

Establishing Relationships Among Nutrient Concentrations, Phytoplankton Abundance, and Biochemical Oxygen Demand in Minnesota, USA, Rivers

Steven Heiskary and Howard Markus

*Minnesota Pollution Control Agency
Environmental Outcomes Division
520 Lafayette Road
St. Paul, MN 55155*

ABSTRACT

Heiskary, S. A. and H. Markus. 2001. Establishing relationships among nutrient concentrations, phytoplankton abundance, and biochemical oxygen demand in Minnesota, USA, rivers. *Lake and Reservoir Management*. 17(4):251-262.

In this study, we demonstrated significant and predictable relationships among nutrients, algae, and biochemical oxygen demand (BOD) in five medium to large Minnesota, USA, rivers. These rivers were distributed across three ecoregions ranging from the Northern Lakes & Forests (NLF) (low nutrients), to the North Central Hardwood forests (NCHF) (intermediate nutrients), to the Western Corn Belt Plains (WCBP) (high nutrients). River order varied, allowing comparisons of periphyton-dominated rivers to phytoplankton-dominated rivers. Summer flows in 1999 were significantly higher than 2000 and, as a result, the "age" of the water (residence time) was greater in 2000. The lower and more stable flows generally resulted in higher algal concentrations in 2000 as evidenced by paired comparisons between sites and years. Seston composition varied not only in terms of origin of the seston: benthic vs. planktonic, but also along a gradient of nutrient enrichment. Benthic diatoms were a significant proportion in clear, low nutrient rivers in the NLF but declined in significance in more nutrient rich NCHF rivers where planktonic green and blue-green algae became more prominent. In the more turbid and high nutrient WCBP rivers, highly tolerant blue-greens were common. Regardless of origin of the seston, rivers with high nutrients exhibited high chlorophyll and high BOD while those with low nutrients exhibited the inverse. The linkages established here will contribute to nutrient criteria development and nutrient or dissolved oxygen (DO)-based Total Maximum Daily Loading (TMDL) studies.

Key Words: rivers, eutrophication, nutrients, chlorophyll, algae, biochemical oxygen demand, flow, residence time.

The purpose of this study was to document relationships among nutrient concentrations, phytoplankton concentration and composition, and biochemical oxygen demand in larger Minnesota rivers. This understanding will support national efforts for ecoregion-based nutrient criteria development, enhance predictive modeling and load allocation studies for medium to large rivers, and provide an improved basis for setting nutrient goals for rivers. In this study we demonstrated significant and predictable relationships among nutrients, chlorophyll, and BOD in a range of Minnesota rivers. We also demonstrated the significant role that flow, watershed size, and residence time play in this relationship. We also found that algal community composition varied as a function of nutri-

ent concentrations, watershed size and flow. Comparisons to other relevant studies were made as well.

The role of excess nutrients (phosphorus and nitrogen) in the eutrophication of lakes and reservoirs has been long known (USEPA 1998) and well documented in the literature (USEPA 2000a). This knowledge of cause (excess nutrients) and effect (e.g., nuisance algal blooms, reduced transparency, low hypolimnetic dissolved oxygen) provides ample basis for the development of nutrient criteria for lakes and reservoirs (Heiskary and Wilson 1989) and for the development of nutrient-based wasteload allocations (USEPA 1999b). The role of excess nutrients in the eutrophication of rivers is not, however, as well documented nor are there clear linkages between nutrients

and response variables (e.g., algal abundance, turbidity, etc.). Work that has been done on North American rivers has focused primarily on periphyton growth in shallow (wadeable) rivers (Dodds et al. 1997 and Dodds and Welch 2000). Much less work has been done on river phytoplankton in larger non-wadeable rivers (USEPA 2000b).

Various studies have sought to describe factors that might control the production of phytoplankton in rivers. Baker and Kromer-Baker (1979) note the role of temperature and current discharge on the production of phytoplankton in the Mississippi River, south of the Minneapolis-St. Paul metropolitan area. They note further that algal concentrations have increased up to 40-fold the concentrations of the 1920s since the installation of locks and dams (Kromer-Baker and Baker 1981). Søballe and Kimmel (1987) made comparisons between the response of lakes to reservoirs to rivers – noting a gradient in response to nutrients related to retention time and other factors. More recent studies from North America (Van Nieuwenhuysse and Jones 1996 and Basu and Pick 1995 and 1996) and Europe (e.g., Billen et al. 1994) document linkages between phosphorus and in-stream chlorophyll *a*. Other studies describe phytoplankton dynamics in rivers and contributing environmental factors (Rojo et al. 1994, DeRuijter van Steveninck et al. 1992). While these studies contribute significantly to our knowledge of phytoplankton in streams and environmental factors that might control abundance and growth they do not often provide further linkages with other variables such as biochemical oxygen demand (BOD) or other factors which could contribute to the identification of quantifiable thresholds of impairment in rivers.

Documenting these relationships will be useful for nutrient criteria development, load allocations, and establishing effluent limitations as a part of National Pollutant Discharge Elimination System (NPDES) permits. USEPA (1997), in guidance for developing total maximum daily loads (TMDLs), alludes to the role of algae in the consumption (respiration) and production (photosynthesis) of oxygen, however a link back to carbonaceous BOD appears to be missing. This linkage is later implied in the USEPA (1999b) protocol for developing nutrient based TMDLs but is not explicitly described. The Minnesota Pollution Control Agency (MPCA) has made use of the interrelationships of nutrients, chlorophyll *a* and BOD₅ in recent NPDES permits. The USEPA and MPCA established a TMDL for BOD at the Lower Minnesota River below River Mile 25 in 1988 (Anderson and Klang 1997). Subsequent work by MPCA staff, including Erwin Van Nieuwenhuysse (formerly of the MPCA), recognized linkages among phosphorus, algal production and BOD for this portion of the Minnesota River (MPCA

unpubl. data). This recognition led to point-nonpoint source trading for a new discharge in this reach. This trade called for the new discharger to fund upstream nonpoint source projects in order to reduce nutrient loading (algal production) in the Lower Minnesota River (Anderson and Klang 1997). This in turn would offset additional BOD they would contribute in this reach and provide for overall reductions in BOD as a part of the TMDL for this reach. This TMDL is also influencing other NPDES discharges in the Minnesota River Basin with respect to phosphorus control.

Study Area

This study focused on medium to large rivers that are typical of several Minnesota ecoregions. Between-region differences in land use, soil characteristics and geomorphology influence water runoff, nutrient loading, and processing of nutrients in the rivers (USEPA 2000b). The rivers selected for this study (Fig. 1) drain one or more of the following ecoregions: Northern Lakes and Forests (NLF), North Central Hardwoods

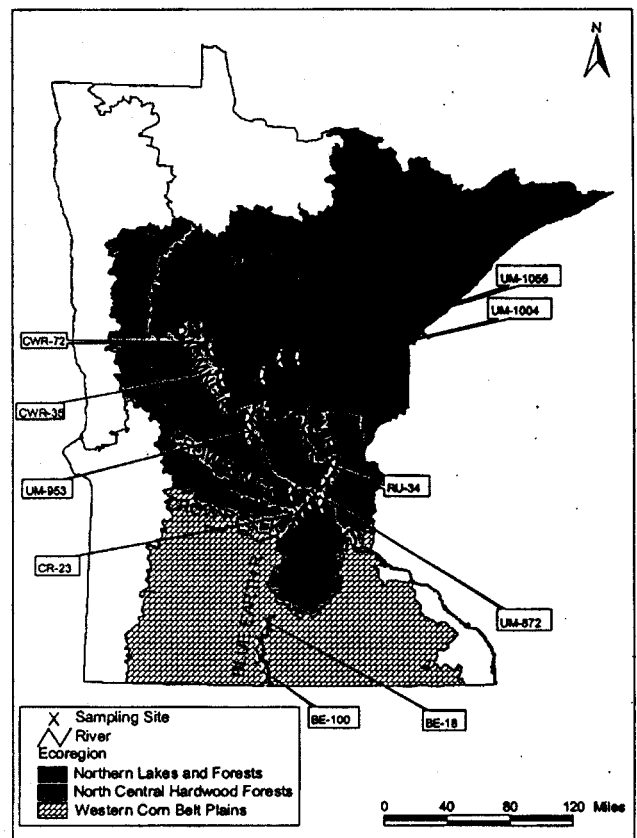


Figure 1.—Minnesota river-nutrient study sites with major watershed and ecoregion boundaries. Select sites noted for reference purposes.

