Journal of the Minnesota Academy of Science

Volume 54 | Number 1 Article 5

1988

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Recommended Citation
Ellingson, S. B., & Hopwood, A. J. (1988). Seasonal Variations in Water Quality Parameters of the Mississippi River near St. Cloud, MN. *Journal of the Minnesota Academy of Science, Vol. 54 No.1*, 17-22. Retrieved from https://digitalcommons.morris.umn.edu/jmas/vol54/iss1/5

Seasonal Variations in Water Quality Parameters of the Mississippi River near St. Cloud, MN

STEPHEN B. ELLINGSON* and ALFRED J. HOPWOOD**

ABSTRACT — Water quality parameters were monitored in the Mississippi River and three tributaries (Harris Channel, Watab Creek, and Sauk River) from July 1980 to April 1981. Results were correlated with water temperature and discharge to assess seasonal changes. Effects of tributary inflow on the river were determined. Planktonic carbon was estimated with the firefly luciferin-luciferase system which measures adenosine triphosphate extracted from viable cells. Particulate organic matter, planktonic carbon, and percentage viable carbon were correlated with temperature ($\rho \geq 0.6$) while nitrate plus nitrite was inversely correlated with temperature and discharge. Only the Sauk River affected the water quality of the Mississippi River by adding elevated levels of dissolved electrolytes, total phosphorus, particulate organic matter, and planktonic carbon. Relatively low levels of planktonic carbon (155 μg/l) in the river indicated good water quality. Seasonal changes in water quality parameters of rivers must be considered in designing useful monitoring programs.

Introduction

Previous limnological research has been biased toward temperate lakes. However, more significant anthropogenic demands are placed on the water quality of rivers, which necessitate a more refined understanding of this important resource. This project was an effort to add to the sparse information regarding water quality and planktonic carbon in large rivers. These rivers are used both as sources of domestic and industrial water supply and as waste repositories. Diligent water quality monitoring is required to ensure the best use of this resource. It is well known that most water quality parameters in rivers change markedly with variations in season and discharge. Natural variations can easily range from 100 to 400 percent of observed mean values (1). Unfortunately, it is common to allow equal intervals between sampling and use inappropriate statistics in an attempt to interpret changes. An appreciation of this natural variation is needed to correctly assess water quality changes.

This investigation was conducted in a relatively pristine headwater reach of the Mississippi River. The river drains the third largest watershed (322.5 x 10^6 ha) in the world and is of immense importance to North Americans. The specific objectives of this project were to: (1) monitor spatial and temporal changes in water quality parameters along the study reach, (2) determine if tributaries in the reach had an effect on river water quality, and (3) suggest a better method of indirectly measuring planktonic carbon in large rivers. This paper was abstracted from a thesis submitted by Ellingson (2) in partial fulfillment of the requirements for the Master of Arts degree in biology at St. Cloud State University.

Materials and Methods

Six sampling transects were established across the Mississippi River above and below the Harris Channel, Watab Creek, and the Sauk River with tributary samples gathered upstream from each confluence (Figure 1). Each transect contained a left and right bank station spaced equally across the river. A total of 115 water samples were collected from July 29, 1980 to April 4, 1981 during 14 trips. Field measurements and grab samples were taken at 2 m or one-half the maximum depth. Tributary discharge was calculated from current velocity and cross-sectional area with river flow data obtained from the St. Cloud Water Utility and St. Regis Paper Company (SRPC).

Determinations of specific conductivity (corrected to 25°C), pH, and phosphorus (total & dissolved) were according to *Standard Methods* (3) with Millipore HA (0.45 μm pore) filters used for dissolved phosphorus. Nitrate plus nitrite levels were determined with the low range Hach Chemical Co. test. The test registers both nitrate (NO_3) and nitrite (NO_2); however, NO_2 concentrations are usually insignificant compared to NO_3 levels. Organic matter was separated into particulate and dissolved components with Whatman GF/F filters (0.7 μm pore) and quantified by wet oxidation with dichromate (4,5).

