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Suspended sediment, C, N, P, and Si yields from the Mississippi River Basin

R. Eugene Turner[1] & Nancy N. Rabalais[2]
[1]*Coastal Ecology Institute, Louisiana State University, Baton Rouge, LA 70803, U.S.A.*
[2]*Louisiana Universities Marine Consortium, 8124 Highway 56, Chauvin, LA 70344, U.S.A.*

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Abstract

The annual loads of C,N,P, silicate, total suspended sediment (mass) and their yields (mass area^{-1}) were estimated for six watersheds of the Mississippi River Basin (MRB) using water quality and water discharge records for 1973 to 1994. The highest load of suspended sediments is from the Missouri watershed (58 mt km^2 yr^{-1}), which is also the largest among the six major sub-basins. The Ohio watershed delivers the largest load of water (38%). The Upper Mississippi has the largest total nitrogen load (32%) and yield (1120 kg TN km^2 yr^{-1}). The loading of organic carbon, total phosphorus and silicate from the Upper Mississippi and Ohio watersheds are similar and relatively high (range 2.1–2.5, 0.068–0.076, and 0.8–1.1 mt km^2 yr^{-1}, respectively). The yields of suspended sediments, total phosphorus, total nitrogen, and silicate from the Lower Mississippi watershed are disproportionately the highest for its area, which is the smallest of all the watersheds and has the weakest monitoring network. The loading from the Red and Arkansas watersheds are of lesser importance than the others for most parameters investigated. The total nitrogen loading to coastal waters increased an additional 150% since the early 1900s, and is now dominated by loads from the Upper Mississippi watershed, rather than the previously dominant Ohio watershed. An analysis of trends for 1973–1994 suggests variability among years, rather than uni-directional change for most variables among 11 key stations. Explanatory relationships were established or confirmed to describe TN and TP loadings in terms of the now largely human-created landscape arising mostly over the last 150 years.

Introduction

The Mississippi River watershed is 41% of the area of the contiguous 48 states (Fig. 1) and the third, eighth and sixth largest river in the world in terms of its length, discharge and sediment yield, respectively (Milliman & Meade, 1983). Most of its natural vegetation has been replaced over only the last 200 years, as a mostly European agricultural model arose and evolved into the present intensively-farmed form. The river debouches its load onto a continental shelf which harvests about 25% of the US coastal fisheries landings (tonnage) and whose nutrient load stimulates marine phytoplankton in sufficient quantities to cause the formation of the largest coastal hypoxic zone (<2 mg oxygen l^{-1}) in the north Atlantic Ocean (Rabalais et al., 2002). The diverse physiography of the sub-basins (also defined as watersheds) includes relatively flat midwestern prairies, alluvial riparian soils and the Appalachian mountain valleys. In a way, learning about water quality in these watersheds is to know the history of land use and vice-versa. One purpose of this analysis was to determine the present annual C, N, P, Si and suspended sediment load (mass) and yields (mass area^{-1}) for six watersheds of the Mississippi River Basin (MRB) using water quality monitoring records for 1973 to 1994. The stations included the major tributary sources for fresh water and sediments. Various analyses of water quality trends were completed for dissolved nitrogen, phosphorus, and silicate, suspended sediments, and organic carbon. These constituents are important because of their probable effects on aquatic primary production, food webs, and on health compliance issues. We compared these results to those of others, and examined the data for trends at 11 key stations. The variations in total nitrogen (TN) and total phosphorus (TP) were related to land use, especially population density and agricultural practices.

Methods

Basin divisions

We divided the MRB into 6 major watersheds: Upper Mississippi River, Missouri River, Ohio River, Arkansas River, Lower Mississippi River, and Red River. We combined the Upper and Middle Mississippi watersheds of Goolsby et al. (1999) into an 'Upper Mississippi' watershed, which makes the data comparable to the results of Smith et al. (1996), Keown et al. (1986) and Malcomb & Durum (1976). Malcomb & Durum (1976) included the Red River watershed with the Arkansas River. Finally, the Middle Mississippi River watershed defined here, and also by Goolsby et al. (1999), drains into a part of the main channel of the Mississippi River which is without good discharge records. Estimating yields and loadings for the Lower Mississippi watershed is problematic in this regard. For this one station, the loadings can be determined by difference of several upstream loadings from the downstream loadings (usually determined at St. Francisville, LA). Yields for the Lower Mississippi were therefore obtained by subtraction of the upstream loadings from the downstream loadings to 'force' a numerical solution. The nutrient and sediment yields from the Lower Mississippi watershed are small relative to the whole basin yields, which means that small errors in constituent concentrations for upstream and downstream of the Lower Mississippi watershed have potentially large consequences to the estimate for the Lower Mississippi watershed.

