Seasonal and Diel Changes of Dissolved Organic Matters and Urea in a Small Eutrophic Pond

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Abstract

Seasonal changes of DOC, DON, DOP and urea were measured on the outside and the inside of the cylinder set up in a small eutrophic pond, and diel observation of these dissolved organic matters was carried out in August when dense phytoplankton blooming was observed.

Seasonal changes of DOC : DON : DOP atomic ratio ranged widely from 780 : 20 : 1 in spring to 2100 : 33 : 1 in autumn, mainly due to the variations of DON and DOP concentrations. Urea concentrations decreased in summer and autumn. The percentage of urea carbon in DOC was from 0.2% to 6.3% and urea nitrogen in DON was 2% to 39%. Urea was one of the major compound in DON. The lower percentages were observed in the period with lower urea concentrations. This suggests that urea is a changeable compound in dissolved organic nitrogen compounds.

On the outside DON concentrations were higher from midnight to morning but lower on the inside during the nighttime. Whereas DOC and DOP showed no clear diel changes. The variation of urea revealed no significant periodicity. The concentrations of dissolved organic matters showed higher values in the upper layer than in the lower one during the diel observation when the strong chemical stratification was found. Urea showed a distinctive vertical profile, with values in the middle layer higher than in the upper and lower layers.

Introduction

Observation of the distribution and the behavior of dissolved organic carbon (DOC), nitrogen (DON) and phosphorus (DOP) would presumably further knowledge of biogeochemical cycles of carbon, nitrogen and phosphorus in natural waters. Several workers have reported the distribution of dissolved organic matters in the sea (DUURSMA, 1961[1]; HOLM-HANSEN *et al*., 1966[2]; BANOUB and WILLIAMS, 1973[3]). According to DUURSMA (1961)[1] and BANOUB and WILLIAMS (1973)[3], the seasonal changes of dissolved organic matters are related to phytoplankton blooming. However, little study of the distribution of DOC, DON and DOP in freshwater lake has been reported. HOLM-HANSEN *et al*. (1976)[4] measured dissolved organic matters and phytoplankton biomass in Lake Tahoe and found the gradient with depth in the distribution of dissolved organic matters

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persisting throughout the year dispite the physical mixing of the water column. MITAMURA and SAIJO (1981)[5] studied the seasonal changes of DOC, DON, DOP and urea in relation to phytoplankton blooming in Lake Biwa. They suggested a close relationship between the distribution of dissolved organic matters and the biological activity of phytoplankton.

In freshwater, the seasonal changes of urea were reported by BERMAN (1974)[6] in Lake Kinneret, SATOH and HANYA (1981)[7] in Lake Yunoko, and MITAMURA and SAIJO (1981)[5] in Lake Biwa. Urea is actively utilized as an important nitrogen source for the natural phytoplankton community (e.g., MCCARTHY, 1972[8]; EPPLEY *et al.*, 1973[9]; MCCARTHY *et al.*, 1977[10]; MITAMURA and MATSUMOTO, 1981[11]) and is decomposed concerning the photosynthesis by phytoplankton (MITAMURA and SAIJO, 1975[12]; WEBB and HAAS, 1976[13]). Urea is usually a changeable compound and one of the major constituents of DON. Urea in a key indicator for understanding the behavior of dissolved organic matters in natural waters.

To know in more detail the bahavior of these matters in natural freshwater, in the present study the seasonal changes of DOC, DON, DOP and urea were investigated in a small eutrophic pond, where phytoplankton blooming appeared in summer. MANNY and WETZEL (1973)[14] studied the diel changes of DOC and DON in a hardwater stream in southern Michigan. However, data on the diel changes of dissolved organic matters and urea are very few. In this study, the diel observation was carried out in a dense phytoplankton blooming period to obtain information on the changes of dissolved organic matters and urea in relation to the diel changes of biological activity.

Methods

Measurement of dissolved organic matters was carried out in a small eutrophic pond (13,500m^2; average depth, 2m) located in Osaka. A transparent plastic cylinder (3m, high; 1.7m, dia.) was set up near the center of the pond to avoid the influence of the horizontal water movement by wind and the supply of allochthonous substances. The observations were carried out on the outside (open station) and the inside (closed station) of the cylinder. Water samples for measurements of seasonal changes of dissolved organic matters were collected every 0.5m depth from the surface to near the bottom once a month from December 1972 to November 1973. Diel changes were measured at the same depths at each station at 2 or 3 hour intervals on August 4 and 5 in 1973.

