## Supporting Information for the Article

# Nitrate in the Mississippi River and its tributaries, 1980 to 2008: Are we making progress?

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Contains 7 pages, Tables SI-S1 through SI-S4, Figures SI-S1 through SI-S5.

## *Site Detail*

Figure SI-S1 has a map of the study sites and a schematic detailing the relative location of the sites and major tributaries. Table SI-S1 has detail on the characteristics of the study sites, including U.S. Geological Survey site number, drainage area, and model calibration period.

## *Additional Detail on Methods*

For each combination of streamflow and time ($Q_0$,$t_0$), the coefficients of the model equation ( equation 1 in the text) are estimated in the Weighted Regressions on Time, Discharge, and Season (WRTDS) model using a weighted regression, where the weights on each observation in the calibration data set are based on the distance between the observation ($Q_i$, $t_i$) and the estimation point ($Q_0$, $t_0$). This distance has three dimensions—the time difference between $t_0$ and $t_i$, the seasonal difference between the time of year at $t_0$ and the time of year at $t_i$ (for example, the seasonal difference between July 1, 2009 and July 1, 2000 is 0), and the difference between ln($Q_0$) and ln($Q_i$). For all three dimensions, the tricube weight function originally defined by Tukey[1] is used:

$$w = \begin{cases} \left(1-(d/h)^3\right)^3 \ if \ |d| \leq h \\ 0 \ if \ |d| > h \end{cases} \qquad (1)$$

where $w$ is the weight, $d$ is the distance from the observation to the estimation point, and $h$ is a predefined half-window width. In this study, half-window widths were set to 10 years for time, 0.25 (one-quarter of the year) for season, and 1 natural log cycle for sites with a drainage area >250,000 km$^2$ or 2 natural log cycles for sites with a drainage area ≤250,000 km$^2$ for streamflow. The overall weight for each observation to be used in the weighted regression is determined as the product of the three component weights. The influence of any given observation declines gradually to zero as distances become greater, and when any one of the three weights goes to zero, the overall weight is zero. WRTDS has a minimum requirement of 100 or more observations with nonzero weights to be used in the regression for each estimation point. At some estimation points, the predefined windows are restrictive enough that fewer than 100 observations have nonzero weights. This is most likely to happen at the edges of the estimation space near the beginning or end of the record and at the most extreme ends of the streamflow distribution. In such cases, all three of the half-window widths are increased by 10% until at least 100 observations with nonzero weights are included in the regression.

The flow-normalization approach currently used in WRTDS can be problematic where the probability distribution of streamflow on a given day has changed over time, such as after construction of a large dam or initiation of large groundwater withdrawals.[2] In addition, the flow-normalized estimates provide a relatively smooth description of changes in the system. When the changes are gradual (such as with changes in land use), this approach is likely to be appropriate; when the changes are more abrupt (such as a major treatment upgrade at a single influential point source), the approach could have the effect of making an abrupt change appear gradual.[2] For the large watersheds included in this study, the effects of any such changes were likely small. Finally, the flow-normalization approach removes the variation in nitrate concentration or flux due to random streamflow variations on the day of sampling. However, the history of streamflow also may be important.[3] For example, interannual variation in antecedent soil-moisture conditions can affect nitrate transport to streams—nitrate concentrations in streams in Quebec increased during storm events with dry antecedent conditions due to leaching of nitrogen that had accumulated in the soil during dry periods.[4]

Annual streamflow in 2008 was high in many parts of the Mississippi River basin, and as a result, estimated flux also was high in 2008 at several of the sites (figure 1 in the text). These high estimated flux values did not directly influence the temporal pattern of flow-normalized flux, which showed a large increase around 2008, particularly at MSSP-CL and MIZZ-HE. This increase was not a result of the high streamflow in 2008; rather, it was a result of the pattern of recent increases in concentrations over a wide range of seasons and streamflow conditions. The fact that the last year of the record used in this analysis happened to be a year of high streamflow makes it all the more important that the analysis be repeated in the future with new data to determine if this observed up-turn persists. As is the case with all smoothing techniques, re-estimation with the addition of new data is a vital part of the overall analysis process.

To determine whether the large net decreases in flow-normalized flux observed in the nested area above MSSP-TH were in any way an artifact of the WRTDS flow-normalization approach, we examined WRTDS flux estimates without flow normalization and found that the same general results occurred, although the year-to-year variability made the changes much less clear cut. Further, by multiplying means of the raw concentration data for specific seasons and for different parts of the period of record by the respective means of streamflow, we found that the large net decrease in flux in the nested area above MSSP-TH can be derived by empirical methods that do not employ any of the techniques used in WRTDS.

## *Model Comparison and Evaluation*

Nitrate fluxes previously have been estimated for these sites through the U.S. Geological Survey National Stream-Quality Accounting Network (NASQAN) program.[5] Fluxes were estimated using a seven-parameter regression model equation of the form:

$$\ln(L_i) = \beta_0 + \beta_1 \ln Q + \beta_2 \ln Q^2 + \beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t) + \beta_5 t + \beta_6 t^2 + e \qquad (2)$$

where ln is the natural logarithm, $L_i$ is the calculated flux for sample *i*, lnQ is ln(daily mean streamflow) – center of ln(daily mean streamflow), t is decimal time minus the center of decimal time (as defined by

Cohn et al.[6]), e is error, and $\beta_i$ are the fitted parameters in the multiple regression model. The daily mean streamflow was used to estimate $L_i$ for each day; daily flux values were summed each year to obtain an estimate of annual flux. The first five years of fluxes were estimated by calibrating the regression model using the first five years of available nitrate data. Each subsequent year of flux estimates was calculated by calibrating the regression model using samples from the current year and the previous four years. This "moving window" approach allows a sufficient number of samples in each model run to represent the full range of streamflow and nitrate concentrations. This approach also is somewhat more comparable with the WRTDS approach than a single calibration of the regression model in equation (2) using data from the full period of record at a site.

