

Effects of Point Source Loadings, Sub-basin Inputs and Longitudinal Variation in Material Retention on C, N and P Delivery from the Ohio River Basin

P. A. Bukaveckas,^{1*} D. L. Guelda,² J. Jack,³ R. Koch,² T. Sellers,⁴
and J. Shostell⁵

¹Department of Biology, Center for Environmental Studies, 1000 W. Cary Street, Richmond, Virginia 23284, USA; ²Bemidji State University, Bemidji, Minnesota 56601, USA; ³Department of Biology, Center for Watershed Research, University of Louisville, Louisville, Kentucky 40292, USA; ⁴Division of Natural Sciences, Keuka College, Keuka Park, New York 14478, USA; ⁵Department of Biology, Pennsylvania State University – Fayette, Uniontown, Pennsylvania 15401, USA

ABSTRACT

Spatial variability in material fluxes within large river basins may arise from point source inputs, variable contributions from sub-basins and longitudinal variation in material transformation and retention. By measuring instantaneous fluxes throughout the Ohio River basin, we were able to draw inferences about the importance of these factors in determining the overall export of C, N and P from the basin. Our study spanned the lower 645 km of the Ohio River and included all tributaries that contributed at least 1% of the volume of the Ohio River at its confluence with the Mississippi. The intensively cultivated northern sub-basin (Wabash River) contributed a large fraction of N and P entering the Ohio River. In the southern sub-basins (Tennessee and Cumberland Rivers), impoundments and less intense cultivation appear

to diminish and delay material delivery particularly with respect to N. The southern rivers account for a proportionately larger fraction of the water entering the Mississippi River during low discharge conditions and this fraction has increased during the past 50 years. The upper portion of the study reach was found to be a net source of CHLa and DOC and a net sink for inorganic N suggesting that this portion of the river provided a generally favorable environment for autotrophic production. Point source loadings of NH₄ were significant inputs to the upper sub-reach but a relatively small component of the overall budget for dissolved inorganic N.

Key words: river; Ohio River; nutrients; nitrogen; phosphorus; mass balance; point sources.

INTRODUCTION

Large rivers play an important role in regional and global biogeochemical cycles by transporting materials from terrestrial sources to downstream

and marine environments (Howarth and others 1996). Recent work in the central basin of the United States has demonstrated that riverine nitrogen export regulates the areal extent of hypoxia in the Gulf of Mexico (Scavia and others 2003) and that riverine alkalinity export is large in the context of the net carbon balance for North America (Raymond and Cole 2003). Particulate and

Received 6 April 2004; accepted 2 September 2004; published online 21 October 2005.

*Corresponding author; e-mail: pabukaveckas@vcu.edu

dissolved materials in river water vary over a small range of concentrations in comparison to the range of variation in river discharge. As a result, the export of materials from river basins is largely determined by the amount of runoff (Lewis and others 1999). Large rivers integrate drainage waters from distant points in the landscape that may differ in topography, soils, climate and vegetation. These differences give rise to variable yields of water and materials resulting in intra-basin variation in material fluxes. Anthropogenic influences may contribute to spatial variability when nutrient yields are enhanced by N and P inputs from diffuse and point sources (Harris 2001; Caraco and others 2003). Agricultural and urbanized areas contribute a disproportionate fraction of riverine nutrient fluxes due to the high mobility of N (as NO_3), erosion losses of P-amended soils and wastewater inputs enriched in N and P.

Riverine processes regulating the transformation of materials may also play a role in determining basin yields. Downriver fluxes may be attenuated by removal (atmospheric losses of CO_2 and N_2 via respiration and denitrification) and short-term storage through biotic uptake (autotrophic and heterotrophic assimilation of inorganic N and P). Large rivers are typically net heterotrophic systems in which community respiration is greater than primary production (Cole and Caraco 2001). Positive algal carbon balances may be maintained when hydrologic and geomorphic constraints permit favorable light conditions. In the Ohio River, estimates of light dosage that integrate variable light intensity and algal transit time were used to predict when and where photosynthesis exceeded respiration (Sellers and Bukaveckas 2003). Under these conditions, autotrophic demand may be large in relation to remineralization of autochthonous and allochthonous organic matter such that the river functions as a net sink for inorganic N and P.

Modern methods for quantifying nutrient uptake in lotic systems are based on injection of conservative and non-conservative tracers. As these are impractical for large rivers, comparative work has been based largely on streams and small (wadeable) rivers. Recent studies have shown that ammonia uptake in headwater streams is largely determined by rates of net primary production (Hall and others 2002, 2003). Small streams differ from large rivers in that their lower volume to benthic area ratio allows for higher rates of nutrient uptake by surficial and sub-surface (hyporheos) microbial communities (Alexander and others 2000). As large rivers have high volume to surface area ratios, pelagic processes are likely to assume greater impor-

tance and may augment benthic metabolic activity during periods of the flow regime that are favorable to the proliferation of plankton. Most of the large rivers in the temperate zone have been altered through the construction of dams and other channel modifications (Dynesius and Nielsson 1994; Vorosmarty and others 1997). These may enhance the importance of pelagic processes in two ways. First, channel modifications disconnect the river from its floodplain by reducing lateral exchange and diminishing the role of floodplain communities in nutrient retention and transformation. Second, dams induce pelagic conditions by increasing storage capacity and lengthening water residence time. Many recent studies have shown that regulated rivers are capable of supporting large and diverse resident plankton communities (Kohler 1994; Reynolds and Descy 1996; Servais and others 2000). Peaks in community development are often associated with seasonal depletion of inorganic nutrients (NO_3 , PO_4 , dissolved Si) although it is unclear whether this is driven by internal metabolic demand or a result of reduced inputs from upstream source areas.

A mass balance approach can be used to test the hypothesis that biotic processes in rivers result in the attenuation of downstream transport through selective retention of various fractions of C, N and P. If outputs from the river are comparable to the sum of inputs from upstream, tributary and point sources, then the net effect of ecosystem processes is assumed to be negligible. Input and output fluxes are typically derived from continuous measurements of discharge and periodic sampling of dissolved and particulate constituents whose concentrations are extrapolated by time-averaging or flow-weighting techniques (Bukaveckas and others 1998). Integration over the period of interest allows identification of specific fractions that behave in a non-conservative fashion. In this study, we use a synoptic approach whereby we compare instantaneous input and output fluxes over a range of discharge conditions to determine whether the river functions as a source or sink (Richey and others 1990; Salvia and others 1999). We compare input fluxes from tributaries and point sources to assess their importance in determining the timing and magnitude of output fluxes from the Ohio River basin.

SITE DESCRIPTION AND METHODS

The Ohio River is the second largest river in the United States and the principal source (38%) of

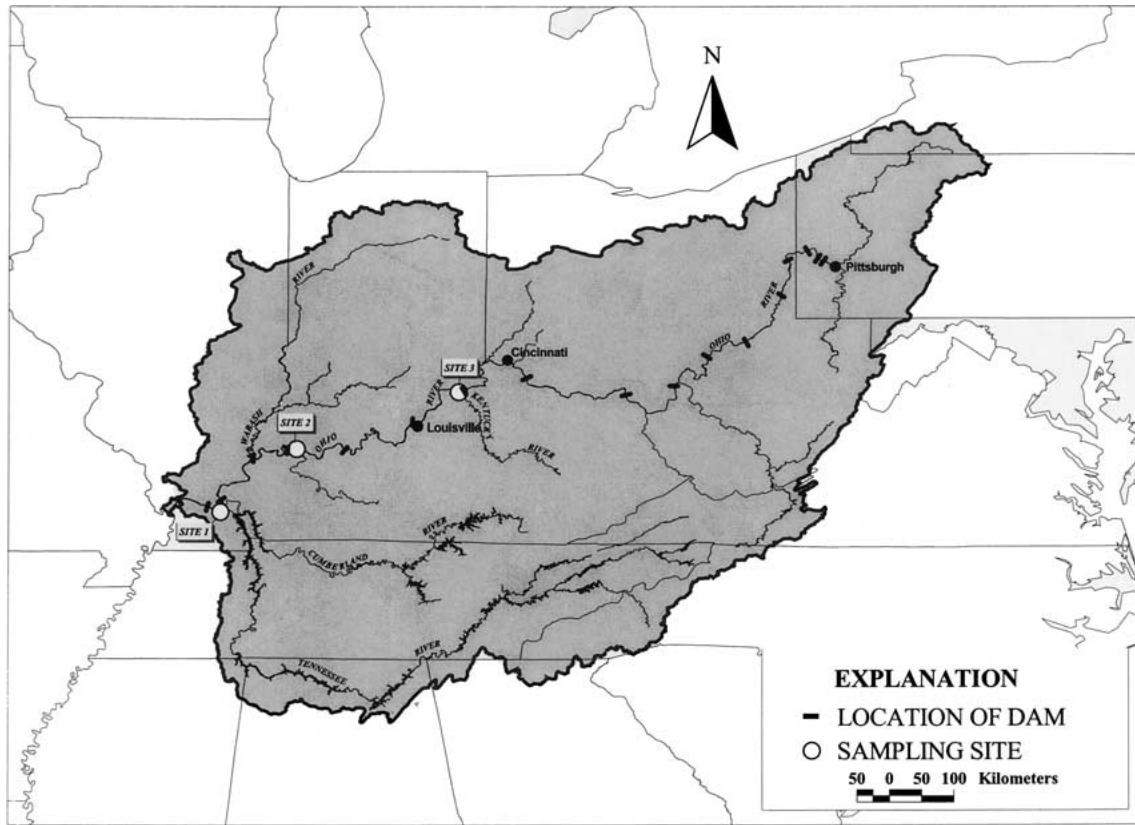


Figure 1. Map of Ohio River watershed showing locations of dams, sampling sites and major urban centers along the mainstem of the Ohio River. Tributaries sampled as part of this study were the Kentucky, Green, Wabash, Tennessee and Cumberland Rivers.