The collected samples were immediately filtered through Whatman GF/C glass-fiber filters. The filters and filtrates were frozen and stored at $-20^{\circ}C$ for subsequent chemical analyses. DOC was determined by the dichromate oxidation method, DON by the Kjeldahl technique, DOP according to MENZEL and CORWIN (1965)[15], and urea by the method of NEWELL *et al.* (1967)[16]. Ammonia was determined by the method of SAGI (1966)[17], nitrite according to BENDSCHNEIDER and ROBINSON (1952)[18], nitrate by WOOD *et al.* (1967)[19], and phosphate by MURPHY and RILEY (1962)[20]. Chlorophyll-a was determined by the method of SCOR-UNESCO (1964)[21]. Dissolved oxygen was measured by the WINKLER method with azide modification. Water temperature and pH values were also measured at every sampling time.

Results

Seasonal changes of dissolved organic matters and urea

The strong stratification of dissolved oxygen and pH values was found during June to August as shown in the previous study (MITAMURA and MATSUMOTO, 1976)[22]. High chlorophyll-a amounts (more than 200 mg chl.a•m^{-3}) were found in the euphotic layer (0 to 1 m depth judging from transparency) at both stations in August. In summer, the blue-green alga *Microcystis aeruginosa* was dominant, and notable depressions of dissolved inorganic nitrogen, showing the average value 4.4 μg at.N•l^{-1} which was only about one thirtieth of the yearly average value, were observed in the euphotic layer at both stations. Ammonia was a major constituent of total dissolved nitrogen (as the sum of dissolved inorganic and organic nitrogen) in the euphotic layer at both stations throughout the year except summer. In summer, ammonia concentrations were consistently low, accounting for only about 10% in total dissolved nitrogen. This suggests that ammonia is actively consumed as a nitrogen source for phytoplankton.

Seasonal changes of DOC, DON and DOP were shown in Tables 1 and 2. The concentrations of DOC ranged from 1.00 to 2.71 mg at.C•l^{-1}. The concentrations of DON ranged from 17.2 to 45.9 μg at.N•l^{-1}, and lower values were observed in late autumn and winter. MITAMURA and SAIJO (1981)[5] observed the yearly lowest value of DON during the phytoplankton blooming period in Lake Biwa. In the present study, the concentrations of DON slightly decreased during phytoplankton blooming at the closed station, but there was no clear correlation between the seasonal changes of DON and chlorophyll-a at the open station. The concentrations of DOP ranged from 0.73 to 1.93 μg at.P•l^{-1} except in May, and lower values were continually observed in summer and autumn. The extremely high DOP concentrations found at the closed station in May were presumably caused by wagtail excretion. Seasonal changes of phosphate resembled that of DOP at both stations, although the concentration of phosphate was almost a quarter of the DOP level. The DOC, DON and DOP concentrations in this pond were considerably higher than those obtained by HOLM-HANSEN *et al.* (1974)[4] in Lake Tahoe or by MITAMURA and SAIJO (1981)[5] in Lake Biwa. The pond under study was a rather eutrophic one.

There were no clear correlations between DOC and DON nor between DOC and DOP at either station. The correlation coefficient between DON and DOP was high ($r=0.73$) at the closed station except for May, but low ($r=0.23$) at the open station. As seen in Fig. 1, the atomic ratios of DOC/DON, DOC/DOP and DON/DOP changed from 26 to 85, 360 to 2700 and 14 to 37, respectively, at both stations. Seasonal changes of these ratios showed similar patterns, showing low values in spring and high values in summer and autumn. The seasonal changes of DOC : DON : DOP atomic ratio was ranging from 510 : 16 : 1 in May to 2500 : 32 : 1 in October. Our yearly average DOC : DON : DOP atomic ratios (1100 : 24 : 1 at the closed station and 1300 : 22 : 1 at the open one) resemble those obtained by MITAMURA and SAIJO (1981)[5] in Lake Biwa (843 : 35.8 : 1 in the northern basin and 496 :