Unlike with the flux estimates in our study, the NASQAN program modified the model structure in equation (2) for MSSP-OUT to include additional streamflow terms (both streamflow and streamflow-squared terms) from two upstream stations (MSSP-TH and the Ohio River at Metropolis). Upstream streamflows were lagged ten days to account for travel time between the streamflow stations and MSSP-OUT. For the purposes of comparing the WRTDS and previous NASQAN flux estimates, the NASQAN estimates for MSSP-OUT were regenerated without the inclusion of the two upstream stations.

A comparison of WRTDS and previous NASQAN flux estimates indicates that most annual estimates with the two methods were within ±15% of each other (figure SI-S4). At many of the sites, annual flux estimates for years with high streamflow were lower with WRTDS. Aspects of the NASQAN approach have been shown to produce systematic bias toward overestimation of nitrate fluxes in certain situations.[7] The flexible approach to model fitting employed by WRTDS allows a more accurate representation of the relation between streamflow and concentration at high streamflows by limiting the influence of concentration data collected at low streamflows. The WRTDS approach also recognizes that the model error variance can differ substantially across the range of conditions for which estimates are being made; this error variance has a direct impact on the size of the re-transformation bias correction applied. The WRTDS approach to model fitting and bias correction can, in some situations, lead to lower flux estimates than those provided by the NASQAN approach. If we define the annual difference (AD) between the two methods as the NASQAN estimate minus the WRTDS estimate, there are seven sites with negative mean AD values and one (MSSP-CL) with a positive mean AD value. When viewed as a percentage of the annual mean NASQAN estimate for the site, these mean AD values range from +6.8 % for MSSP-CL to -13.0% for MIZZ-HE. The mean over all sites is -5.1%. Combined with figure SI-S4, these comparisons show that WRTDS annual flux estimates are in broad general agreement with the previous NASQAN estimates, but that the WRTDS annual flux estimates do have a general tendency to be lower.

A full evaluation of the differences between the two methods was beyond the scope of this study. However, we can say that for most years at most sites the NASQAN and WRTDS approaches provide similar results. Where they differ substantially, we have good reason to believe the WRTDS estimates are generally less biased—the WRTDS approach has the flexibility to describe changes in system behavior over time (such as changes in the shape of the streamflow versus concentration relation or changes in seasonality) and it also includes the capability to develop flow-normalized concentration and flux estimates.

We also explored the biases of individual daily flux estimates from WRTDS for the days on which samples were collected. Stenback et al.[7] used a ratio of the mean value of the estimated fluxes to the mean value of the actual flux on the sampled dates (which they call the partial load ratio) as a metric of bias. We applied a similar approach to evaluate possible biases in the WRTDS estimates used in this study. Figure SI-S5 shows observed and predicted annual fluxes of nitrate at the study sites. Generally, there was good correspondence between the two, with no obvious curvature from the 1:1 line. The bias in the WRTDS predictions was calculated as:

$$Flux\ bias = \left( \frac{\sum_{i=1}^{n} L_{p,i} - \sum_{i=1}^{n} L_{o,i}}{\sum_{i=1}^{n} L_{o,i}} \right) * 100 \qquad (2)$$

where $L_{p,i}$ is the predicted flux from WRTDS for day *i*, $L_{o,i}$ is the observed flux for day *i*, and *n* is the number of days in the monitoring record. Flux biases for WRTDS were less than ±5% at all sites; most were less than ±3% (figure SI-S5). The bias was negative at seven sites, indicating that WRTDS tended to underestimate flux to a small extent. The bias was positive at MSSP-CL, indicating that WRTDS tended to overestimate to a small extent at this site. These results demonstrate that WRTDS estimates at these sites have little or no bias, unlike the large positive bias for some data sets that has been observed when using different estimation methods, as reported by Stenback et al.[7] Note that an analysis of the residuals is not possible with the flow-normalized estimates, as there is no "observed" equivalent.

## WRTDS Output

Tables SI-S3 and SI-S4 have WRTDS output of nitrate concentration (in mg/L) and flux (in kg/yr) for all sites. Table SI-S3 has annual mean estimated and flow-normalized concentration and total annual estimated and flow-normalized flux. Table SI-S4 has spring mean estimated and flow-normalized concentration and total spring estimated and flow-normalized flux.

## Supplementary Information References

(1) Tukey, J. W. *Exploratory data analysis*; Addison-Wesley: Reading, MA, 1977.

(2) Hirsch, R. M.; Moyer, D. L.; Archfield, S. A. Weighted regressions on time, discharge, and season (WRTDS), with an application to Chesapeake Bay river inputs. *J. Am. Water Resour. As*. **2010**, *46*, 857–880.

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(5) Aulenbach, B. T.; Buxton, H. T.; Battaglin, W. A.; Coupe, R. H. *Flow and nutrient fluxes of the Mississippi-Atchafalaya River basin and subbasins for the period of record through 2005*, Open-File Report 2007-1080; U.S. Geological Survey: Reston, VA, 2007.

