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Concentrations and controls of dissolved organic matter in a constricted-channel region of the Ohio River

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Abstract. A 12-month study was conducted to measure the concentrations of dissolved organic matter (DOC, TDN, TDP) in four sites within a 119 km long reach of the Ohio River, near Louisville, KY. In this study we test whether specific geomorphological and biological factors influenced variations in dissolved organic matter. Concentrations of DOC in the river averaged ≈1200 μmol/L, and varied by nearly two orders of magnitude seasonally (mean DOC during base flow ≈620 μmol/L). Peak periods for DOC at all sites were during April–May. The site nearest a navigation dam (deeper, lower current velocities) had significantly lower concentrations of TDN and greater C:N ratios than upstream sites. The largest tributary entering this reach (Kentucky River) had no significant effect on levels of DOM in the main river, despite having significantly greater concentrations of TDN and lower levels of DOC during most months of the year. Concentrations of DOC, TDN, and TDP were not significantly different in littoral and pelagic habitats at all sites studied, suggesting little floodplain influence on DOM in this constricted-channel section of the Ohio River. C:N ratios of DOM in the Ohio were significantly different among seasons; C:N exceeded or equaled Redfield ratios in summer and fall (6 to 10), but were below Redfield (1.8 to 3.0) during winter and spring. Regression models suggest that total phytoplankton densities and flow conditions are the two most important factors regulating DOM in this very large river.

Introduction

Dissolved organic matter (DOM), typically measured as dissolved organic carbon (DOC) plus other organic fractions (esp. N, P), is central to secondary production and microbial foodwebs in aquatic ecosystems (Cole et al. 1988; Benner et al. 1995; Hoch et al. 1995). It is estimated that the dissolved fraction (versus particulate) represents between 80 and 95% of the total organic-C in most fresh waters (Wetzel 1985; Spitzy & Leenheer 1991; Sabater et al. 1993). However, concentrations of DOM and controls on its flux in large rivers are still not well understood (Junk et al. 1989; Sedell et al. 1989; Hoch et al. 1995). This lack of clarity is partially due to the complex interactions between physical controls (e.g., geomorphology, discharge, watershed, temperature)

and biological and chemical influences (e.g. carbon sources, DOM quality, bacterial transformation), both in the river and its watershed (Sedell et al. 1989; Thorp & Delong 1994).

The forms of dissolved organic matter (DOM) in rivers are diverse and vary according to the type of watershed, quantity of *in situ* primary production, presence of adjacent wetlands, season, and degree of floodplain influences (Thurman 1985). For example, the primary source of DOM to the Amazon River is terrestrial humic material which is largely refractory, with a high C:N ratio (Ertel et al. 1986; Richey et al. 1990). However, the gradual degradation of a large pool of refractory carbon coupled with the rapid cycling of a small labile pool of DOM permit substantial heterotrophic microbial activity and carbon cycling in this tropical river (Richey et al. 1990; Benner et al. 1995). The sources, inputs, and dynamics of carbon in the Amazon formed the basis for the "Flood Pulse Concept," by Junk et al. (1989). Lateral movement of complex forms of DOM from the floodplain into the river is thought to be an important and conspicuous feature of many large floodplain rivers. The possibility that complex forms of DOM can be partially degraded into simpler and more easily metabolized forms through exposure to natural levels of UV radiation also means that refractory allochthonous DOM may be sufficient to support riverine bacterial production (e.g., Tranvik 1993; Wetzel et al. 1995).

In contrast, DOM in freshwater tidal portions of the Hudson River (NY), is supplied by a combination of autochthonous and allochthonous sources, including submersed macrophytes, wetland detritus, phytoplankton, and local tributaries (Findlay et al. 1991a,b, 1992). Macrophyte-derived DOM in the Hudson can support high rates of microbial production, which exceed by several-fold the rates of carbon fixed by phytoplankton (Findlay et al. 1991a). In the upper Mississippi, forested floodplains and *in situ* primary production have seasonally important impacts on particulate organic carbon (POC; generally > 0.45 μm) and DOM in rivers (Grubaugh & Anderson 1989). Direct terrestrial leaf fall (as opposed to indirectly through tributaries, floods, or soil percolation) provides substantial POC and DOC to the Mississippi during autumn (the largest seasonal influx). During low-flow summer periods, phytoplankton and macrophyte production are thought to dominate DOC supply (Henebry & Gorden 1989). It has been proposed that the primary supply of organic carbon to the foodwebs of some large rivers may come from direct inputs of riparian litter and autochthonous primary producers, including both phytoplankton and submersed macrophytes (Thorp & Delong 1994). This condition is thought to be especially relevant for large rivers whose channels are more constricted and lack substantial floodplains. Understanding and quantifying these sources for rivers is important, as different forms of organic

matter will affect the chemical composition of DOM available for bacteria and nutrient cycling (Tezuka 1990; Hoch et al. 1995; Williams 1995).

The Ohio River near Louisville is an 9th or 10th-order river, which for the majority of its length occupies a geologically-constricted valley. On the basis of discharge, the Ohio is the second largest river in the United States, after the lower Mississippi. The mean annual discharge (at Louisville) is roughly 3300 m^3/s (64y record; McClain et al. 1994). Studies on the biology and chemistry of the river span several decades (see Mitsch et al. 1989; Thorp et al. 1994; Wehr & Thorp 1997 for references), but we know of only two brief accounts of DOM in the Ohio (Malcolm & Durum 1976; Warta et al. 1995). The more widely-cited study (Malcolm & Durum 1976) was part of a multi-river comparison of carbon dynamics in major rivers in the United States. Data from the Ohio represent eight samples from a single site, and they reveal no obvious relationships between discharge and either POC or DOC concentration. However, data indicate that carbon transport in the Ohio is about half that of the lower Mississippi, suggesting that the Ohio may be an important source of carbon to the Mississippi delta. Further, very little is known about the effects of regulated flow (e.g., from navigation dams) on variations in riverine DOM, despite the commonness of these conditions in most of the world's major rivers.

Because we need more thorough information on riverine DOM to support ongoing studies of food webs, carbon dynamics, and ecosystem production in large rivers like the Ohio, we initiated a study to obtain more data on the concentrations of DOM (as DOC, total dissolved phosphorus [TDN], and total dissolved nitrogen [TDP]) in a lower portion of this river, and the factors which influence them. One of our goals was to examine some of the tenets stated in the Flood Pulse Concept. In particular, we tested whether the concentration and composition of riverine DOM was affected by season, longitudinal location within a reach, tributaries, horizontal position within a reach (i.e., littoral vs. pelagic), or the presence of navigation locks and dams. Second, a particular interest was whether predictions of Redfield stoichiometry (106C:16N:1P) hold for DOM in a large river (Redfield 1958; Williams 1995). Third, we tested whether specific physical or biological factors are important in regulating riverine DOM.

Methods

Site, design, and sampling

All samples were collected from sites along the McAlpine pool, a 119 km reach of the Ohio River which runs from Markland, Indiana downriver to

Louisville, Kentucky (KY) (Figure 1). The Ohio is an enormous river system, whose watershed includes parts of 14 states. The largest cities along the Ohio River are Pittsburgh, Pennsylvania (>900 km upriver of study reach), Cincinnati, Ohio (150 km upriver), and Louisville, KY (just downriver). The McAlpine pool is located within a large, geologically-constricted portion of the river, and has one major tributary, the Kentucky River. Steep hills and cliffs characterize this river valley for a large section above and including this reach; hence the floodplain expanse covers no more than about 100 km^2 (on each bank) for the entire 119 km stretch. The McAlpine pool is populated only by small towns and receives few industrial or urban discharges; a small steel works in Carrollton, KY probably contributes little to the DOM pool of the river; an electrical power plant at Westport, KY discharges slightly heated water. There are no quantitative data on non-point sources of pollution in the region. River flow in the pool is partially regulated by a low-head (11 m) navigation dam (McAlpine dam) near Louisville; at this location the average discharge is 3032 m^3/s.