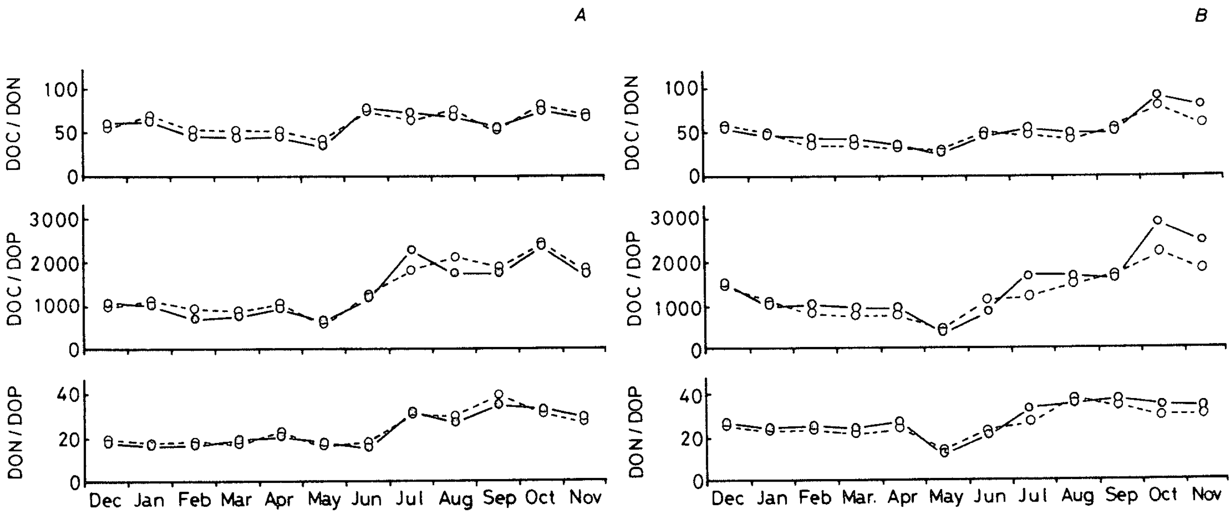

Fig. 1 Seasonal changes of DOC/DON, DOC/DOP and DON/DOP atomic ratio at the open station (*A*) and the closed station (*B*). (⊙) and (○) indicates the average value for 0–1 m and 1–2 m depth.

22.8 : 1 in the southern basin).

The urea concentrations ranged from 0.39 to 7.03 μmole • l^{-1} showing the highest value in April and the lowest in October at both stations (Tables 1 and 2). Urea decreased as of June, following the abrupt decrease of ammonia. The seasonal change of urea was similar to those of ammonia, nitrite and nitrate. It is considered that urea is one of the major nitrogen sources for phytoplankton. The average percentage of urea nitrogen in total nitrogenous nutrients (as the sum of ammonia, nitrite, nitrate and urea) was 3% in autumn and winter to 32% in mid-summer in the euphotic layer at both stations. These values were comparable to those obtained in Lake Yunoko by SATOH and HANYA (1981)[7]

The patterns of seasonal changes of urea nitrogen in DON resemble those of urea carbon in DOC at both stations (Fig. 2). Urea carbon ranged from 0.2% to 6.3% in DOC and urea nitrogen from 2% to 39% in DON. It seems that urea is one of the major compounds in DON. The seasonal change of DON values substracting urea nitrogen was not as appreciable as those of DON and urea. These results suggest that urea is the most