(6) Cohn, T. A.;, Caulder, D. L.; Gilroy, E. J.; Zynjuk, L. D.; Summers, R.M. The validity of a simple statistical model for estimating fluvial constituent loads—An empirical study involving nutrient loads entering Chesapeake Bay. *Water Resources Res*. **1992**, *28*, 2353–2363.

(7) Stenback, G. A.; Crumpton, W. G.; Shilling, K. E.; Helmers, M. J. Rating curve estimation of nutrient loads in Iowa rivers. *J. Hydrol*. **2011**. *396*, 158–169.

## Table SI-S1. Study site characteristics.

| Site abbreviation | U.S. Geological Survey site number | Site name | Drainage area, in square kilometers | Start of model calibration period | End of model calibration period |
|---|---|---|---|---|---|
| MSSP-CL | 05420500 | Mississippi River at Clinton, IA | 221,703 | 11/12/1974 | 7/8/2009 |
| IOWA-WAP | 05465500 | Iowa River at Wapello, IA | 32,375 | 11/10/1977 | 9/1/2009 |
| ILLI-VC | 05586100 | Illinois River at Valley City, IL | 69,264 | 12/12/1974 | 8/11/2009 |
| MSSP-GR | 05587455 [1] | Mississippi River below Grafton, IL | 443,665 | 1/27/1975 | 9/9/2009 |
| MIZZ-HE | 06934500 | Missouri River at Hermann, MO | 1,353,269 | 10/28/1969 | 9/10/2009 |
| MSSP-TH | 07022000 | Mississippi River at Thebes, IL | 1,847,180 | 1/30/1973 | 9/8/2009 |
| OHIO-GRCH | 03612500 [2] | Ohio River at Dam 53 near Grand Chain, IL | 526,027 | 10/11/1972 | 8/26/2009 |
| MSSP-OUT | -- [3] | Mississippi River above Old River Outflow Channel, LA | 2,914,514 | 10/5/1967 | 6/2/2010 |

[1] streamflow measured at the Mississippi River at Grafton, IL (U.S. Geological Survey site 05587450)

[2] streamflow measured at the Ohio River at Metropolis, IL (U.S. Geological Survey site 03611500)

[3] streamflow is sum of that measured at Mississippi River at Tarbert Landing, MS (U.S. Army Corps of Engineers site 01100) and Old River Outflow Channel near Knox Landing, LA (total outflow; U.S. Army Corps of Engineers site 02600); nutrient data measured at Mississippi River near St. Francisville, LA (U.S. Geological Survey site 07373420). The MSSP-OUT site, as defined here, is intended to provide an approximation of the concentration and flux of nitrate from the Mississippi River basin just upstream from the Old River Outflow Channel.

## Table SI-S2. Percent difference between NASQAN and WRTDS estimates of annual nitrate flux.

| Site | Number of years[1] | Mean percent difference |
|---|---|---|
| MSSP-CL | 20 | 6.8 |
| IOWA-WAP | 29 | -11.3 |
| ILLI-VC | 26 | -4.2 |
| MSSP-GR | 26 | -3.5 |
| MIZZ-HE | 29 | -13.0 |
| MSSP-TH | 29 | -4.5 |
| OHIO-GRCH | 29 | -8.0 |
| MSSP-OUT | 29 | -4.2 |

[1] The calculation for some sites included fewer than 29 years due to an insufficient number of water-quality samples—NASQAN flux-estimation protocols generally require a minimum of four water-quality samples per water year for five contiguous years to estimate fluxes.

## Table SI-S3. WRTDS output of annual mean estimated and flow-normalized nitrate concentration and total annual estimated and flow-normalized nitrate flux.

[WRTDS, Weighted Regressions on Time, Discharge, and Season model; --, estimates not reported because no samples were collected in that year. All estimated and flow-normalized concentrations and fluxes are reported as nitrate as nitrogen.]