Table 1.—Watershed area, channel morphometry, and flow characteristics for Minnesota river-nutrient study sites. Summer flow and residence time unless otherwise noted.

Site	Water-shed Area	Width meter	Mean Depth	Flow Annual mean	Flow Summer mean	Flow Summer 1999	Flow Summer 2000	Res. Time ^a Summer mean	Res. Time 1999 mean	Res. Time 2000 mean
	km ²	m	m	m ³ ·s ⁻¹	m ³ ·s ⁻¹	m ³ ·s ⁻¹	m ³ ·s ⁻¹	days	days	days
Crow Wing										
CWR-72	2,668	40	1.0	13.7	12.7	22.4	14.2	7.1	6.7	7.0
CWR-35	5,517	65	1.0							
Mississippi										
UM-1056	15,242	35	2.2	84.1	81.0	152.9	58.2	16.7	15.6	17.2
UM-1029	15,768	35								
UM-1004	18,959	75	2.3	104.1	98.0	183.1	77.1	18.6	17.5	19.1
UM-953	30,044	130	2.6	135.6	132.6	252.6		23.9	22.4	
UM-895	34,076	205						25.0	24.0	26.0
UM-872	44,289	300	3.3	233.1	228.3	338.6	152.9	28.5	27.4	29.7
Rum										
RU-34	3,294	55						7.6	7.6	8.2
RU-18	3,546	60	1.1	17.8	16.6	16.9	7.8	8.1	8.1	8.7
Crow										
CR-23	6,527	70	1.3	23.1	23.8	25.1	8.5	12.4	12.3	13.7
CR-0	7,141	75						11.3	11.3	12.6
Blue Earth										
BE-100	811	20	0.6					3.7	3.5	3.7
BE-94	2,082	30	0.7					5.9	5.6	5.9
BE-73	3,541	40	0.6					7.7	7.2	7.7
BE-54	3,603	46						7.7	7.3	7.8
BE-18	3,955	48	1.5	30.3	33.5	68.0	30.4	8.1	7.6	8.2

^a Represents "age of water" estimates based on flow and watershed area.

Forests (NCHF), or the Western Corn Belt Plains (WCBP). These three correspond to three aggregated Level III (USEPA 2000b) Nutrient ecoregions (VIII, VII, and VI, respectively) that characterize Minnesota and much of the Upper Midwest. Watershed areas are 2,590 km² (1,000 mi²) or greater above 15 of 17 sites (Table 1). 1,000 mi² has been used as a basis to differentiate large streams from small streams (Miltner and Rankin 1998). Selecting rivers (sites) from each ecoregion and of varying watershed area allowed us to capture a range of responses.

The upper site on the Crow Wing at CWR-72 drains about 2,668 km² (1,030 square miles) on the western edge of the NLF ecoregion. The downstream site at CWR-35 has a watershed of about 5,517 km² (2,130 square miles) of which about 58 percent is from the NLF and 42 percent is from the NCHF ecoregion (Fig. 1).

The Mississippi River has its origin in the NLF ecoregion (Fig. 1). In 1999, the furthest upstream site monitored was at UM-1004 in Brainerd, Minnesota. As the Mississippi River flows from the Brainerd area,

the watershed becomes more characteristic of the NCHF ecoregion (Fig. 1). At the most downstream site, UM-872 (just north of the Twin Cities Metropolitan Area), the majority of the watershed (65 percent by area) lies in the NCHF ecoregion. In 2000, we replaced sites UM-1004 and UM-965 with two sites further upstream (UM-1056 and UM-1029) that are more characteristic of the NLF ecoregion and exhibit less direct influence from upstream reservoirs.

The Rum River, with the exception of Lake Mille Lacs at its headwater (accounting for about 15 percent of the watershed at RU-18), primarily drains the NCHF ecoregion. Two downstream sites at Isanti, Minnesota (RU-34) and St. Francis, Minnesota (RU-18) were monitored in 1999 and 2000. No major tributaries enter between the two sites and about 250 km² additional watershed area is drained over this 26-km (16-mile) reach. There are no lakes or reservoirs on the main stem of this reach, however several small lakes are located in the watershed between these two sites.

The Crow River has two very distinct subwatersheds. The North Fork comprises about 53 percent of

the watershed, drains from the NCHF ecoregion with numerous lakes and wetlands throughout the watershed (Fig. 1). The South Fork, comprising about 47 percent of the watershed, drains primarily from the agricultural WCBP ecoregion. The highly agricultural land use, combined with numerous small wastewater discharges dotted throughout both subwatersheds, contributes to the "nutrient-rich" conditions in the Crow. The two sites monitored in 1999 and 2000 (CR-23 and CR-0) are located on the mainstem downstream from the confluence of the North and South Forks at river mile 23 and near the mouth to the Mississippi River. No major tributaries enter between these two sites, however about 614 km² of watershed are added over this 36-km (23-mile) reach.

The Blue Earth River, in south central Minnesota, has its headwaters in Iowa and drains an area of about 9,174 km² (3,542 square miles) before entering the Minnesota River. Five sites arrayed from near the Iowa border (BE-94) to a site upstream of the Rapidan Dam (BE-18) were included in 1999. In 2000, the site at BE-77 was replaced with BE-100 to allow for an improved characterization of headwater conditions.

Methods and Materials

At least two sites were sampled on each river to allow upstream and downstream comparisons of concentration and flux in the sampled parameters. Site designators are represented by an abbreviation for that river and miles from the river mouth, for example CWR-72 (Crow Wing River, 72 miles upstream from the mouth). Sites are located at, or near, U.S. Geological Survey (USGS) stream gage locations whenever possible to allow for accurate estimates of flow for each sample date, with a minimum of one USGS gage per river.

The morphometry of each river reach (study site) was determined based on available data and estimated values from published equations (Table 1). The length of each reach and watershed area above the reach was based on existing MPCA and USGS data. The width of the river (wetted cross-section) was estimated over various river stages in 1999 and 2000, at each sample site, and an average value was included to provide a general description of the site. Mean depth at the sample site was estimated based on Søballe and Kimmel (1987) [after Leopold et al. 1964] where:

$$\text{mean depth (m)} = \text{annual mean flow (m}^3 \text{ s}^{-1})^{0.42} / 2.95 \quad (1)$$

To evaluate the effect of stream flow, we used

USGS discharge data for the summers of 1999 and 2000. Residence time or "age of water in the system," was estimated based upon equations provided by Søballe and Kimmel (1987) [after Leopold et al. 1964] where:

$$\text{residence time (days)} = 0.08 * \text{watershed area (km}^2)^{0.6} / \text{discharge (m}^3 \text{ s}^{-1})^{0.1} \quad (2)$$

For sites without actual flow data, residence time was estimated based on the watershed area of the site as a proportion of the watershed area for the nearest gaged site.