Water quality data

Water quality data were extracted from the United States Geological Survey (USGS) water quality data files summarized in Alexander et al. (1996). Eleven primary stations in the MRB have sufficient water quality and discharge data to estimate the constituent yields and loadings for each for 1973 to 1994. Nearby stations were substituted to re-construct historical trends in some cases. The mean annual flux (1973 to 1994) of each constituent was calculated as the sum of the product of average monthly concentration times average monthly discharge. The annual yield was calculated as the mean annual flux/watershed area.

Clarke (1924) is the source of water quality data from 1905 to 1907. Additional data for the upper Mississippi and Missouri rivers are in water quality reports prepared by Palmer (Reynolds, 1902) as part of an analysis of the opening of a drainage canal that was thought to affect the St. Louis, MO, drinking water supplies.

Suspended sediment records have been collected at the New Orleans water supply treatment plant at Carrollton, LA, since 1903, when the existing unified treatment system was under construction. The data are from the intake pipe at the Carrollton Sewerage Treatment Plant (CSTP) established in 1905, and is still in service, and located at the same depth. Water quality samples have been taken since 1905, but many of these records were not found at either the CSTP or at the present administrative headquarters. Reports from the first part of the 20th century sometimes record the results as though taken at the year of the publication date, although detailed examination and comparisons reveal that the data were collected 10 or even 30 years earlier. The CSTP data files yielded records for 1933–1934, and for weekly measurements since 1960. Many of the records after the 1970s were collected by the USGS, and are reported in various electronic and digital formats.

Regression analyses

Multiple and linear regression analyses were run on untransformed water quality data to determine trends, if any, for 1973 to 1994, and to compute descriptive relationships between nutrient yields and land use. The number of data points in each analysis is listed by station in Table 1.

Land use

The calculated variations in watershed TN yields were compared to variations in land use and population density. The population and land use data were calculated by Goolsby et al. (1999) using data from the 1990 US Census. Also included in this analysis were the nutrient data and land use data from Lurry & Dunn (1997), Goolsby et al. (1999) and Turner et al. (2000). One of 40 data points was not used from the Lurry & Dunn (1997) data set, which was for the White River, at Oacoma, S. Dakota. This watershed had the 2nd

