (Ebise, 1984). Hence, there are two principal advective flows, successively from stations 1 to 2 to 3 to 9 through 12 and from stations 7 to 9 through 12. The apparent retention times (basin volume divided by influent water load) are 2.7 months for Takahamairi, 7.8 months for Tsuchiurairi, and 8.3 months for the central basin. Nevertheless, the water is usually well mixed within and between the three basins because the wind-driven currents are fairly strong. Judging from the lag in the seasonal chlorophyll-a concentration peaks, we suppose that the average time for water to flow from St. 1 to St. 3 is about one month and that from St. 1 to St. 9 takes about three months. In addition, Lake

Kasumigaura is so shallow that vertical stratification is easily destroyed by a moderately strong wind (Muraoka and Fukushima, 1986).

The organic matter and nutrient loads flowing into the northwestern bays comprised 76%, 74%, 80%, and 77% of the total COD ($KMnO_4$ method), COD for dissolved matter, total nitrogen, and total phosphorus loads into the whole lake, respectively (Ebise, 1984). We then asssume a one-dimensional model of water and organic matter transport with the primary inputs into the northwestern bays. Thus all changes in DOC subsequent to its input into the lake in these north-western bays is assumed to due to in situ processes whose impacts increase as the water flows downstream from these bays to the central basin and eventually out into the Hitachitone River.

Water samples were collected with a 2 m-column sampler at stations 1, 2, 3, 7, 9, and 12 (Fig. 1) monthly from Oct. 1992 to Sep. 1994. The samples were immediately cooled in an ice box and brought back to our laboratory where we passed them through precombusted (450 °C for 3 hours) Whatman GF/F filters (effective pore size 0.7 μm). The filtrates were kept at 3 °C in glass bottles until analysis.

In May, Aug. and Nov. 1994 and in Feb. 1995, water samples were also obtained at downstream stations of 10 influent rivers which collectively account for 86% of the total discharge into Lake Kasumigaura. These river samples were treated in the same manner as the lake samples. Details about discharge rates and water quality of the rivers will be reported elsewhere.

Chemical analysis

After removal of inorganic carbon from the acidified filtrates (by addition of 2 N HCl to pH 2 and purging with nitrogen gas), the DOC concentrations were determined on a commercially available total organic carbon analyzer (model TOC-5000; Shimadzu) equipped with 2.8 g of a 20% Pt catalyst on quartz wool. Because nearly all volatile organic matter would be excluded from analysis by this procedure, the DOC values reported here represent the amounts of non-volatile organic matter. Analytical precision was typically within ±1% and we used the mean value of three or more measurements for each sample.

Absorbance measurements were made in a 1 cm quartz cell at 220, 230, 240, 250, 260, 270, 280, and 290 nm with a Beckman DU-7 spectrophotometer. Milli-Q water was used as the blank for both absorbance and fluorescence measurements. The pH of the samples, which was always within the range from 8 to 10, was not adjusted. The absorption spectra of almost all samples exhibited a monotonous decrease with wavelength, with no characteristic band similar to the patterns reported by Buffle et al. (1982). The decrease in absorbance with wavelength was not sample-specific, thus for the subsequent analyses we chose to use the absorbance at 260 nm, the same wavelength adopted by Tambo and Kamei (1978), as an index for the amount of humus-, lignin- and tannin-like compounds in water.

A Shimadzu RF-540 was used for fluorescence measurements. The instrument was calibrated with salicylic acid solutions, but the intensity was arbitrarily set to make only relative comparisons. Fluorescence spectra of the samples revealed that the values of the maximum excitation and emission wavelengths (λ_{ex}^{max} and λ_{em}^{max}, res-

pectively) were largely independent of season and station. Therefore, all the fluorescence measurements were made at λ_{ex} = 260 nm and λ_{em} = 450 nm, which were fairly close to the wavelengths of 260 nm/440 nm ($\lambda_{ex}/\lambda_{em}$) observed for samples from the Black Sea (peak C; Coble et al., 1990), but were a little different from the wavelengths of 360 nm/460 nm used by Stewart and Wetzel (1980) and those of 345 nm/415 nm used by Zumstein and Buffle (1989) for lake water samples.

The concentrations of protein (Lowry-Folin method; Lowry et al., 1951), carbohydrate (anthrone method; Scott and Melvin, 1953), and lignin/tannin – like compounds (tungstophosphoric and molybdophosphoric acid method; APHA, 1985) were determined colorimetrically using bovine serum albumin (Carbon content 49.3 %), D-glucose (40.0 %) and tannic acid (52.2 %), respectively, as standards. The samples for protein and carbohydrate measurements were pre-concentrated to one-fifth or one-tenth of their original volumes by lyophilization. The particulate organic carbon (POC) and nitrogen (PON) contents on dried (110 °C for 2 hours) GF/F filtes were determined with a Yanagimoto MT-5 CHN-analyzer.

Biodegradability experiments

Filtrates which had passed through precombusted Whatman GF/F filters were incubated in sterile 100 ml glass bottles at 20 °C in the dark without shaking. Each sample was inoculated with 0.5 ml of sand-filtered lake water (explained in the next section), but there was little difference in the biodegradability of the inoculated and non-inoculated samples (data not shown). This lack of a difference is probably due to the filtration with Whatman GF/F filters not efficiently removing all microorganisms. We took sub-samples of about 5 ml and determined DOC concentrations about 10, 20, 30, 40, 60, 80, and 100 days after the incubation began. The maximum bacteria number at four different incubation times for three experimental pond samples was 7.7×10^6 ml^{-1} and that at seven different incubation times for two lake water samples was 4.1×10^6 ml^{-1}. By the use of a conversion factor, 106 fgC μm^{-3}, and a mean bacterial volume, 0.14 μm^3, from Nagata (1986; samples obtained in a mesotrophic lake), we estimate the bacterial contributions to labile DOC in the pond and lake samples to have been at most 0.11 mgC l^{-1} and 0.06 mgC l^{-1}, respectively. Thus the contribution of bacteria to labile DOC (mean concentrations: 1.1 mgC l^{-1} in the experimental ponds and 0.90 mgC l^{-1} in Lake Kasumigaura as shown below) was < 10 %. The UV absorbance was also determined for the samples which had been incubated for 100 days.