freshwater discharge into the Gulf of Mexico (Turner and Rabalais 2004). A historical perspective on management and water quality of the Ohio River is provided by Pearson (1992). The river is formed by the confluence of the Allegheny and Monongahela Rivers near Pittsburgh, PA and runs 1579 km to its confluence with the Mississippi (Figure 1). The river drains an area of 528,205 km² that is predominantly (48%) human-appropriated land use (urban, crop, pasture; Table 1). Major urban centers located along the Ohio River include Pittsburgh, PA, Cincinnati, OH and Louisville, KY. Our study spanned the lower 645 km of the Ohio River (beginning below Cincinnati, OH) and included all tributaries that contributed at least 1% of the volume of the Ohio River at its confluence with the Mississippi. Major sub-basins include the upper Ohio (above Cincinnati, OH), Kentucky, Green, Wabash, Tennessee and Cumberland Rivers. The sub-basins differ in their land use and extent of hydrologic regulation (Table 1). Agricultural activities are concentrated in the northern sub-basin (Wabash River) where croplands account for 67%

of land use. The eastern (upper Ohio) and southern (Tennessee and Cumberland) basins are less intensively cultivated (crop lands = 13–28%) with a greater proportion of forested lands (31–49%).

The flow regimes of the Ohio River and its principal tributaries are characterized by peak discharge in spring (February–April) and low discharge in late summer (July–October). The rivers differ somewhat in the timing and magnitude of the seasonal flow pulse. The discharge of the Ohio River and its principal tributaries is regulated by “low head” dams (height < 10 m) that are designed to maintain a minimum depth for navigation during low flow. Low dams regulate but do not eliminate flowing conditions and, unlike flood control (high head) dams, do not inundate large areas (Sparks and Spink 1998). The number and storage capacity of mainstem dams differs among the rivers of the Ohio basin resulting in varying degrees of water regulation (Table 1). The Ohio River is subdivided along its length by 20 navigation dams, eight of which are located within our study reach (Figure 1). The combined storage capacity of the

Table 1. Sampling Locations and River and Sub-basin Characteristics for the Mainstem Ohio River and its Principal Tributaries

	Distance		HUC	Basin Area (km ²)	Discharge (km ³ y ⁻¹)	River Length (km)	Population			Land Use		Retention (days)
	(km)	(km)					Density (ind km ⁻²)	Crop	Pasture	Urban (basin %)	Forest	
Ohio River (upper)	716		5090203	215,410	103	862	62	22	13	6	48	
Kentucky River	699		5100205	16,006	8	417	39	10	26	3	49	
Ohio River (mid)	320		5140201	251,230	116	1258	60	21	15	6	47	
Green River	317		5110005	21,896	11	595	23	28	29	2	31	
Wabash River	214		5120113	75,716	25	765	47	67	7	5	14	
Cumberland River	93		6040005	45,579	33	1106	38	17	19	4	44	
Tennessee River	74		5140206	104,455	57	1050	37	13	17	5	47	
Ohio River (lower)	71		5140206	526,029	247	1507	49	28	15	5	40	

Distances denote the location of mainstem sampling sites and, for tributaries, their point of confluence, relative to the mouth of the Ohio River. Hydrologic Unit Codes (HUC), basin area, discharge, population data (from 1990) and land use data (from 1987) are from the USGS National Stream Water Quality Monitoring Network (USGS 2000). Retention is the cumulative storage volume of mainstem dams listed in the National Dam Inventory (NID 2000) divided by the annual discharge.

Ohio River mainstem dams (9 km³) is equivalent to 4% of the annual discharge or approximately 13 days of discharge (at annual-average flow; Table 1). Mainstem dams on the Kentucky and Cumberland Rivers have storage volumes comparable to the Ohio River when expressed relative to the annual discharge of these rivers. In contrast, the Green and Tennessee Rivers are subject to greater water regulation with storage volumes of mainstem dams equivalent to 10 and 26% (respectively) of annual discharge (37 and 96 days of retention). The Wabash is a relatively free-flowing river with only a single mainstem impoundment that stores a volume less than 1% of the annual discharge.

Sampling locations included three sites on the Ohio River (hereafter: up-, mid- and down-river sites) and five tributaries (Figure 1). The up- and down-river sites delineated the study reach for which input and output fluxes were quantified. Their locations were selected on the basis of accessibility to the river during varying flow conditions and proximity to gauging stations. The up-river site was located 716 km from the confluence of the Ohio River with the Mississippi River. This site (near Vevay, IN) was 7 km downriver of a gauging station (Markland Dam) and 17 km upriver of the confluence with the uppermost tributary (Kentucky River). The downriver site (near Paducah, KY) was 12 km above the gauging station at Metropolis, IL and 3 km below the confluence with the lowermost tributary (Tennessee River). This site was located 71 km from the mouth of the Ohio River as characterization of fluxes below this point are compromised by occasional backwater effects from the Mississippi River. The location of the mid-river site (320 km from the mouth of the Ohio River) was chosen to delineate an upper sub-reach characterized by shallow pools and high autotrophic potential from a lower sub-reach in which pools were deeper and hypothesized to be more heterotrophic. This site (above Evansville, IN) was 3 km upriver of the confluence with the Green River. The lack of access points in this section of the river necessitated a greater distance (105 km) from the proximal gauging station (Cannelton Dam). Seven surveys were completed between 1998 and 2000. In each year, two surveys were conducted, one at the onset of the warmwater, low-discharge period (June or July) and one at the conclusion (October). An additional survey was performed in March, 2000 to characterize transport processes during low water temperature and elevated discharge. Sampling followed a Lagrangian design with upriver sites visited 3–10 days prior to

downriver sites depending on transit time (estimated from river stage and discharge).

Water samples and ancillary field data (temperature, dissolved oxygen) were taken at a mid-point (thalweg) of the river channel within 1 m of the surface. In our prior studies of the Ohio River we have compared samples collected at various locations along the width and depth of the channel and have not found consistent differences. The well-mixed conditions may be attributed to the fact that our sampling locations lacked side channel and backwater areas (as is generally true for the lower Ohio River) and did not include areas above navigation structures. Tributary samples were collected 1–2 km above the confluence with the Ohio River to ensure that samples were representative of waters originating in the sub-basin. Water samples were analyzed for particulate organic carbon (POC), dissolved organic carbon (DOC), nutrients (dissolved and total) and chlorophyll *a* (CHL_a). Chloride was measured on a subset of samples for use as a conservative tracer in comparing input and output fluxes. Particulate organic carbon (POC) concentrations were determined from material collected on pre-combusted glass fiber filters (Gelman A/E; 0.5 μm). Filters were dried over night at 70°C, weighed, combusted at 84–50°C for four hours and re-weighed. POC was estimated to be 41% of the ash-free dry mass as determined from sub-samples run on a Perkin–Elmer CHN analyzer. DOC was measured on an automated total carbon analyzer (Shimadzu Model TOC-5050A) after acidification and sparging to remove inorganic carbon. Nutrient analyses followed standard methods (APHA, 1998) using filtered samples and automated procedures (Skalar San Plus) for the determination of NO₃ (cadmium reduction), NH₄ (phenate), soluble reactive phosphorus (SRP; ascorbic acid), and dissolved silica (SiO₂; molybdate-reactive). Total (TP, TN) and total dissolved (TDN, TOP) fractions were determined from unfiltered and filtered samples that had been subjected to persulfate digestion. Particulate N and P were estimated from the difference between total and total dissolved fractions. Dissolved organic N and P were estimated by subtracting DIN (NO₃ plus NH₄) or SRP from the total dissolved fraction. Chloride analyses were performed manually using the ferricyanide method (APHA 1998). Samples for CHL_a analyses were collected on 0.5 μm filters, extracted in acetone (12 h) and analyzed by fluorometry (Turner Designs 10-AU) with acid correction (Arar and Collins 1997).

To quantify the effects of riverine processes on material throughput we compared instantaneous

input and output fluxes. Flux rates were calculated as the product of discharge and concentration at each site. Stage and discharge data for the Ohio River and its tributaries were obtained from the United States Geological Survey (USGS 2000) and Tennessee Valley Authority (TVA). Discharge was represented by a 10-day average centered on the date of sample collection. The sum of input fluxes from tributaries and the upper Ohio River were compared to output fluxes to determine whether in-river processes resulted in a net gain or loss for various fractions of C, N and P. To facilitate comparisons with previously published values we calculated the first-order rate of N loss per unit of water travel time (as % d⁻¹) using the formula $R = -t^{-1} (1-L)$ where t is the water time of travel and L is riverine N loss expressed as a fraction of external inputs (Alexander and others 2000). We compared input and output fluxes over the entire reach (length = 645 km; ORK, 862–1507) and for two subsections delineated by the mid-river site. The mass balance for the upper sub-reach (length = 396 km; ORK, 862–1258) was based on a comparison of inputs from the upper Ohio (above Cincinnati) and Kentucky Rivers against outputs measured at the mid-river sampling location. Outputs from the lower sub-reach (length = 249 km; ORK, 1258–1507) were measured fluxes at the downriver site and these were compared to inputs from the upper Ohio (above mid-river sampling location), Green, Wabash, Cumberland and Tennessee Rivers.