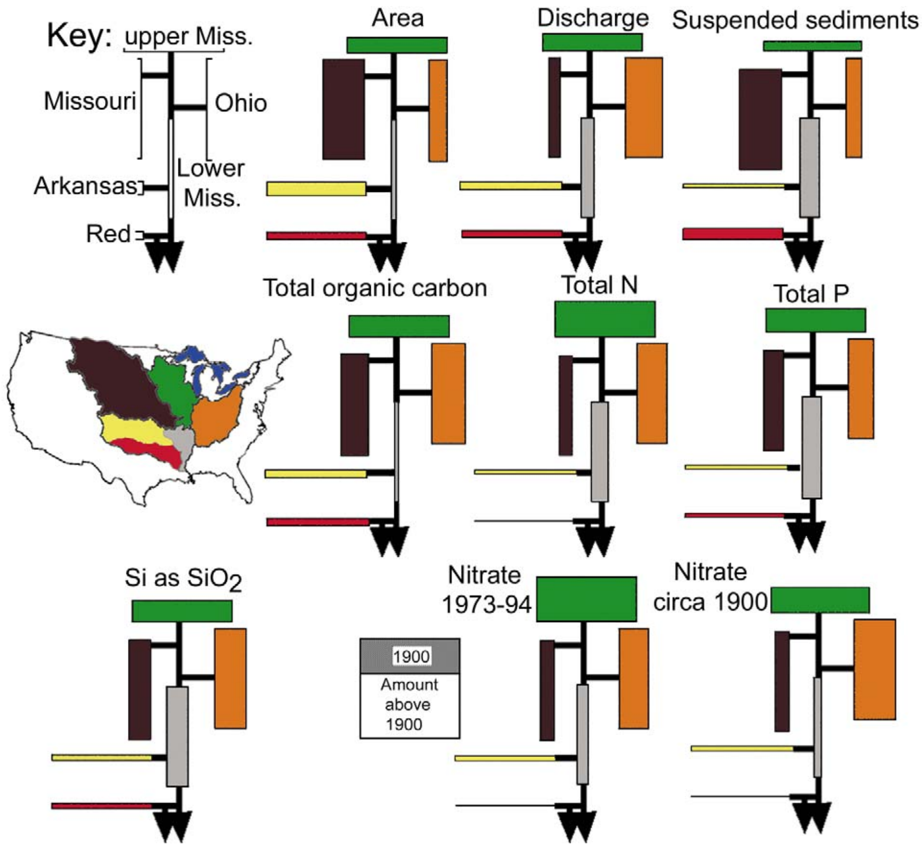

Figure 1. The proportional amount (expressed as a percentage of the total) of watershed area, water discharge, suspended sediment loading, total organic carbon, total nitrogen, total phosphorus, and nitrate in 1974–1994 (mass) from each of 6 watersheds. The estimated proportional amount of nitrate loading (mass) for circa 1900 is also shown. The nitrate loading circa 1900 for the whole watershed was about 38% of what it is today. The two arrows leaving the watershed are for the Mississippi River (right) and the Atchafalaya River (left) which joins the Red River with about 30% of the Mississippi River flow.

lowest discharge and lowest population density and whose TN:TP ratio was an outlier (at < 5% of the mean TN:TP ratio for all stations).

Results

Discharge

The Ohio watershed delivers an average 38% of the fresh water discharge into the Gulf of Mexico for 1973 to 1994 (Fig. 1). The Upper Mississippi discharges 19%, followed by the Missouri (13%), Lower Mississippi (13%), Red River (11%) and the Arkansas (11%). The land surface area is dominated by the Missouri, which has 42% of the land surface, compared to almost equal percentages by the Ohio, Upper Mississippi, and Arkansas (16, 15 and 13%, respectively). The remaining 14% of land area is almost equally divided between the Red and Lower Mississippi watersheds. The Missouri is the largest watershed among the six, by at least 2.5×, but the water yield in the Ohio watershed is 3× higher than the others.

Suspended sediments

Estimates of the suspended sediment yields (kg km^{-2} yr^{-1}) from the Mississippi River watershed varied among investigators (Tables 2 and 3). Some of this variation is due to the variability in water discharge and also to the period of record. For example, the relatively low estimate by Smith et al. (1996) included the 1988 drought year, whereas the 1993 record flood year is included in our estimate. The highest value in Table 2, for before the 1900s, is about 3× the lowest estimate (1980 to 1988). Some of the variability in estimates arose because different land areas were included, where sediment delivery per land mass, as well

Table 1. Sample size for nutrient data obtained from the USGS water quality files in Alexander et al. (1996). The data are from 1973 to 1994.

Watershed/Rivers (USGS Station #)	Suspended sediments	Total phosphorus	Nitrate-N	Total nitrogen	Si	TOC
1. Ohio/Cannelton Dam, KY (#03303280)	86	102	45	97	106	36
2. Ohio/Grand Chain, IL (#03612500)	230	243	171	241	158	61
3. Mississippi/Clinton, IA (#05420500)	136	162	123	158	96	31
4. Mississippi/Grafton, IL (#05587455)	40	62	60	62	59	5
5. Missouri/Omaha, NB (#06610000)	2024	74	55	74	96	29
6. Missouri/Hermann, MO (#06934500)	374	271	207	258	188	53
7. Mississippi/Thebes, MO (#07022000)	170	266	153	254	157	102
8. Arkansas/Little Rock, AR (#07263620)	171	197	108	183	179	54
9. Mississippi/St. Francisville, LA (#07373420)	185	247	149	178	184	260
10. Atchafalaya/Melville, LA (#07381495)	116	198	105	106	109	192
11. Red/Alexandria, LA (#7355500)	299	213	83	211	172	144

as record length and completeness, differ. Many technical problems may arise in calculating sediment supply, including accommodations to include the effects of variations of velocities with depth, logistical issues related to working in a large river, and sampling frequency. Sediment yield is also not constant, because of climatic fluctuations, and, importantly, because of land use developments over the last 150 years (Turner & Rabalais, 2003). The highest sediment yields for the MRB are for after when European colonization began in the 1800s, which involved land clearing and plowing, and, decades later, large-scale land drainage. Sediment yields from circa 1850 to the early 1900s are $>$10000 kg km^{-1} yr^{-1} and were reduced by half in the 1960s, after a significant number of dams were constructed on the Missouri River (Meade et al., 1990; Table 3). Estimating the sediment delivery before the 1850s is problematic because of the understandable lack of records, but were undoubtedly lower than in the late 1800s.