Outdoor experimental ponds

In order to characterize autochthonous DOC, we sampled water from six outdoor experimental ponds (surface area: 24 m^2, depth: 1.5 m, volume: 36 m^3). Lake water to fill and flush the ponds (20 d retention time) had been sand filtered through 400 mm of anthracite (mean particle diameter 0.9 mm) and 400 mm of sand (mean particle diameter 0.45 mm) at a rate of 6.6 m h^{-1}. $NaNO_3$ and KH_2PO_4 solutions were continuously added to the inflowing filtered water by peristaltic pump to

add 2 and 0.2 mgl^{-1} of nitrogen and phosphorus, respectively. At the start of the experiment (Aug. 3, 1993), a bucket (20 l) of phytoplankton-rich lake water (dominated by *Microcystis* sp. and *Oscillatoria* sp.) was put into each pond. Fish were maintained at different densities in the ponds for more than one year (Fukushima et al., 1995a). During the summers of 1993 and 1994, water samples were taken at the center of each pond using a 1-m column water sampler daily (Ponds 1, 2 and 3) or three times a week (Ponds 4, 5 and 6) for 40 days. The DOC concentrations and UV-absorbances of the filtrates were measured during the biodegradability tests of the weekly samples using the same method mentioned above.

After passing through the sand filter, the labile fractions of DOC in the pond inflow water were almost quantitatively consumed by the microorganisms in the sand as shown below; hence, only refractory DOC some of which is carried from the watershed (pedogenic-refractory) or produced in Lake Kasumigaura (autochthonous-refractory) remains after this process. Since there was high primary production in these ponds (mean concentrations of chlorophyll-a and POC of 50–150 $\mu g\, l^{-1}$ and 3.2–11.0 $mg\, l^{-1}$, respectively, in each pond compared with 2 $\mu g\, l^{-1}$ chlorophyll-a and 0.3 $mg\, l^{-1}$, respectively, in the inflow water), substantial autochthonous DOC production (autochthonous-refractory and autochthonous labile, but produced in the ponds) is presumed to have occurred and their characteristics can be determined as the difference in some feature of DOC between the pond and inflow waters. Particular for autochthonous labile components, we can calibrate their characteristics by comparing the feature between before and after the biodegradability tests because the labile ones have been lost during the period.

Quantification DOC into four components

We can derive a simple model for dividing the measured DOC into four components: PR (Pedogenic – Refractory), PL (Pedogenic – Labile), AR (Autochthonous – Refractory), and AL (Autochthonous – Labile) ($mgC\, l^{-1}$) based upon characteristic ratios of chemical and/or photometric properties to mass (DOC) for each DOC component (X_{PR}, X_{PL}, X_{AR}, X_{AL}). If these ratios are constant, then the budgets for DOC give the following equations:

$$DOC_{ini} = PR + PL + AR + AL \tag{1}$$

$$DOC_{last} = PR + AR \tag{2}$$

$$X_{ini}\, DOC_{ini} = X_{PR}\, PR + X_{PL}\, PL + X_{AR}\, AR + X_{AL}\, AL \tag{3}$$

$$X_{last}\, DOC_{last} = X_{PR}\, PR + X_{AR}\, AR \tag{4}$$

Where, DOC_{ini} is the initial DOC concentration in a sample ($mgC\, l^{-1}$), DOC_{last} is the DOC at the end of incubation, X_{ini} is the characteristics ratio at the start of incubation and X_{last} is this ratio at the end of incubation.

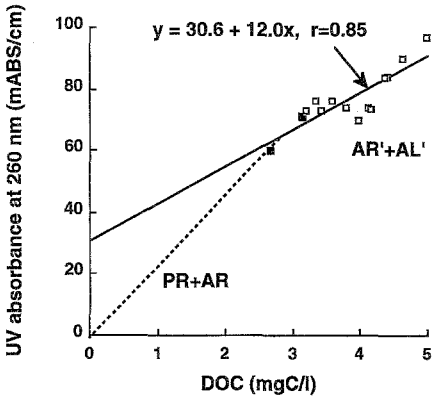

Figure 2. DOC vs. UV-absorbance for outdoor experimental ponds' dissolved organic matter. Open square indicates the average for one of six outdoor experimental ponds for 40 days during the summers of 1993 and 1994. Solid square indicates the inflow water (sand filtrated lake water). Solid line indicates the regression line (independent variable (x): DOC, dependent variable (y): UV absorbance, n = 14). Dotted line connects the origin of the coordinate axes and one of the solid squares straightly. Constituents are explained in the text

Results and discussions

Characteristics of autochthonous DOC

Prior to reporting the DOC dynamics in the lake, we show the calibration of the data obtained from the outdoor experimental ponds and determine the characteristics of autochthonous DOC (Fig. 2). As explained previously, the slope of the model-regression line in Fig. 2 expresses the UV-absorbance: DOC ratio of autochthonous DOC (AR' + AL' as explained below). This value is 12 ± 2 mABS cm^{-1} $mgC^{-1}l$ (± standard error of the slope; this value should be multiplied by 2.2 to estimate 95% confidence interval; ABS: Absorbance at 260 nm) and is considerably smaller than the values observed in Lake Kasumigaura's water (as shown below in Table 4). We suppose that the autochthonous DOC was produced by the biological processes in the water column rather than release from sediment, because there was little sediment in the ponds.