The design of the present study was intended to examine effects of (1) season, (2) longitudinal site, (3) tributary, (4) navigation dam, and (5) littoral habitats on concentrations of dissolved organic matter in a large river. Despite being well-mixed, there is a true littoral zone in this portion of the Ohio, with distinctly reduced current velocities (<10% mid-river), submersed macrophytes (*Vallisneria, Potamogeton*) during the summer, retention of particular matter in backwaters, and greater densities of zooplankton (esp. cladocerans, copepods; see also Thorp et al. 1994). We sampled the river over twelve months from February 1991 through January 1992. Four major sites were sampled each month in the Ohio (Figure 1, inset): 20 km below the Markland dam and 3 km above the (tributary) Kentucky River (ATR); within the Kentucky at a location 3 km upriver of its confluence (ITR); in the Ohio 3 km below the Kentucky; and approximately 9 km above McAlpine locks and dam (LOW). At each site, two habitats were sampled: pelagic (Channel) and littoral (Bank) locations (see Thorp et al. 1994 for details). Each site × habitat location was spatially replicated 5 times. This resulted in 40 samples per month.

Samples were collected from each location using 20 L plastic buckets at each site from a boat at a depth of 0.5–1.0 m. Water samples for chemical analysis were filtered (<2 h after collection) in line (Whatman GF/F; $\approx 0.7\ \mu m$ poresize), using a peristaltic pump. Samples were acidified to pH < 2.0 with H_2SO_4 (U.S.E.P.A. 1987), kept cool (ca. 4 °C) while on the boat, and then frozen (<8 h after collection; −15 °C) for later processing. Current velocity in the pelagic and littoral areas were measured with a Marsh McBirney velocity meter (model 201-D), and water temperatures were recorded with a YSI

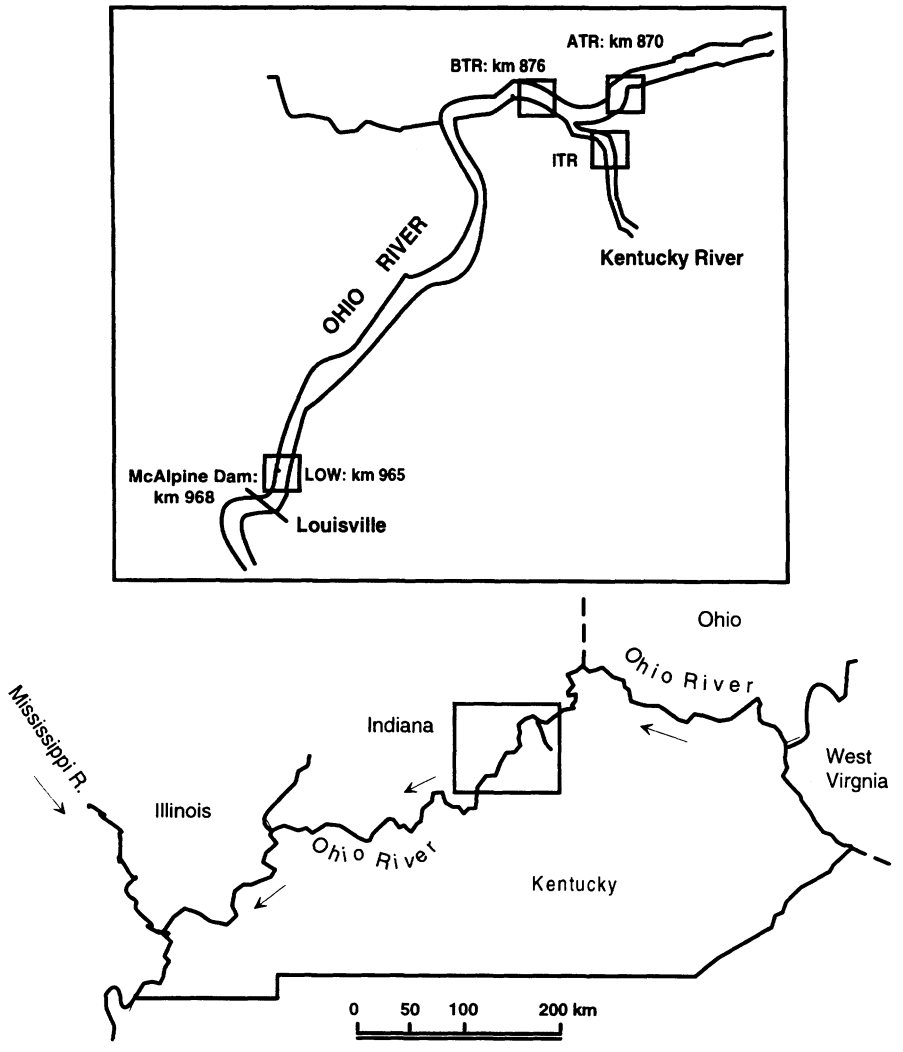

Figure 1. Location of the McAlpine Pool of the Ohio River. Detail of the study area, major tributary and sampling sites are shown inset (ATR = above tributary, ITR = in tributary, BTR = below tributary, LOW = near navigation dam; km distances measured downriver from Pittsburgh; arrows indicate direction of river flow).

temperature probe. Water samples were retrieved for turbidity analysis from the main river sites and measured in NTU units with a Hach turbidimeter.

Laboratory analyses

Samples were analyzed for concentrations of dissolved inorganic [= soluble-reactive] phosphorus (DIP) using antimony-ascorbate-molybdate (A.P.H.A.

1985; Bran+Luebbe Analyzing Technologies 1986a), NH_4^+-N using phenol-hypochlorite, and NO_3^- (after reduction to NO_2^- in a Cd-Cu column) via reaction with sulfanilamide-NNED (A.P.H.A. 1985; Bran+Luebbe Analyzing Technologies 1986b, 1987a). Soluble reactive Si (as SiO_2) was measured via the molybodosilicate method (A.P.H.A. 1985; Bran+Luebbe Analyzing Technologies 1987b).

Dissolved organic carbon (DOC) was measured following removal of inorganic-C via acid sparging, then digested with acid persulfate and high-energy UV. The resultant CO_2 was dialyzed and reacted with buffered phenolphthalein and measured at 550 nm (Goulden & Brooksbank 1975; Bran+Luebbe Analyzing Technologies 1989). Total dissolved P (TDP) was first predigested in smaller aliquots using acid persulfate (Eisenreich et al. 1975) and then analyzed for DIP as described above. Total dissolved nitrogen (TDN) was measured following digestion with alkaline persulfate and high-energy UV, and oxidized to inorganic-N and then measured as NO_3^- (Le & Wehr 1996). Recovery of known P and N compounds in distilled and lake water samples by this method averaged >90%. All procedures were modified for automated analysis and run on a TrAAcs 800 automated analyzer (Bran+Luebbe Inc., Buffalo Grove, IL). From these analyses we calculated concentrations of TDP, TDN, DOC, % organic-P, % organic-N, and ratios of C:N, C:P, and N:P in DOM. Calcium and Na concentrations were measured using flame atomic absorption spectroscopy (Perkin-Elmer model 1100B). Biological data (phytoplankton densities, taxonomic categories) used for regression analyses (see below) were reported by Wehr & Thorp (1997).