Stream order was estimated based on 1:190,000 scale quadrangle maps in the Minnesota Atlas and Gazetteer (DeLorme 1994). BE-100, with the smallest watershed in this study (811 km²), was deemed a third-order stream. The remaining sites on the Blue Earth, Crow Wing at CWR-72, and Rum were deemed fourth-order. The Crow Wing at CWR-35, Crow River, and Mississippi River at UM-1004 to UM-1056 were deemed fifth-order. The remaining sites on the Mississippi (downstream of UM-1004) were deemed sixth order.

Samples were collected at mid-channel on five to six occasions from mid-July to mid-September in 1999 and seven to eight occasions from June through September in 2000. Samples were collected from bridges at each site by means of a bucket on a rope. The bucket was rinsed with ambient water prior to sample collection. For quality assurance purposes duplicate samples were collected on about ten percent of the visits.

Nutrient samples were acidified upon collection with H₂SO₄. Chlorophyll *a* samples were field filtered on the day of collection and the volume filtered was noted. The filter was then placed in a petri-dish and wrapped in foil. Samples were frozen prior to shipment to laboratory and analyzed for chlorophyll *a* and pheophytin *a*. Other samples are un-preserved but chilled to 4 °C prior to shipment to the laboratory.

Phytoplankton samples were subset from the grab samples and preserved with Lugol's solution (APHA 1998). Three samples, typically one each from July, August and September, from nine sites (CWR-35, UM-1004, UM-953, UM-872, RU-34, RU-18, CR-23, BE-94 and BE-54) were forwarded to Phycotech, Inc. for identification to genera and biovolume calculation. The methods may be found under "General Technical Approach" on the Phycotech web site (www.phycotech.com). Three slides per sample were prepared by the HPMA (2-hydroxypropyl methacrylate) method for analysis. An Olympus BHT compound microscope was used to identify the algae. Approximately 10 percent of the counts were recounted from the same slides for both abundance and biovolume to determine detailed counting efficiency.

All water chemistry samples were analyzed at Minnesota Department of Health (MDH) and relevant information is summarized in Table 2 (USEPA 1999a). Precision estimates were derived from the analysis of ten duplicate samples taken during the course of this study. The mean and percentage difference, for these duplicates samples, was equivalent to or better than routinely reported results of MDH laboratory duplicates.

Dissolved oxygen, pH, temperature, and conductivity were measured in the field with a multiparameter probe. Transparency tube measurements were made with a 60 cm long, 3.8 cm diameter, clear plastic tube. A well-mixed sample is poured into the tube. While looking down into the tube, water is released from a valve at the bottom until the black and white (Secchi) symbol at the bottom of the tube is visible. The depth of the water when the symbol becomes visible is recorded. Typically, two separate readings are averaged to yield the recorded measurement. Previous use of the transparency tube has revealed significant correlations with turbidity and total suspended solids (Sovell et al. 2000).

Data analysis was conducted primarily by EXCEL spreadsheet (V97, Microsoft, 1997). Linear regression was used to describe relationships between variables and F-tests were used to assess the significance of these relationships. T-tests and/or comparisons of means and standard error were used to determine significant between-site and between-year differences. Summer-means and select maxima are noted for each site in 1999 and 2000 (Table 3).

Detailed channel morphometry for the Crow and Mississippi Rivers (MPCA unpubl. data) allowed for calculation of travel time as a function of flow

and provided a basis for evaluating "age of water" estimates. For the Crow, travel time over the reach from CR-23 to CR-0 varied from about 20 hours at $42 \text{ m}^3 \cdot \text{s}^{-1}$ (1,500 cfs) up to about 50 hours at $5.7 \text{ m}^3 \cdot \text{s}^{-1}$ (200 cfs). Considering average flows of about $25.5 \text{ m}^3 \cdot \text{s}^{-1}$ (900 cfs) and $8.5 \text{ m}^3 \cdot \text{s}^{-1}$ (300 cfs) respectively for 1999 and 2000 (Table 1) this would translate to travel (residence) time over this reach of about 25 to 35 hours. "Age of water" estimates (based on extrapolated flow at CR-0) suggest that the "age of water" at CR-0 would be on the order of 12.3 days (24 hour increase) at $25.5 \text{ m}^3 \cdot \text{s}^{-1}$ (1999) and 13.7 days (26 hour increase) at $8.5 \text{ m}^3 \cdot \text{s}^{-1}$ (2000). Based on this comparison the "age of water" estimates provide a reasonable basis for estimating between-site changes in residence time for the Crow River. A similar time-of-travel comparison for the Mississippi River sites suggested that "age of water" estimates might overestimate residence time for this much larger system. Time-of-travel measurements from UM-1004 to UM-872 averaged about 110 hours (4.6 days) during summer 1999. In comparison, "age of water" estimates indicated a time-of-travel on the order of 10 days. In summer 2000, time-of-travel from UM-1004 to UM-872 averaged 8.3 days, which was twofold greater than summer 1999. For the Mississippi sites, time-of-travel estimates were more accurate and will be referred to later in the discussion.

Results and Discussion

Using regression analysis we were able to demonstrate significant, consistent and positive relationships between total phosphorus (TP) and sestonic total

Table 2.—Laboratory methods and precision estimates for Minnesota river-nutrient study.

Parameter	Reporting Limit & Units	EPA parameter number	Precision mean difference	Percent of observed
Total Phosphorus	$10.0 \mu\text{g} \cdot \text{L}^{-1}$	365.2	$4.8 \mu\text{g} \cdot \text{L}^{-1}$	2.7%
Total Kjeldahl N	$0.1 \text{ mg} \cdot \text{L}^{-1}$	351.2	$0.048 \text{ mg} \cdot \text{L}^{-1}$	2.8%
$\text{NO}_2 + \text{NO}_3$	$0.01 \text{ mg} \cdot \text{L}^{-1}$	353.1		
Total Suspended Solids	$0.5 \text{ mg} \cdot \text{L}^{-1}$	160.2	$2.8 \text{ mg} \cdot \text{L}^{-1}$	9.6%
Total Suspended Volatile Solids	$0.5 \text{ mg} \cdot \text{L}^{-1}$	160.4		
Turbidity	0.2 NTU	180.1		
BOD_5		405.1	$0.15 \text{ mg} \cdot \text{L}^{-1}$	6.6%
Chlorophyll a	$0.16 \mu\text{g} \cdot \text{L}^{-1}$	446.0	$1.7 \mu\text{g} \cdot \text{L}^{-1}$	7.4%
Pheophytin	$0.27 \mu\text{g} \cdot \text{L}^{-1}$	446.0		

Table 3. Summer-means and maxima from Minnesota river-nutrient study for selected parameters in 1999 and 2000.