The long-term incubations of the inflow water revealed negligible concentrations of labile DOC (0.1 ± 0.1 mgC l^{-1}; n = 6) compared with those in the ponds (1.1 ± 0.6 mgC l^{-1}; n = 36, mean ± standard deviation). Then, we can suppose that the inflow water originally contained only pedogenic-refractory (PR) and autochthonous-refractory (AR) components and that the relationship between DOC and UV absorbance for the components would be described by the dotted line passing the origin of the coordinate axes and the point indicating the inflow water as shown in Fig. 2. Therefore, the pond waters would have contained PR, AR, AR', and AL' where AR' and AL' are the autochthonous DOC produced in the ponds and distinguished from AR and AL produced in Lake Kasumigaura. Then, the UV-absorbance: DOC ratio of this AL' component has been determined from the

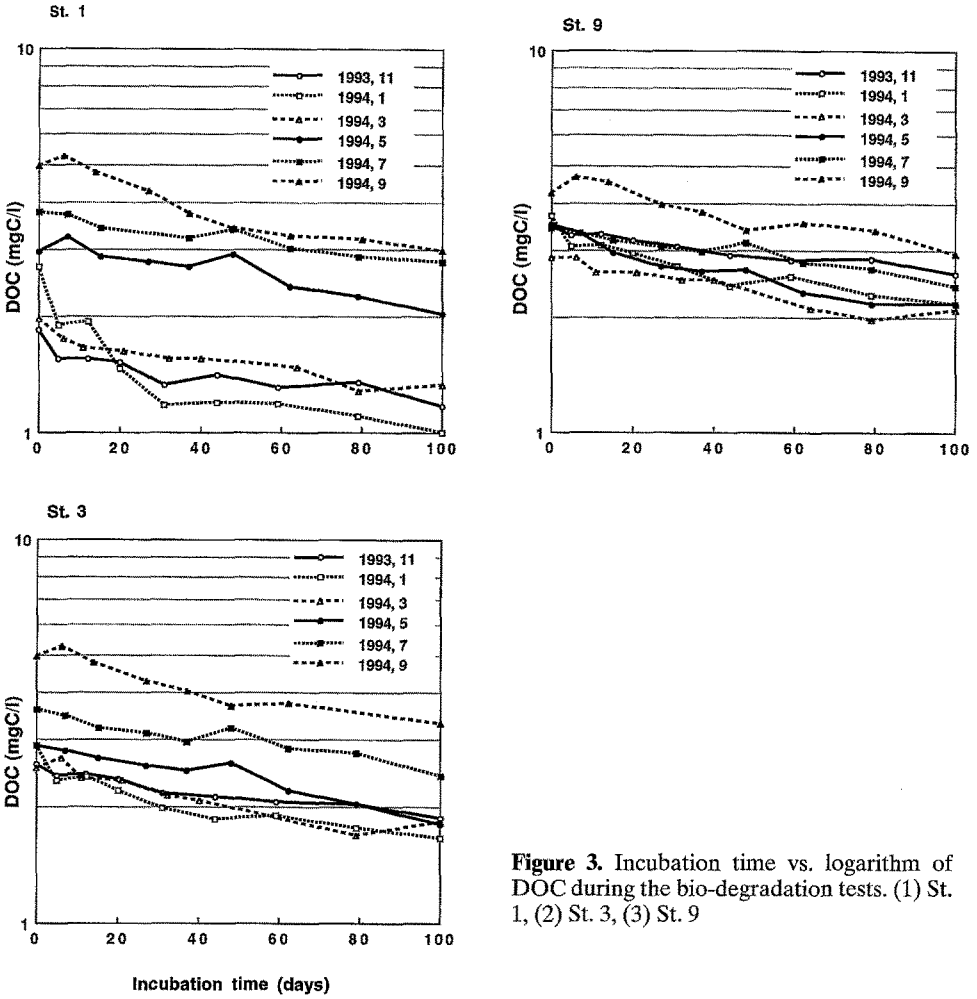

Figure 3. Incubation time vs. logarithm of DOC during the bio-degradation tests. (1) St. 1, (2) St. 3, (3) St. 9

change in UV-absorbance during the incubation/change in DOC during the incubation to be 12 ± 4 (n = 9) mABS cm^{-1} mg C^{-1} l. This value is only approximate, but it is fairly close to the ratio determined for AR' + AL' DOC above. Consequently, we can postulate a negligible change in the UV-absorbance: DOC ratio of autochthonous DOC during the bio-degradation process.

Biodegradation of DOC in lake and river waters

Similar to the results reported by Ogura (1975), Geller (1983), and Satoh et al. (1987), DOC declined relatively rapidly in the early stages of incubations until 20 days after the start when the rates slowed (Fig. 3). The rate constants for decomposition of DOC were calculated for both the early stage (T_1; from 0 to 20 days;

Table 1. First-order decomposition coefficients of DOC (d^{-1}). k_1: for the first 20 days. k_2: from 20 to 100 days. ±: standard deviation. n = 24

	k_1	k_2
St. 1	0.0084 ± 0.0069	0.0036 ± 0.0016
St. 2	0.0067 ± 0.0049	0.0035 ± 0.0012
St. 3	0.0050 ± 0.0036	0.0036 ± 0.0013
St. 7	0.0061 ± 0.0058	0.0032 ± 0.0014
St. 9	0.0041 ± 0.0043	0.0033 ± 0.0014
St. 12	0.0037 ± 0.0038	0.0033 ± 0.0012

k_1 = ln (DOC (0 day)/DOC (20 days))/20) and the latter stage (T_2; from 20 to 100 days; k_2 = ln (DOC (20 days)/DOC (100 days))/80), assuming the decomposition proceeds as a first-order reaction during each stage (Table 1). The values of k_1 ranged from 0.0037 d^{-1} at St. 12 to 0.0084 d^{-1} at St. 1, indicating a gradual but significant decrease with flow downstream (for example, $p < 0.05$ between St. 1 and St. 3 and $p < 0.01$ between St. 1 and St. 9 by unpaird sample t-test; similar values were obtained with the Mann-Whitney U-test). This decrease is probably due to the fact that the proportion of refractory DOC increases in the downstream direction. On the other hand, k_2 remains relatively constant at 0.003 – 0.004 d^{-1} at all lake stations ($p > 0.90$ between St. 1 and St. 3 and $p > 0.50$ between St. 1 and St. 9 by unpaired sample t-test).