Data analysis and statistics

We had two aims in our data analyses. First, we examined effects of season and hydrological features (e.g., floodplain, tributary, navigation dam) on DOM concentrations. Season was defined by flow and temperature conditions (Thorp et al. 1994); Dec–Feb designated as "winter," Mar–May = "spring," Jun–Aug = "summer," and Sep–Nov = "fall." We grouped these chemical observations and tested for differences in DOM using ANOVA (groups >2) or Student's *t*-test (groups = 2; Sokol & Rohlf 1995). Effects were judged to be significant if the probability of an event due to chance (P) was <0.05. Second, effects of physical and biological variables on DOM concentrations were first considered using correlation (Pearson's). A step-wise multiple linear regression considered individual and combined effects of six hypothesized factors (*physical*: temperature, current velocity, turbidity; *biological*: total phytoplankton, diatom, and colonial cyanobacteria densities) on DOM concentrations and their ratios. The maximum criterion for inclusion

of independent variables was $\alpha = 0.05$, the minimum for exclusion was $\alpha = 0.10$. All data were checked for assumptions of normality and homogeneity of variances. All chemical variables and their ratios were skewed; a $\log_{10}$ transformation enabled the use of the statistical tests described. Temperature, current velocity and turbidity measurements were either nearly normal or not sufficiently improved by several transformations; these variables were left untransformed. We compiled and analyzed data using SYSTAT 5.1 (Wilkinson 1992).

Results

Physical factors and nutrients

While temperature and current velocity varied significantly by month (ANOVA; $p < 0.001$), annual averages were similar among the four sites studied (Table 1; ANOVA, $P > 0.05$ for both). Turbidity levels varied spatially, with some indication of a downstream increase, but these apparent differences were non-significant ($P = 0.427$). Chemical conditions varied among locations but with few obvious downstream patterns. Concentrations of DIP differed significantly among sites ($F = 5.01$, $P = 0.003$), with greater levels near the dam and lowest DIP above the Kentucky River. Other inorganic nutrients (NH_4^+, NO_3^-, Si, and Ca) had similar average concentrations among sites. There were no significant effects of the tributary itself on levels of these variables in the Ohio.

Concentrations of dissolved organic matter were spatially more complex. Dissolved organic carbon (DOC) concentrations in Kentucky River averaged 28% lower than in the Ohio River just above their confluence (Tukey's post-hoc analysis: $P = 0.034$). However, this tributary had no significant impact on downstream DOC levels. TDN concentrations were greatest in the Kentucky and least (38% decline) in the Ohio near McAlpine dam. In contrast, TDP levels were greatest near the dam. The net effect of these downstream patterns was nearly a 50% increase in C:N ratio of dissolved organic matter over the 119 km stretch. The C:P and N:P ratios declined by approximately 37 and 30% downstream, although the minimum each was observed in the "below tributary" site.

Temporal and seasonal patterns

Overall, monthly patterns of all three elements were similar. Temporal patterns indicated that in general, DOM levels tended to be greatest during the spring, when discharge declined, but while temperatures were still cool (Figure 2).

Table 1. Summary of physical and chemical variables measured in the McAlpine Pool of the Ohio River between February 1991 and January 1992 (n = 120 per site; ATR = above the tributary, ITR = in the Kentucky River tributary, BTR = below the tributary, LOW = near the navigation dam; chemical variables expressed in μmol/L; current velocity (cm/s) and turbidity (NTU) measured only in channel habitats (n = 60 per site)).

	ATR		ITR		BTR		LOW	
	Mean	SE	Mean	SE	Mean	SE	Mean	SE
Physical								
Temperature	15.1	± 0.8	15.3	± 0.7	15.2	± 0.8	16.1	± 0.9
Current velocity	15.1	± 1.1	15.0	± 1.1	15.3	± 1.0	15.2	± 1.3
Turbidity	13.0	± 1.8	12.3	± 1.6	15.3	± 1.7	18.6	± 3.9
Dissolved inorganic								
DIP	0.92	± 0.07	1.00	± 0.009	1.20	± 0.06	2.05	± 0.07
NH_4-N	12.0	± 0.99	10.6	± 1.20	13.0	± 1.03	8.86	± 0.69
NH_3-N	71.4	± 2.71	53.0	± 1.68	63.8	± 2.56	67.0	± 2.72
Si	139.9	± 6.37	176.1	± 7.41	141.1	± 9.14	129.0	± 5.70
Ca	737	± 27	872	± 32	801	± 33	801	± 46
Na	810	± 43	295	± 14	716	± 44	707	± 37
Dissolved organic								
DOC	1382	± 131	991	± 84	1345	± 132	1186	± 101
TDN	701	± 89	728	± 94	509	± 69	436	± 66
TDP	2.91	± 0.28	2.49	± 0.22	2.68	± 0.16	3.62	± 1.02
% organic-P	66.5	± 3.1	60.9	± 2.5	59.9	± 2.1	57.1	± 3.2
% organic-N	73.2	± 3.1	73.9	± 3.1	62.6	± 3.0	61.3	± 3.7
C:N ratio	4.5	± 0.4	4.5	± 0.4	4.8	± 0.4	6.7	± 1.1
C:P ratio	630	± 63	645	± 58	396	± 49	715	± 110
N:P ratio	376	± 62	391	± 60	252	± 39	307	± 71

Lower levels were observed late summer through most of the winter. Temporal fluctuations were more extreme in the Ohio than the smaller Kentucky River (ITR), although patterns were similar. The timing of nutrient peaks appeared to be affected by location along the river. Near the dam, maximum DOM levels occurred in April, then sharply declined. Further upstream maximum levels were somewhat more prolonged and tended to peak in May or April–May. TDP levels exhibited a distinct secondary peak at all sites in July, but both DOC and TDN levels remained low. Almost cyclical high-low patterns in TDP were observed in the water column near McAlpine dam but at no other sites.

Temporal constraints on DOM were next considered by grouping months into four season-classes according to temperature and current conditions (Figure 3). There were marked seasonal differences in the concentrations