Planktonic carbon was estimated with the firefly luciferin-luciferase system modified after Holm-Hansen and Booth (6). Biomass was concentrated into small glass-fiber filters (Whatman GF/F, 2.5 cm dia.) and adenosine triphosphate (ATP) was extracted with 10 ml of boiling Tris buffer. Lyophilized firefly lantern extract (Sigma Chemical Co.) was reconstituted, added to the extracted ATP, and luminescence monitored with a liquid scintillation counter. The area under the decay curve is proportional to ATP concentration. Planktonic carbon was calculated from a C:ATP ratio of 417

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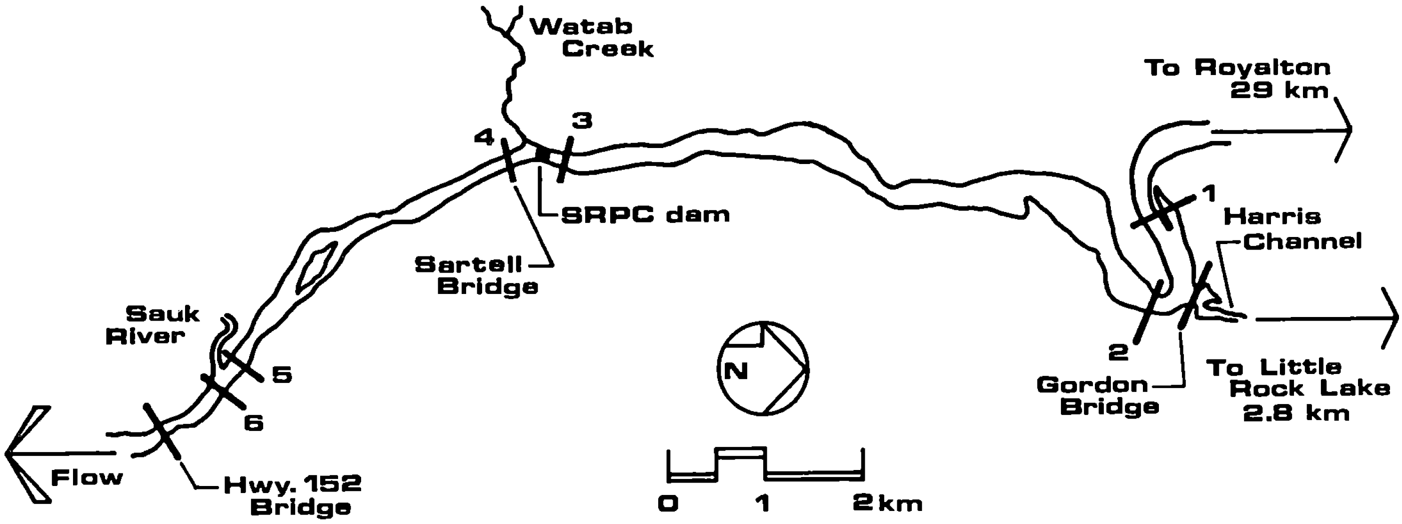

Figure 1. Study area along Mississippi River with sampling transects (no. 1 to 6) and tributaries indicated. St. Cloud Water Utility is 2.0 km downstream from Hwy. 152 (Sauk Rapids) bridge. SRPC = St. Regis Paper Company.

(3) and divided by particulate organic matter (POM) to yield percentage viable carbon. Land use/land cover information was provided by the Minnesota State Planning Agency (7).

Statistical calculations were completed with UNIVARIATE, CORR (Spearman's ρ), and NPAR1WAY (Kruskal-Wallis Test) procedures of Statistical Analysis Systems (8,9). Analysis of skewness and kurtosis indicated that all parameters lacked a normal distribution. Consequently, nonparametric statistics were employed.

Results and Discussion

Seasonal Changes in River

Since water temperature varies according to seasonal changes, parameters correlated with water temperature can be said to have a seasonal pattern. In rivers this pattern can be modified by fluctuating discharge. During runoff events very high or low levels of a constituent can result from the increased discharge. Parameters significantly correlated with discharge or temperature appear in Table 1. All of these parameters demonstrated a stronger correlation with temmperature (i.e., seasonal patterns) than discharge. The effects of discharge and temperature could not be separated using partial correlations since these parameters were not related (ρ = - 0.05, P = 0.61). Water temperature ranged from 0.0° to 27.9°C and discharge ranged from 32.94 to 93.34 m^3/sec.