1999 Site	mean Tube cm	mean Temp. °C	max °C	mean pH SU	mean Cond. µmhos	mean Turb. NTU	mean BOD ₅ mg·L ⁻¹	mean TSS mg·L ⁻¹	mean TSV mg·L ⁻¹	mean TKN mg·L ⁻¹	mean NO ₃ mg·L ⁻¹	mean TP µg·L ⁻¹	mean Chl-a µg·L ⁻¹	mean Pheo µg·L ⁻¹	mean ChlT µg·L ⁻¹	max µg·L ⁻¹
CWR-72	60	16	26	8.1	283	3	1.0	3.5	1.4	0.58	0.21	32	3.1	1.4	4	7
CWR-35	60	16	25	7.8	386	4	1.0	6.0	2.8	0.77	0.22	59	2.4	1.9	4	9
UM-1004	25	20	25	7.4	216	18	1.1	23.3	3.4	0.81	0.09	71	4.5	3.8	8	14
UM-965	40	20	26	7.6	259	12	1.2	15.4	2.7	0.75	0.14	63	4.0	3.9	8	12
UM-953	37	21	26	7.7	263	10	1.1	13.1	2.7	0.72	0.15	62	4.4	2.9	7	11
UM-895	48	21	28	7.7	275	9	1.2	12.8	3.1	0.76	0.20	67	5.2	4.5	10	15
UM-872	37	22	28	7.9	278	12	1.5	18.9	4.9	0.88	0.38	92	15.6	6.6	22	33
RU-34	46	20	26	7.5	272	10	1.6	16.8	4.2	1.14	0.27	137	13.3	6.6	20	36
RU-18	49	21	27	7.7	279	8	1.8	15.5	4.9	1.11	0.26	131	18.8	7.9	27	55
CR-23	12	22	29	8.1	588	53	4.5	73.0	18.0	2.06	2.11	359	83.4	21.2	105	154
CR-0	15	21	28	8.0	574	49	4.0	75.0	17.0	1.92	1.86	329	74.1	19.6	94	132
BE-94	15	19	25	7.9	668	59	2.1	125.0	17.8	1.17	7.64	247	29.1	12.0	41	84
BE-73	13	20	25	7.9	636	57	3.6	110.0	17.7	1.55	6.28	243	47.7	14.7	62	99
BE-54	12	21	26	8.0	636	68	3.4	126.0	20.4	1.47	6.41	248	64.4	17.0	81	150
BE-18	13	22	27	8.1	621	68	3.4	135.0	20.9	1.44	6.28	240	57.6	16.1	74	147
2000 Site	mean Tube cm	mean Temp. °C	max °C	mean pH SU	mean Cond. µmhos	mean Turb. NTU	mean BOD ₅ mg·L ⁻¹	mean TSS mg·L ⁻¹	mean TSV mg·L ⁻¹	mean TKN mg·L ⁻¹	mean NO ₃ mg·L ⁻¹	mean TP µg·L ⁻¹	mean Chl-a µg·L ⁻¹	mean Pheo µg·L ⁻¹	mean ChlT µg·L ⁻¹	max µg·L ⁻¹
CWR-72	>60	20	25	8.4	313	2.5	1.2	3.3	2.3	0.57	0.12	34	3.4	1.5	5	14
CWR-35	>60	20	24	8.2	372	3.3	1.2	6.1	2.7	0.70	0.23	49	3.7	1.7	5	9
UM-1056	53	20	24	8.0	262	11.7	1.1	19.5	2.9	0.72	0.07	59	4.7	2.1	7	9
UM-1029	42	20	24	7.9	256	14.0	1.0	22.4	3.1	0.74	0.08	60	5.1	2.7	8	10
UM-953	53	21	25	8.3	295	7.6	1.3	9.1	2.4	0.72	0.11	54	7.6	4.8	12	22
UM-895	53	23	27	8.4	269	6.9	1.6	10.9	3.4	0.82	0.19	77	11.0	6.2	17	30
UM-872	47	23	27	8.4	342	8.8	2.1	15.7	5.0	0.93	0.23	84	22.7	6.4	29	41
RU-34	56	18	24	8.1	337	6.2	1.8	10.6	3.7	0.97	0.28	143	20.5	7.2	29	41
RU-18	52	18	24	8.4	329	6.3	2.3	11.2	4.8	0.97	0.18	133	31.4	10.7	44	65
CR-23	13	21	26	8.5	736	40.6	6.6	74.6	18.1	1.94	1.69	349	120.3	25.5	143	213
CR-0	15	19	24	8.5	721	31.5	7.0	63.8	17.6	1.76	1.56	284	112.4	26.6	136	207
BE-100	42	18	24	8.3	723	16.4	1.1	35.0	5.4	0.57	7.18	116	6.4	4.8	11	23
BE-94	23	19	25	8.1	698	30.6	2.7	60.8	10.7	1.14	6.11	192	41.8	6.7	48	121
BE-73	17	20	26	8.3	675	40.6	5.1	74.4	15.3	1.63	5.55	205	87.4	15.4	101	188
BE-54	15	21	26	8.3	662	46.3	6.3	90.9	18.1	1.60	5.35	207	86.7	11.5	97	195
BE-18	15	21	27	7.3	620	57.4	5.3	108.3	18.9	1.63	5.37	223	73.1	10.2	82	177

*Notes: Cond. = specific conductivity in µmhos/cm; TSS = total suspended solids, TSV = total suspended volatile solids; TN = TKN + NO₃; Total chlorophyll a = chlorophyll a (chl a) + pheophytin (pheo).

chlorophyll a (ChlT = chlorophyll a + pheophytin a) in Minnesota rivers (Table 4, Eq. 3 & 4 and Fig. 2). The slope for the 2000 data appeared steeper, as compared to the 1999 regression, but was not significantly different (95% confidence level). The significant relationship between TP and ChlT is consistent with a worldwide study conducted by Van Nieuwenhuysse and Jones (1996) and a Canadian study by Basu and

Pick (1996). In each of these studies significant linear regressions (log-log) of TP and total chlorophyll a exhibited significant R² values of 0.72 and 0.76 respectively.

In our relationships, sites from the different ecoregions fall into distinct regions of the regression (Fig. 2, Table 3). The predominately NLF ecoregion sites (Crow Wing and UM-1065, 1029, and 1004) were

Table 4.—Regression equations derived based on Minnesota river-nutrient study. Regression based on summer-mean concentrations for 1999 and 2000 unless otherwise noted.

1999: ChlT ($\mu\text{g} \cdot \text{L}^{-1}$) = 0.34 TP ($\mu\text{g} \cdot \text{L}^{-1}$) - 13.2	($R^2 = 0.89$)	(3)
2000: ChlT ($\mu\text{g} \cdot \text{L}^{-1}$) = 0.44 TP ($\mu\text{g} \cdot \text{L}^{-1}$) - 20.0	($R^2 = 0.91$)	(4)
1999: ChlT ($\mu\text{g} \cdot \text{L}^{-1}$) = 7.98 TN ($\text{mg} \cdot \text{L}^{-1}$) + 11.45	($R^2 = 0.49$)	(5)
2000: ChlT ($\mu\text{g} \cdot \text{L}^{-1}$) = 8.17 TN ($\text{mg} \cdot \text{L}^{-1}$) + 21.86	($R^2 = 0.25$)	(6)
1999: ChlT ($\mu\text{g} \cdot \text{L}^{-1}$) = 75.53 TKN ($\text{mg} \cdot \text{L}^{-1}$) - 48.39	($R^2 = 0.94$)	(7)
2000: ChlT ($\mu\text{g} \cdot \text{L}^{-1}$) = 100.84 TKN ($\text{mg} \cdot \text{L}^{-1}$) - 61.39	($R^2 = 0.96$)	(8)
1999: TP ($\mu\text{g} \cdot \text{L}^{-1}$) = 231.23 TKN ($\text{mg} \cdot \text{L}^{-1}$) - 105.32	($R^2 = 0.95$)	(9)
2000: TP ($\mu\text{g} \cdot \text{L}^{-1}$) = 188.67 TKN ($\text{mg} \cdot \text{L}^{-1}$) - 63.35	($R^2 = 0.95$)	(10)
1999: BOD ₅ ($\text{mg} \cdot \text{L}^{-1}$) = 0.031 ChlT ($\mu\text{g} \cdot \text{L}^{-1}$) + 0.89	($R^2 = 0.97$)	(11)
2000: BOD ₅ ($\text{mg} \cdot \text{L}^{-1}$) = 0.043 ChlT ($\mu\text{g} \cdot \text{L}^{-1}$) + 0.88	($R^2 = 0.95$)	(12)
1999: BOD ₅ ($\text{mg} \cdot \text{L}^{-1}$) = 0.011 TP ($\mu\text{g} \cdot \text{L}^{-1}$) + 0.42	($R^2 = 0.92$)	(13)
2000: BOD ₅ ($\text{mg} \cdot \text{L}^{-1}$) = 0.019 TP ($\mu\text{g} \cdot \text{L}^{-1}$) - 0.14	($R^2 = 0.87$)	(14)
1999: BOD ₅ = 0.043 Chl-a + 0.95	($R^2 = 0.98$)	(15)
2000: BOD ₅ = 0.053 Chl-a + 0.87	($R^2 = 0.98$)	(16)
1999: BOD ₅ = 0.18 Pheo + 0.48	($R^2 = 0.80$)	(17)
2000: BOD ₅ = 0.26 Pheo + 0.64	($R^2 = 0.80$)	(18)