| Site | Drainage area, in km$^2$ | Calendar year | Annual mean estimated concentration, in mg/L | Annual mean flow-normalized concentration, in mg/L | Total annual estimated flux, in $10^8$ kg/yr | Total annual flow-normalized flux, in $10^8$ kg/yr |
|---|---|---|---|---|---|---|
| MSSP-CL | 221,703 | 1980 | 0.95 | 1.13 | 0.39 | 0.66 |
| MSSP-CL | 221,703 | 1981 | 1.04 | 1.20 | 0.42 | 0.70 |
| MSSP-CL | 221,703 | 1982 | 1.30 | 1.26 | 0.79 | 0.73 |
| MSSP-CL | 221,703 | 1983 | 1.58 | 1.33 | 1.0 | 0.76 |
| MSSP-CL | 221,703 | 1984 | 1.62 | 1.39 | 1.0 | 0.79 |
| MSSP-CL | 221,703 | 1985 | 1.58 | 1.44 | 0.93 | 0.81 |
| MSSP-CL | 221,703 | 1986 | 1.91 | 1.49 | 1.5 | 0.84 |
| MSSP-CL | 221,703 | 1987 | 1.22 | 1.52 | 0.42 | 0.85 |
| MSSP-CL | 221,703 | 1988 | -- | -- | -- | -- |
| MSSP-CL | 221,703 | 1989 | -- | -- | -- | -- |
| MSSP-CL | 221,703 | 1990 | -- | -- | -- | -- |
| MSSP-CL | 221,703 | 1991 | 1.91 | 1.67 | 1.3 | 0.96 |
| MSSP-CL | 221,703 | 1992 | 1.80 | 1.67 | 1.1 | 0.95 |
| MSSP-CL | 221,703 | 1993 | 2.29 | 1.67 | 2.1 | 0.94 |
| MSSP-CL | 221,703 | 1994 | -- | -- | -- | -- |
| MSSP-CL | 221,703 | 1995 | 1.85 | 1.64 | 1.1 | 0.90 |
| MSSP-CL | 221,703 | 1996 | 1.79 | 1.62 | 1.1 | 0.88 |
| MSSP-CL | 221,703 | 1997 | 1.78 | 1.59 | 1.1 | 0.87 |
| MSSP-CL | 221,703 | 1998 | 1.67 | 1.57 | 0.94 | 0.86 |
| MSSP-CL | 221,703 | 1999 | 1.70 | 1.56 | 0.94 | 0.85 |
| MSSP-CL | 221,703 | 2000 | 1.50 | 1.55 | 0.70 | 0.84 |
| MSSP-CL | 221,703 | 2001 | 1.69 | 1.57 | 1.2 | 0.86 |
| MSSP-CL | 221,703 | 2002 | 1.81 | 1.61 | 1.0 | 0.88 |
| MSSP-CL | 221,703 | 2003 | 1.41 | 1.66 | 0.64 | 0.91 |
| MSSP-CL | 221,703 | 2004 | 1.68 | 1.70 | 0.94 | 0.93 |
| MSSP-CL | 221,703 | 2005 | 1.73 | 1.74 | 0.81 | 0.96 |
| MSSP-CL | 221,703 | 2006 | 1.59 | 1.81 | 0.70 | 0.99 |
| MSSP-CL | 221,703 | 2007 | 1.78 | 1.89 | 0.84 | 1.0 |
| MSSP-CL | 221,703 | 2008 | 2.05 | 1.99 | 1.3 | 1.1 |
| IOWA-WAP | 32,375 | 1980 | 4.48 | 5.02 | 0.30 | 0.59 |
| IOWA-WAP | 32,375 | 1981 | 4.59 | 4.93 | 0.28 | 0.57 |
| IOWA-WAP | 32,375 | 1982 | 6.26 | 4.92 | 0.90 | 0.57 |
| IOWA-WAP | 32,375 | 1983 | 6.12 | 4.85 | 0.87 | 0.56 |
| IOWA-WAP | 32,375 | 1984 | 5.44 | 4.82 | 0.69 | 0.56 |

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|---|---|---|---|---|---|---|
| IOWA-WAP | 32,375 | 1985 | 3.92 | 4.78 | 0.28 | 0.55 |
| IOWA-WAP | 32,375 | 1986 | 6.26 | 4.76 | 0.78 | 0.55 |
| IOWA-WAP | 32,375 | 1987 | 4.01 | 4.76 | 0.23 | 0.55 |
| IOWA-WAP | 32,375 | 1988 | 2.40 | 4.77 | 0.12 | 0.56 |
| IOWA-WAP | 32,375 | 1989 | 1.36 | 4.79 | 0.035 | 0.56 |
| IOWA-WAP | 32,375 | 1990 | 4.38 | 4.82 | 0.53 | 0.57 |
| IOWA-WAP | 32,375 | 1991 | 5.71 | 4.85 | 0.87 | 0.57 |
| IOWA-WAP | 32,375 | 1992 | 5.89 | 4.89 | 0.71 | 0.58 |
| IOWA-WAP | 32,375 | 1993 | 6.66 | 4.91 | 1.7 | 0.58 |
| IOWA-WAP | 32,375 | 1994 | 4.92 | 4.91 | 0.37 | 0.58 |
| IOWA-WAP | 32,375 | 1995 | 4.81 | 4.89 | 0.52 | 0.58 |
| IOWA-WAP | 32,375 | 1996 | 4.34 | 4.89 | 0.43 | 0.58 |
| IOWA-WAP | 32,375 | 1997 | 4.94 | 4.92 | 0.47 | 0.58 |
| IOWA-WAP | 32,375 | 1998 | 6.34 | 4.98 | 0.88 | 0.59 |
| IOWA-WAP | 32,375 | 1999 | 5.11 | 5.05 | 0.78 | 0.59 |
| IOWA-WAP | 32,375 | 2000 | 3.81 | 5.12 | 0.31 | 0.60 |
| IOWA-WAP | 32,375 | 2001 | 5.07 | 5.18 | 0.70 | 0.60 |
| IOWA-WAP | 32,375 | 2002 | 4.64 | 5.20 | 0.26 | 0.60 |
| IOWA-WAP | 32,375 | 2003 | 4.17 | 5.22 | 0.28 | 0.60 |
| IOWA-WAP | 32,375 | 2004 | 5.35 | 5.26 | 0.56 | 0.59 |
| IOWA-WAP | 32,375 | 2005 | 4.81 | 5.27 | 0.36 | 0.59 |
| IOWA-WAP | 32,375 | 2006 | 4.76 | 5.26 | 0.33 | 0.58 |
| IOWA-WAP | 32,375 | 2007 | 6.39 | 5.23 | 0.90 | 0.58 |
| IOWA-WAP | 32,375 | 2008 | 5.75 | 5.19 | 1.1 | 0.57 |
| ILLI-VC | 69,264 | 1980 | 3.71 | 3.81 | 0.72 | 0.99 |
| ILLI-VC | 69,264 | 1981 | 4.06 | 3.79 | 1.1 | 0.99 |
| ILLI-VC | 69,264 | 1982 | 4.08 | 3.80 | 1.5 | 0.99 |
| ILLI-VC | 69,264 | 1983 | 4.00 | 3.83 | 1.3 | 1.0 |
| ILLI-VC | 69,264 | 1984 | 3.96 | 3.86 | 1.1 | 1.0 |
| ILLI-VC | 69,264 | 1985 | 3.82 | 3.90 | 1.2 | 1.0 |
| ILLI-VC | 69,264 | 1986 | 4.04 | 3.93 | 0.93 | 1.0 |
| ILLI-VC | 69,264 | 1987 | 3.78 | 3.96 | 0.59 | 1.0 |
| ILLI-VC | 69,264 | 1988 | 3.47 | 3.98 | 0.57 | 1.0 |
| ILLI-VC | 69,264 | 1989 | 3.51 | 3.99 | 0.38 | 1.0 |
| ILLI-VC | 69,264 | 1990 | 4.41 | 4.00 | 1.4 | 1.0 |
| ILLI-VC | 69,264 | 1991 | 4.19 | 4.01 | 1.3 | 1.0 |
| ILLI-VC | 69,264 | 1992 | 4.01 | 4.03 | 0.81 | 1.0 |
| ILLI-VC | 69,264 | 1993 | 4.69 | 4.05 | 2.1 | 1.1 |
| ILLI-VC | 69,264 | 1994 | 4.12 | 4.06 | 0.99 | 1.1 |
| ILLI-VC | 69,264 | 1995 | 4.22 | 4.08 | 1.3 | 1.1 |
| ILLI-VC | 69,264 | 1996 | 4.00 | 4.09 | 0.92 | 1.1 |
| ILLI-VC | 69,264 | 1997 | 3.97 | 4.10 | 0.89 | 1.1 |
| ILLI-VC | 69,264 | 1998 | 4.50 | 4.12 | 1.5 | 1.1 |