To assess the influence of point source inputs on mass balances, we obtained data from the EPA Permit Compliance System (PCS) Database for facilities holding National Pollutant Discharge Elimination System (NPDES) permits (USEPA 2003). Point sources located within our study reach discharge effluent to the Ohio River at an average rate of 12 m³ s⁻¹. The majority (72%) enters within the upper sub-reach where the largest single point source is a wastewater treatment plant serving the Louisville metropolitan area (Morris-Forman WWTP; NPDES ID KY0024411). We estimated point source contributions to NO₃, NH₄ and TP budgets based on effluent discharge and concentration (no data on effluent Cl concentrations available). Effluent NH₄ concentrations were measured monthly at Morris-Forman WWTP from October 1999 through October 2003 (USEPA 2003). To characterize TP fluxes, we used NPDES (effluent) and Ohio River Valley Water Sanitation Commission (influent, unpublished) concentrations for Morris-Forman WWTP (collected October 1998–December 2002; total = 21 observations).

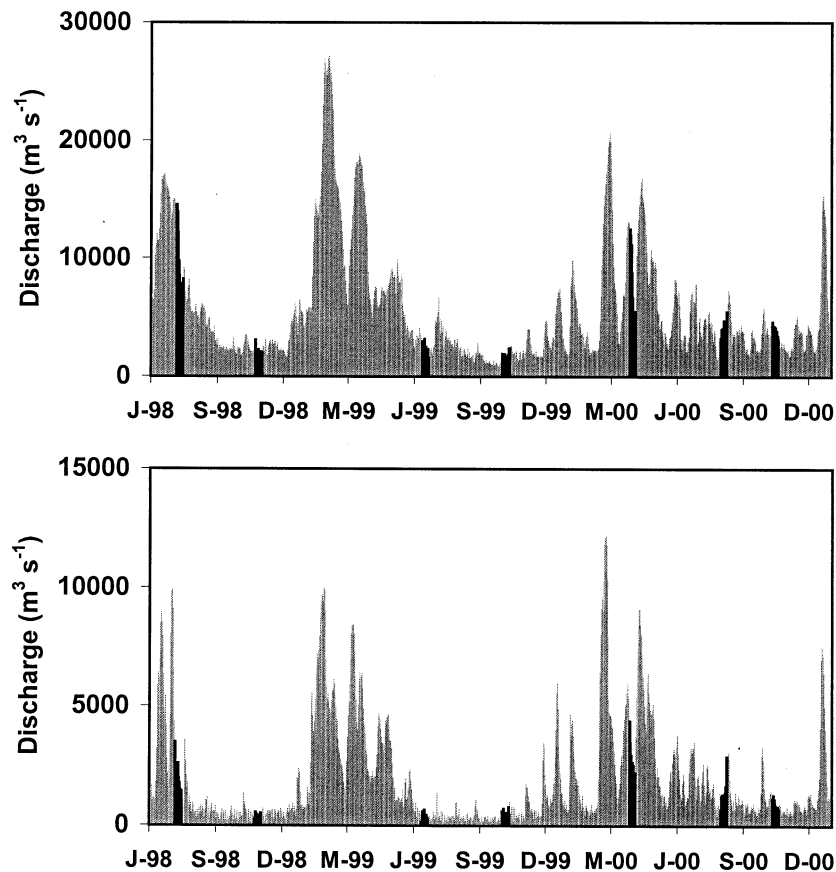


Figure 2. Daily average discharge of the Ohio River at Site 1 (downriver; upper panel) and Site 3 (upriver; lower panel). Data are for the period from June 1, 1998 to December 31, 2000 with survey dates shown in bold. Downriver and upriver discharges represent outflow and inflow to the study reach and are based on data from USGS gauging stations at Metropolis, IL and the Markland Dam (respectively).

Effluent NO_3 concentrations were not available for Morris–Forman WWTP and therefore we used data from the Hamilton County WWTP (NPDES ID OH0025461, collected monthly from January 1998 to October 2003). This facility serves the Cincinnati metropolitan area and has a comparable discharge to the Morris–Forman WWTP. We estimated input fluxes associated with all point sources within the study reach by extrapolating data for Morris–Forman WWTP based on its proportional contribution to the effluent discharge (54%) entering the upper sub-reach.

RESULTS

Discharge from the Ohio River basin ranged from 1000 to 26000 $\text{m}^3 \text{s}^{-1}$ (daily averages) between June 1998 and December 2000 with highest values in winter–spring (Figure 2). Surveys in July 1998 and March 2000 were conducted during periods of elevated discharge (9700 $\text{m}^3 \text{s}^{-1}$ and 8000 $\text{m}^3 \text{s}^{-1}$

respectively). Remaining surveys occurred during low discharge (<3000 $\text{m}^3 \text{s}^{-1}$). Inputs from the upper Ohio River sub-basin (Site 3) ranged from 500 to 12000 $\text{m}^3 \text{s}^{-1}$ and exhibited similar seasonal patterns to those observed at the downriver station (Figure 2). The upper Ohio River sub-basin contributed on average 28% (7 survey periods) of the output from the entire basin while the principal tributaries (Tennessee, Wabash and Cumberland Rivers) contributed 23, 16 and 12% (respectively). The combined inputs of the Kentucky and Green Rivers were relatively minor accounting for 3% of the output from the entire basin. The proportion of water originating within each of the major sub-basins was variable among survey dates. The contribution from the upper Ohio River sub-basin ranged from 20 to 50% with proportionally higher values occurring during the two surveys when output from the basin as a whole was highest (Figure 3). The Tennessee and Cumberland Rivers accounted for a smaller proportion of inputs during

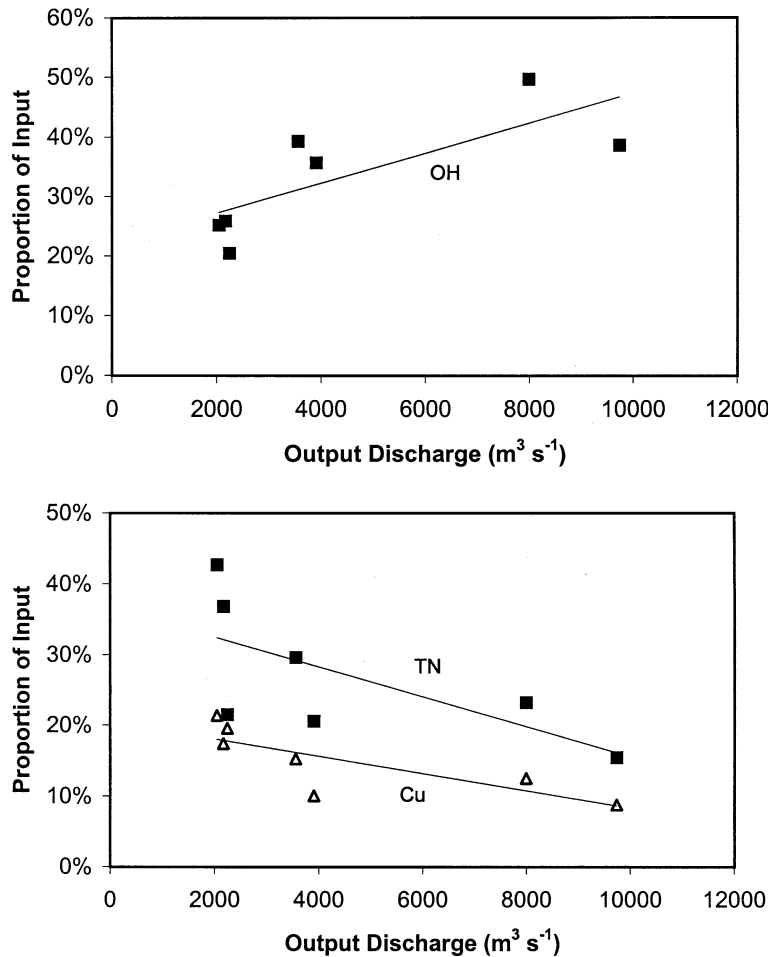


Figure 3. Discharge of the upper Ohio River (Site 3; upper panel) and the Cumberland and Tennessee Rivers (lower panel) as a proportion of the discharge of the Ohio River at the downriver sampling location (Site 1). Regression lines denote statistically significant associations for the Tennessee ($R^2 = 0.45$), Cumberland ($R^2 = 0.63$) and upper Ohio ($R^2 = 0.58$) Rivers.

these two surveys but contributed a greater proportion of inputs (40 and 20%, respectively) when total basin outflow was low. The proportion of water originating within the Wabash River sub-basin was not correlated with the discharge of the Ohio River.