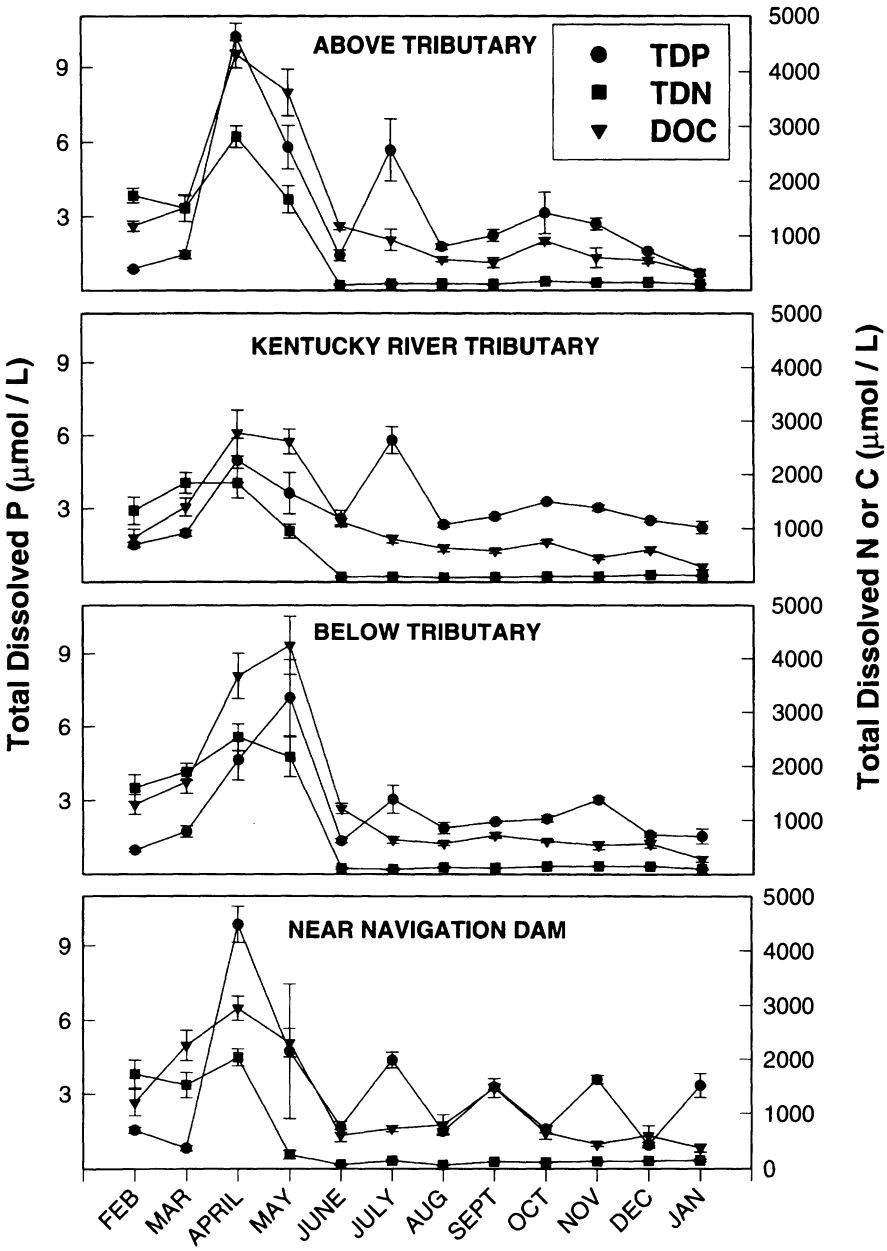

Figure 2. Downstream changes (four sites) in concentrations of total dissolved phosphorus (TDP), total dissolved nitrogen (TDN), and dissolved organic carbon (DOC) in the McAlpine Pool of the Ohio River, plotted monthly from Feb 1991 through Jan 1992 (error bars represent ± 1 SE; $n = 10$ per point; all concentrations in μmol/L; note different scales for P (left axis) versus N and C (right axis)).

of all three variables. In general, DOM concentrations were greatest in the spring, although similar TDP levels were observed in the Kentucky River in each season. Minimum TDP and DOC concentrations were observed in the winter, while minimum TDN was observed in summer and fall. In general the seasonal effect was most pronounced in DOC concentrations, with roughly a 3-fold difference before and after the spring period. During the summer and fall, TDN was depleted to levels less than 10% of springtime maxima river-wide. These seasonal effects were very highly significant (Table 2) for all DOM variables considered. Sites effects were more specific; TDP and TDN concentrations varied significantly with site, but DOC levels were not significantly different. The Kentucky River (tributary) had no significant effect on levels of DOM or ratios of these elements. The site near the navigation dam had significantly lower TDN levels, significantly greater C:N, and lower N:P values. If littoral zones supply DOM to the Ohio, we would expect significant differences in some of these variables versus pelagic sites. No significant differences were observed. Post-hoc analyses (Tukey's HSD) revealed no seasons or sites within which littoral zones contained significantly greater concentrations of DOC. In particular, the high-flow winter period did not alter the lack of similarity observed between littoral and pelagic sites during other seasons.

Ratios of elements measured in DOM also varied with season and did not always match the predicted Redfield value of 6.6 (Figure 4). C:N ratios consistently exceeded Redfield predictions during the summer (one-sample *t*-tests; all $P < 0.001$), but roughly matched Redfield predictions during the fall at all sites ($P > 0.05$). During the winter, C:N ratios were significantly below Redfield predictions (all sites, $P < 0.05$); and during spring, C:N at three out of four sites were also below predictions ($P < 0.05$, exception = LOW). In contrast, seasonal C:P ratios were always significantly above the Redfield prediction of 106, and often five-fold greater in the winter and spring, suggesting strongly P-depleted DOM. Measured N:P ratios also consistently exceeded the Redfield model (16), but there was a strong seasonality in N:P which followed an inverse pattern to that observed for C:N ratios.

Effects of physical and biological factors on Ohio River DOM

Certain physical and biological factors were considered for their possible effects on levels of DOM in the Ohio. Correlations among these variables indicate that TDP and DOC concentrations were significantly greater when temperatures were warmer, turbidity was high, and total phytoplankton densities were greater (Table 3). TDN levels were significantly greater during periods of increased current velocity, turbidity, and phytoplankton densities. C:N ratios correlated significantly, more strongly with temperature than did

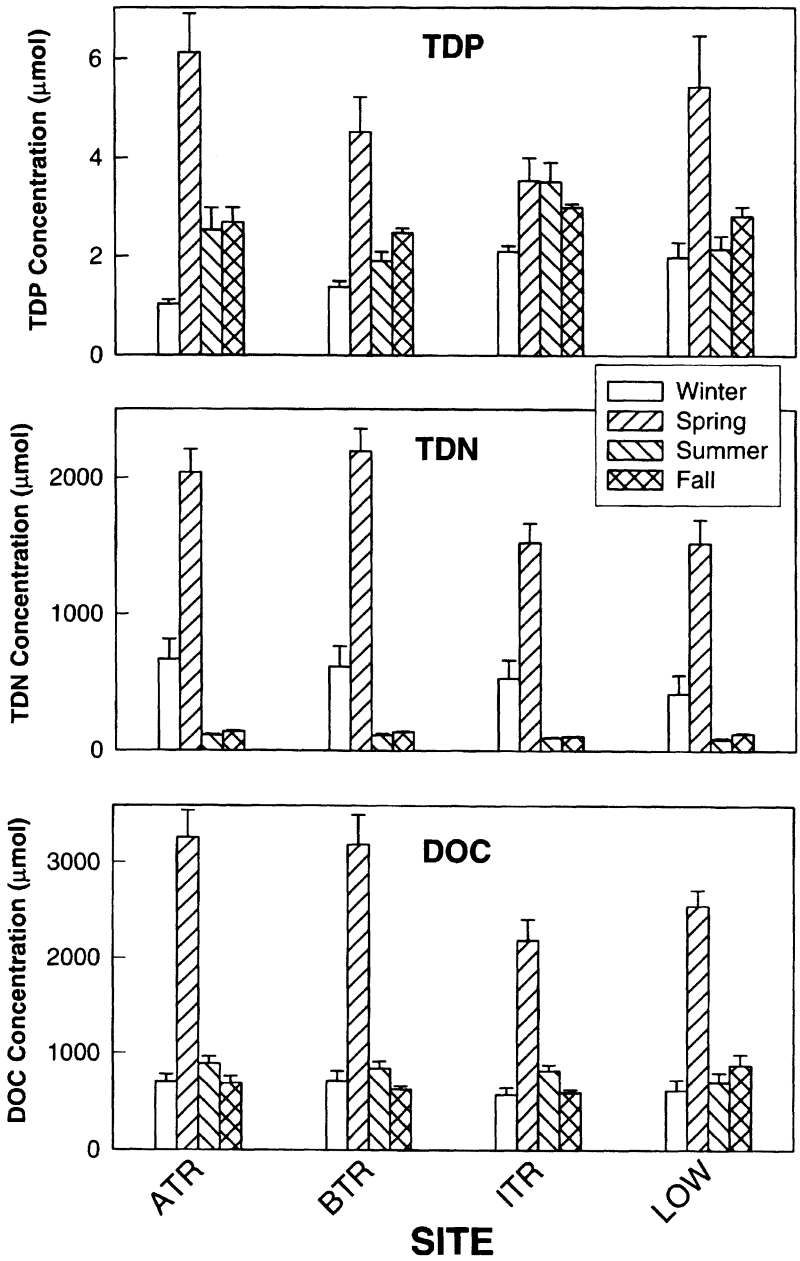

Figure 3. Effects of season on concentrations of TDP, TDP and DOC in four sites in the McAlpine Pool during 1991–1992 (seasons based on temperature, flow conditions, see Methods; Winter = Dec–Feb (n = 115); Spring = Mar–May (n = 120); Summer = Jun–Aug (n = 120); Fall = Sept–Nov (n = 120); error bars indicate +1 SE).