Sediment yields from 1973 to 1994 are highest in the Lower Mississippi watershed, which is about 2$\times$ higher than any of the other watersheds, and 4$\times$ higher than the MRB as a whole (Table 2). The Arkansas watershed has the lowest yield (20% of the average for the MRB). The proportional amount of suspended sediment supply is dominated by the Missouri watershed (Figure 1), which yields 42% of the total supply, and is 2 $\times$ times that of the Lower Mississippi.

Nutrient concentration

The concentration of silicate and various forms of nitrogen and phosphorous has been measured frequently over the last 40 years in the lower end of the MRB at St. Francisville and New Orleans, LA. These data show that the average annual nitrate concentration since the 1960s has risen while that of silicate has fallen, resulting in a decline in the Si:nitrate ratio from 4:1 to 1:1 that began in the 1960s (Turner & Rabalais, 1991). A trend analysis of nutrient concentrations at 11 stations suggests that the trends in concentration have been somewhat stable over the last 20 years (Table 4). The total nitrogen concentration increased

Table 2. Estimated yields (kg km^{-2} yr^{-1}) of suspended sediment, total phosphorus, nitrate-N, total nitrogen, silicate and organic carbon by watershed. ND = no data

Watershed/Rivers	kg km^{-2} yr^{-1}					
	Suspended sediments	Total phosphorus	Nitrate-N	Total nitrogen	Si	TOC
Ohio-Tennessee (Grand Chain, IL)						
Keown et al. (1986)	125 166	ND	ND	ND	ND	ND
Smith et al. (1996)	29 772	44	297	ND	ND	ND
Lurry & Dunn (1997)	ND	98	ND	1019	ND	ND
Goolsby et al. (1999)	ND	75	610	940	1220	ND
This study	42 930	68	504	765	1074	2513
Upper Mississippi River (by difference: Thebes, MO, less Hermann, MO)						
Keown et al. (1986)	42 429	ND	ND	ND	ND	ND
Smith et al. (1996)	35 727	55	346	ND	ND	ND
Goolsby et al. (1999)	ND	87	840	1229	1110	ND
This study	35 189	76	902	1120	874	2171
Missouri (Hermann, MO)						
Keown et al. (1986)	52 375	ND	ND	ND	ND	ND
Smith et al. (1996)	15 763	9.8	21	ND	ND	ND
Malcom & Durun (1976)	ND	ND	ND	ND	ND	540
Lurry & Dunn (1997)	ND	20.5	ND	167	ND	ND
Goolsby et al. (1999)	ND	19	90	180	300	ND
This study	47 913	19	78	140	297	857
Lower Mississippi River (by difference)						
Smith et al. (1996)	38 879	36	117	ND	ND	ND
Goolsby et al. (1999)	ND	58	295	630	1510	ND
This study	218 399	194	677	1712	1975	1727
Arkansas-White (Little Rock, AR)						
Keown et al. (1986)	22 866	ND	ND	ND	ND	ND
Lurry & Dunn (1997)	ND	11	ND	110	ND	ND
Goolsby et al. (1999)	ND	13	50	130	370	ND
This study	9963	14	41	141	262	783
Red (Shreveport and Alexandria, LA)						
Keown et al. (1986)	119 026	ND	ND	ND	ND	ND
Goolsby et al. (1999)	ND	53	80	250	1240	ND
This study	75 770	24	26	147	366	1264
Entire Watershed to Gulf of Mexico (St. Francisville, LA)						
Keown et al. (1986)	65 380	ND	ND	ND	ND	ND
Malcomb & Durum (1976)	ND	ND	ND	ND	ND	1052
Smith et al. (1996)	33 975	37.7	244	ND	ND	ND
Lurry & Dunn (1997)	ND	34	ND	398	ND	ND
Goolsby et al. (1999)	ND	32	302	497	733	ND
This study	52 347	45	300	483	610	1403

Table 3. Different estimates of suspended sediment loading to the Gulf of Mexico from the Mississippi River Basin.