| | | | | | | |
|---|---|---|---|---|---|---|
| ILLI-VC | 69,264 | 1999 | 4.10 | 4.15 | 1.1 | 1.1 |
| ILLI-VC | 69,264 | 2000 | 3.64 | 4.17 | 0.52 | 1.1 |
| ILLI-VC | 69,264 | 2001 | 4.27 | 4.15 | 1.1 | 1.1 |
| ILLI-VC | 69,264 | 2002 | 4.05 | 4.12 | 1.2 | 1.1 |
| ILLI-VC | 69,264 | 2003 | 3.74 | 4.09 | 0.58 | 1.1 |
| ILLI-VC | 69,264 | 2004 | 4.11 | 4.05 | 0.96 | 1.1 |
| ILLI-VC | 69,264 | 2005 | 3.56 | 4.00 | 0.80 | 1.1 |
| ILLI-VC | 69,264 | 2006 | 3.85 | 3.94 | 0.69 | 1.0 |
| ILLI-VC | 69,264 | 2007 | 3.89 | 3.85 | 1.1 | 1.0 |
| ILLI-VC | 69,264 | 2008 | 4.15 | 3.77 | 1.5 | 0.98 |
| MSSP-GR | 443,665 | 1980 | 2.31 | 2.56 | 2.0 | 3.3 |
| MSSP-GR | 443,665 | 1981 | 2.48 | 2.58 | 2.8 | 3.4 |
| MSSP-GR | 443,665 | 1982 | 3.16 | 2.59 | 5.6 | 3.4 |
| MSSP-GR | 443,665 | 1983 | 3.02 | 2.59 | 4.9 | 3.4 |
| MSSP-GR | 443,665 | 1984 | 2.88 | 2.60 | 4.4 | 3.4 |
| MSSP-GR | 443,665 | 1985 | 2.88 | 2.60 | 4.2 | 3.4 |
| MSSP-GR | 443,665 | 1986 | 3.28 | 2.60 | 5.2 | 3.4 |
| MSSP-GR | 443,665 | 1987 | 2.40 | 2.59 | 2.0 | 3.4 |
| MSSP-GR | 443,665 | 1988 | 1.67 | 2.59 | 1.2 | 3.4 |
| MSSP-GR | 443,665 | 1989 | 1.44 | 2.59 | 0.82 | 3.5 |
| MSSP-GR | 443,665 | 1990 | 2.52 | 2.58 | 3.1 | 3.5 |
| MSSP-GR | 443,665 | 1991 | 3.03 | 2.58 | 4.2 | 3.5 |
| MSSP-GR | 443,665 | 1992 | 2.81 | 2.58 | 3.5 | 3.5 |
| MSSP-GR | 443,665 | 1993 | 3.46 | 2.59 | 7.9 | 3.5 |
| MSSP-GR | 443,665 | 1994 | 2.81 | 2.62 | 3.1 | 3.5 |
| MSSP-GR | 443,665 | 1995 | -- | -- | -- | -- |
| MSSP-GR | 443,665 | 1996 | 2.80 | 2.70 | 3.5 | 3.6 |
| MSSP-GR | 443,665 | 1997 | 2.77 | 2.73 | 3.3 | 3.6 |
| MSSP-GR | 443,665 | 1998 | 3.09 | 2.77 | 4.6 | 3.6 |
| MSSP-GR | 443,665 | 1999 | 2.95 | 2.80 | 4.1 | 3.7 |
| MSSP-GR | 443,665 | 2000 | 2.43 | 2.83 | 2.3 | 3.7 |
| MSSP-GR | 443,665 | 2001 | 2.98 | 2.85 | 4.6 | 3.7 |
| MSSP-GR | 443,665 | 2002 | 2.95 | 2.88 | 3.8 | 3.7 |
| MSSP-GR | 443,665 | 2003 | 2.43 | 2.89 | 2.1 | 3.7 |
| MSSP-GR | 443,665 | 2004 | 2.93 | 2.91 | 3.6 | 3.7 |
| MSSP-GR | 443,665 | 2005 | 2.80 | 2.92 | 2.8 | 3.7 |
| MSSP-GR | 443,665 | 2006 | 2.65 | 2.94 | 2.1 | 3.7 |
| MSSP-GR | 443,665 | 2007 | 3.11 | 2.98 | 3.6 | 3.8 |
| MSSP-GR | 443,665 | 2008 | 3.31 | 3.05 | 5.8 | 3.8 |
| MIZZ-HE | 1,353,269 | 1980 | 0.82 | 0.96 | 0.50 | 0.90 |
| MIZZ-HE | 1,353,269 | 1981 | 0.82 | 0.97 | 0.58 | 0.91 |
| MIZZ-HE | 1,353,269 | 1982 | 1.05 | 0.98 | 1.2 | 0.93 |
| MIZZ-HE | 1,353,269 | 1983 | 1.14 | 1.01 | 1.3 | 0.94 |