Table 2. Effects of season, site, tributary river (Kentucky River), navigation dam, and littoral zones on concentrations of total dissolved phosphorus (TDP), total dissolved nitrogen (TDN), dissolved organic carbon (DOC), and elemental ratios of dissolved organic nutrients in the McAlpine pool of Ohio River during twelve months of 1991–1992. Differences based on ANOVA (F) for multi-level factors and Student's t-tests (t, with pooled variances) for two-level factors (a positive t-score indicates values are greater below the tributary, near the dam, or in the littoral zone; P = probability of a significant difference; * = $P < 0.05$; ** = $P < 0.01$; *** = $P < 0.001$; NS = non-significant, defined as > 0.05).

	Season		Site		Tributary		Navigation dam		Pelagic vs. littoral	
Variable	F	P	F	P	t	P	t	P	t	P
TDP	38.29	***	4.56	**	−0.16	NS	0.61	NS	1.17	NS
TDN	276.32	***	4.22	**	0.06	NS	−2.02	*	−0.09	NS
DOC	163.57	***	1.85	NS	−0.27	NS	−0.58	NS	0.10	NS
C:N ratio	141.15	***	2.52	NS	−0.16	NS	2.14	*	0.05	NS
C:P ratio	43.11	***	7.09	***	−0.09	NS	−1.12	NS	−0.97	NS
N:P ratio	163.97	***	8.19	***	0.20	NS	−2.48	*	−0.70	NS

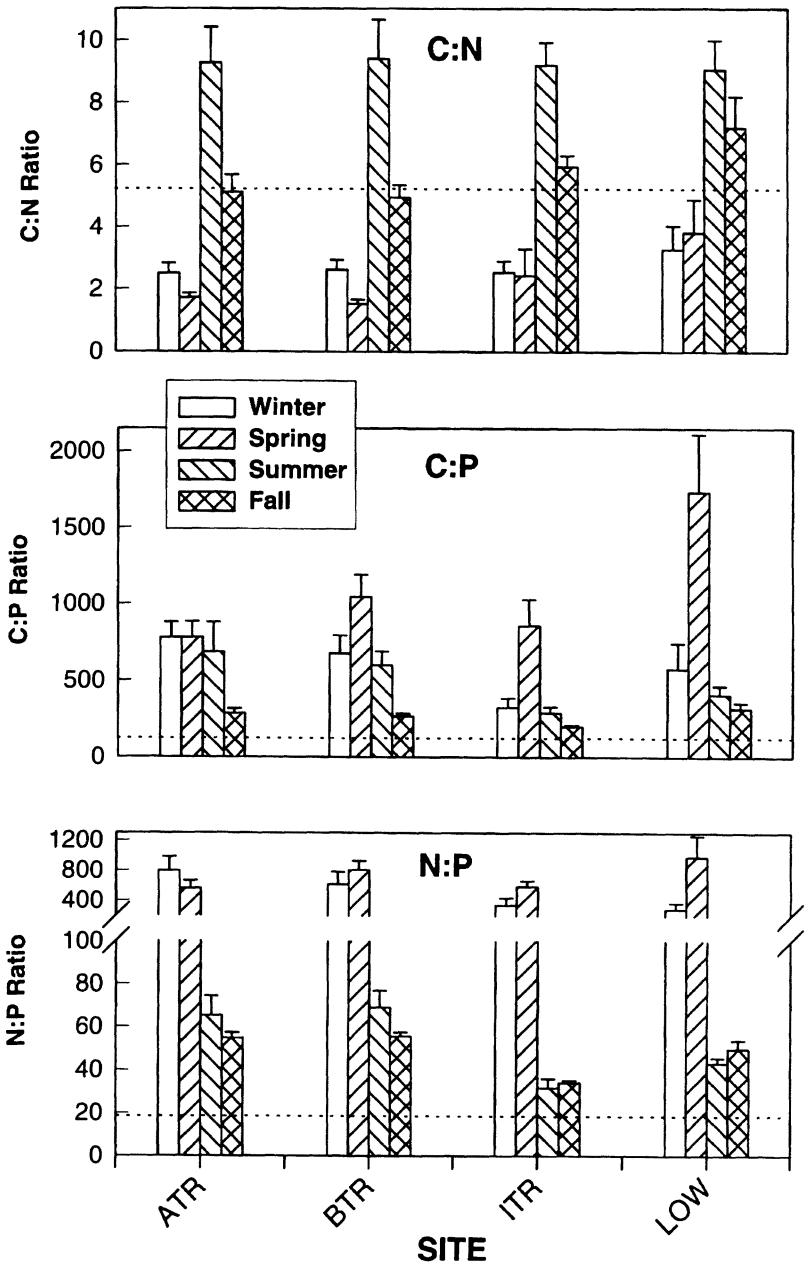

Figure 4. Effects of season on C:N, C:P, and N:P ratios in dissolved organic matter in four sites in the McAlpine Pool during 1991–1992 (dashed line indicates Redfield Ratio for pairs of elements; error bars indicate +1 SE; see Figure 3 for details).

any other DOM variable; this corresponds with earlier results for the summer time period. It was the only variable that correlated negatively with turbidity and phytoplankton density. C:P ratios differed, these correlated strongly and negatively with densities of colonial cyanobacteria.

We considered these relationships further by using multiple linear regression (MLR) to identify which factors may be most important in controlling levels of DOM (Table 4, Figure 5). Spatial and temporal variations in TDP and DOC concentrations both correlate most strongly with one biological variable, total phytoplankton density. The complete model describes nearly half of the total variation in TDP. Variation in DOC was predicted to be controlled mainly by phytoplankton abundance, although this variable explains only about 23% of the variation in DOC. Nearly 60% of the total variation in DOC was described by a multivariate model consisting of total cell density, cyanobacteria, temperature and current velocity. Total-N levels in the Ohio were predicted to be controlled principally by current velocity. Plots of all three sets of regressions reveal not only the closeness of fit but also the fact that, for TDN and DOC, the predictive models were very close to 1:1 relationships (Figure 5). DOC and TDN concentrations each ranged nearly two orders of magnitude over the year, but most of their variability could be accounted for by two biological and two physical variables.