clustered near the lower end and transitioned to the NCHF sites. The Blue Earth (WCBP) and Crow River (WCBP-NCHF transition) sites were on the upper end. Variability in the relationship was evident for the Blue Earth sites in both years with the downstream (higher order) sites above the regression line and the lower order (BE-100 and BE-94) below the line.

Likewise we found a positive, but weaker, relationship between ChlT and total nitrogen (TN) (Table 4, Eq. 5 & 6). The consistently high nitrate-N concentrations in the Crow and Blue Earth Rivers (Table 3) contributed to the poor relationship. TKN exhibited much stronger and significant relationships (F-test, $p < 0.001$) with total chlorophyll in both years (Fig. 3,

Table 4, Eq. 7 & 8). This was anticipated though, since TKN is largely organically bound nitrogen and much of the measured N is likely tied up in the algal cells (similar to TP). TKN is highly correlated with TP as well in both years (Table 4, Eq. 9 & 10). Basu and Pick (1996) noted a significant relationship between log TN and log chlorophyll a in their streams ($R^2 = 0.66$). They noted, however, that it is unlikely that TN concentration regulated chlorophyll in their study rivers.

Watershed area, flow and residence time are highly related (Table 1) and contribute to between-year and between-site differences in water quality in these rivers.

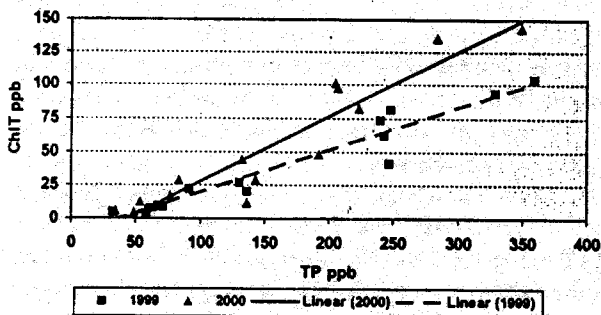


Figure 2.—Summer-mean total chlorophyll a (ChlT) vs. total phosphorus for Minnesota rivers sampled in 1999 and 2000.

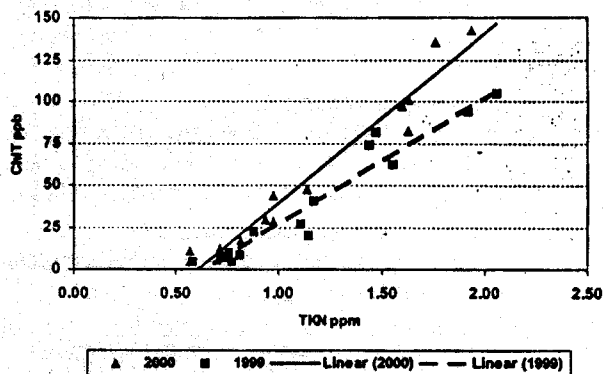


Figure 3.—Summer-mean total chlorophyll a (ChlT) vs. total Kjeldahl nitrogen (TKN) for Minnesota rivers sampled in 1999 and 2000.

In the nutrient-poor Crow Wing, TP concentrations were consistently higher at the down stream site in 1999 and 2000 (Table 3), however there was no significant difference in ChlT between these sites in either year (Fig. 4). Overall, Crow Wing ChlT concentrations were quite low and varied positively with flow (Fig. 5). In contrast, the nutrient-rich Blue Earth River exhibited a marked downstream increase in ChlT in both years. The largest between-site increases were noted among the third order site BE-100 and the downstream fourth order sites (Fig. 4). Increased residence time (watershed area) and TP (Tables 1 and 3) between BE-100 and BE-94 contributed to the increased ChlT between these two sites, while increased residence time between BE-94 and the three downstream sites was likely the reason for the downstream ChlT increase in both years (Fig. 4). The Crow did not exhibit a downstream increase in ChlT in either year however, as with the Blue Earth River, it exhibited peak chlorophyll during periods of low or stable flow (Fig. 5). The Rum River, intermediate between these extremes, exhibited a downstream increase in ChlT (Fig. 4) but did not exhibit a consistent relationship between chlorophyll and flow (Fig. 5).

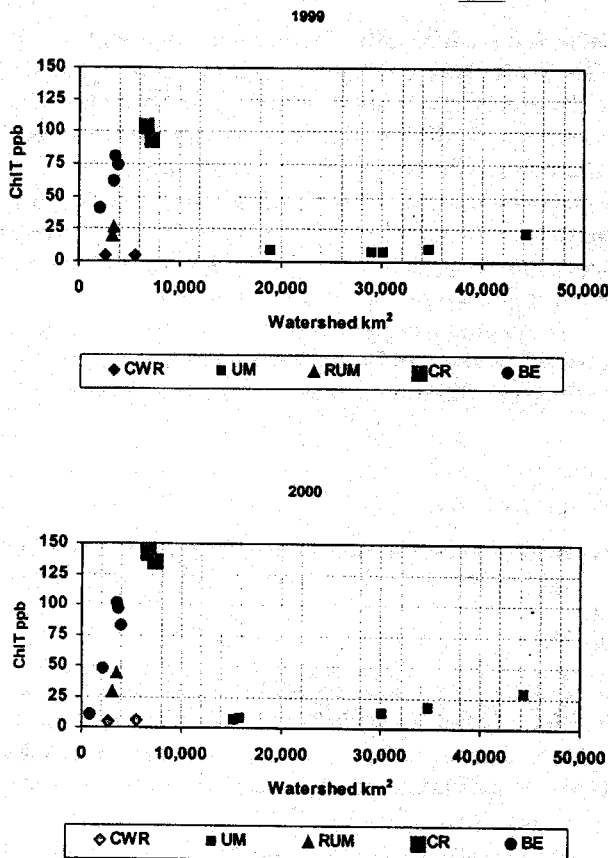


Figure 4.—Summer-mean total chlorophyll a (ChlT) versus watershed area for Minnesota river sites sampled in 1999 and 2000.

The fifth and sixth order Mississippi River sites exhibited minimal change in ChlT relative to watershed area in both years (Fig. 4). Stable TP concentrations in 1999 (Table 3) and short time-of-travel (about three to four days) between UM-1004 and UM-895 contribute to this lack of change in ChlT. TP concentrations again were relatively stable over this reach (Table 3) in 2000 but time-of-travel was on the order of seven to eight days and a gradual increase in ChlT from the upstream sites to UM-895 was noted. In both years, however, a marked increase in TP and ChlT was noted between UM-895 and UM-872. A lack of a relationship between ChlT and watershed area for the high order Mississippi sites was consistent with Basu and Pick (1996) who noted that the biomass of phytoplankton in large (greater than fifth order) rivers was strongly correlated with TP concentrations but not with water residence time.

