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Synchronous variation of dissolved organic carbon and color in lakes

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Abstract

Temporal variation in dissolved organic carbon (DOC) and water color (light absorption at 440 nm) was measured in 20 lakes in northern Michigan that varied in DOC, pH, morphometry, and relative productivity as indicated by chlorophyll and total phosphorus (TP). Monthly observations during May–August over 6 yr revealed that DOC and color varied by 6- and 28-fold among lakes and varied substantially through time within lakes. The pattern of temporal variation differed among years but was synchronous among lakes. Of the 190 possible correlations among lake time series, most were positive for DOC (158) and color (160), and 50% of the positive correlations were significant ($P < 0.05$). Other variables, such as total phosphorus, chlorophyll, and pH, were less synchronous and had fewer significant positive correlations (13–25%). Temporal dynamics in DOC and color were related to ice-out date as well as spring and summer precipitation. Years of late ice-out and high spring rain were associated with high DOC and color in spring. A summer drought in one year led to declines in color (up to 40%) and DOC (up to 38%) in nearly all of the lakes. The common temporal dynamics of DOC and color were most likely the result of climatic conditions that affected loading of allochthonous carbon as well as losses due to photodegradation. The variations in DOC were sufficient to cause large changes in light penetration, standing stocks of carbon, and ecosystem metabolism.

Dissolved organic carbon (DOC) is increasingly recognized as a critical property of aquatic ecosystems. DOC influences a wide variety of physical, chemical, and biological processes. Light absorption by DOC has a strong influence on the penetration of ultraviolet and photosynthetically active radiation (Morris et al. 1995) as well as the mixing and thermal properties of lakes (Fee et al. 1996; Snucins and Gunn 2000). DOC interacts with dissolved nutrients and metals and thereby influences their concentrations and availability (Perdue 1998; Shaw et al. 2000). DOC mainly comprises acids and, therefore, affects pH and in some acidic waters acts as a buffer (Driscoll et al. 1994). DOC also represents a large reservoir of carbon in many systems, including the ocean (Benner et al. 1992). Small changes in DOC concentrations can be of considerable significance for carbon

cycling and ecosystem metabolism because the pool is so large (e.g., Cole et al. 2000).

Globally, the concentration of DOC varies from <100 to $>4,000 \mu\text{mol L}^{-1}$ in freshwaters (Perdue and Gjessing 1990). In many lake districts where cultural eutrophication has had minimal effects, DOC is a primary feature that distinguishes lakes. Lakes in these areas with low DOC concentrations have high water clarity and appear blue in color. High-DOC lakes have brown water because of the high concentrations of light-absorbing humic and fulvic acids. One index of the relative humic content of water is referred to as “color” and has been measured by a variety of optical methods (Molot and Dillon 1997). The large variation in DOC and color observed among lakes is determined by relative rates of loading, in-lake transformations, and hydrologic losses (Engstrom 1987; Dillon and Molot 1997; del Giorgio et al. 1999). Large lakes with long water residence times tend to have lower DOC and color because of lower areal loading rates and higher in-lake rates of photo- and biological mineralization. Lakes in watersheds with extensive wetlands and peatlands often have high DOC loading and typically high DOC concentrations and color (Gergel et al. 1999).

Although DOC concentrations can vary dynamically in small lakes with short water residence times and high allochthonous loading (e.g., Hessen et al. 1997), DOC in systems with larger, longer residence time can appear to have low

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seasonal and interannual variance. This low variance reflects the slow dynamics of a large and relatively recalcitrant pool of organic matter (Wetzel 1995). Despite the apparent slow dynamics and low variability, some observations reveal that DOC can change substantially in lakes. At the Experimental Lakes Area (ELA) in Canada, DOC has declined in lakes as a consequence of experimental acidification and long-term climate warming (Schindler et al. 1997). In other studies of Canadian boreal watersheds, lake DOC has increased in watersheds with clear-cutting and wildfires relative to unaltered watersheds (Carignan et al. 2000; France et al. 2000). Long-term observations of lakes and rivers in Sweden reveal increases in DOC during years of elevated precipitation (Andersson et al. 1991). Thus, DOC can vary in response to large-scale environmental changes with attendant effects on lake ecosystems.

Most studies of variability in lake DOC and color have been either broad comparative analyses of among-lake variation (e.g., Kortelainen 1993; D'Arcy and Carignan 1997) or studies focused on mass balances and changes in a smaller set of lakes in response to environmental or experimental conditions (e.g., Dillon and Molot 1997; Schindler et al. 1997; Carignan et al. 2000). Few studies have considered the temporal variation of a collection of lakes through time, especially in the context of whether DOC might vary synchronously among lakes. Synchrony is defined as the concurrent variation of time series among ecosystems.

There is a growing interest in considering the ensemble dynamics of lakes in a landscape context, because such variation reveals common environmental forcing and responses and allows extrapolation of results (Magnuson et al. 1990; Kratz et al. 1997). Some lake properties such as surface-water temperature are highly synchronous in a region because of a shared climate (Baines et al. 2000). Biological variables might be expected to vary more independently among lakes because of greater intrinsic regulation through ecological interactions (Magnuson et al. 1990). Yet, Baines et al. (2000) found relatively high synchrony in chlorophyll dynamics for seven lakes in northern Wisconsin, indicating common interactions between environmental forcings and ecological responses for phytoplankton communities. Synchrony in the annual abundances of zooplankton populations has also been identified in eight Ontario lakes (Rusak et al. 1999). Less is known about the temporal dynamics of DOC and color despite evidence cited above that DOC can vary with climatic conditions. Kling et al. (2000) document synchrony in DOC among 10 Arctic lakes in a drainage series. There was positive synchrony of DOC, although the mean correlation for DOC was lower than for many other variables.

Neither the spatial scale of DOC synchrony among lakes nor the tendency for other collections of lakes to exhibit synchrony is known. Furthermore, the magnitude of variation in DOC and color, especially for lakes with high concentrations of DOC, remains poorly described despite the significance of DOC and color to many lake ecosystem processes. In this paper, we report measurements of DOC and color made in 20 lakes over 6 yr. We document significant variation, both among lakes and temporally within lakes, in DOC and color. We test whether the observed temporal var-

iation is synchronous. We examine whether the variation in DOC and color is associated with externally driven environmental conditions such as precipitation and drought, as well as internal lake properties such as lake nutrient concentrations, pH, and morphometry.