Predictions about the ratios of the variables reveal other important features regarding controls on DOM in the Ohio. The plots of the simple bivariate regressions with the most important single predictors (Figure 6, left panel) reveal the possible effect of these factors, and they also may be used to identify the conditions under which Redfield ratios may be expected to occur. With C:N ratio, the expected value of 6.6 in organic materials falls almost exactly on the Y-intercept of the first plot. Thus, our data suggest that the predicted Redfield C:N ratio should occur in the Ohio River under low turbidity conditions. Further, results also suggest that with greater turbidity, C:N is predicted to decline by more than 5-fold. With C:P ratios, the predicted value of 106 also falls very close to the Y-intercept of the bivariate plot with current velocity. When the Ohio River experiences slower current speeds (e.g., near navigation dams or late summer), C:P ratios may meet the nutritional balance predicted by Redfield, but with velocities greater than about 40 cm/s, river conditions become strongly P-deficient. With N:P ratios, the expected value of about 16 does not match the Y-intercept of the Ohio River plot. Indeed, only five out of 94 observations in this dataset were 18 or less. Despite this extreme pattern, our data predict that N:P ratios will far exceed Redfield predictions as turbidity increases. The three MLR models make predictions that describe between 40 and 60% of the variability in these element ratios, and describe a line that is in all three cases, very close to 1:1.

Table 3. Correlations between physical and biological factors with concentrations of dissolved organic matter in the McAlpine pool of Ohio River during twelve months of 1991–1992 (for abbreviations see Table 2; correlations based on pelagic (mid-channel) samples with balanced observations ($n = 94$); r = Pearson product-moment correlation; P = probability of a significant difference, * = $P < 0.05$; ** $P < 0.01$; *** = $P < 0.001$; NS = non-significant, defined as > 0.05).

	Temperature		Current velocity		Tributary		Total phyto density		Cyano >2 μm density	
Variable	*r*	*P*	*r*	*P*	*r*	*P*	*r*	*P*	*r*	*P*
TDP	0.348	**	0.178	NS	0.315	**	0.647	***	0.105	NS
TDN	−0.013	NS	0.543	***	0.625	***	0.506	***	−0.166	NS
DOC	0.373	**	0.418	***	0.399	***	0.463	***	−0.208	NS
C:N ratio	0.611	***	−0.408	***	−0.613	***	−0.250	*	−0.003	NS
C:P ratio	0.126	NS	0.479	***	0.263	*	−0.003	NS	−0.405	***
N:P ratio	−0.325	**	0.602	***	0.603	***	0.167	NS	−0.266	*

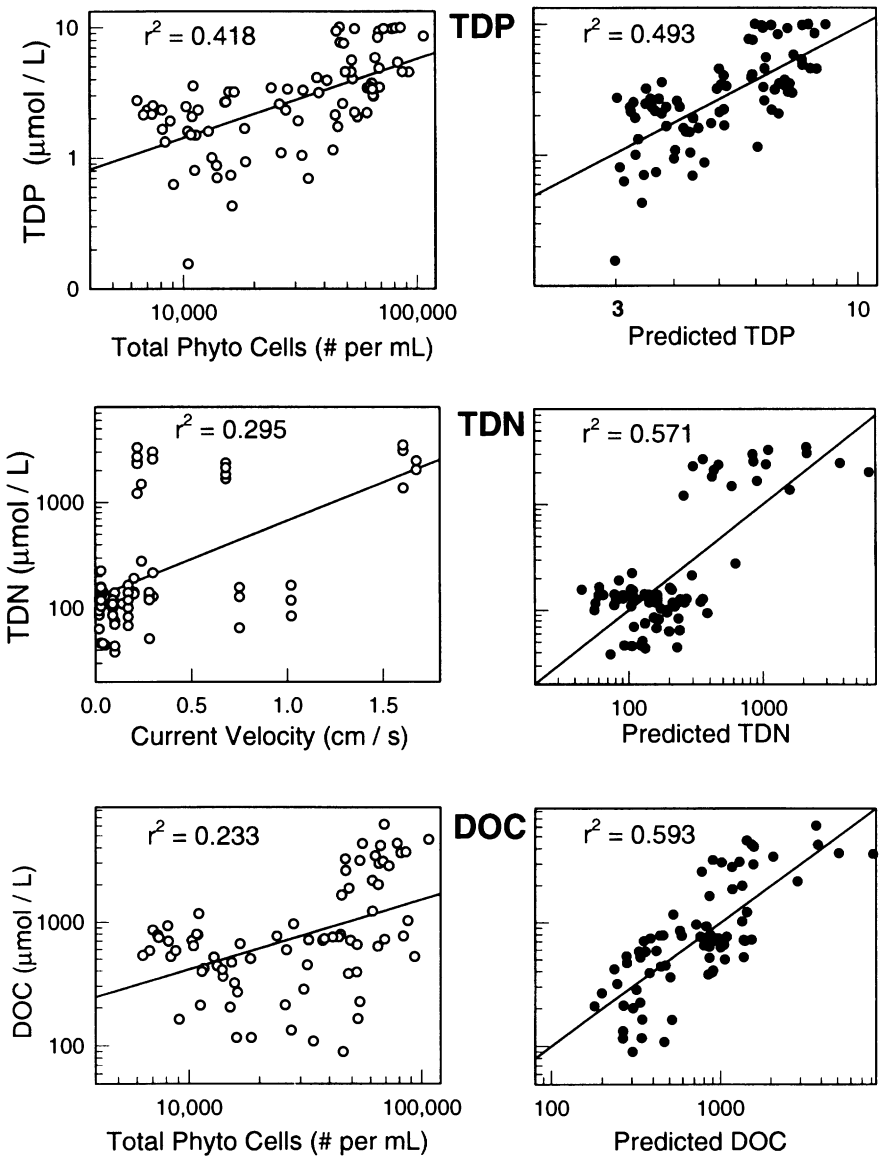

Figure 5. Bivariate and multiple linear regressions (MLR) testing factors affecting concentrations of TDP, TDN, and DOC in the McAlpine Pool on the Ohio River during 1991–1992. Independent variables in each bivariate regression are the factors selected by MLR as the primary factor affecting concentrations of DOM in each category. The "predicted" elements (right panels) are the multivariate model established by MLR (see Table 3 for details).