A second primary goal of this study was to establish the relationship between chlorophyll *a* and BOD_5 . ChlT and BOD_5 exhibited strong and significant (F-test, $p < 0.001$) relationships in the rivers studied (Fig. 6 and Table 4, Eq. 11 & 12). The slope for the 2000 data was steeper and significantly different (95% confidence interval) than the slope for 1999. As with TP, the NLF sites exhibited low chlorophyll and BOD_5 , while values were much higher for both parameters in the Blue Earth and Crow Rivers (Table 3). The transitional NCHF sites were intermediate between these two extremes. These between-year comparisons suggested that the combination of less dilution, increased algal growth (respiration), and algal decomposition played a more important role in the production of BOD during the lower flows of 2000 as compared to the higher flows of 1999.

Chlorophyll *a* (living cells) and pheophytin (degradation product) data from individual sites and dates can further describe the influence of algae on BOD . The living cells (at the sample site) contribute to respiration, while the dead cells transported from upstream reaches contribute via bacterial decomposition. Individual regression of mean chlorophyll *a* and BOD_5 (Table 4, Eq. 15 & 16) and pheophytin *a* and BOD_5 (Table 4, Eq. 17 & 18) showed significant relationships (F-test, $p < 0.01$) for each. Chlorophyll *a*, however, explained a higher percentage of the variation in BOD_5 in both years. A comparison of chlorophyll *a* and pheophytin *a* to BOD_5 at CR-23 showed good correspondence if the two values are combined (i.e., total chlorophyll) with the exception of June 12, 2000 when BOD_5 was high relative to the chlorophyll *a* (Fig. 7). The June 12th sample was taken at the peak of the hydrograph (Fig. 5). High runoff brought organic and inorganic material into suspension, as evidenced by the elevated TSS ($120 \text{ mg} \cdot \text{L}^{-1}$) on that

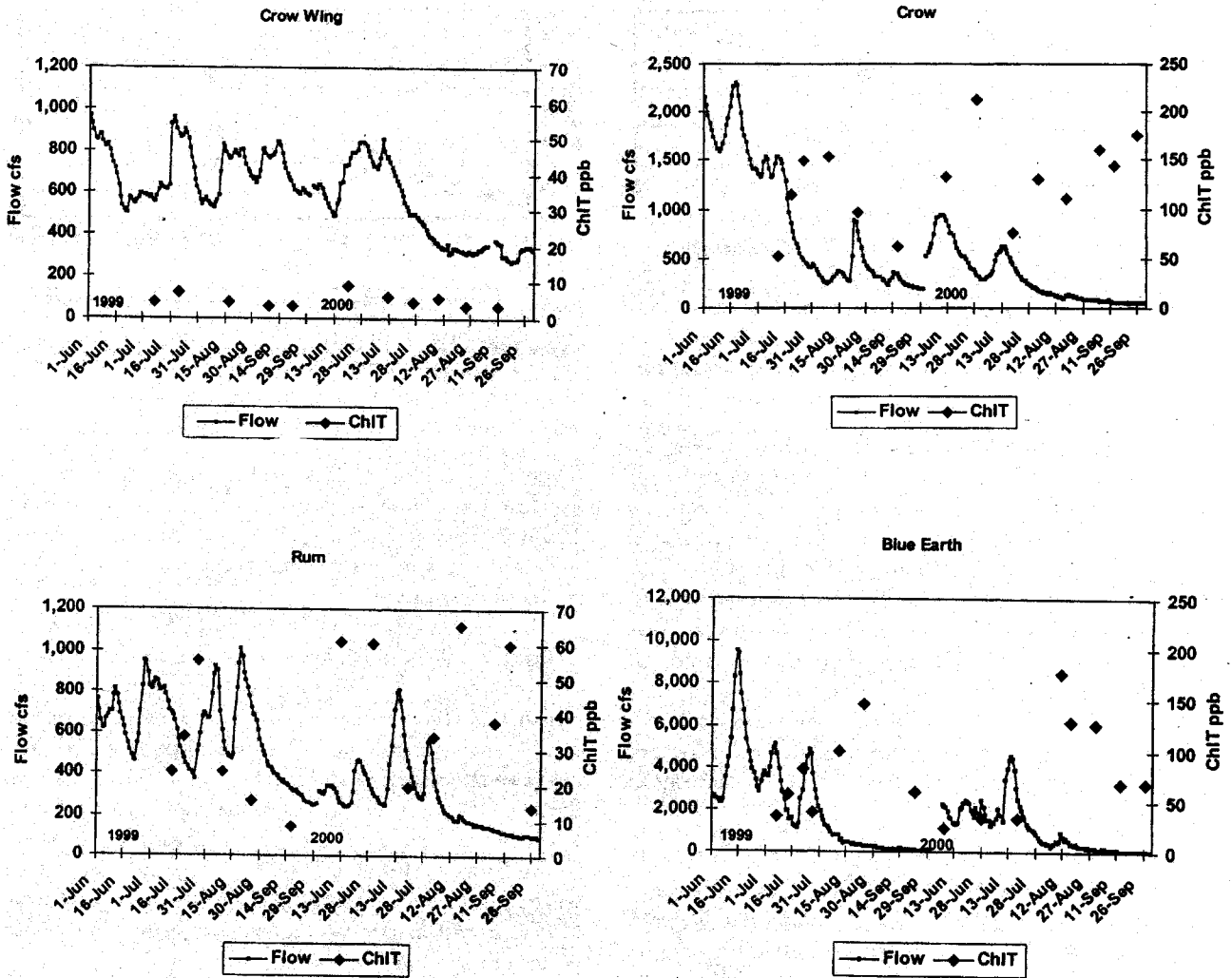


Figure 5.-Total chlorophyll a (ChlT) and flow comparisons for Crow Wing (CWR-72), Rum (RUM-18), Crow (CR-23) and Blue Earth (BE-18) Rivers for 1999 and 2000.

date, which would contribute to the BOD load in the river (in addition to algal respiration and decomposition). All other samples were taken on the declining limb of the hydrograph or during low flow (Fig. 5) when TSS was about 60 to 70 mg · L⁻¹.

BOD₅ values were higher, on average, for BE-18 than anticipated based on Fig. 6. BOD₅ and chlorophyll a values track very closely at BE-18 in 2000; pheophytin in contrast was at relatively low concentrations (relative to chlorophyll a) throughout summer 2000 (Fig. 7). The one date with poor correspondence was June 28, 2000 when BOD₅ was elevated relative to chlorophyll a. Again, as with the Crow River, increased flow (Fig. 4) and peak TSS (270 mg · L⁻¹) were noted on this date. In contrast, peak BOD₅ and chlorophyll a co-occurred on August 11, 2000, under low flow condition (Fig. 5). TSS was 86 mg · L⁻¹ on that date which is a very low value as compared to the peak concentra-

tion of 270 mg · L⁻¹. In each of these two examples there was very good correspondence between BOD₅ and total chlorophyll based on individual sample dates, which further supported the excellent correlations previously noted. These data (BE-18 and CR-23) also suggested that flow and TSS periodically affect this relationship as well.

Lastly, as anticipated based on Figs. 2 and 6, the relationship between TP and BOD₅ was equally strong and significant (F-test <0.001) for both ears (Fig. 8) (Table 3, Eq. 13 & 14). The slope for the 2000 data was steeper and significantly different (95% confidence interval) than the slope for 1999.