Methods

Twenty lakes were sampled during summer in 1995–2000. All lakes were visited monthly within a few days (usually 2 d) from May through August. From each lake a 1-L sample of surface water was collected for subsequent analysis of pH, DOC, chlorophyll, and color. A total phosphorus (TP) sample was collected separately in an acid-washed bottle.

TP samples were frozen on return to the laboratory. For other analyses, duplicate subsamples (usually 200 ml) from the 1-L sample were passed through 47-mm GF/F filters under low vacuum (<200 mm pressure). Filters were frozen for later analysis of chlorophyll *a* (Chl *a*). Duplicate samples of filtrate (20 ml) were collected in glass scintillation vials and acidified to pH 2 with 2N H₂SO₄ and stored in the dark for later analysis of DOC. Filtrate was also collected and stored at 4°C for analysis of water color. pH was measured in the laboratory immediately after sample collection using an Orion digital meter with two-point calibration and electrodes with automatic temperature compensation.

DOC was measured on a Shimadzu model 5050 high-temperature organic carbon analyzer. Duplicate measurements were made for each sampling time. Concentrations were determined using a range of standards. Water color was determined within a few days of sample collection by reading absorbance on a spectrophotometer at 440 nm in a 10-cm cuvette. Samples were read against a blank prepared from Nanopure water. Color is expressed as a wavelength-specific absorption coefficient in units of inverse meters.

$$a_{440} = 2.303 \times (\text{absorbance at 440 nm} \div 0.1 \text{ m}) \quad (1)$$

This value is a relative measure of the brown color of lake water and reflects the content of light-absorbing, primarily humic material in the water. Total phosphorus was measured on a Lachat AE autoanalyzer after persulfate digestion using the molybdate blue method. Chl *a*, with corrections for phaeopigments, was determined by extracting filters in a refrigerator overnight in 25 ml of 100% methanol and measuring the fluorescence of extracts before and after acidification using a Turner 450 fluorometer and SC665 emission filter and NB440 excitation filter. Calibration of the fluorometer was conducted annually using a spectrophotometer.

Statistical analysis—Synchrony was measured by calculating the Pearson correlation coefficient among all possible pairs of lakes ($n = 190$). Although synchrony is often assessed for annual or seasonal means, we used all the data for the analyses reported here. We tested several assumptions and concerns (Rusack et al. 1999; Baines et al. 2000) involved in using the time series correlations as an indicator of synchrony, including: (1) the assumption that the null model of zero correlation between lake pairs is appropriate, (2) the effect of nonhomogeneity of variances on the analysis of correlation patterns, (3) the consequences of autocorre-

Table 1. Selected physical, chemical, and biological characteristics of the study lakes. Means of pH, total phosphorus (TP), and chlorophyll *a* are for all samples.

| Lake | Area (ha) | z_{\max} (m) | pH | TP (nM) | Chlorophyll (mg m^{-3}) | Visible outlet? |
|--------------------|-----------|----------------|------|---------|----------------------------|-----------------|
| Bergner | 17.8 | 12.0 | 5.67 | 449 | 6.72 | Yes |
| Bog Pot | 1.8 | 2.0 | 5.98 | 1,106 | 17.68 | Yes |
| Bolger | 1.1 | 3.5 | 6.62 | 1,165 | 19.85 | Yes |
| Brown | 32.9 | 5.5 | 8.10 | 1,875 | 19.60 | Yes |
| Crampton | 25.8 | 15.2 | 6.26 | 296 | 3.81 | No |
| Cranberry | 1.3 | 7.9 | 4.87 | 444 | 8.05 | No |
| Eds Bog | 0.1 | 7.0 | 5.18 | 634 | 4.18 | No |
| Forest Service Bog | 0.2 | 4.9 | 5.46 | 345 | 4.44 | No |
| Hummingbird | 0.8 | 7.6 | 4.99 | 962 | 23.54 | Yes |
| Inkpot | 6.6 | 5.2 | 7.69 | 1,103 | 8.65 | Yes |
| Kickapoo | 7.9 | 2.7 | 7.42 | 1,263 | 12.15 | Yes |
| Morris | 5.9 | 6.7 | 7.46 | 852 | 12.41 | Yes |
| North Gate Bog | 0.3 | 8.0 | 4.38 | 565 | 5.14 | No |
| Plum | 91.4 | 7.3 | 7.60 | 811 | 8.86 | Yes |
| Raspberry | 4.6 | 6.1 | 6.18 | 473 | 6.91 | Yes |
| Reddington | 1.2 | 4.9 | 6.26 | 687 | 11.34 | Yes |
| Roach | 45.1 | 10.0 | 5.92 | 331 | 3.73 | No |
| Tenderfoot | 194.2 | 9.1 | 7.79 | 1,208 | 9.42 | Yes |
| Tuesday | 0.9 | 15.0 | 6.04 | 392 | 6.59 | No |
| Ward | 2.7 | 8.2 | 7.77 | 858 | 4.67 | Yes |

lation in the time series, (4) the effect of maximum values in the time series on measures of synchrony, and (5) the possible effects of trends in the time series related to repeated seasonal patterns or long-term directional change. Briefly, we found that none of these concerns seriously affected assessments of synchrony based on correlations. Randomized lake time series yielded correlations centered on zero supporting the standard null model expectation. Non-parametric Spearman rank correlations gave results almost identical to Pearson correlations. Some of the time series had lag-1 autocorrelations, but correlations between differenced series were typically similar to those of autocorrelated series. Deleting maximum values from time series did not strongly alter correlations among most lake pairs. Finally, z -transformations of the time series to assess possible effects of seasonal or other trends did not produce significantly different patterns in the Pearson correlations than untransformed series.

For some questions related to the overall response of the lakes, we categorized the number of lakes having greater or lesser values of DOC and color. The exact probability associated with any given number of lakes was calculated using the binomial distribution.