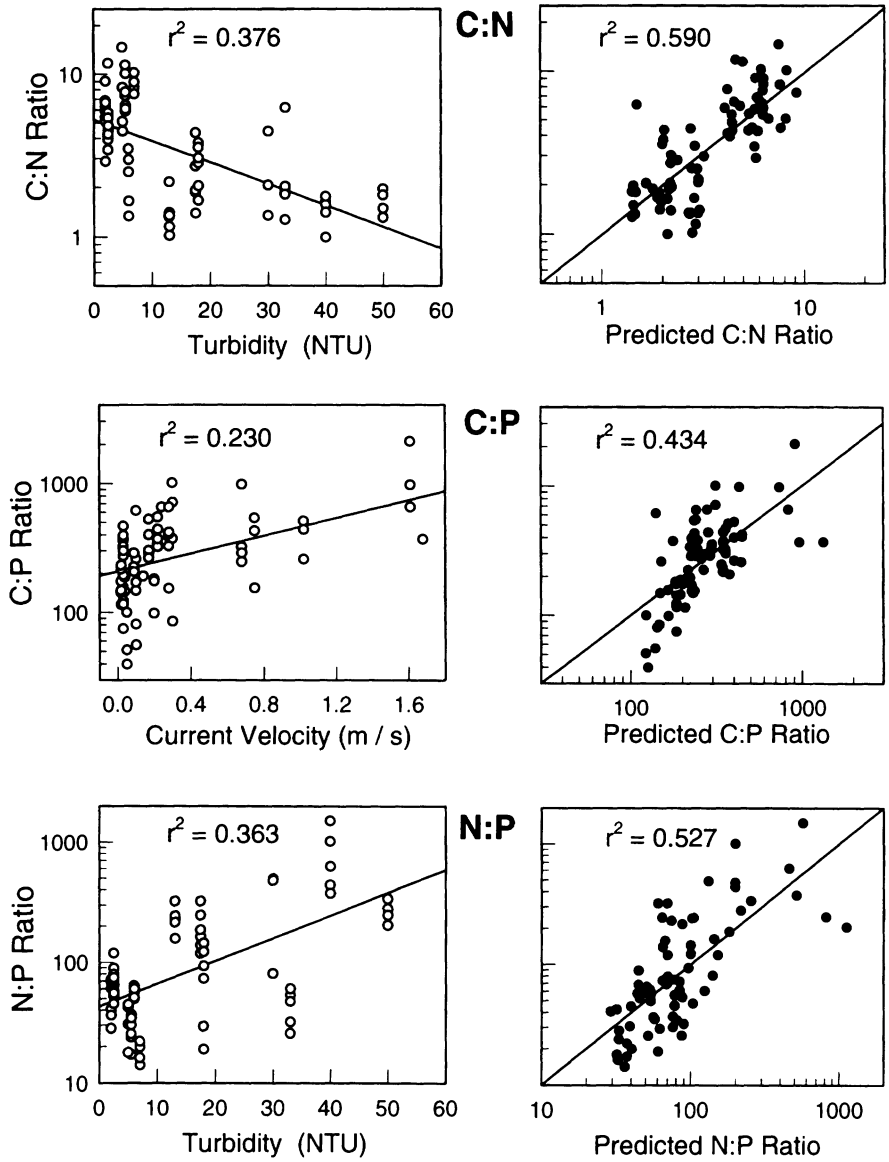

Figure 6. Bivariate and multiple linear regressions (MLR) testing factors affecting C:N, C:P, and N:P ratios in dissolved organic matter in the McAlpine Pool on the Ohio River during 1991–1992. Independent variables in each bivariate regression are the factors selected by MLR as the primary factor affecting concentrations of DOM in each category. The "predicted" ratios (right panels) are the multivariate model established by MLR (see Table 3 for details).

Table 4. Results of multiple regression analysis used to identify predictors of dissolved organic matter concentrations and ratios in the McAlpine Pool of the Ohio River. Six independent variables tested include three physical variables (temperature, current velocity, turbidity) and three biological variables (Total phytoplankton, Bacillariophyta (diatoms), and Cyanobacteria >2 μm densities). Significance of individual variables tested via Student's *t*-test (r^2 = coefficient of determination of the complete model; *P* = probability of a significant effect; * = $P < 0.05$; ** = $P < 0.01$; *** = $P < 0.001$).

Step	Independent variable	Slope	*t* Score	*P*
Dependent variable = TDP		$r^2 = 0.493$		
1	Total phyto cells	0.362 ± 0.049	7.31	***
2	Temperature	0.012 ± 0.005	2.43	*
3	Cyano cells >2 μm	−0.030 ± 0.013	−2.20	*
Dependent variable = TDN		$r^2 = 0.571$		
1	Current velocity	0.804 ± 0.295	2.73	**
2	Cyano cells >2 μm	−0.153 ± 0.039	−3.91	***
3	Total phyto cells	0.734 ± 0.175	4.20	***
4	Turbidity	0.020 ± 0.011	1.90	*
Dependent variable = DOC		$r^2 = 0.593$		
1	Total phyto cells	0.584 ± 0.115	5.08	***
2	Cyano cells >2 μm	−0.142 ± 0.029	−4.88	***
3	Temperature	0.051 ± 0.011	4.66	***
4	Current velocity	0.788 ± 0.198	3.99	***
Dependent variable = C:N ratio		r^2 0.590		
1	Turbidity	−0.015 ± 0.003	−4.61	***
2	Temperature	0.036 ± 0.006	6.01	***
3	Diatom cells	−0.094 ± 0.039	−2.40	*
Dependent variable = C:P ratio		$r^2 = 0.434$		
1	Current velocity	0.838 ± 0.152	5.53	***
2	Cyano cells >2 μm	−0.093 ± 0.021	−4.36	***
3	Temperature	0.026 ± 0.009	2.91	**
Dependent variable = N:P ratio		$r^2 = 0.527$		
1	Turbidity	0.031 ± 0.007	4.21	***
2	Current velocity	0.801 ± 0.241	3.33	**
3	Cyano cells >2 μm	−0.091 ± 0.028	−3.22	**

Discussion

One of the first studies of DOM in the Ohio River is a paper by Malcolm & Durum (1976), in which the authors reported on the concentrations and transport of DOC and POC in six U.S. rivers, including the Ohio and Mississippi. Samples were collected from study sites during 1969, from which average

concentrations, discharge levels, and transport rates of POC and DOC were determined (eight DOC values from the Ohio). With these data the authors estimated that average DOC concentrations in large temperate rivers range between 250 to 330 μmol/L (≈3 to 4 mg C/L). Other early reviews also report that the "average" DOC concentration for large rivers in temperate regions fall between about 250 and 500 μmol/L (Meybeck 1982; Thurman 1985; Spitzy & Leenheer 1991). However, studies cited by these reviews undersampled rivers during winter or other high flow periods. For example, the presumed average DOC of 250 μmol/L (3.1 mg/L) in the Ohio River for 1969 was based on samples collected between July and December, with no data between January and June (Malcolm & Durum 1976). In our study of the Ohio (1991–1992; n = 474), we measured greatest concentrations of DOC between the months of April and June. We estimate the annual average to be closer to 1200 μmol/L (≈10 mg C/L). We estimate the mean DOC concentration during base flow to be ≈620 μmol/L, which is closer to values reported by earlier studies.

One reason for discrepancies among averages given from different studies is certainly the lack of adequate coverage during critical times of year, such as peak floods, plankton blooms, or autumn leaf fall. Early data for the Mississippi may reflect insufficient sampling over time. The 1969 average DOC estimate for the Mississippi of 290 μmol/L (3.5 mg/L), was based on six dates (Malcolm & Durum 1976). A more complex and recent study (1984–1985) of the upper Mississippi estimated the annual average DOC levels to be closer to 1040 μmol/L (12.5 mg/L; Grubaugh & Anderson 1989); these are very similar to our 1991–1992 levels in the Ohio. These authors employed a more complete spatial sampling strategy which included a broader range of flow conditions and seasonal processes. A year-long study of DOC and bacterial activity in the River Danube revealed annual average DOC concentrations at two stations of 280 and 528 μmol/L (3.4 and 6.3 mg/L, respectively). Peak concentrations in the Danube (station 1: >650; station 2: >1200 μmol/L) were observed after spring floods and subsequent phytoplankton blooms in the river (Hoch et al. 1995). We suggest that later studies need to consider these temporally unpredictable factors when assembling data to characterize annual average levels of DOC in large rivers.