Water chemistry data were averaged across dates for each of the eight sites to characterize longitudinal variation in the Ohio River and differences among the major sub-basins (Figure 4). Highest average concentrations of CHLa, POC, DOC, N and P were found in the Wabash River. POC concentrations in the Wabash River (mean = 12.7 mg L⁻¹) were two- to five-fold higher than those measured in other tributaries and the mainstem of the Ohio River (range = 2.6 to 6.3 mg L⁻¹). DOC concentrations in the Wabash River (mean = 11.9 mg L⁻¹) exceeded those of other sites (5.8 to 8.4 mg L⁻¹) by two-fold or less. DOC was on average 62% of total

organic carbon (range = 48–74%) across all sites. Chlorophyll in the Wabash River averaged 48.3 $\mu\text{g L}^{-1}$ whereas concentrations did not exceed 20 $\mu\text{g L}^{-1}$ among the remaining sites. Higher TN values for the Wabash River reflected elevated concentrations of both inorganic and organic fractions relative to other sites in the basin. Lowest TN concentrations were observed in the two rivers draining the southern region (Tennessee and Cumberland Rivers). This was largely due to low NO₃ in these rivers (<100 $\mu\text{g L}^{-1}$) relative to the Ohio River and other tributaries (range = 648 to 1690 $\mu\text{g L}^{-1}$). TP concentrations in the Wabash River were two-fold greater than average values for other sites and were largely due to higher concentrations of the organic fraction. The three sites in the mainstem of the Ohio River exhibited consistent downriver gradients of increasing CHLa (from 1.8 to 7.9 $\mu\text{g L}^{-1}$) and decreasing dissolved

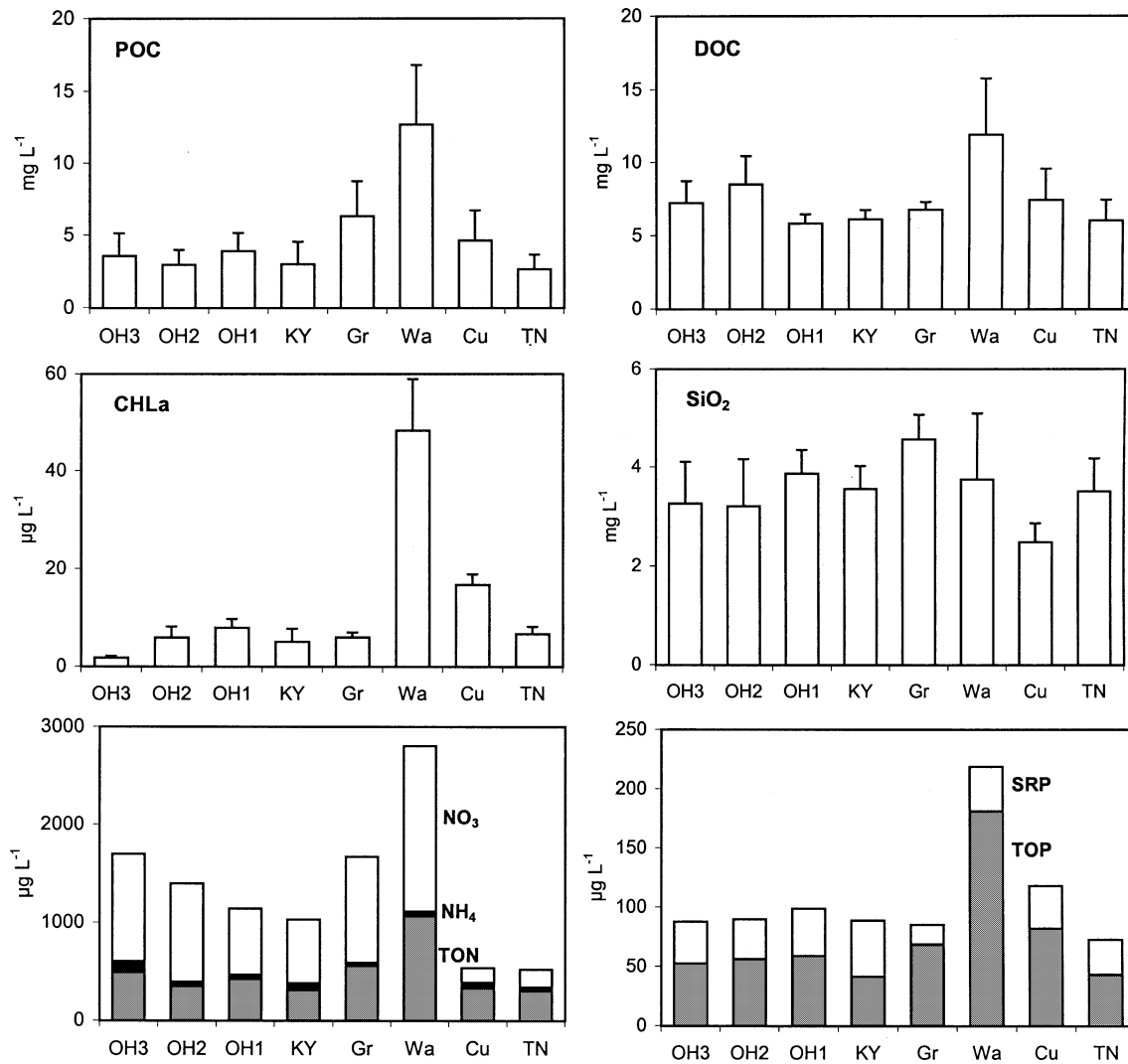


Figure 4. Chlorophyll, dissolved silica and particulate and dissolved fractions of C, N and P for the Ohio River and its principal tributaries. Values are averages (\pm Standard Error) for seven surveys completed between June 1998 and December 2000. Ohio River samples are from upper-(OH3), mid- (OH2) and down- (OH1) river stations; tributaries are listed in order (upriver to downriver) according to their confluence with the Ohio River.

inorganic nitrogen (from 1206 to 721 $\mu\text{g L}^{-1}$). The decrease in inorganic nitrogen (predominantly NO_3) coupled with a small increase in TP resulted in a reduction in TN:TP (from 20 to 10) along the longitudinal gradient. Lowest TN:TP ratios were measured in the Tennessee and Cumberland Rivers (mean = 5.1 and 4.2; respectively). Dissolved silica ranged from 2.5 to 4.6 mg L^{-1} with lowest concentrations measured in the Cumberland River.

Water balances generally showed good agreement as input discharge (upper Ohio River plus tributaries) equaled 85–91% of output discharge from the basin (Figure 5). The 10–15% underestimation of inputs may be due to ungauged sources which account for 9% of watershed area.

An exception was the July, 1998 survey which was conducted during a period of declining river stage (transition from high to low discharge). We used river stage and morphometric data obtained from the US ACoE to calculate the loss of storage volume during the survey period. The decrease in storage volume accounted for 83% of the imbalance in the water budget. For this date only, we calculated mass balances with a correction for the change in storage by assuming an outflow volume equivalent to the inflow volume. Water balances derived separately for the two sub-sections of our study reach also showed good agreement with inputs accounting for 85–95% of outputs (excluding July, 1998). To assess the effects of

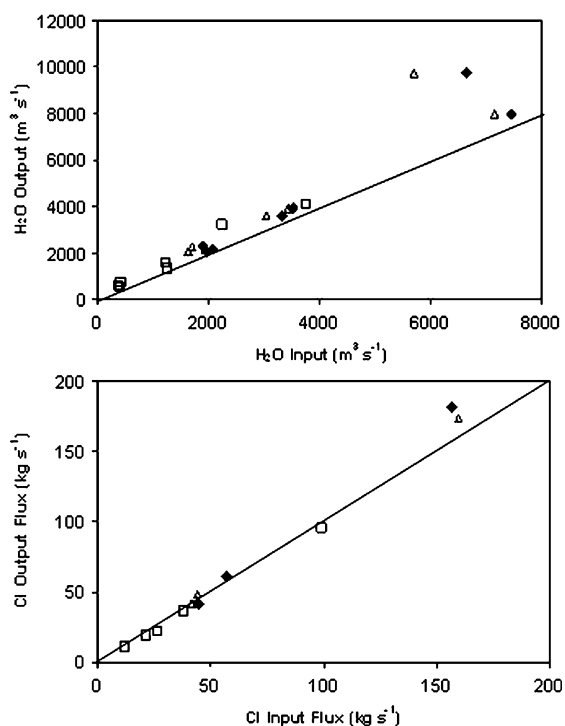


Figure 5. Input and output fluxes of water (7 dates) and Cl (3–5 dates) for the mainstem Ohio River. Input fluxes are the sum of upstream and tributary sources. Symbols denote fluxes for the entire study reach (Sites 1–3; triangles) and for upper (Sites 2–3; squares) and lower (Sites 1–2; diamonds) sub-sections.

underestimating water inputs on mass balances we compared inputs and outputs of a conservative tracer for a subset of dates when chloride was measured (five for upper sub-reach and three for lower sub-reach). Input fluxes of Cl corresponded to 86–122% of output fluxes (mean = 103%) and showed no consistent pattern of over- or underestimation (Figure 5). Good agreement in Cl balances despite underestimation of water inputs may be due to unaccounted point source inputs making up for ungauged inputs. We conclude that our mass balances are accurate to within 20% and assume that departures exceeding this value are evidence for source or sink processes occurring within the mainstem of the Ohio River (Richey and others 1990).