Meteorological data—Precipitation was measured with a rain gauge at the University of Notre Dame field laboratory located within a few kilometers of all 20 lakes. We supplemented our records, available only for the summer months (June through August), with additional data from the North Temperate Lakes (NTL) Long Term Ecological Research site (LTER) at Trout Lake near Boulder Junction, Wisconsin, approximately 30 km from our study site. The NTL-LTER site

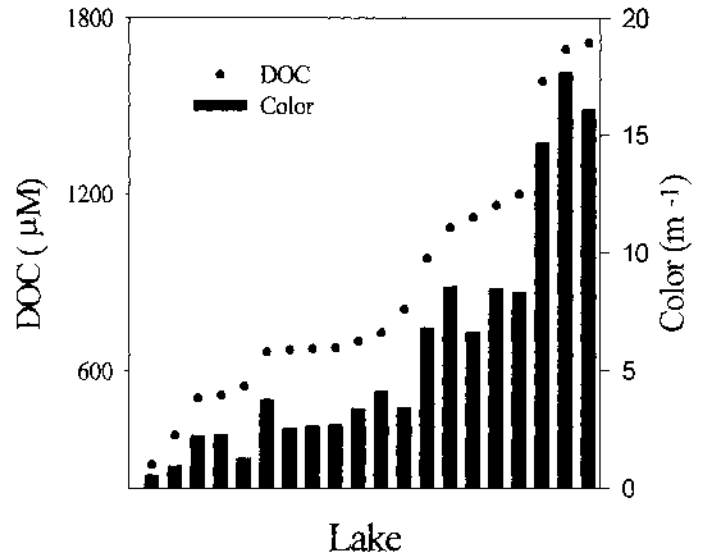


Fig. 1. Average DOC and color in the 20 study lakes for the period May–August 1995–2000. Lakes are ranked from lowest to highest DOC.

maintains extensive meteorological data (<http://limnosun.limnology.wisc.edu/catalog.html>). We used daily spring precipitation data (April and May) and records of the last date of complete ice cover for the LTER study lakes. We calculated spring precipitation as the sum of daily precipitation from April 1 to our first sampling date for each year (consistently the third week of May).

General lake characteristics—The 20 lakes considered in this study are located at the University of Notre Dame Environmental Research Center (UNDERC) on the border of Wisconsin and Michigan near Land O' Lakes, Wisconsin, at 46°13'N latitude and 89°32'W longitude (see UNDERC web site for further details and map at <http://129.74.130.84/>). Lakes are surrounded by wetlands and upland forests with little to no human development in their watersheds. Thirteen lakes had visible outlets leading to either temporary or permanent streams. The remainder had no obvious outlets. The lakes range in size and depth (Table 1) from small, relatively deep, kettle hole-type lakes (e.g., Tuesday Lake) to large, relatively shallow basins (e.g., Brown and Plum lakes).

Results

The study lakes had a strong gradient of DOC and color varying over 6-fold in DOC and 28-fold in color (Fig. 1). Some lakes, such as Crampton and Roach, had low DOC (<400 μM) and low color (<1 m^{-1}). Most lakes, however, had moderate to high concentrations of DOC and were visibly stained (color >2 m^{-1}). High DOC lakes included Hummingbird and North Gate Bog, where average concentrations exceeded 1,600 μM and color was >15 m^{-1} . Lakes at the highest end of the DOC gradient (Hummingbird, North Gate Bog, and Reddington) were also acidic with average pH <6 (Table 1). Not all lakes with moderate to high DOC, however, were acidic. For example, Inkpot, Morris, Kickapoo,

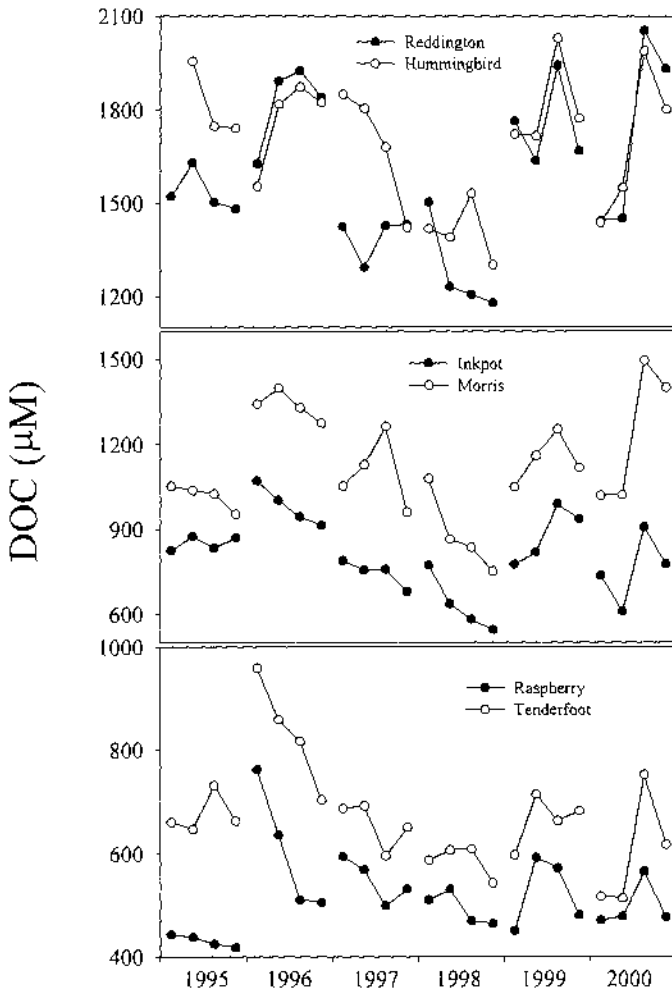


Fig. 2. Exemplary time series of DOC for pairs of lakes illustrating how synchrony was determined. Data are monthly values for May–August in each year. Correlations (r) for the pairs are: Reddington–Hummingbird, $r = 0.69$, $P = 0.001$; Inkpot–Morris, $r = 0.74$, $P < 0.001$; Raspberry–Tenderfoot, $r = 0.71$, $P < 0.001$.

and Bolger all had average DOC concentrations $>700 \mu\text{M}$ and $\text{pH} > 7$ (Table 1).