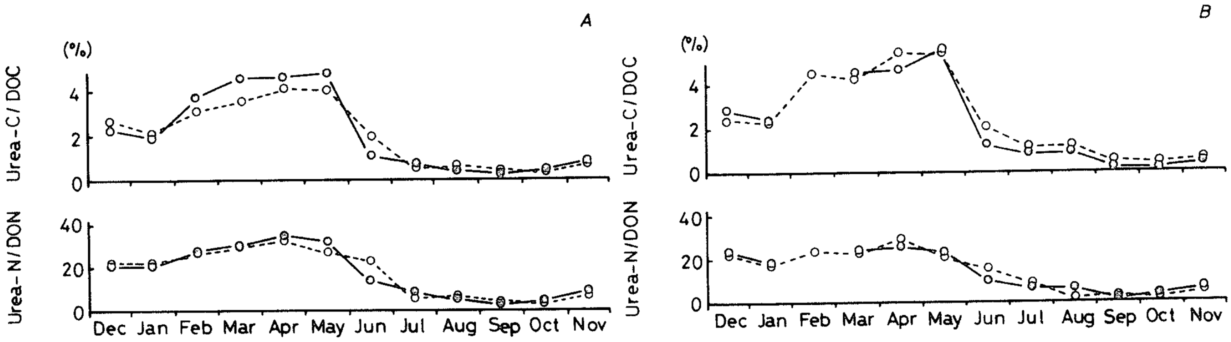

Fig. 2 Seasonal changes of urea carbon in DOC and urea nitrogen in DON at the open station (*A*) and the closed station (*B*). (⊙) and (○) indicates the average percentage value for 0– 1 m and 1–2 m depth.

Table 1 Seasonal changes in DOC (mg at .$\cdot l^{-1}$), DON, DOP (μg at.$\cdot l^{-1}$), and urea concentration (μ mole$\cdot l^{-1}$) at the open station from December 1972 to November 1973.

Depth (m)	Dec.	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.
Dissolved organic carbon												
0.0	1.42	1.17	1.08	1.25	1.42	1.17	1.50	2.17	2.00	2.00	1.75	1.33
0.5	1.33	1.42	1.17	1.25	1.33	1.17	1.50	2.71	1.83	1.83	1.83	1.50
1.0	1.17	1.17	–	1.25	1.33	1.08	1.58	2.17	1.83	1.25	1.75	1.50
1.5	–	1.25	–	1.58	1.92	1.33	1.42	1.92	2.08	2.08	1.92	1.42
2.0	1.17	1.50	1.17	1.46	1.50	1.17	1.42	1.67	2.08	1.42	2.00	1.58
Dissolved organic nitrogen												
0.0	21.8	19.5	22.3	29.0	38.2	27.9	20.2	32.1	29.8	32.5	24.9	23.1
0.5	19.7	19.2	28.5	29.8	25.4	32.6	17.2	35.2	29.0	32.8	23.6	22.4
1.0	20.4	19.7	–	27.7	28.7	28.7	21.6	32.5	27.1	31.4	24.3	23.0
1.5	22.5	19.5	–	30.3	38.5	31.7	20.9	33.1	27.7	32.6	25.4	22.0
2.0	21.9	21.2	22.9	27.2	29.8	28.4	21.0	27.8	29.1	32.7	22.7	22.7
Dissolved organic phoshorus												
0.0	1.12	1.16	1.57	1.57	1.57	1.61	1.25	1.02	1.13	0.99	0.73	0.75
0.5	1.16	1.25	1.48	1.50	1.34	1.70	1.12	0.97	1.04	0.94	0.75	0.82
1.0	1.03	1.12	1.52	1.55	1.34	1.57	1.34	1.10	1.00	0.87	0.73	0.80
1.5	1.07	1.21	–	1.48	1.61	1.52	1.12	1.08	0.93	0.85	0.80	0.95
2.0	1.21	1.34	1.25	1.59	1.43	2.55	1.03	0.92	0.86	0.74	0.79	0.69
Urea												
0.0	–	1.94	2.86	4.52	6.06	4.90	1.94	0.86	0.66	0.50	0.53	0.92
0.5	–	2.17	4.18	4.31	5.00	5.04	0.79	1.25	0.43	0.40	0.53	0.79
1.0	2.27	2.24	–	4.20	4.97	4.15	1.55	1.32	1.06	0.40	0.46	0.69
1.5	–	2.21	–	4.28	–	4.31	2.93	1.19	0.99	0.50	0.43	0.76
2.0	2.73	2.57	3.09	4.18	4.84	3.72	2.70	0.56	0.99	0.63	0.43	0.76

Table 2 Seasonal changes in DOC (mg at .$\cdot l^{-1}$), DON, DOP (μg at.$\cdot l^{-1}$), and urea concentration (μ mole$\cdot l^{-1}$) at the closed station.