Period of record	$kg\,km^{-1}\,yr^{-1}$	Source
<1850	?	–
1879 to 1880	107 297	Fisk (1952); estimate 1
1879 to 1880	102 691	Fisk (1952); estimate 2
1851 to 1930s	117 933	postulated in Curtis et al. (1973)
circa 1890s	94 220	Dole & Stabler (1909)
1949–1961	85 463	Judson & Ritter (1964)
1956–1967	90 600	Curtis et al. (1973)
1963–1979	64 201	Milliman & Meade (1983)
1970 to 1988	65 380	Keown et al. (1986)
1980 to 1988	33 975	Smith et al. (1996)
1974 to 1993	52 347	This study

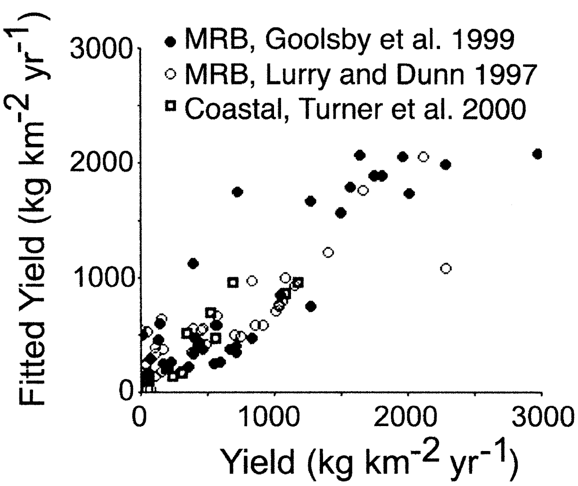

Figure 2. The actual and estimated yield of total nitrogen (TN; $kg\,km^{-2}\,yr^{-1}$) for watersheds within the Mississippi River Basin (MRB, from 2 data sources) and US coastal systems (from data in Turner et al., 2000). The fitted values are from a multiple regression equation whose two independent variables are population density and the % land as harvested cropland.

at about one-third of all sites in two studies, but also decreased at others. There were no changes, either up or down, at more than half the sites and for all parameters investigated. The era of rapid changes in nutrient concentrations appears to be stabilized now at a higher level for the period 1973 to 1994.

Watershed yields and loads

The yields of nutrients by watershed ($kg\,km^{-2}\,yr^{-1}$) are in Table 2, and the proportions of nutrient loads ($kg\,yr^{-1}$) by watershed are in Fig. 1. Different methods for computing yields were used by the authors in Table 2. All of these authors except for Goolsby et al. (1999) used some combination of monthly or annual averages of solute concentration times discharge to calculate the average yield. Goolsby et al. (1999) used multiple regression models (Cohn et al., 1992) relating various quadratic, sine, and cosine functions, with discharge, solute concentration, and empirically-defined constants to estimate average daily fluxes which were then summed to produce an annual long-term average. Our estimates of TN, TP, nitrate and Si yields can be compared with those of Goolsby et al. (1999), while remembering that they used 1980 to 1998 data, whereas we used data from 1974 to 1993. For the three largest basins, the ratio of their TP, TN, nitrate and Si yield data to ours is between 0.9 to 1.3, and 0.7 to 1.1 for the whole river basin. This suggests that the estimates are comparable for other solutes and different (earlier) time intervals used by others.

The yields of TP are within the same range as for previous estimates, and based on a similar water quality data record. The range of yields for TP varies from 14 to 194 $kg\,km^{-2}\,yr^{-1}$, 26 to 902 $kg\,km^{-2}\,yr^{-1}$ for nitrate, 141 to 1120 $kg\,km^{-2}\,yr^{-1}$ for total nitrogen, 262 to 1074 $kg\,km^{-2}\,yr^{-1}$ for silicate, and 783 to 2513 $kg\,km^{-2}\,yr^{-1}$ for total organic carbon. Four of the lowest values (including suspended sediments) are for the Arkansas watershed. The highest nitrate yield is from the Upper Mississippi watershed, and the highest silicate and total organic loading is from the Ohio-Tennessee watershed. The highest TP and TN yields are from the lower Mississippi River, which also has the highest suspended sediment yields.