DOC concentrations in the McAlpine pool of the Ohio varied seasonally by more than two orders of magnitude, from 60 to 7000 μmol/L (≈0.7 to 84 mg C/L). Roughly half of DOC values observed in the Ohio ranged between 500 and 1400 μmol/L (≈6 to 17 mg C/L). DOC concentration ranges for other major rivers of the world, such as the Mississippi, St. Lawrence, Amazon, Zaire, and Niger, appear to fall in a similar range (Spitzy & Leenheer 1991). However, 20% of all 1991–1992 observations in the Ohio exceeded 1800

μmol/L ($\approx$22 mg/L). Few studies have examined what conditions may result in extreme low or high values, which can be observed in flowing waters. In some large rivers, researchers have observed an increase in POC and DOC with greater discharge, presumably the result of resuspension and partial dissolution of bottom materials, plus the introduction of materials from the littoral zone and adjacent floodplain (Thurman 1985; Junk et al. 1989; Hoch et al. 1995). Other rivers show no such pattern (Malcolm & Durum 1976). Our data (Table 3) indicate that DOC concentrations are greater in the Ohio during periods of increased current velocity (and discharge). In contrast, DOC maxima in the upper Mississippi appears to be negatively correlated with flow (dilution effect), where floodplain forests are an important part of the carbon budget of the river and are the dominant carbon source during the fall (Grubaugh & Anderson 1989). In the Hudson River which is a geologically-constricted freshwater tidal system for much of its length, there is no strong positive or negative relationship between DOC concentration and discharge, suggesting floodplain inputs are also not the primary source of DOC to the river (Findlay et al. 1991a). Instead, phytoplankton, macrophytes, littoral wetlands, and bottom sediments are thought to supply carbon for bacterial metabolism most of the year (Findlay et al. 1991a, b, 1992). Summer bacterial production in portions of the upper Mississippi also appears to be driven by carbon supplied by submersed macrophytes and resuspended sediments (Henebry & Gorden 1989).

In many temperate rivers, the period from late winter to early spring is typically a flood period with elevated turbidity (see also Thorp et al. 1994). In some larger rivers a predictable winter-spring pulse of carbon occurs from the floodplain into the river channel (Junk et al. 1989). The Ohio River differs from several other well-studied large rivers, because it lacks a substantial floodplain for much of its length which could import large quantities of POC and DOC into the river during flood-pulse periods. DOC, TDN and TDP data for the Ohio show little influence of littoral habitats on pelagic DOM and support earlier suggestions that the supply of organic carbon to constricted rivers is principally derived from autochthonous sources and direct riparian inputs, rather from the floodplain (Thorp & Delong 1994).

Variations in C:N ratios of Ohio River DOM (0.4 to 25; mean = 5.2) correlated strongly with season (Figure 4, Table 2). The annual average of C:N ratios in the river were, probably coincidentally, near the Redfield ratio of 6.6 Carbon-rich DOM (C:N 29) predominates during the summer (June through August), when biological activity is greatest (Thorp et al. 1994; Wehr & Thorp 1997). We presume that more rapid recycling and incorporation of nitrogen (versus C) in the water column is the primary cause and is likely the result of enhanced bacterial and phytoplankton activity during the summer

(warmer temperatures, greater sunlight). A very similar pattern has been observed in the euphotic zone of the open ocean, where greater removal rates of TDN relative to DOC are thought to be biologically driven (Sambrotto et al. 1993; Williams 1995). Over time, the result is lower quality, high C:N dissolved organic matter, following (at least partial) bacterial degradation and incorporation. Changes in DOC quality (or "availability") have also been observed along the river gradient of several rivers. DOC quality, based on molecular weight or bacterial growth responses, has been shown to decline on progressing downstream in the Moisie, Ogeechee, and lower Mississippi Rivers (Ford et al. 1990; Left & Meyer 1991; Sabater et al. 1993; Cotner & Gardner 1993). This pattern was presumed to be the result of interactions between biotic (decomposition) and physical (floodplain inputs, downstream transport of retractile DOC) processes. In the Ohio, floodplain influences appear to be minor, although we do not yet have sufficient data to quantify the effects of adjacent wetlands or submersed macrophytes on the river itself.

Steep declines in the C:N ratio of DOM in the Ohio River during winter to less than half of Redfield predictions, is further evidence of the importance biological control of carbon availability in the river. Labile organic matter (based on a lower C:N ratio; Meybeck 1982; Williams 1995; Anderson & Sarmiento 1994) will be rapidly degraded unless other factors limit bacterial utilization. Our data suggest that during winter, when phytoplankton abundance and presumably biological activity is low (Wehr & Thorp 1997), labile carbon will remain in the water column longer, much as it does in the open ocean (Williams 1995). The results from multiple regression analysis of our Ohio River data indicate that phytoplankton density is the most important variable explaining changes in DOC in the river (Table 4), and this source may be presumed to be more N-rich (Tezuka 1990). Decomposition and regeneration of nitrogen from N-rich organic matter must occur later in the year when bacterial activity increases, as supported by other data. For example, in the lower Mississippi, bacterial growth and ammonium regeneration are closely coupled in the summer, but not in winter months (Cotner & Gardner 1993). Patterns such as these should lead to an accumulation of N-rich POC and DOC in rivers during the winter and early spring, as was observed in the Ohio.

Few data exist on C:N or C:P ratios of DOM in rivers. The composition of DOM in the Amazon system is perhaps the best studied of all large rivers. In general, C:N ratios of riverine DOM (mainly humic substances) in most rivers are fairly nitrogen-poor, with humic acids (HA) averaging about 20; while C:N of the HA in the Rio Negro averages nearly 60 (Ertl et al. 1986; Hedges et al. 1986). Further, these authors pointed out that C:N ratios of fulvic acid in the Amazon system are greater (low N content) than

corresponding humic acids from the same sites (mean ≈60). The Pawcatuck River in Rhode Island (USA), a smaller river system also influenced by humic materials, had C:N ratios of DOM (excluding Little Naragansett Bay) ranging from about 8–13 (Doering et al. 1993). Both systems receive their primary subsidy of DOC from terrestrial sources. We know of no comparable data for more autotrophic river systems. However, the C:N of DOM in mesotrophic Lawrence Lake (Michigan, USA) varied from about 10 to 30 (slightly above Redfield); while in hypertrophic Wintergreen Lake, it ranged from about 4–8 (≈Redfield), suggesting that a greater dependence on autochthonous (phytoplankton and macrophyte) production will alter the C:N ratio of organic matter to the ecosystem (Ward & Wetzel 1984). Causes for increases or decreases in dissolved C:N in rivers may also be considered by examining the C:N ratios of particulate matter in rivers. In general, C:N ratios of riverine (aquatic) POC have been measured to be between 6 and 9, while POC from terrestrial sources range between 20 and 40 (Malcolm & Durum 1976). The supply of allochthonous POC and DOC from the watershed should tend to increase the C:N ratio of dissolved (and less-easily degraded) organic carbon (e.g., Thurman 1985; Ertel et al. 1986; Leenheer 1994), while autochthonous sources may be more N-rich and easily degradable (e.g., Tezuka 1990). The exact nature of the carbon supplied by submersed macrophytes and adjacent wetlands in large rivers requires more study. Presumably the highest quality DOM (C:N ratios <3) is found in rivers during the winter and spring, when bacterial activity may be limited by low temperatures, and during a period when littoral and submersed macrophytes are in their early stages of decay (e.g., studies by Findlay et al. 1991a, 1992).

Almost no data exist for dissolved C:P ratios in streams or rivers. Dissolved C:P ratios in the Ohio exceeded the Redfield ratio of 106 year round and at all sites (Figure 4). Ratios were closest to Redfield predictions (about 250–300) during the fall. Using data presented in a study on the Pawcatuck River (Doering et al. 1993), we estimate that C:P ratios of that system vary from about 170 to 500. We presume that this condition exists because freshwater bacteria are commonly P-limited (Toolan et al. 1991; Coveney & Wetzel 1992) and are able to hydrolyze organic-P with extracellular enzymes, while leaving most of the organic-C unchanged (Lock 1993). Because of the very marked seasonal changes in C:N and C:P ratios in DOM measured in the Ohio, experiments are needed to determine which mechanisms may be responsible for driving changes in carbon supply and bacterial metabolism over the year.

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