Depth (m)	Dec.	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.
Dissolved organic carbon												
0.0	1.42	1.08	1.33	1.67	1.58	1.00	1.42	1.83	1.67	1.25	2.25	2.17
0.5	1.50	1.42	1.67	1.79	1.33	1.08	1.33	1.67	1.50	1.25	2.67	2.00
1.0	–	1.17	1.17	1.21	1.17	1.00	1.50	1.42	1.25	1.58	1.58	1.33
1.5	1.58	1.67	1.08	1.33	1.25	1.17	1.33	1.25	1.42	1.50	1.67	1.33
2.0	1.75	1.17	1.25	1.25	1.33	1.00	1.33	1.08	1.17	1.59	1.92	1.25
Dissolved organic nitrogen												
0.0	28.7	24.1	30.5	38.6	42.6	41.8	33.8	34.5	36.1	28.7	26.0	25.1
0.5	27.0	27.9	37.0	41.6	40.5	41.7	37.5	31.7	29.7	32.1	25.9	27.9
1.0	25.7	28.1	32.0	34.8	38.7	45.9	27.5	30.2	32.2	31.7	23.3	20.9
1.5	33.0	27.3	33.7	39.5	38.6	40.9	35.0	27.5	32.1	31.3	21.6	23.5
2.0	25.6	25.6	30.0	38.3	37.6	33.2	26.5	23.2	30.6	32.3	21.6	21.9
Dissolved organic phosphorus												
0.0	0.90	1.21	1.52	1.73	1.61	3.22	1.43	1.04	1.01	0.87	0.74	0.83
0.5	1.03	1.21	1.70	1.53	1.48	3.04	1.93	1.03	0.91	0.83	0.76	0.72
1.0	1.07	1.16	1.25	1.66	1.66	3.27	1.43	0.99	0.90	0.86	0.77	0.76
1.5	1.12	1.34	1.57	1.70	1.52	2.60	1.25	0.99	0.88	0.96	0.74	0.78
2.0	1.12	1.25	1.70	1.70	1.57	2.37	1.12	1.05	0.81	0.96	0.77	0.67
Urea												
0.0	3.83	2.71	–	5.05	6.57	4.90	1.44	2.22	1.41	0.49	0.43	0.98
0.5	3.14	2.45	–	4.90	5.20	4.94	1.24	0.53	1.02	0.39	0.63	1.02
1.0	–	2.45	–	5.13	4.58	4.90	2.03	1.05	1.15	0.53	0.50	0.59
1.5	3.79	2.68	4.15	4.56	5.59	5.20	2.32	1.38	–	0.59	0.39	0.59
2.0	3.27	2.68	–	4.64	7.03	–	2.88	1.31	1.47	0.62	0.49	0.69

changeble compound in DON, which changed with biological activity.

Diel changes of dissolved organic matters and urea

The diel measurements of dissolved organic matters and urea concentrations were carried out in August, when strong stratification of dissolved oxygen and pH values was found. The average dissolved oxygen concentration showed 10.6 mg $0_2 \cdot l^{-1}$ (140% saturation) at 0m depth, but only 0.2 0_2 mg $\cdot l^{-1}$ (2%) at 2m depth. The thermocline also advanced near the 1m depth. The daily average amounts of chlorophyll-a in the euphotic layer ware 122 and 56 mg chl. a $\cdot m^{-3}$ at the closed station and the open station, respectively. In the upper layer, the diel change of ammonia was observed, showing low values from noon to early night and high values just after sunrise, whereas no obvious changes in nitrite, nitrate and phosphate concentrations were found as reported in the previous study by MITAMURA and MATSUMOTO (1976)[22]. The diel change of ammonia in the euphotic layer suggests the utilization of ammonia by phytoplankton during the daytime. This finding agrees with those of BEERS and KELLY (1965)[23], GOERING *et al.* (1964)[24], EPPLEY *et al.* (1971)[25], and MASHIKO (1975)[26].

The diel changes of DOC, DON, DOP and urea were shown in Tables 3 and 4. DOC and DOP showed no clear changes at either station. The DON concentrations were higher from midnight to morning at the open station, but lower during the night at the closed station. MANNY and WETZEL (1973)[14] indicated that the DOC concentration was constant parameter during the diel period and the concentrations of DON considerably changed at each station. DOC seems to be rather stable matter than DON in the eutrophic pond. These dissolved organic matters slightly decreased with depth as can be seen in Tables 3 and 4.