The relative loadings among watersheds are not the same as for the relative yields because of varying land mass size among watersheds. The upper three watersheds have about equal loadings of total organic carbon (range 23 to 32% of the total; Fig. 1). The loadings of TP and silicate are about equally divided among the Upper Mississippi, Lower Mississippi, Ohio and Missouri watersheds (Fig. 1). The dominant watershed in terms of total nitrogen and nitrate loading is the Upper Mississippi watershed (35 and 45%, respectively), followed by the Ohio watershed (28 and 30%, respectively). The TN and nitrate loadings from the Red and Arkansas are relatively small compared to the others (<7%, each; Fig. 1).

The nitrate load at the beginning of the century compared to more recent decades are higher, by 150% for the watershed as a whole (Fig. 1). The proportions of nitrate loading from each watershed have been redistributed towards a higher yield from the Up-

Table 4. Trends in concentration (mg l^{-1} yr^{-1}) of selected parameters at 11 stations (identified in Table 1) in the Mississippi River Basin. These are the results of a simple linear regression analysis. The mean trends ± 1 Standard Error are given where the significance level is at $p < 0.05$. 'nc' = no statistically-significant change. Increases are in **bold**. The data are for 1973 to 1994.

Parameter	Station										
	1	2	3	4	5	6	7	8	9	10	11
Suspended sediments	nc	−3 ± 1	nc	nc	−15 ± 3	nc	nc	nc	−8.0 ± 2.1	nc	−22 ± 8.9
TOC	nc	nc	nc	nc	nc	nc	nc	**0.08** ± 0.04	−0.13 ± 0.03	nc	−0.17 ± 0.03
Nitrate-N	nc	nc	nc	nc	**0.2** ± 0.07	nc	nc	nc	nc	nc	−0.008 ± 0.003
Dissolved inorganic-N	nc	nc	**0.1** ± 0.01	nc	−0.4 ± 0.2	**0.04** ± 0.01	**0.09** ± 0.02	**0.01** ± 0.006	−0.04 ± 0.01	nc	nc
Total nitrogen	nc	nc	**0.07** ± 0.01	nc	nc	nc	**0.04** ± 0.01	−0.01 ± 0.006	nc	−0.04 ± 0.01	−0.02 ± 0.005
Ortho-phosphate	nc	nc	nc	nc	nc	**0.003** ± 0.0007	nc	nc	nc	nc	−0.002 ± 0.0006
Total phosphorus	nc	nc	nc	**0.01** ± 0.007	nc	−0.006 ± 0.003	−0.003 ± 0.004	−0.002 ± 0.0006	nc	nc	−0.003 ± 0.001
Silicate	nc	nc	**0.3** ± 0.1	**0.8** ± 0.3	**0.2** ± 0.09	nc	**0.16** ± 0.05	nc	nc	nc	nc

Table 5. Multiple linear regression equations describing the variation in total nitrogen yield (TN; kg km^{-2} yr^{-1}) for various watersheds of the Mississippi River Basin, and the independent variables: % cropland, per capita density and kg N fertilizer. Data sets 1 and 4 are from watersheds without overlapping watersheds that are found within another within the same data set. Data set 2 has overlapping watersheds. All results are significant at a $p = 0.0001$ level of confidence. NA = not applicable.

A. Data set	Number	Average size (1000 km^2)	Intercept kg TN km^{-2} yr^{-1}	Adjusted R^2	kg TN (± 1 std. error)	
					Per capita	% Cropland
Mississippi River Basin						
1. Goolsby et al. (1999)	42	57	101	0.82	5.27 (± 1.2)	27 (± 2.5)
2. Lurry & Dunn (1997)	40	493	−80	0.80	9.7 (± 1.0)	11.7 (± 2.5)
3. Combined 1 + 2	81	NA	12.9	0.69	7.7 (± 1.0)	17.6 (± 2.2)
B. Coastal						
4. Turner et al. (2000)	11	294	−121	0.78	2.6 (± 0.4)	121 (± 10.4)
C. Combined data sets						
5. All combined	93	NA	−16.8	0.60	2.4 (± 4.5)	17.6 (± 17.6)
6. Only data sets without overlapping watersheds (1 and 4)	52	NA	61	0.78	2.3 (± 0.5)	30.1 (± 2.3)

B. Data set	Number	Adjusted R^2	Intercept kg TN km^{-2} yr^{-1}	TN (± 1 std. error)		
				km^2	Per capita	kg N fertilizer
Goolsby et al. (1999)	42	0.75	242	−2.9 (± 1.2)	5.5 (± 1.4)	0.22 (± 0.3)

per Mississippi watershed and the percentage from the Ohio watershed has declined (Fig. 1). The proportional amount from the Missouri watershed has remained about the same. The percentage from the Red and Arkansas watersheds remained less than 5% in both calculations.