Compared with previously reported values of k_1 = 0.01 – 0.09 d^{-1} and k_2 = 0.001 – 0.009 d^{-1} (T_1: 0 to 2 – 7 days; T_2: from 2 – 7 to 40 days; final percentage of recalcitrant DOC: 40 – 78%; Ogura, 1975) for the waters of a eutrophic inland bay and those of k_1 = 0.043 d^{-1} and k_2 = 0.004 d^{-1} for a eutrophic lake (T_1: 3 days; T_2: from 3 to 30 days; final percentage of recalcitrant DOC: 80%; Watanabe, 1984), the values of k_1 obtained were rather small, but those of k_2 were fairly similar to those from previous reports. The longer T_1 in our experiment would be expected to yield a smaller k_1. The nearly constant k_2 values represent the average decomposition rate of refractory DOC derived from the watershed and/or produced in situ.

Geller (1986) showed that 12 – 22% of the original dissolved organic macromolecules obtained from a mesotrophic lake were decomposed. Aging under mildly photolytic conditions increased the amount decomposed by a further 5–10%, and provision of glutamic acid enhanced degradation by an additional 3–20%. The acceleration of degradation upon supplementation with labile substances is due to cometabolism. Because of the high attenuation of UV-light in lake water, decomposition by photolysis is, however, likely to be rather small compared with the above results. In addition, the concentrations of glutamic acid provided were much higher than the total labile DOC concentration calculated for Lake Kasumigaura. Thus, the in situ enhancement of DOC degradability is unlikely to have been large, but we should keep in mind that our experiments somewhat underestimated DOC degradation rates in Lake Kasumigaura.

In this study, in consideration of the retention time of water in Lake Kasumigaura and also the low degradability after 60-days of incubation we termed as

Table 2. Summary of data on organic matter in L. Kasumigaura for October 1992 through September 1994 (n = 24)

St.	DOC mgC l^{-1}	UV mABS cm^{-1}	Fluo	Lignin mgC l^{-1}	Carbohydrate mgC l^{-1}	Protein mgC l^{-1}	R-DOC: 40 d mgC l^{-1}	R-DOC: 100 d mgC l^{-1}	L-DOC mgC l^{-1}	POC mgC l^{-1}	Chlorophyll-a $\mu g\ l^{-1}$	UV/DOC	Fluo/DOC
1	2.76 ± 1.04	64.7 ± 29.5	29.7 ± 12.9	0.10 ± 0.05	0.47 ± 0.27	0.94 ± 0.34	2.13 ± 0.95	1.80 ± 0.74	0.96 ± 0.41	4.86 ± 2.62	73.8 ± 45.8	22.8 ± 4.2	10.7 ± 2.3
2	3.00 ± 0.83	65.0 ± 20.6	29.1 ± 10.3	0.09 ± 0.03	0.46 ± 0.20	0.87 ± 0.35	2.35 ± 0.74	2.01 ± 0.57	0.98 ± 0.35	4.78 ± 2.11	78.2 ± 40.5	21.0 ± 3.4	9.5 ± 1.8
3	3.19 ± 0.71	65.4 ± 17.4	28.5 ± 8.2	0.09 ± 0.04	0.47 ± 0.19	0.83 ± 0.33	2.62 ± 0.60	2.23 ± 0.51	0.96 ± 0.35	4.82 ± 1.72	75.4 ± 30.2	20.5 ± 3.6	8.9 ± 1.8
7	3.05 ± 0.57	64.9 ± 14.6	27.9 ± 6.5	0.10 ± 0.05	0.41 ± 0.17	0.87 ± 0.31	2.47 ± 0.49	2.12 ± 0.36	0.93 ± 0.33	3.58 ± 1.32	55.0 ± 27.2	21.6 ± 5.4	9.3 ± 2.1
9	3.38 ± 0.38	61.5 ± 11.6	26.8 ± 6.3	0.08 ± 0.03	0.44 ± 0.11	0.75 ± 0.31	2.89 ± 0.34	2.46 ± 0.32	0.91 ± 0.32	4.37 ± 1.11	69.5 ± 22.2	18.2 ± 2.3	7.9 ± 1.5
12	3.43 ± 0.40	63.9 ± 10.3	27.8 ± 6.4	0.09 ± 0.05	0.44 ± 0.16	0.87 ± 0.39	2.97 ± 0.36	2.52 ± 0.33	0.89 ± 0.32	4.58 ± 1.07	65.0 ± 20.4	18.5 ± 2.3	8.0 ± 1.2
Corr. 1	*						**	**				**	***
Corr. 2	***					*	****	****				****	****

±: standard deviation, DOC: dissolved organic carbon, UV: absorbance at 260 nm, Fluo: Fluorescence-excitation: 260 nm, emission: 450 nm, relative concentration, Lignin: lignin or tannin-like compounds, R-DOC 40 d and 100 d: refractory DOC which remained after 40 day- and 100 day-incubations, respectively, L-DOC: labile DOC which decreased during 100 day incubation, POC: Patriculate organic carbon. Corr 1: correlation between St. 1 and St. 3, Corr. 2: correlation between St. 1 and St. 9, level, *: significant at the 10% level, **: 5% level, ***: 1% level, ****: 0.1% level.

refractory that DOC (R-DOC) which remained after 100-days of incubation. The labile DOC (L-DOC) was then calculated by difference (total DOC – R-DOC).