The DOC/DON, DOC/DOP and DON/DOP ratios were calculated. The diel changes of DOC/DON and DON/DOP ratios were closely related to the changes of DON concentrations at both stations. DON seems to be the most changeable of dissolved organic matters. The daily average atomic ratio of DOC : DON : DOP was calculated as 1600 : 9 : 1 at the closed station and 1300 : 11 : 1 at the open station. These ratios were lower in DON compared with the yearly average DOC : DON : DOP ratios.

Urea showed no clear diel periodicity during the observation period, although the diel variation of urea was expected to observe the similar trend with ammonia. As seen in Tables 3 and 4, average urea concentrations in the middle layer were consistently high, showing 1.2- and 1.7-fold higher levels than in the upper layer and near the bottom.

Discussion

DUURSMA (1961)[1] in DOC and DOP, and BANOUB and WILLIAMS (1973)[3] in DOC and DON, observed higher concentrations after the phytoplankton blooming in the sea. They suggested that the increased concentration of dissolved organic matters was due to the breakdown of phytoplankton. TAKAHASHI and SAIJO (1981)[27] reported that the DON maximum was accompanied with a particulate organic nitrogen maximum, the major part of which was constituted by phytoplankton, in Lake Kizaki. MITAMURA and SAIJO (1981)[5] reported no increase of dissolved organic matters during or after the phytoplankton

Table 3 Diel changes in DOC (mg at .$\cdot l^{-1}$), DON, DOP (μg at.$\cdot l^{-1}$), and urea concentration (μ mole$\cdot l^{-1}$) at the open station from August 4 to 5 1973.

Depth (m)	13:00	15:00	17:00	19:00	21:00	0:00	3:00	5:00	7:00	9:00	11:00	13:00
Dissolved organic carbon												
0.0	2.12	2.21	2.02	2.15	2.02	2.19	1.94	2.13	2.06	2.01	1.93	2.13
0.5	2.08	2.20	2.03	2.23	2.06	1.99	1.87	2.13	2.01	2.16	1.94	2.24
1.0	1.94	1.95	2.01	1.98	1.98	1.79	1.88	1.94	1.98	1.82	1.94	2.41
1.5	2.05	1.88	1.84	1.94	1.97	1.83	1.87	1.87	1.86	1.87	1.91	2.30
2.0	1.94	1.78	1.81	1.77	1.87	1.72	1.77	1.77	1.79	1.65	1.85	2.32
Dissolved organic nitrogen												
0.0	16.3	14.4	13.8	14.0	12.6	19.6	18.6	20.7	19.9	17.4	18.2	18.5
0.5	14.8	14.0	14.2	13.8	—	18.9	17.8	19.2	19.4	18.4	17.8	19.8
1.0	13.3	13.5	13.7	13.5	12.9	18.5	18.2	18.7	18.7	18.3	18.3	18.2
1.5	—	13.8	12.4	13.5	12.7	17.8	17.9	19.6	18.1	17.9	18.7	17.7
2.0	—	12.3	12.3	12.4	11.8	15.8	17.5	17.5	12.3	15.0	16.5	17.6
Dissolved organic phosphorus												
0.0	1.46	1.73	1.54	1.59	1.51	1.43	1.41	1.51	1.54	1.52	1.52	1.73
0.5	1.59	1.58	1.54	1.63	1.45	1.52	1.47	1.45	1.41	1.54	1.48	1.59
1.0	1.65	1.66	1.58	1.54	1.46	1.44	1.40	1.36	1.48	1.56	1.57	1.43
1.5	1.67	1.51	1.49	1.45	1.51	1.68	1.45	1.45	1.62	1.48	1.54	1.43
2.0	1.53	1.36	1.46	1.68	1.41	1.40	1.53	1.23	1.46	1.34	1.46	1.42
Urea												
0.0	2.96	2.54	2.56	2.36	2.46	2.86	2.42	2.61	2.33	2.45	2.24	1.95
0.5	2.95	2.56	3.25	2.46	3.67	2.64	2.53	2.62	2.55	2.56	2.54	2.35
1.0	3.32	3.12	2.85	2.97	2.97	2.95	2.34	2.46	3.01	2.67	2.57	2.29
1.5	3.88	3.42	3.36	3.08	3.06	2.83	2.46	2.76	2.45	2.80	2.85	2.50
2.0	2.34	2.94	2.00	1.85	2.44	2.15	1.74	0.86	1.21	1.28	1.19	1.47

Table 4 Diel changes in DOC (mg at .$\cdot l^{-1}$), DON, DOP (μg at.$\cdot l^{-1}$), and urea concentration (μ mole$\cdot l^{-1}$) at the closed station.