Water quality relationships to population density and land use

Various estimates of nitrogen yields from the MRB and coastal watersheds are described by the percent of land in cropland and population density (Fig. 2). There is some difference in the X and Y plot for each data set, in part because of a mismatch of census data, stream discharge records, and land use for both data sets. Population density is another representative indicator of nitrogen transformation and sources in the landscape. Howarth et al. (1996) and Peierls et al. (1991), for example, described a strong relationship between population density and nitrogen yields for several large river watersheds. A multiple regression equation, predicting nitrogen yield on the basis of the land in crops and population density, explains 78 to 83% of the variation for the three individual data sets, and 60% for all data sets combined (Table 5). The results are strikingly robust. Both population density and land use affect water quality. The annual per capita yield in these regression equations ranges from 2.3 to 9.7 kg TN per capita, with the coastal data sets having a lower per capita yield (2.6 kg TN per capita compared to 5.3 to 9.7 kg TN per capita for the MRB).

There is a strong correlation between the nitrogen concentration as nitrate and total nitrogen, and of nitrate and silicate over the broad landscape of the various soils, slopes, vegetation, climate and land use found in the MRB (Fig. 3). Virtually all of the rise in TN is the result of increases in nitrate above a threshold value of about 2 mg l^{-1}. As nitrate rises, the atomic ratio of dissolved Si : nitrate declines, and is $<$1:1 when the nitrate concentration is $>$1 mg l^{-1} (Fig. 3).

Total phosphorus

The variability in TP yield (TP; kg km^{-2} yr^{-1}) and per capita density (persons km^{-2}) and for watersheds within the Mississippi River Basin is shown in Fig. 4 (using data in Goolsby et al., 1999, and Lurry & Dunn, 1997). The apparent strong statistical relation-

Table 6. Multiple linear regression equations describing the variation in total phosphorus yield (TP, kg km^{-2} yr^{-1}) for various watersheds of the Mississippi River Basin, and the independent variables: % cropland and per capita density. All results are significant at a $p = 0.001$ level of confidence. NS = not significant.

A. Data set	Number	Average size (1000 km^2)	Intercept kg TN km^{-2} yr^{-1}	Adjusted R^2	TP (± 1 std. error)	
					Per capita	% Cropland
Mississippi River Basin						
1. Goolsby et al. (1999)	41	57	26.8	0.46	0.39 (± 0.12)	0.80 (± 0.24)
2. Lurry & Dunn (1997)	38	493	23.9	0.86	0.55 (± 0.82)	N.S.

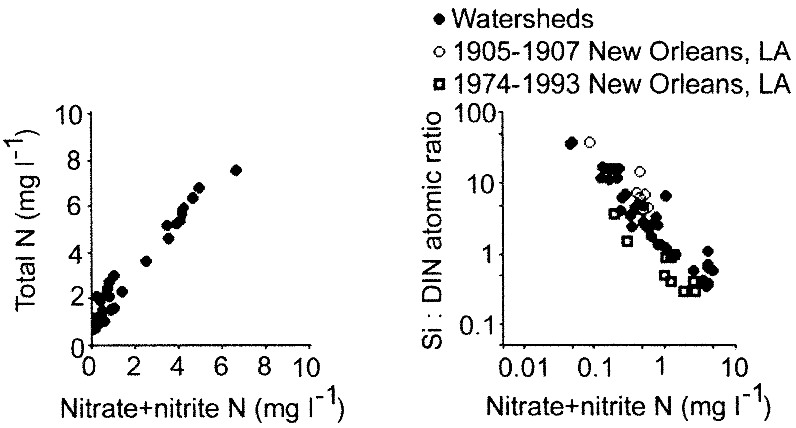

Figure 3. Left: The relationship between total nitrogen (Y axis) and nitrate+nitrite concentration (X axis) for 42 watersheds of the Mississippi River Basin (from data in Goolsby et al., 1999). Right: The atomic ratio of the dissolved Si-silicate: nitrate+nitrite ratio versus dissolved nitrate+nitrite concentration for 42 watersheds of the Mississippi River Basin (from data in Goolsby et al., 1999 and for 529 individual sampling events at New Orleans.