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|---|---|---|---|---|---|---|
| MIZZ-HE | 1,353,269 | 1984 | 1.18 | 1.03 | 1.5 | 0.96 |
| MIZZ-HE | 1,353,269 | 1985 | 1.16 | 1.05 | 1.3 | 0.97 |
| MIZZ-HE | 1,353,269 | 1986 | 1.22 | 1.07 | 1.3 | 0.98 |
| MIZZ-HE | 1,353,269 | 1987 | 1.17 | 1.09 | 1.1 | 0.99 |
| MIZZ-HE | 1,353,269 | 1988 | 0.90 | 1.10 | 0.53 | 1.0 |
| MIZZ-HE | 1,353,269 | 1989 | 0.91 | 1.12 | 0.42 | 1.0 |
| MIZZ-HE | 1,353,269 | 1990 | 1.13 | 1.15 | 0.95 | 1.0 |
| MIZZ-HE | 1,353,269 | 1991 | 1.09 | 1.17 | 0.65 | 1.0 |
| MIZZ-HE | 1,353,269 | 1992 | 1.20 | 1.18 | 0.91 | 1.0 |
| MIZZ-HE | 1,353,269 | 1993 | 1.27 | 1.19 | 2.1 | 1.1 |
| MIZZ-HE | 1,353,269 | 1994 | 1.19 | 1.18 | 1.1 | 1.0 |
| MIZZ-HE | 1,353,269 | 1995 | 1.24 | 1.18 | 1.5 | 1.0 |
| MIZZ-HE | 1,353,269 | 1996 | 1.28 | 1.18 | 1.3 | 1.0 |
| MIZZ-HE | 1,353,269 | 1997 | 1.25 | 1.18 | 1.4 | 1.0 |
| MIZZ-HE | 1,353,269 | 1998 | 1.26 | 1.19 | 1.5 | 1.1 |
| MIZZ-HE | 1,353,269 | 1999 | 1.22 | 1.21 | 1.4 | 1.1 |
| MIZZ-HE | 1,353,269 | 2000 | 1.18 | 1.22 | 0.57 | 1.1 |
| MIZZ-HE | 1,353,269 | 2001 | 1.24 | 1.23 | 1.1 | 1.1 |
| MIZZ-HE | 1,353,269 | 2002 | 1.17 | 1.26 | 0.74 | 1.1 |
| MIZZ-HE | 1,353,269 | 2003 | 1.17 | 1.30 | 0.51 | 1.2 |
| MIZZ-HE | 1,353,269 | 2004 | 1.33 | 1.35 | 0.91 | 1.2 |
| MIZZ-HE | 1,353,269 | 2005 | 1.32 | 1.40 | 0.84 | 1.2 |
| MIZZ-HE | 1,353,269 | 2006 | 1.38 | 1.47 | 0.52 | 1.3 |
| MIZZ-HE | 1,353,269 | 2007 | 1.56 | 1.56 | 1.3 | 1.3 |
| MIZZ-HE | 1,353,269 | 2008 | 1.69 | 1.67 | 1.9 | 1.4 |
| MSSP-TH | 1,847,180 | 1980 | 1.61 | 1.93 | 2.5 | 4.7 |
| MSSP-TH | 1,847,180 | 1981 | 1.77 | 1.95 | 3.5 | 4.8 |
| MSSP-TH | 1,847,180 | 1982 | 2.25 | 1.97 | 6.7 | 4.8 |
| MSSP-TH | 1,847,180 | 1983 | 2.28 | 2.00 | 6.9 | 4.9 |
| MSSP-TH | 1,847,180 | 1984 | 2.37 | 2.04 | 7.2 | 5.0 |
| MSSP-TH | 1,847,180 | 1985 | 2.22 | 2.07 | 6.1 | 5.0 |
| MSSP-TH | 1,847,180 | 1986 | 2.44 | 2.10 | 6.8 | 5.1 |
| MSSP-TH | 1,847,180 | 1987 | 2.05 | 2.12 | 3.8 | 5.1 |
| MSSP-TH | 1,847,180 | 1988 | 1.70 | 2.15 | 2.4 | 5.1 |
| MSSP-TH | 1,847,180 | 1989 | 1.53 | 2.17 | 1.8 | 5.2 |
| MSSP-TH | 1,847,180 | 1990 | 2.15 | 2.18 | 5.0 | 5.2 |
| MSSP-TH | 1,847,180 | 1991 | 2.37 | 2.19 | 5.2 | 5.2 |
| MSSP-TH | 1,847,180 | 1992 | 2.24 | 2.19 | 4.6 | 5.2 |
| MSSP-TH | 1,847,180 | 1993 | 2.44 | 2.19 | 9.9 | 5.2 |
| MSSP-TH | 1,847,180 | 1994 | 2.28 | 2.18 | 4.9 | 5.2 |
| MSSP-TH | 1,847,180 | 1995 | 2.30 | 2.16 | 6.0 | 5.1 |
| MSSP-TH | 1,847,180 | 1996 | 2.26 | 2.13 | 5.4 | 5.0 |
| MSSP-TH | 1,847,180 | 1997 | 2.30 | 2.11 | 5.5 | 5.0 |