The lakes also varied in pH and relative primary productivity. Eight of the lakes have an average pH < 6 . In contrast, seven of the lakes have an average pH > 7 (Table 1). Phosphorus is the primary limiting nutrient for several experimental lakes not included in this study but in close proximity to the lakes listed in Table 1 (Carpenter et al. 2001). Total phosphorus (TP) is, therefore, an indicator of potential planktonic primary production, and TP varied more than sixfold among lakes. As expected, Chl a was related to TP ($r = 0.76$, $P = 0.01$) and also had a sixfold range in means of $3.7\text{--}23.5 \text{ mg m}^{-3}$ (Table 1).

Seasonal and interannual variation—DOC varied through time both within years and among years as illustrated in Fig. 2 for three pairs of lakes. In terms of interannual variation, DOC tended to increase from 1995 to 1996 but was lower in 1997 and even lower in 1998. DOC increased in 1999, and average values in 2000 were close to those observed in

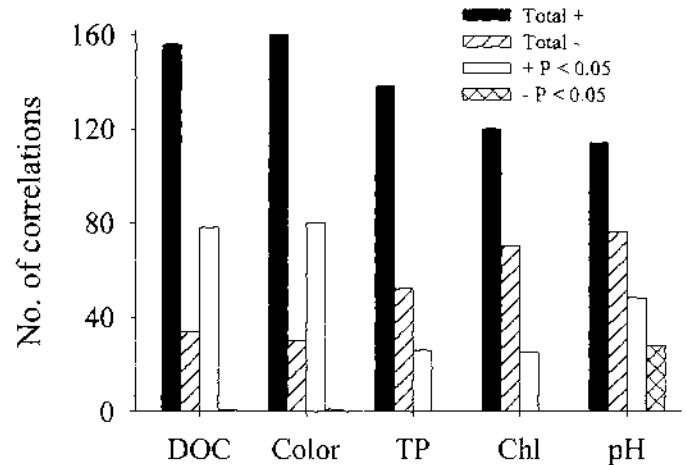


Fig. 3. Number of correlations that were positive ("total +," filled bars), negative ("total -," slashed bars), positive and significant ($P < 0.05$, open bars), negative and significant ($P < 0.05$, crosshatched bars) for DOC, color, total phosphorus (TP), chlorophyll a (Chl), and pH based on correlations between time series for each lake ($n = 190$).

1999. The seasonal patterns of DOC were also not consistent from year to year. In some years, DOC tended to decline from May to August (e.g., 1998). Seasonal variation was relatively low in 1995, whereas all lakes had large increases in DOC during midsummer in 1999 and 2000 (Fig. 2). Similar dynamics were also observed for color (data not shown).

Synchrony—Most remarkably, the lakes illustrated in Fig. 2 had synchronous variation in DOC. Correlations were 0.69, 0.74, and 0.71 (all $P < 0.01$) for the pairs: Reddington and Hummingbird, Inkpot and Morris, Raspberry and Tenderfoot, respectively. These correlations are not based on direct hydrological linkages between these pairs because none share a connecting stream.

The synchronous dynamics illustrated in Fig. 2 reflect a more general result based on correlations between the 190 possible pairs of lakes. There were 156 positive correlations and, of these, half (78) had a $P < 0.05$ (Fig. 3). Thus, temporal variation among the 20 lakes was in general similar, although some lakes demonstrated relatively little synchrony. Specifically, three lakes—Bolger, Crampton, and Forest Service Bog—accounted for 21 of the 34 negative correlations observed. These lakes tended to vary independently of the other 17. We have no explanation for this low synchrony except to suspect that longer lags in hydrological inputs might lead to distinct temporal dynamics for these systems.

The dynamics of color among the lakes and the tendency toward synchrony was similar to DOC, reflecting a general relationship between these two variables. Positive correlations were observed for 160 of the 190 pairwise comparisons, and 80 of these positive correlations had $P < 0.05$ (Fig. 3).

The number of positive as well as positive and significant correlations were similar for DOC and color in many lakes, again reflecting the common dynamics of these two variables (Table 2). Three lakes—Bolger, Crampton, and Tuesday—appeared to be more synchronous for color than DOC (Table

Table 2. Number of positive correlations ($r > 0$) for DOC and color by lake. Positive correlations with $P < 0.05$ are noted in adjacent column. Total possible number is 19 for each entry.

| Lake | DOC | | Color | |
|--------------------|----------|------------|----------|------------|
| | positive | $P < 0.05$ | positive | $P < 0.05$ |
| Bergner | 18 | 14 | 18 | 13 |
| Bog Pot | 16 | 9 | 15 | 7 |
| Bolger | 10 | 4 | 19 | 8 |
| Brown | 16 | 12 | 17 | 8 |
| Crampton | 9 | 0 | 14 | 3 |
| Cranberry | 14 | 9 | 16 | 10 |
| Eds Bog | 16 | 3 | 13 | 4 |
| Forest Service Bog | 9 | 0 | 8 | 0 |
| Hummingbird | 17 | 12 | 16 | 9 |
| Inkpot | 17 | 12 | 18 | 13 |
| Kickapoo | 17 | 11 | 18 | 11 |
| Morris | 19 | 13 | 18 | 14 |
| North Gate Bog | 17 | 10 | 15 | 7 |
| Plum | 17 | 8 | 14 | 6 |
| Raspberry | 17 | 7 | 19 | 6 |
| Reddington | 17 | 11 | 17 | 12 |
| Roach | 11 | 0 | 15 | 1 |
| Tenderfoot | 17 | 10 | 17 | 8 |
| Tuesday | 17 | 2 | 18 | 10 |
| Ward | 17 | 11 | 17 | 10 |

2). For example, Tuesday Lake had 17 positive correlations for DOC, but only two of these had $P < 0.05$. In the case of color, there were 18 total positive correlations, with 10 having $P < 0.05$.

DOC and color were more synchronous than the other variables measured (i.e., TP, Chl α , pH). For example, although there was a tendency toward synchrony in all cases, there were fewer total positive correlations for TP (138), Chl (120), and pH (114) and far fewer significant ($P < 0.05$) positive correlations (TP = 26, chlorophyll = 25, pH = 48) compared to observations for DOC and color (Fig. 3). Similar to DOC and color, there were very few significant negative correlations for TP and chlorophyll.