The third primary goal of this study was to relate algal composition to nutrient status and watershed size for medium to large Minnesota rivers. Phytoplankton composition varied not only in terms of the origin of the phytoplankton, i.e., benthic vs. sestonic, but

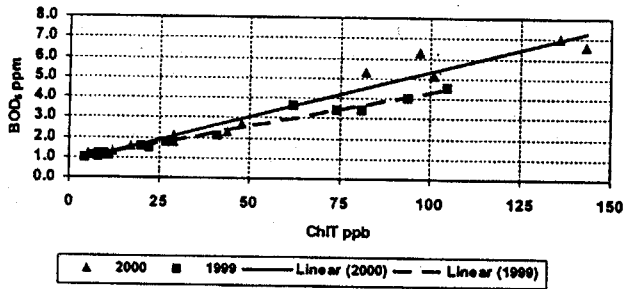


Figure 6.-Summer-mean BOD₅ vs. total chlorophyll a (ChlT) for sites sampled in 1999 and 2000.

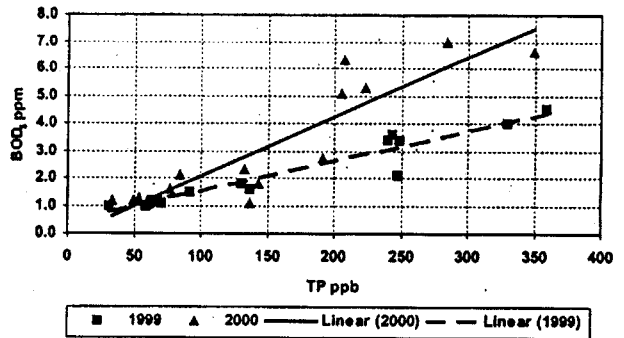


Figure 8.-Summer-mean BOD₅ vs. total phosphorus for sites sampled in 1999 and 2000.

also along a gradient of nutrient enrichment (Fig. 9). In the shallow and clear Crow Wing River periphyton scoured from the substrate of the stream was an important component of the measured seston based on the predominance of benthic diatoms at CWR-35 (Fig. 9). Lohman and Jones (1999) observed this in their work on Missouri third and fourth order streams and Descy et al. (1987) described this as well. In general, the Crow Wing and Upper Mississippi sites: UM-1004 and UM-953 exhibited compositions somewhat similar to a "typical" composition for temperate rivers based on Rojo et al. (1994). Common diatoms at

these sites included less pollution tolerant genera such as *Cocconeis* sp. and *Acananthus* sp. (Palmer 1969). Prygiel and Leitao (1994) noted these genera as well in the headwater stream to the reservoir Val Joly in northern France.

In the Rum River, UM-953, and UM-872 the more pollution tolerant (Palmer 1969) diatoms, such as *Nitzschia* sp., *Melosira* sp. and *Cyclotella* sp. were quite common. The presence of the Cryptomonads: *Rhodomonas minutus* and *Cryptomonas* sp. further attest to the nutrient richness of these sites based on Swale's (1969) observations in the nutrient-rich Stour River in England. And the most common green algae in the Rum, UM-953, UM-872, Crow, and Blue Earth were *Ankistrodesmus* and *Scenedesmus*, which Swale (1969) noted as the two most common green algae genera in the nutrient-rich Severn River.

In the highly nutrient-rich Crow and Blue Earth Rivers pollution-tolerant blue-green algae (including *Oscillatoria*, *Aphanizomenon*, and nonmotile blue-greens) were dominant. Prygiel and Leitao (1994) noted *Oscillatoria* blooms in the highly nutrient-rich

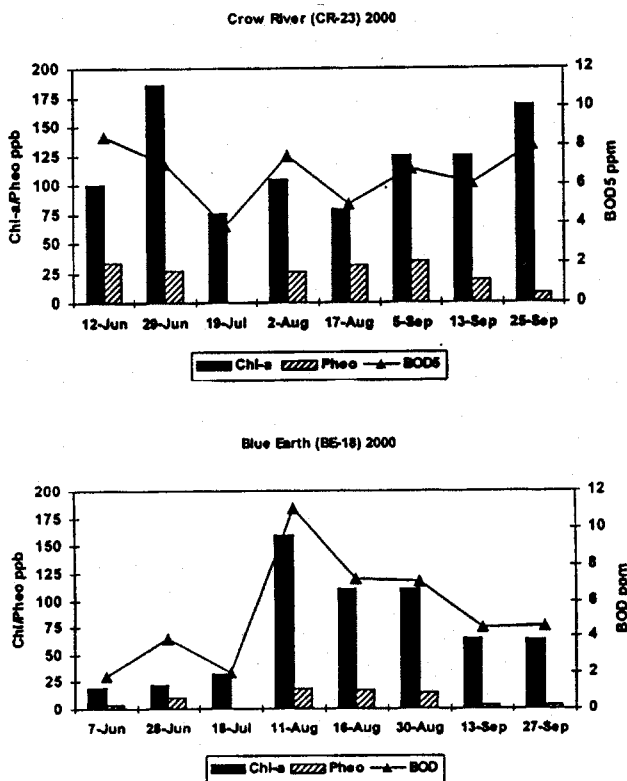


Figure 7.-BOD₅, chlorophyll a, and pheophytin comparisons for Crow and Blue Earth River sites.

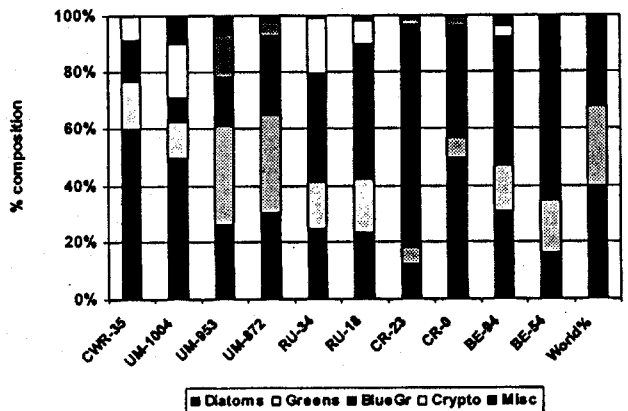


Figure 9.-Mean algal composition for selected Minnesota river sites. Based on three summer samples per site from 1999. Worldwide percentage drawn from Rojo et al. (1994).

river below the reservoir Val Joly as well. They note that while the reservoir "seeded" the *Oscillatoria* and other blue-greens, the river sustained them and allowed for bloom concentrations.

Summary

Strong relationships were evident among in-stream nutrients (TP and TKN in particular) and algae (expressed as total chlorophyll) for medium to high order streams. These findings are similar to that found in other studies (Van Nieuwenhuysse and Jones 1996; Basu and Pick 1996). We have also shown that BOD_5 is highly correlated with phosphorus and chlorophyll and that the living cells (as expressed by chlorophyll a) and the dead or dying cells (as expressed by pheophytin a) both contribute to the BOD. The relationships among nutrients, algae and BOD also varied (between sites and years) as a function of watershed size, flow and residence time. Overall, these relationships should prove useful for nutrient criteria development and waste load allocations (where excess nutrients and dissolved oxygen are a primary concern).

Our regression equations should be applicable elsewhere for rivers with similar characteristics as those in this study. Among the more important considerations are watershed size (which influences flow, residence time, mean depth) and inorganic turbidity. Our sites ranged from ~800 km² up to ~44,000 km² and stream order ranged from 4th to 6th order at most sites. Sites with watershed areas less than about 2,590 km² (1,000 mi²) exhibited slightly lower chlorophyll per unit TP than sites with larger watersheds. An upper threshold (watershed size or stream order) likely exists as well since, as watershed size increases, stream depth increases leading to increased depth of mixing and increased light limitation – as is common in main-stem reservoirs (Heiskary and Walker 1995). Also, systems with excessive and continuously high TSS or turbidity (beyond that observed in this study) will likely yield less chlorophyll a per unit TP than our regressions would estimate. Our rivers exhibited a wide range in TSS and some, such as the blue Earth and Crow, routinely exhibit very high TSS, in conjunction with runoff events. However, as these events subside, TSS declines as well and based on the chlorophyll concentrations recorded in this study, light limitation did not appear to be a major factor at most study sites during the summer index period.