Low current velocity (0.1 m/sec) characterized the three transects above the St. Regis Paper Company dam while rapid current (0.5 m/sec) was present downstream. Flow in the upper Mississippi River is regulated by six headwater reservoirs with a 59-year mean flow of 127.5 m^3/sec reported at Royalton, MN (10). River discharge was relatively constant during the study, with 50 percent of the total ice-free flow occurring in 34.7 percent of the available time. This constancy precluded strong correlations with parameters normally related to discharge. Elevated discharge near St. Cloud took place in September and April with low values during ice cover (December 1 to March 14). Increased discharge tended to dilute NO_3 concentrations suggesting that point-source input to the river was diluted by rainfall and tributary inflow. Typically NO_3 concentration in large rivers increases with discharge as fertilizers are transported from contiguous agricultural land (11). Cultivated farmland adjacent to this stretch of the river is relatively limited. Nitrate exhibited a strong seasonal pattern with high mean concentrations during December and January (0.22 mg N/l) compared to fall and spring sampling (0.03 mg N/l). Data provided by the Minnesota Pollution Control Agency (10) confirmed the pattern of low summer NO_3 values and high winter concentrations. When ammonia and NO_3 levels were compared, they changed together over time (ρ = 0.56, $P < 0.01$). Conversely, during periods of high organic nitrogen levels, the NO_3 concentrations were low (ρ = - 0.28, P = 0.02). Rapid

Table 1. Matrix of Spearman correlation coefficients (ρ) and P-values in parentheses. Parameters significantly related to temperature demonstrate a seasonal pattern, while correlations with discharge can modify seasonal changes.

	Independent Variable	
Dependent Variable	Discharge (m^3/sec)	Temperature (°C)
Nitrate & Nitrite (mg N/l)	- 0.39 (<0.01)	- 0.61 (1.01)
Total Phosphorus (mg P/l)	0.31 (0.01)	0.46 (< 0.01)
Particulate Organic Matter (mg POM/l)	0.27 (0.01)	0.74 (<0.01)
Planktonic Carbon (μg PC/l)	0.34 (<0.01)	0.77 (<0.01)
Percentage Viable Carbon (% VC)	- 0.02 (0.89)	0.55 (<0.01)

assimilation by terrestrial and aquatic biota may have resulted in these low inorganic nitrogen levels during the growing season. Significant increases in NO_3 concentrations occurred when the water temperature dropped below 5°C (10).

Most dissolved phosphorus levels were less than the detection limit (0.010 mg P/l). Only 25.8 percent of samples contained measurable levels of dissolved phosphorus possibly indicating rapid uptake by the aquatic flora. The concentration of total phosphorus (TP) increased with temperature and discharge (Table 1). Total phosphorus is a constituent of planktonic biomass and biomass increases with warmer water temperatures. The erosional transport of total phosphorus during runoff events yields a correlation with discharge. To limit algal blooms and attendant water quality problems, the U.S. Environmental Protection Agency (12) has established a critical value of 0.050 mg TP/l for streams entering a reservoir. This value was equalled or exceeded by 32.8 percent of total phosphorus readings in the river.

Particulate organic matter (POM), planktonic carbon, and percentage viable carbon followed a strong seasonal oscillation with high values associated with elevated water temperatures (Table 1). Positive correlation of percentage viable carbon and temperature (Table 1) coupled with the increased concentrations of POM and planktonic carbon during the summer indicates seasonal development of a true planktonic community. Reports of blue-green algal blooms upstream from the St. Regis Paper Company dam corroborate the formation of an extensive planktonic community. This seasonal pattern in POM, planktonic carbon, and percentage viable carbon can be modified by changes in precipitation and resultant river flow. Runoff flushes particulate matter from the watershed into the river resulting in higher concentrations and mass flowrates. Figure 2 depicts the effects of seasonal change and the unusually large amounts of autumnal precipitation on POM mass flowrates. Rainfall totalled 330 mm, or 166 mm above normal, during August and September. This produced high mass flowrates on September 12 (mean 16,878 kg POM/day) which were slightly lower than those observed in April (mean 18,542 kg POM/day). Patterns similar to Figure 2 were observed with the mass-transport of planktonic carbon and concentrations of POM and planktonic carbon. The largest fraction of organic matter was in dissolved form. It was in constant equilibrium and failed to show any seasonal variations.

Tributary Effects on River

The three tributaries drain watersheds with very different characteristics. Harris Channel drains eutrophic Little Rock Lake in western Benton County. Current velocity in the channel was very low so the flow magnitude was difficult to evaluate. A small (6×10^2 ha) watershed contributes to Watab Creek. Sauk River drains a 2.7×10^4 ha watershed of which 54.8 percent is cultivated and 28.4 percent is open pasture.