Synchrony and lake conditions—Synchrony suggests that some factors common to lakes cause similar temporal variation among lakes. Although external environmental factors related to climatic conditions would seem the most likely cause of such variation, synchrony might also be correlated with features of lakes such as nutrient, chemical, or morphological status. We examined this possibility by calculating mean synchrony as the average correlation coefficient from the 19 time series correlations for each lake and asking if this statistic was related to other properties of the lakes.

Mean synchrony based on the average correlation coefficient for DOC tended to be lower in lakes with low DOC and chlorophyll (Fig. 4); however, some lakes (e.g., Bolger) had relatively high values of these variables and low average synchrony (Fig. 4). The low synchrony observed in the clear-water, low-DOC lakes was at least partly related to the low absolute variability of these systems. We previously determined that alkalinity is strongly correlated with the rate of photobleaching in lakes (Reche et al. 1999). We anticipated that synchrony might be greater in the lakes with higher pH,

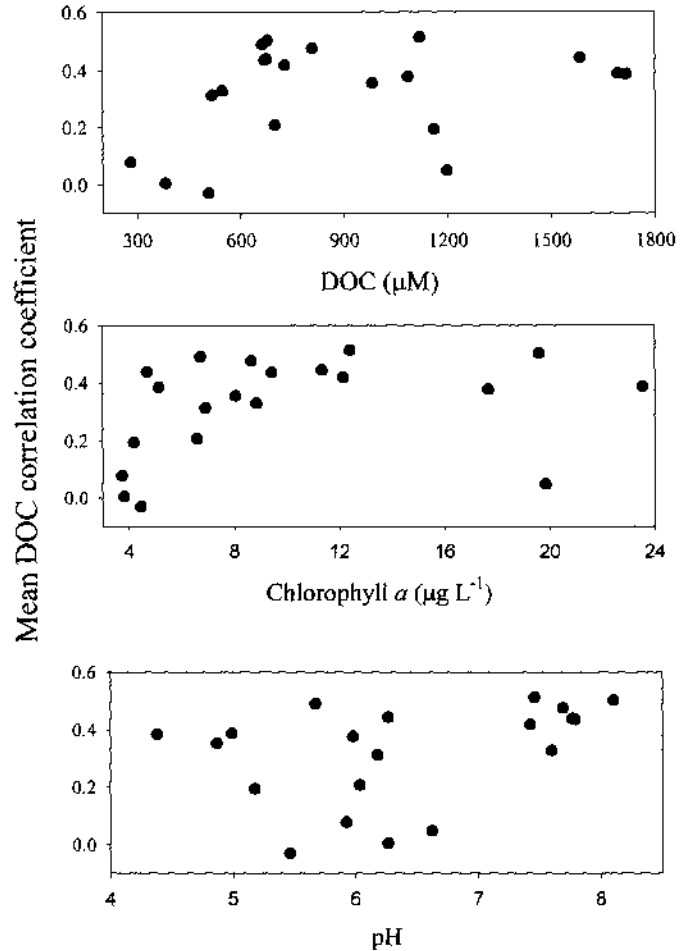


Fig. 4. Average DOC, chlorophyll, or pH versus the mean Pearson correlation coefficient for each lake. The mean DOC correlation of a lake is the average of 19 time series comparisons. Linear regressions for the mean correlation coefficient and DOC, chlorophyll, or pH were all not significant at $P < 0.05$.

alkalinity, or both because photodegradation might be greater, leading to similar loss dynamics. This was not the case (e.g., Fig. 4). Other aspects of lakes such as morphometric features (results not shown) were also unrelated to mean synchrony. In general, mean synchrony based on DOC or as analyzed by the mean correlation coefficient for color (not shown) was unrelated to internal lake conditions. This point is illustrated by the three independent variables of Fig. 4, where linear regressions were not significant at $P < 0.05$.

We hypothesized that lakes with higher synchrony might have stronger hydrological connections to the drainage system, as manifested by the presence of a visible outlet. Lakes with outlets might have shorter relative residence times (per unit volume) and respond similarly to new inputs of DOC. Thirteen lakes had visible outlets, as noted in Table 1. These lakes accounted for 134 and 125 of the total positive and significant correlations ($P < 0.05$) for DOC ($n = 158$) and color ($n = 160$), respectively. In agreement with our hypothesis, the number of positive, significant correlations for outlet lakes was far greater than expected for DOC ($\chi^2 = 27.3$, $P < 0.005$) and color ($\chi^2 = 12.1$, $P < 0.005$).

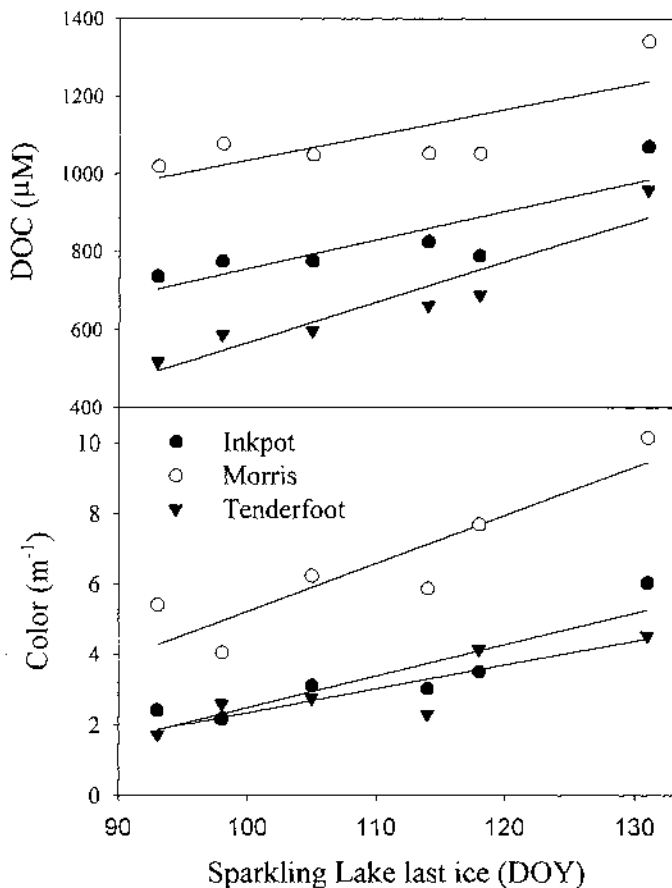


Fig. 5. Relationship between the May value of DOC or color for three of the study lakes and last date of complete ice cover on Sparkling Lake for the years 1995–2000. Symbols are Morris Lake (open circle), Inkpot Lake (closed circle), and Tenderfoot Lake (triangle). Data from Sparkling Lake provided by NTL-LTER.