Shifts in seston composition were evident as a combined function of nutrient status and watershed size (residence time). In the shallower streams with low to moderate nutrient concentrations, such as the

Crow Wing and Rum Rivers, benthic diatoms were a common component of the seston. In these systems there was an abundance of colonizeable habitat and adequate light reaching these substrates, which encouraged the growth of periphyton. These periphyton become part of the seston via sloughing or as a result of flood-event scouring. In deeper streams with larger watersheds and longer residence time, such as the Mississippi, planktonic greens and blue-greens were increasingly common. In highly nutrient-rich rivers, such as the Crow and Blue Earth, periodic light limitation from high inorganic turbidity and short residence time may combine to limit algal growth, however these systems often respond quickly as flow and turbidity decline and planktonic pollution-tolerant greens and blue-greens dominate. Regardless of the "origin" of the sestonic chlorophyll a, rivers with high nutrients exhibited high chlorophyll a and high BOD_5 , while those with low nutrients exhibited the inverse.

ACKNOWLEDGMENTS: This work was funded jointly by the U.S. Environmental Protection Agency, through a nutrient criteria development grant, and the Minnesota Pollution Control Agency. Thanks to staff and student interns whom assisted with fieldwork. Sylvia McCollor and Laurie Sovell, of the MPCA, should be acknowledged for contributions to study design. We also thank MPCA reviewers: Greg Johnson, Mark Tomasek, and Pat Baskfield and two anonymous reviewers for their valuable suggestions on early drafts of the manuscript.

References

- Anderson, W. and J. Klang. 1997. Water pollution trading: from policy to reality. *Environ. Engineer.*
- AMERICAN Public Health Association. 1998. *Standard Methods for the Examination of Water and Wastewater*. 20th Edition.
- Baker, A. and K. Kromer-Baker. 1979. Effects of temperature and current discharge on the concentration and photosynthetic activity of the phytoplankton in the upper Mississippi River. *Freshwat. Biol.* 9:191-198.
- Basu, B. K. and F. R. Pick. 1995. Longitudinal and seasonal development of planktonic chlorophyll a in the Rideau River, Ontario. *Can. J. Fish. Aquat. Sci.* 52:804-815.
- Basu, B. K. and F. R. Pick. 1996. Factors regulating phytoplankton and zooplankton biomass in temperate rivers. *Limnol. Oceanogr.* 41(7):1572-1577.
- Billen, G., J. Garnier and P. Hanset. 1994. Modeling phytoplankton development in whole drainage networks: the RIVERSTRAHLER Model applied to the Seine river system. *Hydrobiol.* 289:119-137.
- DeLorme. 1994. *Minnesota atlas and gazetteer*. Yarmouth, ME. 96 p.
- Descy, J.P., P. Servais, J. Smits, G. Billen and E. Everbecq. 1987. Phytoplankton biomass and production in the River Meuse (Belgium). *Wat. Res.* 21:1557-1566.

- De Ruijter van Steveninck, E. D., W. Admiraal, L. Breebaart, G. M. J. Tubbing and B. vanZanten. 1992. Plankton in the River Rhine: structural and functional changes observed during downstream transport. *J. Plank. Res.* 14(10):1351-1368.
- Dodds, W. E., V. H. Smith and B. Zander. 1997. Developing nutrient targets to control benthic chlorophyll levels in streams: A case study of the Clark Fork River. *Wat. Res.* 7:1738-1750.
- Dodds, W. E. and E. Welch. 2000. Establishing nutrient criteria in streams. *J. N. Amer. Benthol. Soc.* 19(1):186-196.
- Heiskary, S. A. and W. W. Walker, Jr. 1995. Establishing a chlorophyll a goal for a run-of-the-river reservoir. *Lake and Reserv. Manage.* 11(1):67-76.
- Heiskary, S. A. and C. B. Wilson. 1989. The regional nature of lake water quality across Minnesota: An analysis for improving resource management. *J. MN. Acad. Sci.* 55(1):71-77.
- Kromer-Baker, K. and A. Baker. 1981. Seasonal succession of the phytoplankton in the upper Mississippi River. *Hydrobiol.* 83:295-301.
- Leopold, L. B., G. Wolman and J. P. Miller. 1964 *Fluvial processes in geomorphology.* W. H. Freeman, San Francisco, CA.
- Lohman, K. and J. R. Jones. 1999. Nutrient - sestonic chlorophyll relationships in northern Ozark streams. *Can. J. Fish. Aquat. Sci.* 56:124-130.
- Microsoft Corporation. 1997. Microsoft Excel: Version 97. USA.
- Miltner, R. J. and E. T. Rankin. 1998. Primary nutrients and the biotic integrity of rivers and streams. *Freshwat. Biol.* 40:145-158.
- Palmer, M. C. 1969. A composite rating of algae tolerating organic pollution. *J. Phycol.* 5:78-82.
- Prygiel, J. and M. Leitaou. 1994. Cyanophycean blooms in the reservoir of Val Joly (northern France) and the development in downstream rivers. *Hydrobiol.* 289:85-96.
- Rojo, C., M. A. Cobelas and M. Arauzo. 1994. An elementary, structural analysis of river phytoplankton. *Hydrobiol.* 289:43-55.
- Søballe, D. M. and B. L. Kimmel. 1987. A large-scale comparison of factors influencing phytoplankton abundance in rivers, lakes, and impoundments. *Ecology* 68(6):1943-1954.
- Sovell, L., S. Heiskary and J. Anderson. 2000. Using the transparency tube in Minnesota's new Citizen Stream Monitoring Program. Proceedings of the 1999 National Water Quality Monitoring Conference.
- Swale, E. M. F. 1969. Phytoplankton in two English rivers. *J. Ecol.* 57:1-23.
- U.S. Environmental Protection Agency. 1997. Technical Guidance Manual for Developing Total Maximum Daily Loads. Book 2: Streams and Rivers. Part 1: Biochemical Oxygen Demand/Dissolved Oxygen and Nutrients/Eutrophication. Office of Water, Washington D.C. EPA 823-B-97-002 1997.
- U.S. Environmental Protection Agency. 1998. Clean Water Action Plan: Restoring and protecting America's waters. ISBN 0-16-049536-9.
- U.S. Environmental Protection Agency. 1999a. Methods for analysis of water. V2.0. CD-ROM Office of Water, Washington D.C. EPA 821-C-99-004.
- U.S. Environmental Protection Agency. 1999b. Protocol for Developing Nutrient TMDLs. Office of Water, Washington D.C. EPA 841-B-99-007 1999.
- U.S. Environmental Protection Agency. 2000a. Nutrient Criteria Technical Guidance Manual. Lakes and Reservoirs. Office of Water, Washington D.C. EPA-822-B00-001.
- U.S. Environmental Protection Agency. 2000b. Nutrient Criteria Technical Guidance Manual. Lakes and Reservoirs. Office of Water, Washington D.C. EPA-822-B00-002.
- Van Nieuwenhuysse, E. E. and J. R. Jones. 1996. Phosphorus-chlorophyll relationship in temperate streams and its variation with stream catchment size. *Can. J. Fish. Aquat. Sci.* 53:99-105.