Two techniques were employed to determine impacts of the tributaries on the Mississippi River. Initially, water quality in a tributary was compared statistically to water quality at the transect immediately upstream in the Mississippi River. If significant differences were present, a comparison of the river transects up- and downstream of the tributary was completed.

Seasonal patterns in water chemistry observed in the tributaries were similar to those of the river. Representative concentrations of water quality parameters from the Mississippi River and tributaries are given in Table 2. Discharge from Harris Channel and Watab Creek averaged only 2.31 percent and 0.94 percent of Mississippi River flow, thus these inputs had a minimal effect on the Mississippi River water quality. The Sauk River averaged 10.10 percent of Mississippi River discharge. Specific conductivity was significantly higher in the Sauk River ($X^2 = 9.64$, $P < 0.01$) and Watab Creek ($X^2 = 8.23$, $P < 0.01$) when compared to the Mississippi River. These levels were highly variable (range 245 to 610 μS/cm) in Watab Creek. Concentrations of NO_3 in the Sauk River were not unusually high (Table 2) and the average mass flowrate was 24 percent of the mean Mississippi River flow. Total phosphorus inputs from the Sauk River were 44.6 percent of the Mississippi River mass flowrates immediately upstream and the concentration was significantly higher ($X^2 = 7.50$, $P = 0.02$) in the Sauk River. The Sauk River watershed is 83.2 percent cultivated and open pasture land, with runoff from this farmland possibly contributing to the elevated total phosphorus levels. Significantly higher concentrations of POM ($X^2 = 9.60$, $P < 0.01$) and planktonic carbon ($X^2 = 5.63$, $P = 0.02$) occurred in the Sauk River when compared to the Mississippi River. Mass flowrates from the Sauk River for POM and planktonic carbon were 30.52 percent and 64.91 percent of the Mississippi River (Figure 3). Dissolved organic matter and percentage viable carbon levels were similar in the tributaries and Mississippi River.

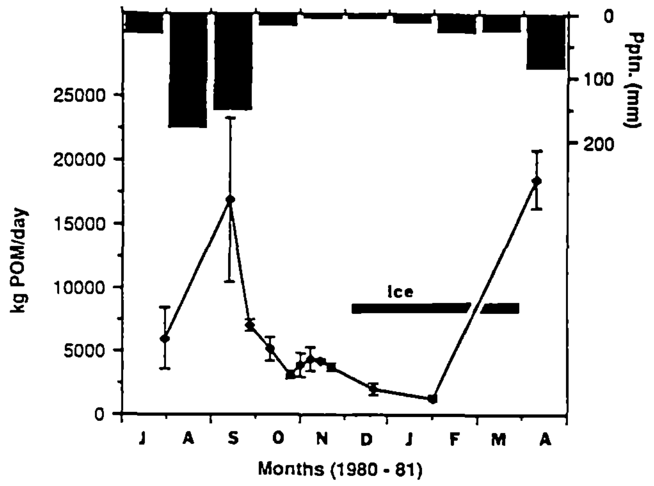

Figure 2. Seasonal changes in particulate organic matter (POM) mass flowrates (kg POM/day) in Mississippi River and corresponding monthly precipitation. Vertical bars denote 90 percent confidence interval.

During the second phase of the statistical analysis, Mississippi River water quality up- and downstream of Watab Creek and the Sauk River were compared. Conductivity in the Mississippi River exhibited no significant changes associated with discharge from Watab Creek. A plume of elevated conductivity ($X_2 = 3.86$, $P = 0.05$), POM ($X_2 = 3.86$, $P = 0.05$), total phosphorus ($X_2 = 2.40$, $P = 0.12$), and planktonic carbon ($X_2 = 2.40$, $P = 0.12$), was present along the right bank (facing downstream) of the river, 0.15 km downstream from the Sauk River. Upon reaching the State Highway 152 bridge, 0.8 km downstream, the Sauk River plume had dissipated.

In summary, Mississippi River water quality was not altered by the small discharge from Harris Channel and Watab Creek. Changes in conductivity, total phosphorus, and biotic parameters were apparent immediately downstream from the Sauk River; however, these additions were dispersed by river flow within one kilometer.