For each of the dissolved and particulate fractions measured (excluding Cl), we observed input–output imbalances exceeding 20% during at least three of the seven surveys. CHLa, NH_4 and NO_3 were the least conservative as inputs to the mainstem Ohio River exceeded outputs by an average factor greater than 1.4. CHLa fluxes were rarely in equilibrium for either the upper or lower sub-reaches (Figure 6). The upper river acted as a modest source of

CHLa with input fluxes (3.0 g s^{-1}) averaging 60% of output fluxes (5.4 g s^{-1}). Net production in the upper reach was highest during low discharge. In contrast, the lower sub-reach was consistently a sink for CHLa where inputs averaged 40 g s^{-1} and outputs averaged 30 g s^{-1} . Chlorophyll fluxes in the lower sub-reach were dominated by the Wabash River which accounted for 56% of inputs on average. Outputs of CHLa ranged from 5 to 78% (average = 32%) of inputs with highest losses occurring during low discharge. The Ohio River overall was found to be a sink for CHLa with an average output equal to 67% of inputs.

Inputs of NH_4 were typically larger than outputs suggesting that the Ohio River acted as a net sink. Inputs to the upper sub-reach (124 g s^{-1}) were almost twofold higher than outputs (65 g s^{-1}) with loss estimates ranging from 24 to 72% (average = 48%). NH_4 removal rates in the upper sub-reach ranged from -0.8 to 9.1% per day of water travel time (mean = 4.8%). The lower sub-reach was in equilibrium with respect to NH_4 inputs and outputs (160 and 158 g s^{-1} , respectively) with average removal rates of 1.5%. The river as a whole was found to be a sink for NH_4 during four of seven surveys (retention = 29–64%). NO_3 fluxes generally followed a conservative pattern in the upper reach but not in the lower reach where input–output balances varied as a function of discharge. For the two sampling dates with highest discharge (July 1998, March 2000), NO_3 outputs (6800 g s^{-1} , 12000 g s^{-1} ; respectively) exceeded concurrent inputs (5100 and 9600 g s^{-1}). During low discharge, inputs (1961 g s^{-1}) exceeded outputs (1242 g s^{-1}) and corresponded to an average loss of 39%. NO_3 removal rates during low discharge ranged from 1.4 to 13.3% (mean = 4.0%). The river as a whole was a sink for NO_3 with input to output ratios ranging from 0.8 to 2.7.

Average fluxes of other parameters (DOC, POC, TN, TP, SRP, SiO_2) were near equilibrium although large imbalances were evident during some surveys (Figure 6). The lower reach was a net sink for DOC on two dates (August and October 2000) with losses equivalent to 68 and 51% (respectively) of inputs. The upper sub-reach was typically a source of DOC (six of seven surveys) with average outputs exceeding inputs (13 and 9 kg s^{-1} , respectively). Modest losses of TN, TP and POC occurred during periods of low discharge but these were offset by net export during high discharge. SRP fluxes were near equilibrium during low discharge whereas high discharge was associated with net export. The river acted as a net source of SiO_2 over a wide range of discharge conditions.

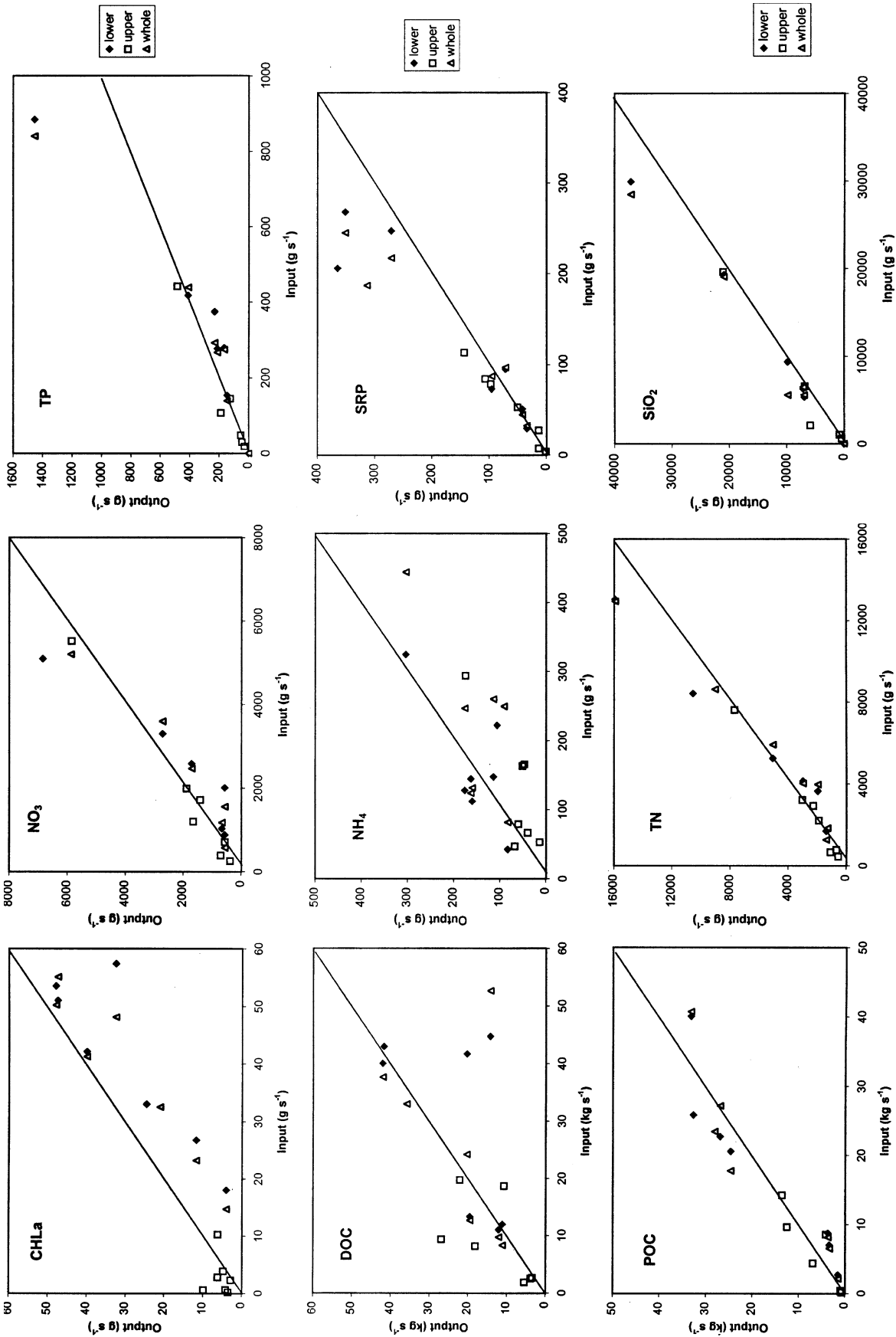


Figure 6. Input and output fluxes of chlorophyll, dissolved silica and particulate and dissolved fractions of C, N and P for the mainstem Ohio River during seven surveys completed between June 1998 and December 2000. Input fluxes are the sum of upstream and tributary sources. Symbols denote fluxes for the entire study reach (Sites 1–3; triangles) and for upper (Sites 2–3; squares) and lower (Sites 1–2; diamonds) sub-sections. Lines depict a 1:1 relationship; symbols falling below the line denote retention.

Table 2. Comparison of NH₄, NO₃ and TP Inputs from the Upper Ohio River Basin, Tributaries (Kentucky River), and Point Sources to the Upper Sub-reach during Baseflow Conditions (June–September)

	N-NH ₄ g s ⁻¹	N-NO ₃ g s ⁻¹	DIN g s ⁻¹	TP g s ⁻¹
Inputs				
Upper Ohio River	100	845	945	68
Tributary	2	12	14	2
Point Sources	80	33	113	20
Total	182	890	1072	90
Outputs	48	945	993	88
% Loss (I-O/I)	74%	6%	7%	2%

Input from the upper Ohio River basin were measured at Site 1 and outputs from the study reach were measured at the mid-river sampling location (Site 2). Ohio River and tributary fluxes are average values for five of the seven surveys excluding those conducted during high flow conditions (July 1998, March 2000).

Point source fluxes are based on effluent discharges for facilities holding National Pollutant Discharge Elimination System (NPDES) and effluent concentrations measured at the Louisville (NH₄, TP) and Cincinnati (NO₃) metropolitan WWTPs.

Point source inputs of NH₄ and TP were important components of the input budgets for the upper sub-reach (Table 2). During baseflow conditions (excluding July 1998 and March 2000 surveys) point source inputs of NH₄ (80 g s⁻¹) were large in comparison to tributary inputs (2 g s⁻¹) and comparable to inputs from the upper Ohio River basin (100 g s⁻¹). Inclusion of point source contributions yielded an average loss rate of 74% for NBU and an average removal rate of 8% per day of water travel time (range = 1 to 15%). Point source inputs of TP (20 g s⁻¹) and NO₃ (33 g s⁻¹) exceeded tributary fluxes into the upper sub-reach (2 and 12 g s⁻¹; respectively). Point sources accounted for 22% of the total TP inputs and their inclusion resulted in a close balance between inputs (90 g s⁻¹) and outputs (88 g s⁻¹). Point sources were not a significant component of the NO₃ budget (<5% of inputs) due to large fluxes associated with the upper Ohio River basin. In the lower sub-reach, point sources did not substantially influence estimates of input or loss due to the lack of major WWTP discharges in this portion of the river and the large fluxes associated with tributaries and the upper Ohio River basin.