Spatial variations in Lake Kasumigaura DOC

While the concentrations of DOC and R-DOC were relatively high in the lake center and low near the mouths of the influent rivers, as discussed below, those of L-DOC were rather uniformly distributed (Table 2). Near uniform distributions were also observed for protein, carbohydrate, lignin/tannin-like compounds, UV-absorbance and fluorescence intensity.

It is well known that algae release extracellularly a large number of organic compounds like carbohydrates and proteins into the water. Because almost all such excreted substances are rapidly metabolized by microorganisms, they should be categorized as L-DOC. Thus, their turnover rates in lake water are so high that they do not accumulate and their concentrations should be proportional to primary productivity and/or the standing stock of phytoplankton. The concentrations of chlorophyll-a were highest in Takahamairi (St. 1, 2, 3), somewhat lower in the central basin (St. 9, 12) and lowest in Tsuchiurairi (St. 7), but the differences between stations were not significant (Table 2). We speculate that L-DOC production is closely related to primary production.

The proportions of L-DOC in total DOC in Lake Kasumigaura, which were somewhat smaller than those observed in one mesotrophic lake (30–50%; Geller, 1986) but higher than those observed in other mesotrophic and eutrophic lakes (8–9%; Sondergaard and Borch, 1992), decreased from 31% at St. 1 to 23% at St. 12.

Due to their specific plant sources and general refractory nature, lignins have been used as molecular-level tracers of land-derived DOC in a variety of marine, lacustrine and riverine environments (Ertel and Hedges, 1984). Therefore, we expected to find a uniform distribution of these compounds in Lake Kasumigaura, and this was the case (Table 2). In addition, the uniform distributions of UV-absorbance and fluorescence indicated that their decreases through biodegradation were nearly compensated by the autochthonous production of dissolved organic matter.

Seasonal variations of DOC in Lake Kasumigaura

At the stations in the bays (St. 1, 2, 3, and 7), the concentrations of POC and chlorophyll-a were highest in spring (April, May) and late summer (August, September) whereas the peaks were delayed to late spring (May, June) and fall (October, November) at the stations in the central basin (Fig. 4). On the other hand, DOC concentrations tended to be high in summer and low in winter, and the extent of seasonal variations was lower downstream. The coefficients of variation of DOC concentrations were very low in the central basin (St. 9: 11%. St. 12: 12%). While the same pattern of seasonal variation seen with DOC was observed for R-DOC and L-DOC, the variation in L-DOC was not so attenuated even in the central basin

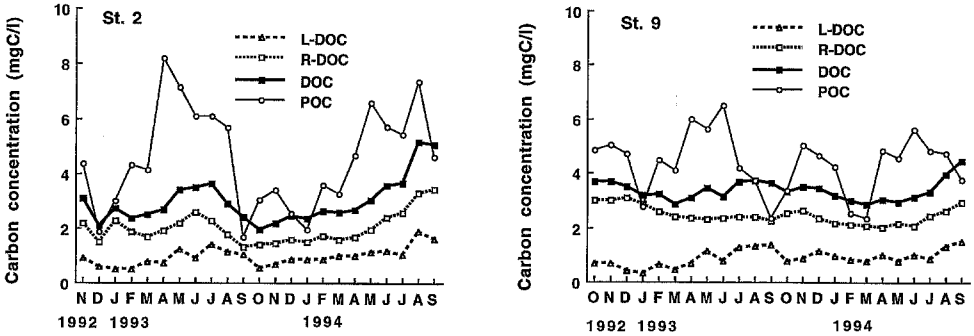

Figure 4. Seasonal variations of particulate organic carbon (POC), dissolved organic carbon (DOC), refractory DOC (R-DOC), and labile DOC (L-DOC). (1) St. 2, (2) St. 9

(coefficients of variation for L-DOC; St. 9: 35%, St. 12: 36%, and R-DOC; St. 9: 13%, St. 12: 13%).

DOC and R-DOC were highly correlated (Table 3) indicating that DOC variation depends largely on that of R-DOC. Although there are significant correlations between DOC and phytoplankton (as measured by POC and chlorophyll-a) near the mouths of influent rivers, they were hardly correlated in the central basin. By considering the time delay between production of particulate matter and dissolved matter, we calculated the cross correlation coefficients between them; in general the highest correlation was between DOC (or R-DOC, L-DOC) and the chlorophyll-a (or POC) one month earlier. For example, the correlation coefficients between POC and DOC at St. 3; 0 month: 0.38, 1 month: 0.64, 2 months: 0.46). In addition, these correlations were higher for R-DOC than for L-DOC (correlation coefficients with POC one month earlier at St. 3; R-DOC: 0.57, L-DOC: 0.44), and higher near the mounth of influent rivers than in the central basin (correlation coefficients between POC one month earlier and DOC; St. 1: 0.79, St. 3: 0.64, St. 9: 0.29).

The average DOC concentrations in 10 influent rivers were relatively higher in spring and summer (3.62 mgC l^{-1} in May, 1994, 3.38 mgC l^{-1} in August) than in fall and winter (2.19 mgC l^{-1} in October and 2.50 mgC l^{-1} in February, 1995). In addition, similar seasonal features were seen for R-DOC (data not shown). We suggest that the seasonal changs in DOC and/or R-DOC near the influent rivers should follow those of the rivers themselves with a small time lag. This kind of seasonal

Table 3. Correlation coefficients (n = 24)

	St. 1	St. 2	St. 3	St. 7	St. 9	St. 12
DOC vs. R-DOC	0.95**	0.96**	0.88**	0.85**	0.60**	0.75**
DOC vs. L-DOC	0.83**	0.88**	0.73**	0.81**	0.62**	0.58**
DOC vs. POC	0.79**	0.59**	0.38	0.53*	0.00	0.37
DOC vs. Chlorophyll-a	0.57*	0.42	0.15	0.41	0.23	0.39

* significance at the 1% level. ** significance at the 0.1% level.

change is probably due to the leaching of the concentrated DOC largely from the upper soil layer during periods of high discharge (Heikkinen, 1989).