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|---|---|---|---|---|---|---|
| MSSP-TH | 1,847,180 | 1998 | 2.34 | 2.09 | 6.6 | 4.9 |
| MSSP-TH | 1,847,180 | 1999 | 2.22 | 2.07 | 5.7 | 4.9 |
| MSSP-TH | 1,847,180 | 2000 | 1.82 | 2.05 | 2.8 | 4.8 |
| MSSP-TH | 1,847,180 | 2001 | 2.17 | 2.06 | 5.4 | 4.9 |
| MSSP-TH | 1,847,180 | 2002 | 2.07 | 2.08 | 4.4 | 4.9 |
| MSSP-TH | 1,847,180 | 2003 | 1.84 | 2.11 | 2.9 | 4.9 |
| MSSP-TH | 1,847,180 | 2004 | 2.20 | 2.14 | 4.6 | 5.0 |
| MSSP-TH | 1,847,180 | 2005 | 2.03 | 2.17 | 3.6 | 5.0 |
| MSSP-TH | 1,847,180 | 2006 | 1.96 | 2.20 | 2.7 | 5.0 |
| MSSP-TH | 1,847,180 | 2007 | 2.38 | 2.25 | 5.1 | 5.1 |
| MSSP-TH | 1,847,180 | 2008 | 2.41 | 2.31 | 7.5 | 5.2 |
| OHIO-GRCH | 526,027 | 1980 | 1.02 | 0.99 | 2.9 | 3.1 |
| OHIO-GRCH | 526,027 | 1981 | 0.97 | 1.00 | 2.1 | 3.1 |
| OHIO-GRCH | 526,027 | 1982 | 1.03 | 1.00 | 3.4 | 3.1 |
| OHIO-GRCH | 526,027 | 1983 | 0.98 | 1.00 | 3.3 | 3.1 |
| OHIO-GRCH | 526,027 | 1984 | 1.01 | 1.00 | 3.3 | 3.1 |
| OHIO-GRCH | 526,027 | 1985 | 1.01 | 1.01 | 3.0 | 3.1 |
| OHIO-GRCH | 526,027 | 1986 | 0.98 | 1.02 | 2.2 | 3.1 |
| OHIO-GRCH | 526,027 | 1987 | 0.98 | 1.03 | 2.0 | 3.2 |
| OHIO-GRCH | 526,027 | 1988 | 0.89 | 1.03 | 1.7 | 3.2 |
| OHIO-GRCH | 526,027 | 1989 | 1.11 | 1.03 | 4.2 | 3.2 |
| OHIO-GRCH | 526,027 | 1990 | 1.07 | 1.02 | 3.8 | 3.1 |
| OHIO-GRCH | 526,027 | 1991 | 0.94 | 1.02 | 3.6 | 3.1 |
| OHIO-GRCH | 526,027 | 1992 | 1.08 | 1.02 | 2.4 | 3.1 |
| OHIO-GRCH | 526,027 | 1993 | 0.97 | 1.02 | 3.0 | 3.1 |
| OHIO-GRCH | 526,027 | 1994 | 0.99 | 1.02 | 3.6 | 3.1 |
| OHIO-GRCH | 526,027 | 1995 | 1.03 | 1.02 | 2.7 | 3.1 |
| OHIO-GRCH | 526,027 | 1996 | 1.07 | 1.03 | 4.2 | 3.1 |
| OHIO-GRCH | 526,027 | 1997 | 1.03 | 1.03 | 3.5 | 3.1 |
| OHIO-GRCH | 526,027 | 1998 | 1.04 | 1.04 | 3.5 | 3.1 |
| OHIO-GRCH | 526,027 | 1999 | 0.99 | 1.04 | 2.4 | 3.1 |
| OHIO-GRCH | 526,027 | 2000 | 1.05 | 1.04 | 2.0 | 3.1 |
| OHIO-GRCH | 526,027 | 2001 | 1.06 | 1.04 | 2.4 | 3.1 |
| OHIO-GRCH | 526,027 | 2002 | 1.02 | 1.04 | 3.1 | 3.1 |
| OHIO-GRCH | 526,027 | 2003 | 1.09 | 1.04 | 3.9 | 3.1 |
| OHIO-GRCH | 526,027 | 2004 | 1.08 | 1.04 | 3.8 | 3.1 |
| OHIO-GRCH | 526,027 | 2005 | 1.01 | 1.04 | 2.8 | 3.1 |
| OHIO-GRCH | 526,027 | 2006 | 1.08 | 1.03 | 2.7 | 3.1 |
| OHIO-GRCH | 526,027 | 2007 | 0.94 | 1.03 | 2.4 | 3.1 |
| OHIO-GRCH | 526,027 | 2008 | 0.95 | 1.02 | 3.1 | 3.1 |
| MSSP-OUT | 2,914,514 | 1980 | 1.24 | 1.25 | 6.7 | 8.1 |
| MSSP-OUT | 2,914,514 | 1981 | 1.25 | 1.29 | 5.8 | 8.5 |
| MSSP-OUT | 2,914,514 | 1982 | 1.39 | 1.33 | 9.4 | 8.8 |