DISCUSSION

The Ohio River integrates drainage waters from sub-basins that differ in their land use and degree of hydrologic regulation. These properties influence the quantity and timing of water and material delivery from the Ohio River. Highest N and P concentrations were measured in the Wabash River and these values were typical of basins with substantial agricultural land use (Harris 2001; Vanni and others 2001). By comparison, the Tennessee and Cumberland Rivers drain more forested areas in the southern region of the basin and generally

exhibited lower nutrient concentrations particularly with respect to N. In a concurrent study (1999) for which monthly samples were collected, we observed summer minima of 17 µg N-NO₃ L⁻¹ (Tennessee River) and 180 µg N-NO₃ L⁻¹ (Cumberland River) whereas Ohio River concentrations were never below 600 µg N-NO₃ L⁻¹ (Koch and others 2004). The southern rivers (particularly Tennessee) experience greater water regulation effects due to the presence of large mainstem impoundments. Nutrient retention in reservoirs can substantially reduce downstream transport (Caraco and Cole 1999; Stanley and Doyle 2002) and the low availability of N relative to P (TN:TP < 8) suggests that denitrification may be important in these rivers (Sjodin and others 1997; Josette and others 1999). Differences in nutrient availability among the rivers corresponded to differences in the nature and severity of growth limitation for phytoplankton. Nutrient limitation (P or N) was commonly observed in the southern rivers but rarely in the Ohio River (only when silica levels declined below 1000 µg L⁻¹) because the latter was predominantly light limited (Koch and others 2004).

Our primary finding is that seasonal variation in the proportion of flow originating from the contributing sub-basins gives rise to predictable patterns in nitrogen export associated with varying stages of the hydrograph. The influence of the southern rivers is greatest during summer baseflow conditions when their combined discharge accounts for 60% of inputs and results in low N concentrations in water entering the Mississippi River (Figure 7). In contrast, periods of elevated discharge for the Ohio River were characterized by proportionately greater contributions from the upper Ohio and Wabash basins and elevated N concentrations. This pattern arises from an inter-

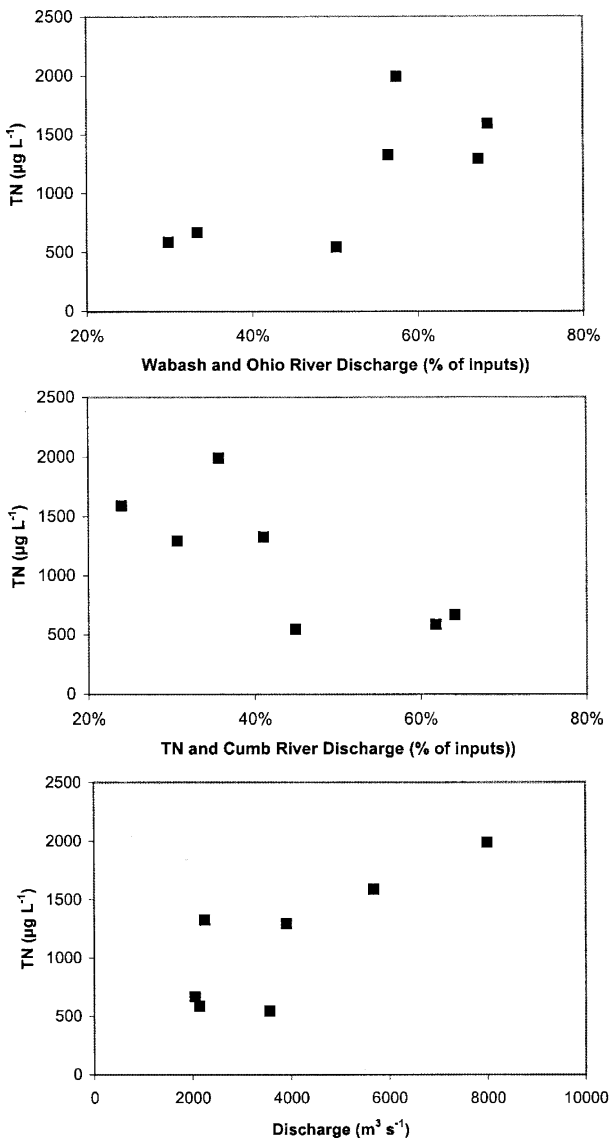


Figure 7. Ohio River TN concentrations as a function of proportion of inputs from the Wabash and upper Ohio River basins (top), the proportion of inputs from the Tennessee and Cumberland River basins (middle) and the discharge of the Ohio River (bottom).

action between climate, land-use and water regulation effects. The northern and eastern sub-basins receive greater N loading associated with agriculture and also experience a proportionately larger peak discharge in spring (ca. five times the average monthly discharge at baseflow). The latter may reflect a contribution from snowmelt runoff. The southern rivers are less intensively cultivated and exhibit smaller spring discharge peaks (ca. three times minimum flow) which minimizes their importance to water and nitrogen budgets when the Ohio River is at elevated flow. Water storage by

regulation structures (particularly in the Tennessee River) may delay the delivery and in part account for the greater contribution of these rivers in late summer.

Seasonally-variable sub-basin contributions foster a positive association between discharge and N concentrations in the Ohio River. A positive association between nitrate concentrations and discharge has been reported previously for the Mississippi River (Goolsby and others 2001) and attributed to leaching of nitrate from agricultural soils following rain events. This relationship would not be expected if point sources were the predominant factor determining concentration, as these inputs would have their maximum influence at low discharge. This finding is consistent with our analyses showing that point loadings are a significant source of NH_4 but a relatively small component of the overall budget for dissolved inorganic N. Prior analyses have emphasized the importance of non-point sources and the transport of NO_3 but it should be recognized that inputs of NH_4 from point sources more closely mimic internal regeneration processes associated with decomposition and consumer excretion. A number of studies have documented the importance of NH_4 production in meeting autotrophic and heterotrophic demands for N (Schaus and others 1997; Pressing and others 2001; Shostell and Bukaveckas 2004) and recent stable isotope analyses of zebra mussels in the Mississippi River suggest that NH_4 may account for a disproportionate fraction of consumer N (Fry and Alien 2003). Our analyses show that point source inputs of NH_4 to the Ohio River are large relative to tributary and upstream sources and suggest they may be important to riverine metabolism and food-webs.

Our synoptic survey of flux rates within the Ohio River and its major tributaries suggests that accurate forecasting of the delivery of N and other materials from this basin depends upon an understanding of hydrologic contributions among the sub-basins. We examined current patterns in the context of long-term (50-year) trends in discharge. Analyses of annual average values revealed increasing trends in discharge comparable to those previously reported for this and other rivers comprising the Great Central Basin (Baldwin and Lall 1999; Raymond and Cole 2003). We estimate that the annual average discharge of the Ohio River has increased by 15% since 1940 with comparable increases observed in the Wabash (18%) and Tennessee (19%) Rivers. In comparison, the annual average discharge of the Cumberland River has increased by 41% and its proportional contribution

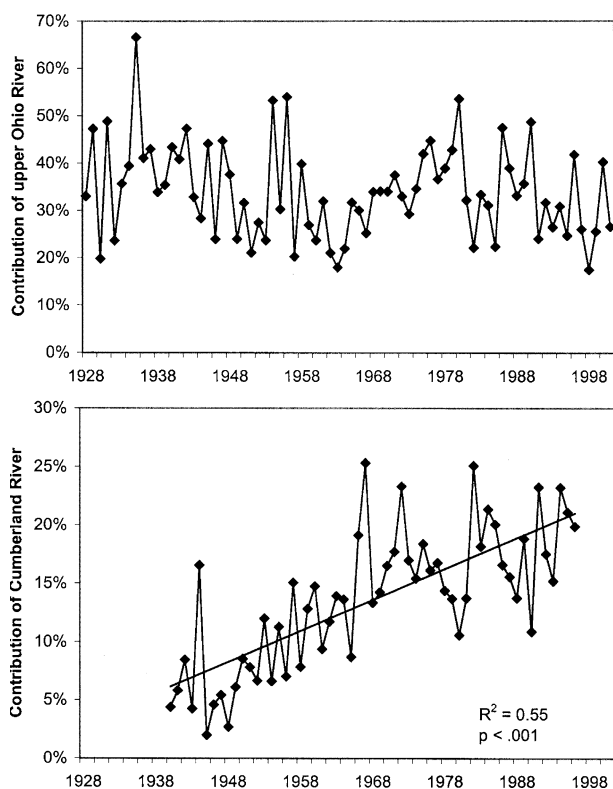


Figure 8. Proportion of inputs to the Ohio River during baseflow (August–October) that originate from the upper Ohio River (top) and Cumberland River (bottom) sub-basins.

to the Ohio River during baseflow (August–October) has risen from 5 to 20% (Figure 8). The greater input of N-depleted waters may partially mitigate high N yields from other portions of the Ohio River basin. A broader analysis (Clark and others 2002) yielded a similar conclusion by showing that concentrations of most chemical constituents in the Mississippi River declined as the proportion of water originating within the Ohio River basin increased. Compared to the upper Mississippi River, much of the Ohio River basin is forested and less intensively farmed, which, in combination with greater precipitation, results in lower concentrations of dissolved and particulate materials. Although the mechanisms driving changes in river discharge within the US Central Basin are not known, our analyses suggest that differential responses in water yield among sub-basins effects material delivery to the Mississippi River.