Sondergaard et al. (1995) showed, from weekly surveys over three months, that L-DOC was positively related to decreases in chlorophyll-a and zooplankton grazing, and that L-DOC increases followed these decreasing concentrations by 3 weeks. Because there are many peaks of chlorophyll-a in a year and because the time interval between our surveys (1 month) is too long to detect such a correlation, we could not find a clear relationship between chlorophyll-a (or POC) and L-DOC in the central basin with any time lag.

Difference between pedogenic and autochthonous DOC

We obtained fairly high positive correlations between UV-absorbance and fluorescence ($r = 0.89$). Stewart and Wetzel (1980) indicated that fluorescence: UV-absorbance ratios changed seasonally in Lake Lawrence and that these ratios might depend on the molecular weight of humic matter. Similar conclusions were also reported for Lake Bret by Zumstein and Buffle (1989). However, there were no seasonal or spatial patterns of this ratio for Lake Kasumigaura. We would not expect sedimentation of DOC with $CaCO_3$ as occurred in Lake Lawrence and Lake Bret, to occur in Lake Kasumigaura.

Compared with the relation between UV-absorbance and fluorescence, lower but positive correlations were observed for the relationships between DOC and UV-absorbance and between DOC and fluorescence ($r = 0.7-0.8$; Fig. 5). Higher correlations were obtained for the upstream stations (r for DOC vs. UV-absorbance; St. 1: 0.95, St. 2: 0.92, St. 3: 0.76, St. 9: 0.73; all station mean: 0.77). In addition, the slopes of the regression lines of UV-absorbance vs. DOC seemed to decrease with flow downstream (St. 1: 27, St. 2: 21, St. 3: 19, St. 9: 19 mABS cm^{-1} mgC^{-1} l), which indicates a differene in dissolved organic matter between stations. The ratios of UV-absorbance: DOC and fluorescence: DOC also decreased in the downstream direction (Table 2). This trend could be explained by changes in the ratios during the dissolved organic matter bio-degradation processes in lake or by different mixing rates between pedogenic and autochtonous DOC.

In order to characterize pedogenic DOC, we investigated the same indices for river waters. The UV-absorbance: DOC ratios of riverine DOC largely surpassed those we measured for autochthonous DOC in the water of the outdoor experimental ponds (Table 4). These ratios were relatively large in spring and summer (average of 10 rivers; spring: 32 ± 5, summer: 30 ± 4, fall: 28 ± 4, winter: 25 ± 3 mABS cm^{-1} mg C^{-1} l). These higher ratios might be attributable to the larger proportion of components leached from soil with high UV-absorbance: DOC ratios. Nevertheless, the seasonal difference (maximum 7 mABS cm^{-1} mgC^{-1} l) was not as large as the difference between the pedogenic and autochthonous components (Table 4).

Very similar UV-absorbance: DOC ratios were observed for PR from all types of river basins we studied. However, in the case of PL, the rivers in watersheds with high proportions of urban land area had somewhat smaller ratios than did the rivers with agricultural or forested basins (Table 4). However, this small ratio for PL

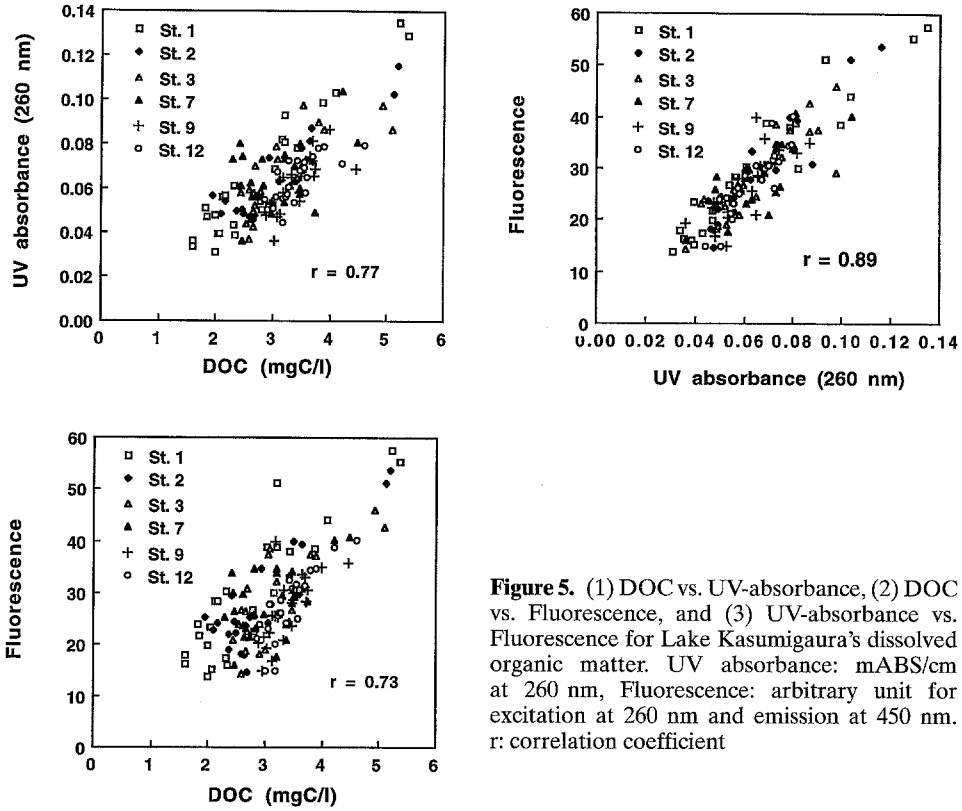

Figure 5. (1) DOC vs. UV-absorbance, (2) DOC vs. Fluorescence, and (3) UV-absorbance vs. Fluorescence for Lake Kasumigaura's dissolved organic matter. UV absorbance: mABS/cm at 260 nm, Fluorescence: arbitrary unit for excitation at 260 nm and emission at 450 nm. r: correlation coefficient