ship between the X and Y variable shown in Fig. 4 are confirmed by a statistical analysis of the data, whose results are in Table 5. The adjusted coefficient of determination (R^2) was 0.86 and 0.46, for the Lurry & Dunn (1997) and Goolsby et al. (1999) data sets, respectively. The difference in R^2 values may be because the average watershed size was 8.6 times larger in the data set developed by Lurry & Dunn (1997) compared to the data developed by Goolsby et al. (1999). The use of data from larger watersheds would tend to dampen out the variability arising from the effects of channel morphology (e.g., Alexander et al., 2000). The area of the watershed in cropland had a statistically significant effect on TP yield at the $p = 0.001$ in the Goolsby et al. (1999) data set, but $p > 0.09$ for the Lurry & Dunn (1997) data set.

Discussion

The nitrate yield was primarily from the Ohio Rver watershed circa 1900, but shifted to the upper Mississippi River basin by 1973–1994, as total nitrogen yield rose several times. The explanation for this shift in relative supply is explained by the results shown in Figs 2 and 4 and described in Tables 4 and 5. That is, both population expansion and land use changes have had a significant effect on watershed yields of these constituents. McIssac et al. (2002) provided a comparison of several empirical models of water quality in the Mississippi River watershed using land use, atmospheric loading and soil organic N. Their results and those presented here substantiate the observations and calculations of many that human intervention within the natural landscape has re-formed stream and river water quality on the scale of the world's largest river basins (e.g., Turner & Rabalais, 1991; Howarth et al., 1996; Jordan & Weller, 1996; Caraco & Cole, 1999). They provide the explanation for the relative rise in nitrogen loading from the Upper Mississippi River basin during the last 100 years.

Analyses of smaller watershed monitoring data also document the effect of present land use on stream

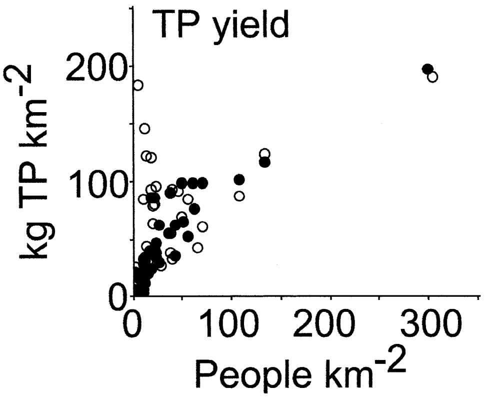

Figure 4. The relationship between per capita density (persons km^{-2}) and TP yield (kg TP km^{-2} yr^{-1}) for watersheds within the Mississippi River Basin (MRB; open circles from data in Goolsby et al., 1999; closed circles from Lurry & Dunn, 1997).

water quality. Jordan et al. (1997) showed that nitrate yields went up, and the Si:N yield down, as the watershed area as cropland increased for 27 watersheds of Chesapeake Bay. Smart et al. (1985) studied watersheds in the Missouri Ozarks in the summer of 1979 and found that the silicate : nitrate ratio and the nitrogen content went up as the land in pasture increased (there were no row crops in that area, apparently). They concluded that the stream nutrient concentrations were more strongly related to land use, than to bedrock geology. Their simple multiple regression equation explained 43% of the variation in TP, using watershed size and the percentage land as urban area. Eighty-percent of the variation in TN was explained (in a statistical sense), using the percentage land in pasture and urban area. Perkins et al. (1998) showed similar results for all four major types of Missouri watersheds, as did Jones et al. (1976) for 34 watersheds in northwestern Iowa (3 year data set). The elemental ratios in the water are subject to the type of land use, as well. For example, Arbuckle and Downing (2001) showed that water flowing from 113 Iowa landscapes dominated by row crops had high N:P ratios (molar ratios >100), whereas landscapes dominated by pasturelands had low ratios (molar ratios about 16:1).

In summary, we provide estimates of C, N. P, Si and suspended sediment loadings and yields for 6 subbasins of the Mississippi River watershed for 1973–1994, and compare these results to those of others. The water quality trends at 11 stations show large fluctuations that are undoubtedly going to be influenced by climate change, but the trends in the eight water quality parameters investigated here are 'stable' in the context of 1973-1994 monitoring records, although there is considerable seasonal and annual variations. Variations in TN and nitrate loadings among basins and over the last 90+ years are explainable on the basis of landscape uses, principally from population growth and agricultural expansion.

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