Recent changes in material delivery from sub-basins of the Ohio River may reflect changes in land use and water regulation but studies in the Amazon River basin suggest that sub-basin effects

are equally important in regions where anthropogenic influences are less pronounced. Greater than 80% of the suspended materials transported by the Amazon River are derived from the small portion of the catchment which is drained by Andean (“white water”) rivers (Devol and Hedges 2001) and these account for a large fraction of the mineral nutrients supporting riverine and flood-plain communities (Melack and Forsberg 2001). An appreciation of water “provenance” is central to predicting material delivery from large river basins where anthropogenic or physiographic effects result in disproportionate yields relative to runoff.

A second finding from our study is that spatial variation in material fluxes along the length of the Ohio River arises in part from transformation of N and P fractions within the river itself. The upper sub-reach was found to be a net source of CHLa suggesting that this portion of the river provided a generally favorable environment for phytoplankton production. Detailed studies of the McAlpine Pool (located at the lower end of the upper sub-reach) showed that light dosages were sufficient to allow photosynthesis in excess of algal respiration and resulted in net gains of algal carbon (Sellers and Bukaveckas 2003). Light dosages increased with decreasing discharge because of the combined effects of longer transit time, reduced turbidity and declining river stage (shallower water column resulting in higher average irradiance). Our survey data suggest that this relationship between discharge and light dosage typifies conditions throughout the upper sub-reach because the ratio of CHLa outputs to inputs increased with declining discharge. The upper sub-reach was also found to be a net sink for NO_3 and NH_4 suggesting that N demand was sufficiently high to offset remineralization rates of autochthonous and allochthonous organic matter.

Loss of inorganic N and P within the upper sub-reach likely reflects transformation to organic forms through biotic uptake and (for N) removal through denitrification. Transformation of inorganic N and P through autotrophic and heterotrophic production should be balanced by the export of dissolved and particulate organic matter. Our budgets indicate that TP and TN mass balances were typically near equilibrium and are consistent with previous findings for the Mississippi River (Goolsby and others 2001). However, because the base-flow period is associated with warm water and peak biotic activity, loss of inorganic fractions may have important implications for downstream environments. Nitrogen supply has been shown to regulate

primary production in estuaries (Gallegos and others 1992; Paerl and others 2001) and river impoundments (Bukaveckas and Crain 2002; Bukaveckas and others 2002) whereas changes in the relative availability of N and Si have been shown to influence coastal food-webs in the Gulf of Mexico (Turner and others 1998). NO_3 removal rates in the Ohio River were comparable to previously published estimates of riverine N loss (0.5–5% d^{-1} ; Alexander and others 2000) whereas NH_4 removal rates were higher (8% inclusive of point sources). The combined effects of N removal and inputs of N-depleted water from southern rivers results in a longitudinal decline in N:P ratios from 20 to 10.

Our present study does not allow us to partition nutrient uptake according to autotrophic vs. heterotrophic demand but it is interesting to note that the lower sub-reach was more heterotrophic (net loss of CHLa) and was not a sink for inorganic N. Cross-sectional geomorphometry data show that pools comprising the lower sub-reach were generally deeper. Modeling analyses revealed that algal respiration typically exceeded photosynthesis resulting in the attenuation of downstream transport in algal carbon (Sellers 2001). Longer transit times within deep pools increase respiration losses and our survey data showed that as discharge declined, loss of CHLa in the lower sub-reach increased. Because losses in the lower sub-reach exceeded gains in the upper sub-reach, the Ohio River was overall a net sink for CHLa. The consequences of algal C loss for downstream food-webs are unclear owing to continuing uncertainty about the importance of autochthonous production in rivers (Devol and Hedges 2001; Thorp and DeLong 2002). Algal C typically comprises less than 10% of the POC in the Ohio River and its tributaries but may account for a disproportionately large fraction of bacterial and zooplankton production given its labile and nutrient-rich composition (Muller-Solger and others 2002; Kritzbeg and others 2004). Our related studies have documented positive responses in zooplankton populations (Guelda and others 2005) and larval fish growth rates in river mesocosms when algal C is elevated to 10–15% (P. Bukaveckas, unpubl. data).

Our assessment of the importance of riverine processes in material transformations is based on an analysis of fluxes during predominantly low flow conditions characteristic of the summer, warm water period (five of seven surveys). We derived basin yields from our dataset to characterize flux conditions and place these in the context of previ-

ously published values that are more representative of intra- and inter-annual variation in discharge from the Ohio River basin. Our average-yield of TOC ($2365 \text{ kg km}^{-2} \text{ y}^{-1}$) was similar to a recently published estimate ($2513 \text{ kg km}^{-2} \text{ y}^{-1}$) based on 61 measurements during 1973 to 1994 (Turner and Rabalais 2004). Our average yields of TN ($322 \text{ kg km}^{-2} \text{ y}^{-1}$) and TP ($22 \text{ kg km}^{-2} \text{ y}^{-1}$) were lower than estimates based on 240 measurements (TN = 765; TP = 68) during this period (Turner and Rabalais 2004). Our estimates of material losses reflect high rates of metabolic activity and reduced horizontal transport during base-flow conditions whereas annualized budgets would yield lower loss estimates due to diminished metabolism and transient storage during high discharge and cold water conditions.

Much progress has been made in recent years to assess material export from large rivers in the context of regional and global biogeochemical cycles. However few studies have examined within-river biogeochemical processes and their potential importance in influencing material export. The scarcity of biogeochemical studies in rivers may be attributed to several factors. First, large rivers are themselves scarce within the landscape thus limiting opportunities for the types of comparative studies that have yielded insights to stream and lake ecosystems (Wolheim and others 2001; Hanson and others 2003). Second, smaller (headwater) streams, because of their low water column to benthic area ratios, have a higher processing potential and may therefore account for a disproportionate fraction of nutrient uptake in river networks (Alexander and others 2000). Our results show that metabolic activity in large rivers can result in significant departures from mass balance equilibrium for a range of C, N and P fractions. Although we know of no studies that have quantified cumulative losses in rivers and their associated tributary networks, we speculate that basin-wide anthropogenic influences act to promote short-term storage in rivers while diminishing uptake in streams. In the Ohio River, the presence of regulation structures lengthens water transit time thereby enhancing the opportunity for biotic processes to attenuate downstream transport of inorganic nutrients during base-flow periods. Channel modifications in small streams typically involve channelization, which decreases water transit time and minimizes metabolic influences. An understanding of the effects of storage and removal on the timing and delivery of materials from large basins requires quantification of these

processes over a range of lotic systems from headwater streams to large rivers.

ACKNOWLEDGEMENTS

The authors would like to thank Rich Schultz for his assistance with sample analyses. Anthony Aufdenkampe and Peter Groffman provided helpful comments. The Ohio River Valley Sanitation Commission provided unpublished data on effluent chemistry for the Morris Forman wastewater treatment plant.