from urban rivers (23 mABS cm^{-1} mgC^{-1} l) far exceeded the ratios for AL and AR (12 mABS cm^{-1} mgC^{-1} l), and is probably attributable to the labile DOC discharged from households. In addition, there was no significant difference between the UV-absorbance: DOC ratio before or after 100-day incubations (before: 29 ± 5, after: 28 ± 4 mABS cm^{-1} mgC^{-1} l; $p > 0.70$ by paired t-test). Thus for almost all riverine DOC, we can expect a negligible change in this during the movement of water from the influent rivers to the lake center.

McKnight et al. (1994) reported such UV-absorbance: DOC ratios for the fulvic acids isolated by XAD-8 resins from different kinds of water bodies and indicated that autochthonous fulvic acids have lower ratios than do pedogenic ones (Table 4). These ratios have been scarcely altered by extraction with XAD-4 (Fukushima et al., 1995b). Zumstein and Buffle (1989) summarized the ratios for 12 oceanic samples and reported a more than one-order of magnitude difference between them and the ratios for pedognic DOC. Our data supported these results, and in addition demonstrated the constancy of the UV-absorbance: DOC ratio during bio-degradation processes. This constancy is extremely important because we can now use this index regardless of the degree of decomposition DOC has undergone. Finally, the rather large increase in the lake water UV-absorbance: DOC ratio during the long-term incubation can be explained by a gradual rise in the proportion of pedogenic

Table 4. UV absorbance at 260 nm divided by DOC concentration (mABS cm^{-1} mgC^{-1} l)

Type	Sample	UV: DOC	Reference	WL*[1]
Pedogenic	Pedogenic refractory organic matter	28–50	Buffle et al. (1982)	285 nm
	Bog water	34	Gorham et al. (1985)	340 nm
	River water	58	Tipping et al. (1988)	340 nm
	River water	30	Zumstein and Buffle (1989)	285 nm
	Suwannee River water; XAD 8	40	McKnight et al. (1994)	260 nm
	PR from Agricultural-river*[2]	29±5	This sthdy	260 nm
	PR from Forest river*[3]	27±4	This study	260 nm
	PR from Urban-river*[4]	27±4	This study	260 nm
	PL from Agricultural-river	32±8	This study	260 nm
	PL from Forest-river	32±13	This study	260 nm
	PL from Urban river	23±8	This study	260 nm
Autochthonous	Ocean and/or Sea	0.4–8	Zumstein and Buffle (1989)	285 nm
	Antarctic pond water; XAD 8	17	McKnight et al. (1994)	260 nm
	AR from experimental ponds	12±4*[5]	This study	260 nm
	AL from experimental ponds	12±4	This study	260 nm
Lake water	L. Kasumigaura near river mouth (St. 1)	23±4	This study	260 nm
	L. Kasumigaura center (St. 9)	18±2	This study	260 nm

*[1]: measured wavelength. The data were corrected to absorbance at 260 nm using the relation $a(x) = a(x_1) \exp 0.014 (x_1 - x)$, *[2]: Agricultural area occupies more than 50% of the watershed, *[3]: Forest occupies more than 35% of the watershed, *[4]: Urbanized areas occupy more than 35% of the watershed. PR: Pedogenic refractory organic matter, PL: Pedogenic labile organic matter, AR: Autochthonous refractory organic matter, AL: Autochthonous labile organic matter. ±: standard deviation except for *[5]. *[5]: standard error of the slope of model-regression line.

constituents (for example, St. 1 before: 23±4, after: 29±5 mABS cm^{-1} mgC^{-1} l; $p < 0.0001$; St. 9 before: 18 ± 2, after: 22 ± 2 mABS cm^{-1} mgC^{-1} l; $p < 0.0001$ by paired t-test).

Quantification of Lake Kasumigaura DOC into four components

If UV-absorbance: DOC is applied as the characteristic ratio and the values of DOC_{ini}, DOC_{last}, X_{ini}, and X_{last} are given, we can determine PR, PL, AR, and AL by solving eq. (1)–(4). From Table 4, the average values of X_{PR}, X_{PL}, X_{AR}, and X_{AL} are 29, 29, 12, and 12 (mABS cm^{-1} mgC^{-1} l), respectively. Hence, we can use X_{pedo} instead of X_{PR} and X_{PL}, and X_{auto} instead of X_{AR} and X_{AL}. As mentioned previously, the change in this ratio during the bio-degradation process is actually negligible.

We applied this model to Lake Kasumigaura. At the center of the lake, PR is the largest component with rather small seasonal variations (Fig. 6; coefficient of variation: 23%). AR increased from fall to winter, when AR exceeded PR by a small extent. PL increased intermittently, but the major part of the labile DOC was AL. The seasonal changes between the DOC concentrations at Stns. 2 and 9 were not so different.