Variation in spring DOC and color in relation to climate—Synchronous variation in DOC and color suggests environmental variables such as precipitation and drought might be important in determining the similar dynamics observed among lakes. Spring values of DOC and color at the May sampling varied from year to year and set the starting point for summer concentrations (e.g., Fig. 2). For example, the initial concentration of DOC in Reddington Lake was 1,764 μM in 1999 and 1,444 μM in 2000. Similarly, spring DOC was 648 versus 959 μM in Tenderfoot Lake in 1995 and 1996, respectively. From these different starting concentrations, dynamics also varied among summers. For example, pronounced declines in DOC (and color) were observed in nearly all lakes during 1998 (e.g., Fig. 2), whereas substantial midsummer increases were observed in many lakes during 1999 and 2000 (e.g., Fig. 2).

Conceptually, variation in the spring levels of DOC and color in the lakes should be related to variation in new inputs during the period of snowmelt. DOC with a high content of light-absorbing humic and fulvic acids (i.e., color) frequently derives from the upper horizons of wetland and upland soils (McDowell and Likens 1988). As the water table rises, accumulated DOC in the upper soil layer tends to mobilize and

flush into adjacent aquatic systems (Boyer et al. 1997). We cannot directly assess the connection of lake DOC and color to soils and watershed hydrology, but some data suggest the importance of these processes to spring concentrations.

We observed that spring DOC and color were higher in lakes during years of late ice-out and lower in years of early ice-out, based on ice-out data from the nearby NTL-LTER lakes. Spring DOC and color in a number of the lakes in our study were predictable from the last date of ice cover recorded each year for LTER lakes (Fig. 5). For example, last ice date for Sparkling Lake (an LTER lake) is related ($P < 0.1$) to spring DOC and color in Bergner, Brown, Inkpot, Kickapoo, Morris, Tenderfoot, and Ward Lakes. Although the relationships illustrated for three lakes in Fig. 5 is representative of a larger group of lakes, 10 (DOC) and 11 (color) lakes did not have significant regressions, so this result is not general. Six years, however, is a limited basis for such an analysis. Another way to examine the association of DOC and color with ice-out date is to assess whether lakes had consistent differences in concentrations and absorbances in extreme years. Over the 6 yr of our study, the extremes for last date of complete ice cover on Sparkling Lake were day 131 in 1996 and day 93 in 2000. Spring DOC and color for 1996 exceeded 2000 in 16 and 14 lakes, respectively. Assuming an equal chance that individual lakes could have a greater or lesser value of DOC or color in each year, the probability that 16 or more lakes had higher values of DOC in 1996 is 0.006, whereas the probability of 14 or more lakes having higher values of color is 0.058.

Spring snowmelt leads to a flush of water into the lakes. This water can be enriched in highly colored DOC or can simply raise lake levels sufficiently that flooding of adjacent wetlands leads to subsequent increases in lake water concentrations. The relationship of DOC and color to ice-out might reflect wetter periods closer to our May sampling time (21 and 22 May in both 1996 and 2000). If so, ice data might be related to the time of highest water and DOC input and hence higher lake concentrations of DOC when samples are taken at a fixed date in spring. Another possibility is that DOC accumulates during darkness under ice cover because photodegradation ceases. The spring sampling time in late ice-out years results in measurements of higher DOC, because less photodegradation has occurred relative to years of early ice-out. There is widespread evidence that lake ice duration is declining, leading to earlier ice-out dates (Magnuson et al. 2000). This trend might cause DOC and color to decline in lakes unless counterbalanced by other mechanisms that increased inputs (e.g., greater precipitation).

Spring precipitation (calculated as cumulative precipitation from 1 April to first sample date) might also be important in determining spring concentrations of DOC and color. In general, spring rainfall was not correlated with DOC or color, but this test is limited by the small number of years. Another way to look at the data is to compare tendencies in the lakes for wet and dry years. Spring precipitation was relatively high in 1995, 1996, and 1999 (>14 cm) and relatively low in the other three springs (<6 cm). We calculated mean DOC and color for the three wet and dry springs, respectively, in each lake and then compared these two values, asking if DOC and color were higher in wetter springs.

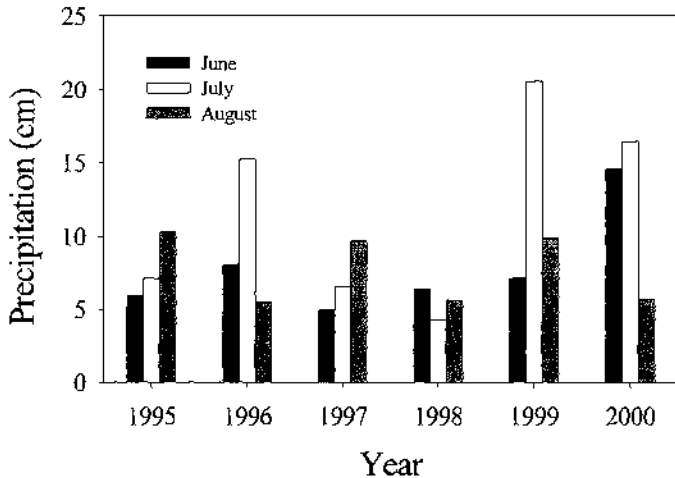


Fig. 6. Summer monthly rainfall at the University of Notre Dame Environmental Research Center for the years 1995–2000.

Sixteen lakes had higher DOC and 14 lakes had higher color in wet springs. The probability of these values is 0.006 (DOC) and 0.058 (color).