Table 2. Representative concentrations of water quality parameters for Harris Channel (HC), Watab Creek (WC), Sauk River (SR), and Mississippi River (MR) from July 29, 1980 to April 4, 1981. 90% = 90th percentile, Med. = median, 10% = 10th percentile.

		LOCATION			
PARAMETER		HC	WC	SR	MR
Discharge	90%	1.80	0.65	7.78	93.30
(m^3/sec)	Med.	1.58	0.64	6.93	73.03
	10%	1.35	0.60	5.45	36.94
	No.	9	7	6	14
Specific Conductivity		342	610	620	370
(µS/cm)		310	480	497	315
		280	245	395	290
		9	7	6	92
pH		8.0	7.9	8.4	8.0
(Std. Units)		7.6	7.6	8.1	7.7
		7.4	7.4	7.8	7.3
		9	7	6	73
Dissolved Phosphorus		0.147	0.018	0.065	0.030
(mg P/l)		<0.010	<0.010	<0.010	<0.010
		<0.010	<0.010	<0.010	<0.010
		8	7	6	67
Total Phosphorus		0.251	0.094	0.211	0.096
(mg P/l)		0.043	0.047	0.163	0.037
		0.020	0.014	0.096	<0.010
		8	7	6	67
Nitrate & Nitrite		0.61	0.25	0.40	0.24
(mg N/l)		0.05	0.12	0.11	0.04
		<0.01	<0.01	<0.01	<0.01
		6	3	6	52
Particulate Organic Matter		5.855	2.061	5.704	2.333
(mg POM/l)		0.741	0.894	3.277	0.863
		0.466	0.741	2.450	0.523
		9	7	6	91
Dissolved Organic Matter		9.794	10.853	9.647	9.865
(mg DOM/l)		7.677	8.206	8.087	7.915
		6.088	6.894	6.984	6.783
		9	7	6	73
Planktonic Carbon		686	491	1177	397
(µg PC/l)		12.9	103	619	77.2
		15.2	20.9	290	26.4
		7	7	6	66
Viable Carbon		35.08	34.22	37.02	34.20
(%VC)		6.79	6.67	18.93	9.51
		2.84	2.54	8.60	4.29
		7	7	6	66

Changes in Planktonic Carbon

With the large number of toxic and biostimulatory substances being introduced to surface waters, there is a need for reliable parameters by which biotic responses can be quickly assessed. Changes imposed on an aquatic resource result in alterations in the biota which can readily be monitored by assaying biomass. Most methods of measuring biomass are time-consuming, complex, and expensive. Chlorophyll (Chl), typically used to measure autotrophic biomass, is subject to inherent variations in the Chl:C ratio which preclude statistically reliable data. Correlations between chlorophyll and other indirect measures of biomass could be difficult because of these inherent variations. High levels of detritus and suspended solids in rivers eliminate estimation of biomass by conventional techniques. A more effective method is required. Only living organisms contain ATP and it exists in relatively constant proportion to cellular carbon (13). The quantification of extracted ATP with bioluminescent assay provides a simple, sensitive and reproducible measure of total living microbial carbon without indicating the types of cells (autotrophic phytoplankton or heterotropic bacterioplankton) in the sample. By a combination of ATP analyses and other microscopic or biochemical measurements, it is possible to estimate relative abundances of different types of organisms.