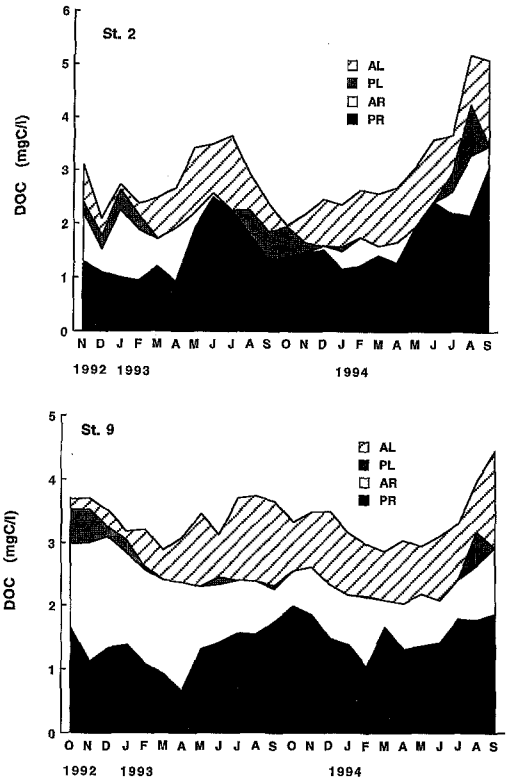

Figure 6. Seasonal change in each component of DOC. Constituents are explained in the text. (1) St. 2 and (2) St. 9

PR seems to be uniform or to diminish very slightly downstream from 1.64 mgC l^{-1} at St. 1 to 1.44 mgC l^{-1} at St. 9 and 1.54 mgC l^{-1} at St. 12 (St. 7: 1.67 mgC l^{-1}) (Fig. 7). As explained previously, the time necessary to flow down from stations 1 or 2 to stations 9 or 12 is roughly 3 months; thus, the refractory components entering the lake from the influent rivers would remain as they were. On the contrary, AR increases from nearly zero (0.17 mgC l^{-1} at St. 1) to approximately 1 mgC l^{-1} at stations 9 and 12 (St. 7: 0.46 mgC l^{-1}). This increase is possibly attributable to release from algae during their growth and decomposition (Cole et al., 1984), sloppy feeding by zooplankton grazing on phytoplankton (Park et al., 1996), release from sediments (Orem et al., 1984) and/or sorption of autochthonous DOC onto pedogenic DOC, etc., but the extent of each of these processes was not determined.

On the other hand, PL decreases from 0.32 mgC l^{-1} at St. 1 to 0.07 mgC l^{-1} at St. 12. The non-zero value at St. 12 can probably be ascribed to the influx near this station. The concentrations of AL (0.79 ± 0.40 mgC l^{-1} at St. 2, 0.73 ± 0.43 mgC l^{-1} at St. 3, 0.71 ± 0.48 mgC l^{-1} at St. 7, 0.82 ± 0.39 mgC l^{-1} at St. 9 and 0.85 ± 0.29 mgC l^{-1} at St. 12) are essentially uniform throughout the lake except at St. 1 (0.64 ± 0.36 mg C l^{-1}; significantly different from AL concentrations at Stns. 2, 9 and 12; not significant differences among Stns. 2, 3, 7, 9, and 12 at a significance level of

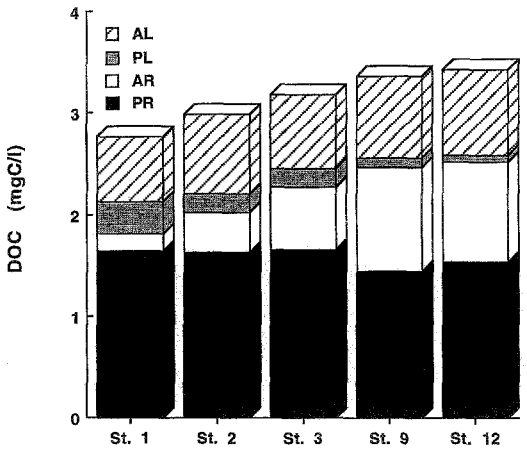

Figure 7. Downstream change in each DOC component. Constituents are explained in the text

5% by paired t-test). The rather low AL at St. 1 suggests an excess of production over loss i.e. downstream increase AL around St. 1 near the influent river mouth.

Even if there were to be a difference between X_{PR} and X_{PL}, or between X_{AR} and X_{AL}, this method of quantifying the pedogenic and autochthonous fractions might still be valid. Such a case might arise when domestic waste is the main source of pedogenic DOC and/or when the labile component from this source remains largely near the points where it enters the lake. The approximate constancy of the UV-absorbance: DOC ratio during the degradation process would be assumed for lakes with high proportions of forested and agricultural areas. However, this assumption must be checked, particularly for pedogenic DOC, because errors in the value used can result in substantial errors in the calculated proportions of the various components of DOC.

Conclusions

The DOC in a shallow, eutrophic lake was chemically analyzed and the proportions comprised by refractory and labile components were quantified with long-term incubations. Simultaneously, the same analysis was applied for river and pond waters which are representative of pedogenic and autochthonous DOC, respectively. Using the UV-absorbance: DOC ratio as an indicator, the proportions in lake water DOC in each of four components, i.e. PR, PL, AR, and AL, we successfully quantified, and their seasonal and spatial dynamics were evaluated with 4 component model. Because the AR concentration is comparable with that of PR, the production of AR DOC should, therefore, be considered as a potentially important element in the carbon cycle of this lake and other water bodies, as is trihalomethane formation during the chlorination process used by water supply systems, etc. The quantification of DOC components by origin provides insights useful for lake management to prevent eutrophication and reduce organic pollution; thus, this method presents a most effective tool for lake restoration.

We have confirmed that the UV-absorbance: DOC ratio changes only slightly during biodegradation of pedogenic and autochthonous DOC. This characteristic argues for the validity of quantification of DOC components by use of this ratio without any consideration of biotic change (two component model; pedogenic – autochthonous). However, we suppose that this is not always the case for other water bodies; hence, variations in the ratio must be checked before applying the two component model elsewhere. Moreover, the applicability of the two or four component model should be investigated in many types of aquatic systems.

Although the dynamics of DOC have been explained, to some extent, their relationships with other characteristics such as molecular weight, hydrophobicity, etc. remain unknown. More studies should be undertaken to clarify the mechanisms of AR production. Furthermore, other methods should be developed to estimate the proportions of various pedogenic DOC sources quantitatively.

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