Depth (m)	13:00	15:00	17:00	19:00	21:00	0:00	3:00	5:00	7:00	9:00	11:00	13:00
Dissolved organic carbon												
0.0	2.51	2.73	1.71	2.29	2.45	2.47	2.48	2.67	1.95	2.56	2.49	2.33
0.5	2.43	2.59	1.78	2.25	2.49	2.57	2.38	2.66	2.33	2.48	2.31	2.45
1.0	2.18	1.68	1.76	2.29	2.23	2.33	2.38	1.97	2.14	2.19	2.31	2.49
1.5	2.29	1.78	1.77	2.32	1.68	2.34	2.42	1.68	2.08	2.22	2.20	1.88
2.0	2.45	1.68	1.84	2.16	2.38	2.19	2.52	1.85	2.18	2.07	2.27	2.08
Dissolved organic nitrogen												
0.0	20.9	14.1	12.5	14.0	14.0	12.9	11.1	12.9	9.4	10.5	14.8	8.5
0.5	18.3	14.5	13.6	13.4	13.6	11.8	10.8	9.0	9.1	13.3	12.2	11.3
1.0	16.4	15.1	14.5	13.2	15.0	9.8	9.8	11.9	9.9	14.2	11.8	11.0
1.5	15.6	14.4	12.9	13.4	–	10.9	–	8.9	10.0	12.8	11.3	11.1
2.0	12.9	12.4	11.6	11.3	11.7	9.5	10.7	11.9	11.4	12.6	11.8	10.6
Dissolved organic phosphorus												
0.0	1.45	1.46	1.51	1.36	1.28	1.34	1.31	2.04	1.33	1.43	1.47	1.54
0.5	1.59	1.51	1.52	1.31	1.31	1.32	1.36	1.41	1.43	1.37	1.41	1.43
1.0	1.37	1.45	1.36	1.27	1.36	1.30	1.60	1.54	1.40	1.39	1.44	1.40
1.5	1.46	1.46	1.44	1.40	1.26	1.37	1.40	1.46	1.52	1.36	1.47	1.44
2.0	1.46	1.49	1.33	1.45	1.47	1.29	1.28	1.31	1.65	1.26	1.52	1.24
Urea												
0.0	3.91	1.51	1.76	1.51	1.66	1.43	1.51	1.43	1.40	1.40	1.40	1.51
0.5	1.99	1.76	1.85	1.57	2.46	1.32	1.40	1.62	1.48	1.68	1.51	1.32
1.0	2.96	2.54	2.38	2.04	2.13	1.90	1.87	1.73	2.94	1.65	1.46	1.68
1.5	2.57	2.40	2.66	2.66	0.53	2.24	1.99	2.15	1.99	1.82	1.87	1.65
2.0	2.28	1.96	1.57	1.46	1.06	1.04	0.76	0.73	0.62	1.15	0.76	0.67

blooming. From the results of seasonal observation in the present study, the DOC concentrations in the euphotic layer showed neither appreciable change, nor a close relation to the change in chlorophyll-a amounts. On the other hand, DON and DOP concentrations changed corresponding to chlorophyll-a amounts at the closed station where the effect of horizontal water movement and the supply of allochthonous substances were restricted.

BERMAN (1974)[6] and MITAMURA and SAIJO (1981)[5] suggested that urea was utilized as a nitrogen source by phytoplankton in the natural freshwater lake from the results of the close relationship between urea concentration and phytoplankton blooming. The percentage of urea nitrogen in DON conspicuously decreased in summer when the lower urea concentrations were observed in the present study. MITAMURA and SAIJO (1981)[5] obtained a similar trend in Lake Biwa. These results suggest that urea is biologically active constituent of DON. McCARTHY (1972)[8] and McCARTHY and EPPLEY (1972)[28] reported that high ammonia concentration suppressed the utilization of urea. McCARTHY *et al.* (1977)[10] suggested that ammonia was preferred to urea and urea was used next to ammonia in Chesapeake Bay. McCARTHY *et al.* (1982)[29] also reported a similar trend in Lake Kinneret. In the present study, the decrease of urea (from early summer) following the abrupt decrease of ammonia was found. This seems to suggest that the phytoplankton prefers ammonia to urea, even in the eutrophic pond. The concentrations of dissolved inorganic nitrogen (mainly cosisting of ammonia) were rapidly regenerated after blooming, but DON did not increase. This seems to suggest that the mineralization of particulate organic nitrogen progresses rapidly, and the consumption and supply of DON are in a state of dynamic balance.