REFERENCES

- Alexander RB, Smith RA, Schwarz GE. 2000. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. *Nature* 403:758–61.
- APHA Standard Methods for the Examination of Water and Wastewater. 1998. American Public Health Association. 20th edition. Washington, DC, USA.
- Arar EJ, Collins GB. 1997. In Vitro Determination of chlorophyll a and pheophytin a in marine and freshwater phytoplankton by fluorescence. Methods for the determination of chemical Substances in marine and estuarine environmental samples. USEPM, p 1–12.
- Baldwin CK, Lall U. 1999. Seasonality of streamflow: The upper Mississippi River. *Water Resour Res* 35:1143–54.
- Bukaveckas PA, Likens GE, Winter TC, Buso DC. 1998. A comparison of methods for deriving solute flux rates using long-term data from streams in the Mirror Lake watershed. *Water, Air, and Soil Pollution* 105:277–93.
- Bukaveckas PA, Williams JJ, Hendricks SP. 2002. Factors regulating autotrophy and heterotrophy in the main channel and an embayment of a large river impoundment. *Aquat Ecol* 36:355–69.
- Bukaveckas PA, Crain AS. 2002. Interannual, seasonal and spatial variability in nutrient limitation of phytoplankton production in a river impoundment. *Hydrobiologia* 481:19–31.
- Caraco NF, Cole JJ. 1999. Human impact on nitrate export: An analyses using major world rivers. *Ambio* 28:167–70.
- Carpato NF, Cole JJ, Likens GE, Lovett GM, Weathers KG. 2003. Variation in N₂O export from flowing waters of vastly different sizes: Does one model fit all? *Ecosystems* 6:344–52.
- Clark GM, Broshears RE, Hooper RP, Goolsby DA. 2002. Evaluating the influence of source basins on downstream water quality in the Mississippi River. *J Am Water Resour Ass* 38:803–18.
- Cole JJ, Caraco NF. 2001. Carbon in catchments; connecting terrestrial carbon losses with aquatic metabolism. *Mar Freshwater Res* 52:101–10.
- Devol AH, Hedges JL. 2001. Organic matter and nutrients in the mainstem Amazon River. In: McClain ME, Victoria R, Richey JE, Eds. *The Biogeochemistry of the Amazon Basin*. New York: Oxford University Press. p 275–306.
- Dynesius M, Nilsson C. 1994. Fragmentation and flow regulation of river systems in the northern third of the world. *Science* 266:753–62.
- Fry B, Allen YC. 2003. Stable isotopes in zebra mussels as bio-indicators of river-watershed linkages. *River Res Appl* 19:683–96.
- Gallegos CL, Jordan TE, Correll DL. 1992. Event-scale response of phytoplankton to watershed inputs in a sub-estuary: timing, magnitude and location of blooms. *Limnol Oceanogr* 37:813–28.
- Goolsby DA, Battaglin WA, Aulenbach BT, Hooper RP. 2001. Nitrogen input to the Gulf of Mexico. *J Environ Qual* 30:329–36.
- Guelda DL, Koch RW, Jack JD, Bukaveckas PA. 2004. Experimental evidence for density-dependent effects and the importance of algal production in determining population growth rates of riverine zooplankton. *River Res Appl* 2005.
- Hall RO, Bernhardt ES, Likens GE. 2002. Relating nutrient uptake with transient storage in forested mountain streams. *Limnol Oceanogr* 47:255–65.
- Hall RO, Tank JL. 2003. Ecosystem metabolism controls nitrogen uptake in streams in Grand Teton National Park, Wyoming. *Limnol Oceanogr* 48:1120–28.
- Hanson PC, Bade DL, Carpenter SR, Kratz TK. 2003. Lake metabolism: Relationships with dissolved organic carbon and phosphorus. *Limnol Oceanogr* 48:1112–19.
- Harris GP. 2001. Biogeochemistry of nitrogen and phosphorus in Australian catchments, rivers and estuaries: effects of land use and flow regulation and comparisons with global patterns. *Mar Freshwater Res* 52:139–49.
- Howarth RW, Bille G, Swaney D, Townsend A, Jaworski NA, Lajtha K, Downing JA, Elmgren R, Caraco NF, Jordan T, Berendse F, Freney J, Kudeyarov V, Murdoch PS, Zhao-liang Z. 1996. Regional nitrogen budgets and riverine N and P fluxes for the drainages to the North Atlantic Ocean; natural and human influences. *Biogeochemistry* 35:181–226.
- Jossette G, Leporcq B, Sanchez N, Philippon X. 1999. Biogeochemical mass-balances (C, N, P, Si) in three large reservoirs of the Seine Basin (France). *Biogeochemistry* 47:119–46.
- Koch RW, Guelda DL, Bukaveckas PA. 2004. Phytoplankton growth in the Ohio, Cumberland and Tennessee Rivers, USA: inter-site differences in light and nutrient limitation. *Aquat Ecol* 38:17–26.
- Kohler J. 1994. Origin and succession of phytoplankton in a river-lake system (Spree, Germany). *Hydrobiologia* 289:73–83.
- Kritzbach ES, Cole JJ, Pace ML, Graneli W, Bade DL. 2004. Autochthonous versus allochthonous carbon sources to bacteria: Results from whole-lake ¹³C addition experiments. *Limnol Oceanogr* 49:588–96.
- Lewis WM, Melack JM, McDowell WH, McClain ME, Richey JE. 1999. Nitrogen yields from undisturbed watersheds in the Americas. *Biogeochemistry* 46:149–62.
- Meack JM, Forsberg BR. 2001. Biogeochemistry of Amazon floodplain lakes and associated wetlands. In: McClain ME, Victoria R, Richey JE, Eds. *The biogeochemistry of the Amazon Basin*. New York: Oxford University Press. p 235–74.
- Muller-Solger A, Jassby AD, Muller-Navarra DC. 2002. Nutritional quality of food resources for zooplankton (*Daphnia*) in a tidal freshwater system (Sacramento-San Joaquin River Delta). *Limnol Oceanogr* 47:1468–76.
- [NID] National Inventory of Dams. 2000. <http://crunch.tec.army.mil/nid/webpages/nid.cfm>.
- Paerl HW, Bales JD, Ausley LW, Buzzelli CP, Crowder LB, Eby LA, Fear JM, Go M, Peierls BL, Richardson TL, Ramus JS. 2001. Ecosystem impacts of three sequential hurricanes (Dennis, Floyd, and Irene) on the United States' largest lagoonal estuary, Pamlico Sound, NC. *Proceedings of the National Academy of Sciences USA* 98:5655–60.

- Pearson WD. 1992. Historical changes in water quality and fishes of the Ohio River. In: Becker CD, Neitzel DA. Eds. water quality in North American river System. Battelle Press, Columbus, pp 209–31.
- Presing M, Herodek S, Preston T, Voros L. 2001. Nitrogen uptake and the importance of internal nitrogen loading in Lake Balaton. *Freshwater Biol* 46:125–39.
- Raymond PA, Cole JJ. 2003. Increase in the export of alkalinity from North America's largest river. *Science* 301:88–91.
- Reynolds CS, Descy JP. 1996. The production, biomass and structure of phytoplankton in large rivers. *Arch Hydrobiol* 113:161–87.
- Richey JE, Hedges JL, Devol AH, Quay PD, Victoria R, Martinelli L., Forsberg BR. 1990. Biogeochemistry of carbon in the Amazon River. *Limnol Oceanogr* 35:352–71.
- Salvia M, Iffly JF, Vander Borgh P, Sary M, Hoffman L. 1999. Application of the 'snapshot' methodology to a basin-wide analysis of phosphorus and nitrogen at stable low flow. *Hydrobiologia* 410:97–102.
- Scavia D, Rabalais NN, Turner RE, Dubravko J, Wiseman WJ Jr. 2003. Predicting the response of Gulf of Mexico hypoxia to variations in Mississippi River nitrogen load. *Limnol Oceanogr* 48:951–6.
- Schaus MH, Vanni MJ, Wissing TE, Bremigan MT, Garvey JE, Stein RA. 1997. Nitrogen and phosphorus excretion by detritivorous gizzard shad in a reservoir ecosystem. *Limnol Oceanogr* 42:1386–97.
- Sellers T. 2001. Effects of water regulation on autochthonous production in a large river: A modeling and mass balance approach. PhD. Dissertation Kentucky: University of Louisville, Louisville.
- Sellers T, Bukaveckas PA. 2003. Phytoplankton production in a large, regulated river: A modeling and mass balance assessment. *Limnol Oceanogr* 48:1476–87.
- Servais P, Gosselain V, Joaquim-Justo C, Becquevort S, Thome JP, Descy JP. 2000. Trophic relationships between planktonic microorganisms in the River Meuse (Belgium): a carbon budget. *Arch Hydrobiol* 149:625–53.
- Shostell J, Bukaveckas PA. 2004. Seasonal and interannual variation in nutrient fluxes from tributary inputs, consumer recycling and algal growth in a eutrophic river impoundment. *Aquat Ecol* [in press].
- Sjodin AL, Lewis WM, Saunders JF. 1997. Denitrification as a component of the nitrogen budget for a large plains river. *Biogeochemistry* 39:327–42.
- Sparks RE, Spink A. 1998. Disturbance, succession, and ecosystem processes in rivers and estuaries: effects of extreme hydrologic events. *Regul Rivers* 14:155–9.
- Stanley EH, Doyle MW. 2002. A geomorphic perspective on nutrient retention following dam removal. *BioScience* 52:693–701.
- Thorp JH, Delong MD. 2002. Dominance of autochthonous autotrophic carbon in food webs of heterotrophic rivers. *Oikos* 96:543–50.
- Turner RE, Qureshi N, Rabalais NN, Dortch Q, Justic D, Shaw RF, Cope J. 1998. Fluctuating silicate:nitrate ratios and coastal plankton food webs. *Proceedings of the National Academy of Sciences USA* 95:13048–51.
- Turner RE, Rabalais NN. 2004. Suspended sediment, C, N, P, and Si yields from the Mississippi River basin. *Hydrobiologia* 511:79–89.
- USEPA. 2003. Permit compliance system database for national pollutant discharge elimination system permits. <http://www.epa.gov/enviro/html/pes/>.
- USGS. 2000. Data on nutrients in the streams, rivers and groundwater of the United States. National water quality assessment program. <http://water.usgs.gov/nawqa/>.
- Vanni MJ, Renwick WH, Headworth JL, Auch JD, Schaus MH. 2001. Dissolved and particulate nutrient flux from three adjacent agricultural watersheds: A five-year study. *Biogeochemistry* 54:85–114.
- Vorosmarty CJ, Sharma KP, Fekete BM, Copeland AH, Holden J, Marble J, Lough JA. 1997. The storage and aging of continental runoff in large reservoir systems of the world. *Ambio* 26:210–9.
- Wollheim WM, Peterson BJ, Deegan LA, Hobbie JE, Hooker B, Bowden WB, Edwardson KJ, Arscott DB, Hershey AE, Finlay J. 2001. Influence of stream size on ammonium and suspended particulate nitrogen processing. *Limnol Oceanogr* 46:1–13.