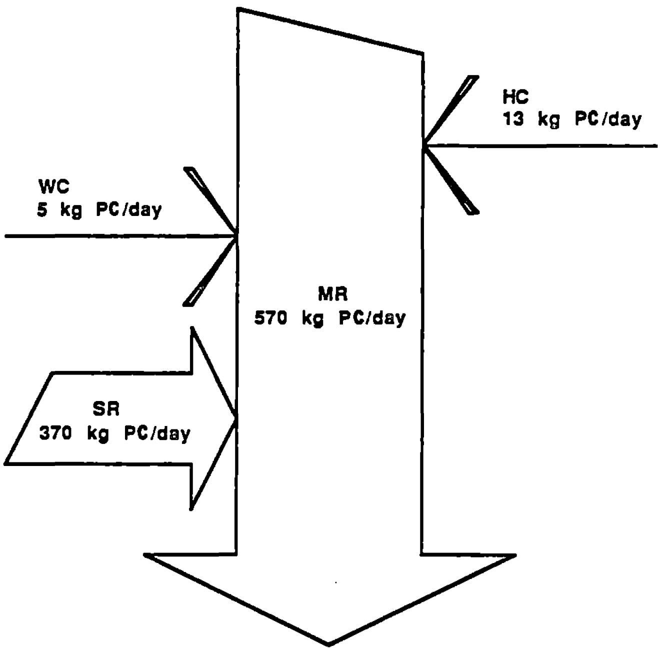

Figure 3. Diagrammatic view of mean planktonic carbon (PC) mass flowrates (kg PC/day) in Mississippi River and tributaries. Arrow width is proportional to flowrate. HC = Harris Channel, WC = Watab Creek, SR = Sauk River, MR = Mississippi River.

As previously indicated, planktonic carbon levels in the Mississippi River were low during the winter (mean 69.6 µg/l) and increased during warmer months (mean 303 µg/l) of the study. A seasonal pattern was exhibited by planktonic carbon levels, which remained high until October 10. Planktonic carbon concentrations later declined from 138 µg/l on October 10 to 28.9 µg/l on October 24 while the mean water temperature decreased from 11.3° to 5.7°C.

Percentage viable carbon in the river ranged seasonally (Table 1) from 2.3 to 58.4 percent with an unusually high mean value (36.9%) on October 10. The water appeared brown on that date and a slight increase (11.2%) in POM was observed. Prior to this the water was green (September 12) and afterward it was clear (October 24). Since no precipitation preceded this event, it is possible that the seasonal senescence of algae, in response to cool water, released a large amount of labile macromolecules. This presumably contributed to a population explosion of the more thermally resilient bacteria, many attached to POM. A similar seasonal pattern was observed in the Dutch Wadden Sea (14). During the summer, 20 percent of the particular carbon was contained within living material while 0.1 percent of the carbon was contained within living material in the winter.

Adenosine triphosphate levels have been used by other researchers to assess water quality changes in lakes, rivers, sediment, and to monitor wastewater treatment plant operation. Values ranged from 0.4 ng ATP/l in the North Atlantic Ocean (15) to 71,600 ng ATP/1 in eutrophic Lake Lilleso (16). Monitoring of ATP levels in the Ohio River and tributaries near Cincinnati disclosed significant spatial differences in biomass (17). Adenosine triphosphate concentrations in the Ohio River were higher below a wastewater treatment plant (300 vs. 1700 ng ATP/l) and planktonic carbon values in the nutrient-rich Little Miami River were higher (833 vs. 155 µg/l planktonic carbon) than mean values obtained for the Mississippi River near St. Cloud.

An autotrophic index was used to assess levels of organic pollution in the lower Tiber River, Italy (18). This ratio was expressed as the concentration of ATP:Chl and increased downstream as more wastes accumulated.

No spatial patterns in planktonic carbon concentration were observed in the Mississippi River with the exception of elevated levels at the transect immediately downstream from the Sauk River. The St. Regis Paper Company, located 5 km upstream from the State Highway 152 bridge, discharges secondarily treated paper milling wastes into the Mississippi River but high planktonic carbon levels were not apparent near this facility.

Conclusions

During the past 15 years, more than $100 billion has been expended to control point-source pollution. It is estimated that an additional $118 billion will be required for new municipal sewage treatment facilities through the end of the century (19). The public and its elected representatives want to know if water quality has improved after spending billions of dollars in clean-up efforts. To address these concerns, the generation of reliable information on representative rivers is imperative. A detailed characterization of the inherent temporal and spatial changes in water quality is required. Temporal changes were assessed in the Mississippi River by statistically correlating water quality parameters with water temperature and discharge. Water quality up- and downstream from tributaries was compared to evaluate spatial patterns. The measurement of ATP was suggested as a practical means of measuring planktonic carbon in large rivers.

With passage of the amended Clean Water Act (PL 100-4), control of nonpoint source pollution (i.e., pollution from diffuse sources such as urban and agricultural runoff) will become more important. Nonpoint source pollution is probably more pervasive than municipal and industrial discharges and its mitigation more onerous. These types of analyses should serve as a paradigm for the regulatory community and water quality managers to evaluate the efficacy of pollution control activities.

Acknowledgements

This research was supported by funds awarded to Drs. A.J. Hopwood and S.F. Williams by the Institutional Studies and Research Office, St. Cloud State University, MN. In memory of Dr. Michael Cichan and family.

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