MANNY and WETZEL (1973)[14] reported that DON concentrations and budget values varied at individual stations and between stations over a diel period in a hardwater stream. KAPLAN and BOTT (1982)[30] reported the diel fluctuations of DOC in a piedmont stream. From the field and laboratory observations, they suggested that benthic algal excretion and bacterial uptake significantly contributed to this periodic diel fluctuation of DOC concentration. Our results showed no significant diel periodicity in accordance with a certain regulation. This suggests that the greater part of dissolved organic matters changes slowly with time or the production and removal rate of dissolved organic matters was in balance during short-term observation. EPPLEY *et al.* (1971)[25] reported that the assimilation rate of urea nitrogen showed no diel periodicity, although observed the periodicity for ammonia and nitrate assimilation in the enriched coastal seawater off southern California. In the upper layer of this pond, the diel change of ammonia was observed. While urea showed no appreciable change. To clarify the relationship between diel change of dissolved organic matters and some parameters such as irradiance and biological activity in natural water, further investigations are required.

MITAMURA and SAIJO (1981)[5] observed that the concentration of dissolved organic matters was higher in the upper layer than in the lower layer of Lake Biwa. TAKAHASHI and SAIJO (1981)[27] also reported that DON concentrations in the trophogenic layer were higher than in the tropholytic layer in Lake Kizaki. A shallower pond like one under study is vertically mixed by wind, so it is difficult to observe any changes in the vertical distribution. The present results indicated that the concentration of dissolved organic matters slightly decreased with depth, during the diel observation when the strong stratification was found.

The distinctive vertical profile of urea was found during the diel observation. Urea concentrations in the upper layer and the lower layer were lower than those of the middle layer. BERMAN (1974)[6] observed higher concentrations of urea in the anoxic hypolimnion during summer. SATOH and HANYA (1981)[7] also reported a similar result. The regeneration of urea from the excretion of zooplankton was suggested by JAWED (1969)[31], EPPLEY *et al.* (1973)[9], and MITAMURA and SAIJO (1980)[32]. The supply by the excretion of zooplankton and the consumption by the assimilation of phytoplankton seems to be one of the important factors to affect the distribution of urea.

In this small eutrophic pond, dissolved organic matters seemed to change with biological activity. This result suggests the importance of study on the behavior of each specific organic compound (such as urea) concomitant with investigation of the gross organic matters.

We wish to thank Dr. Y. NAGATA, Department of Biology, Osaka Kyoiku University, for his kind help in the field surveys.

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要　　約

溶存有機態炭素 (DOC)，窒素 (DON)，リン (DOP) 及び尿素の季節変化と日周変化を富栄養化の進んだ小さな池に設置した円柱の内外において測定した。

DOC : DON : DOP の原子比は，DON と DOP の現存量の季節変化がより大きいために，春は 780 : 20 : 1，または秋は 2100 : 33 : 1 と大きく変動した。尿素態炭素の DOC 中に占める割合は 0.2%から 6.3%，尿素態窒素の DON 中に占める割合は 2 %から 39%であり，尿素は DON を構成する主要な化合物の 1 つであった。尿素の現存量の低い夏と秋にはこれらの割合は低かった。これは尿素が DON の内で変化しやすい化合物であることを示唆するものと考えられる。

日周観測は植物プランクトンの現存量が高く，また顕著な化学成層が認められた 8 月に行った。DOC と DOP には明らかな日周変化はみられなかったが，DON の現存量は円柱の外側では深夜から朝にかけて高く，内側では夜に低かった。また尿素の現存量の日周変化には周期性が認められなかった。日周観測時に，溶存化合物の濃度は下層より上層で高いという傾向が認められた。尿素には，中層の値が上層や下層の値よりも高いという特徴のある鉛直分布がみられた。