Variation in summer DOC and color in relation to climate—The summer dynamics of DOC and color appear to be related to the amounts and timing of rainfall. In several summers—specifically 1996, 1999, 2000—monthly rainfall in July was around 15 cm (Fig. 6). These relatively high levels of precipitation often come in a few heavy storms. In 1996, most lakes were at or near the highest levels of DOC observed over the study in spring (Fig. 2), and these levels were generally dropping during summer. High rainfall might have slowed the rate of decline. In 1999, 11 of 18 lakes (2

lakes missing data) increased in DOC between June and July, whereas in 2000, DOC increased in 18 of 20 lakes between the June and July sampling, and these increases were large (Fig. 2). For example, Reddington Lake gained DOC of over 500 μM . The observations of summer DOC increases associated with higher rainfall are suggestive, but the evidence is limited and not completely consistent. Better resolution of rainfall effects requires a model that accounts for inputs, in-lake processing and losses, and how the timing and amounts of precipitation affect variation in lake DOC.

The years of relatively high summer rainfall contrast with 2 yr of dry weather (1997 and 1998), where color and DOC declined in most lakes (e.g., Fig. 2). These declines were especially large in 1998 when there was a drought during late summer (only 3.2 cm of rain fell between the July and August sampling). Overall, color between the May and August sampling declined 10–40% in most lakes (Fig. 7). DOC losses were also significant in many of the lakes but tended to be lower than color losses, suggesting photobleaching was an important mechanism determining color. Photobleaching is the loss of absorbance that occurs when DOC is exposed to solar radiation. There were also two lakes, Ward and Plum, where changes in color and DOC were uncoupled. Small increases in DOC were observed despite large declines in color. Contrary to all other lakes, Forest Service Bog had a large relative increase in color (18%) and decline in DOC (40%).

Discussion

The principal result of this study is that color and DOC varied synchronously among lakes over the spatial scale of about 3,000 ha. This variation appears to reflect common effects of inputs of allochthonous DOC, arising from uplands

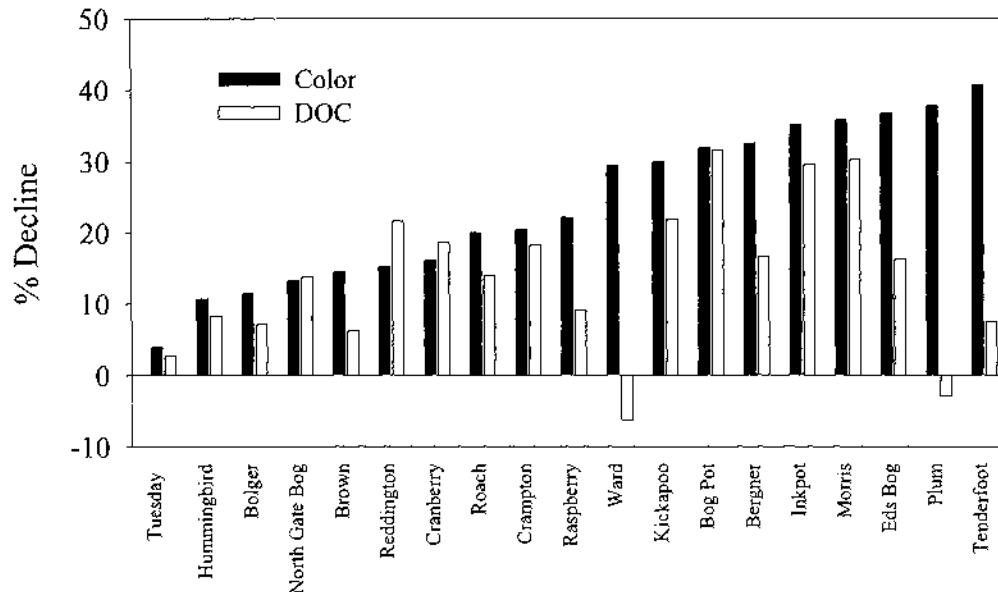


Fig. 7. The percent decline in color and DOC for the survey lakes in summer 1998. Decline was calculated as the difference in concentration or absorbance in the May versus August sample. Lakes are ordered from lowest to highest percent loss of color. Forest Service Bog is not shown (see text). Negative percentages for Ward and Plum lakes indicate an increase in DOC.

and wetlands, that move to lakes via groundwater and surface-water flow. Variable flushing of DOC from upper soil horizons during the spring melt period and during summer storms is likely an important feature in DOC loadings to the lakes based on the relationships observed between DOC and environmental variables such as spring and summer precipitation. It is also possible that common sinks for DOC contribute to synchrony through the effects of environmental variables (e.g., temperature and solar radiation) on processes like bacterial activity and photooxidation.

Our analysis is based on a limited time series of 6 yr and a maximum of 24 observations per lake. We did not attempt to measure analytical or sampling variation in this study. This limits our ability to distinguish among individual observations or the specific dynamics of any particular lake. The study, instead, relies on documenting similar dynamics through analysis of correlations for a large number of systems. Previous studies of synchrony at the nearby NTL-LTER lakes reveal that shorter records (<10 yr) can have reduced synchrony relative to longer records (Baines et al. 2000). Nevertheless, patterns emerge in our data despite variability associated with sampling and analysis as well as the limited length of the time series.

Other studies of synchrony reveal variables that have higher and lower temporal coherence than observed for DOC and color in this study (Magnuson et al. 1990; Rusack et al. 1999; Baines et al. 2000). Highest synchrony is typically found for variables most strongly related to climate (e.g., surface-water temperature), and lower synchrony is observed for biologically determined variables that respond to system-specific properties (e.g., fish abundance) (Magnuson et al. 1990). No previous studies, however, have considered temporal patterns of DOC, except Kling et al. (2000), who observed DOC synchrony for an Alaskan lake series similar in magnitude to the values from this study (most lakes had average correlations of 0.4–0.5). Collectively, the results of our study and Kling et al. (2000) suggest that synchrony in DOC and color might be a general property of lake districts and that extrapolation among lakes of the effects of varying DOC and color is possible.

Although 15 of the lakes considered in this study had relatively high color ($>2.5 \text{ m}^{-1}$) and DOC ($>660 \mu\text{M}$), there were significant differences among these lakes such that synchrony should not be considered a property only of “dystrophic” lakes. There was significant variation among these systems in chemical conditions, as reflected by pH, and in biological productivity, as reflected by TP and Chl *a*. For example, the two highest DOC lakes, Hummingbird and North Gate Bog, were both acidic, but TP and Chl *a* were much higher in Hummingbird (Table 1). Morris and Cranberry represent lakes of quite similar DOC and color. Cranberry, however, is an acidic, low-productivity lake, whereas Morris has pH >7 , extensive macrophyte beds, and higher pelagic productivity based on TP and Chl *a*. These comparisons indicate that high-DOC lakes are not all acidic, low-productivity systems and indicate that synchrony occurs among a diversity of lakes.

We analyzed some of the possible meteorological patterns that were related to synchrony. Specifically, we used records of ice-out date for Sparkling Lake, spring precipitation, and

summer precipitation to test for possible causative relationships. Other variables that might be important but were not examined include winter snow cover, timing of snowmelt and spring run-off, lake level variation, and solar radiation. In most cases, data are not available to examine these other alternatives (e.g., lake level, snow cover, solar radiation including ultraviolet). Given these limitations, we cannot exclude the possibility that other covariables are responsible for the relationships we observed. We can conclude, however, that climatic variables associated with winter/spring and summer conditions set initial levels of DOC and color and subsequent variation within the context of upland, wetland, and lake processes that determine the larger differences observed among lakes (Fig. 1).

The variations in DOC and color observed in the study lakes were large and sufficient to significantly affect processes such as light transmission and ecosystem metabolism. The light-absorbing components of DOC are particularly effective at attenuating ultraviolet radiation and are also strongly related to the attenuation of photosynthetically active radiation (Morris et al. 1995). For example, the changes in DOC observed in Morris Lake cause a large variation in light extinction and an estimated threefold difference in the depth of 10% light transmission. Such changes would significantly alter the light available to support the growth of pelagic and benthic primary producers.

The observed variations in DOC also imply large shifts in carbon standing stocks and fluxes. For example, between May and June 1998, DOC increased $256 \mu\text{M}$ in Tuesday Lake. This increase represents a net change of 845 mmol m^{-2} for the epilimnion (ca. upper 3 m) over a month and is of comparable magnitude to cumulative monthly primary production of 870 mmol m^{-2} (Houser 2001). Assuming the DOC entered the lake as a single pulse and was consumed at a negative exponential rate of $1\% \text{ d}^{-1}$ leads to an estimated consumption of 219 mmol m^{-2} over 30 d. The shift, therefore, in DOC observed in Tuesday Lake in 1998 was of the same magnitude as primary production and potentially provided a large source of carbon to bacteria. This calculation also assumes that no part of the observed change results from net autochthonous DOC production. Monthly changes of similar and greater magnitude were observed in other lakes.

The survey lakes considered here are likely all net heterotrophic ecosystems (respiration $>$ gross primary production) based on observations of similar experimental lakes (Cole et al. 2000). Variable inputs of DOC to these lakes probably result in changes in the balance of autotrophy and heterotrophy. With increased DOC loadings, bacterial production and respiration should increase, but autotrophy might decrease because of lowered light that would accompany increased DOC. Because allochthonous DOC enters a large pool with slow dynamics, alterations of inputs also might have long-lived effects (Wetzel 1995; Carpenter and Pace 1997). The results presented here of relatively large and variable changes in DOC that are similar among lakes warrant further theoretical and experimental analyses of the effects of this variability on ecological processes.

The dynamics of DOC in lakes are driven by inputs, in-lake production and degradation, and hydrologic losses

(Engstrom 1987; Dillon and Molot 1997). The patterns of synchrony documented here suggest that loadings, as well as in-lake sources and sinks, are driven by common environmental processes. There is a need to better document loading rates and dynamic variations in these rates. Furthermore, models are needed that provide estimates of loading to lakes at large scales based on land use and watershed hydrology. Landscape coverage and position, as well as hydrologic connectivity of lakes, might be important to consider in models (Gergel et al. 1999; Soranno et al. 2000). We observed a greater tendency toward synchrony among lakes with visible outlets as opposed to lakes without outlets. This could reflect more rapid water turnover and greater surface water contributions to lakes with hydrologic connections that lead to increases in the variability of DOC and thus the potential for synchrony.

Synchronous variation also suggests that in-lake production or losses of DOC and declines in color can result from environmental processes, such as photodegradation, that might be similar among lakes. The loss of color in nearly all the lakes during the drought period of 1998 is likely the result of reduced inputs of light-absorbing DOC and enhanced photobleaching and photomineralization. Previous studies document the half life of color on the order of 20–50 d in these lakes (Reche et al. 2000). Thus, under drought conditions with accompanying greater exposure to solar radiation, color declined. The greater loss of color relative to DOC has been observed by others (Curtis and Schindler 1997; Molot and Dillon 1997; Moran et al. 2000) and reflects the importance of photobleaching as a mechanism that changes the optical properties of DOC. We expected a relationship between the net loss of color observed during drought (e.g., Fig. 7) and pH based on the previously measured positive relationship between photobleaching and alkalinity (Reche et al. 1999). There was, however, no relationship between the color decline observed in 1998 and lake pH. This result suggests that the interactions of inputs, outputs, and in-lake production and losses of DOC and color vary among lakes sufficiently to obscure a simple relationship.

The major scale of variation in lake DOC and color is among systems. In this study, lakes varied over 6-fold in average DOC concentration and 28-fold in color (Fig. 1). Among years, lakes with high, medium, or low DOC had extremely high fidelity to these categories. Within-lake temporal variation in DOC and color represents a second important scale of variation. In this study, the range of DOC and color was on average two- and threefold, respectively. The among- and within-lake patterns of variation appear to result from similar mechanisms expressed at different hierarchical scales. The greater variation in DOC and color at the among-lake scale primarily reflects how differences in watershed size and structure, which influence loading, interact with lake size and shape, which influence in-lake residence time and degradation. At the within-lake scale, watershed and lake structure are fixed and the principal source of variation is the influence of climatic processes such as ice-out timing, precipitation, and drought, which in turn affect loading, washout, and in-lake production and degradation. Climatic variability influences temporal variation and

the common temporal dynamics of DOC and color of lakes in an area. The synchronous variation indicates a strong connection between lakes and their watersheds and provides further imperative for understanding lakes in a landscape context.

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