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|---|---|---|---|---|---|---|
| MSSP-OUT | 2,914,514 | 1983 | 1.38 | 1.35 | 12 | 8.9 |
| MSSP-OUT | 2,914,514 | 1984 | 1.43 | 1.36 | 11 | 9.0 |
| MSSP-OUT | 2,914,514 | 1985 | 1.38 | 1.36 | 9.9 | 9.0 |
| MSSP-OUT | 2,914,514 | 1986 | 1.43 | 1.36 | 8.9 | 9.0 |
| MSSP-OUT | 2,914,514 | 1987 | 1.22 | 1.36 | 6.2 | 9.0 |
| MSSP-OUT | 2,914,514 | 1988 | 0.96 | 1.35 | 5.3 | 8.9 |
| MSSP-OUT | 2,914,514 | 1989 | 1.38 | 1.34 | 9.3 | 8.9 |
| MSSP-OUT | 2,914,514 | 1990 | 1.39 | 1.33 | 10 | 8.7 |
| MSSP-OUT | 2,914,514 | 1991 | 1.26 | 1.31 | 9.7 | 8.6 |
| MSSP-OUT | 2,914,514 | 1992 | 1.36 | 1.30 | 7.3 | 8.5 |
| MSSP-OUT | 2,914,514 | 1993 | 1.49 | 1.30 | 14 | 8.5 |
| MSSP-OUT | 2,914,514 | 1994 | 1.30 | 1.31 | 9.0 | 8.5 |
| MSSP-OUT | 2,914,514 | 1995 | 1.35 | 1.31 | 8.7 | 8.6 |
| MSSP-OUT | 2,914,514 | 1996 | 1.38 | 1.31 | 9.9 | 8.6 |
| MSSP-OUT | 2,914,514 | 1997 | 1.32 | 1.32 | 9.7 | 8.6 |
| MSSP-OUT | 2,914,514 | 1998 | 1.36 | 1.32 | 10 | 8.5 |
| MSSP-OUT | 2,914,514 | 1999 | 1.29 | 1.31 | 8.4 | 8.5 |
| MSSP-OUT | 2,914,514 | 2000 | 1.28 | 1.31 | 5.6 | 8.5 |
| MSSP-OUT | 2,914,514 | 2001 | 1.32 | 1.31 | 7.8 | 8.5 |
| MSSP-OUT | 2,914,514 | 2002 | 1.31 | 1.32 | 8.6 | 8.5 |
| MSSP-OUT | 2,914,514 | 2003 | 1.36 | 1.33 | 8.4 | 8.5 |
| MSSP-OUT | 2,914,514 | 2004 | 1.36 | 1.33 | 9.5 | 8.5 |
| MSSP-OUT | 2,914,514 | 2005 | 1.35 | 1.34 | 7.4 | 8.6 |
| MSSP-OUT | 2,914,514 | 2006 | 1.39 | 1.35 | 6.0 | 8.6 |
| MSSP-OUT | 2,914,514 | 2007 | 1.40 | 1.36 | 7.8 | 8.6 |
| MSSP-OUT | 2,914,514 | 2008 | 1.32 | 1.38 | 10 | 8.8 |

## Table SI-S4. WRTDS output of spring mean estimated and flow-normalized nitrate concentration and total spring estimated and flow-normalized nitrate flux.

[WRTDS, Weighted Regressions on Time, Discharge, and Season model; --, estimates not reported because no samples were collected in that year. All estimated and flow-normalized concentrations and fluxes are reported as nitrate as nitrogen.]

| Site | Drainage area, in km$^2$ | Calendar year | Spring mean estimated concentration, in mg/L | Spring mean flow-normalized concentration, in mg/L | Total spring estimated flux, in $10^8$ kg/yr | Total spring flow-normalized flux, in $10^8$ kg/yr |
|---|---|---|---|---|---|---|
| MSSP-CL | 221,703 | 1980 | 0.75 | 1.20 | 0.11 | 0.28 |
| MSSP-CL | 221,703 | 1981 | 0.83 | 1.29 | 0.12 | 0.30 |
| MSSP-CL | 221,703 | 1982 | 1.60 | 1.36 | 0.39 | 0.32 |
| MSSP-CL | 221,703 | 1983 | 1.50 | 1.42 | 0.32 | 0.33 |
| MSSP-CL | 221,703 | 1984 | 1.78 | 1.48 | 0.41 | 0.34 |
| MSSP-CL | 221,703 | 1985 | 1.55 | 1.56 | 0.32 | 0.36 |
| MSSP-CL | 221,703 | 1986 | 2.22 | 1.63 | 0.63 | 0.37 |
| MSSP-CL | 221,703 | 1987 | 0.88 | 1.70 | 0.091 | 0.38 |
| MSSP-CL | 221,703 | 1988 | -- | -- | -- | -- |
| MSSP-CL | 221,703 | 1989 | -- | -- | -- | -- |
| MSSP-CL | 221,703 | 1990 | -- | -- | -- | -- |
| MSSP-CL | 221,703 | 1991 | 2.61 | 2.04 | 0.63 | 0.45 |
| MSSP-CL | 221,703 | 1992 | 1.76 | 1.99 | 0.34 | 0.43 |
| MSSP-CL | 221,703 | 1993 | 2.71 | 1.94 | 0.88 | 0.42 |
| MSSP-CL | 221,703 | 1994 | -- | -- | -- | -- |
| MSSP-CL | 221,703 | 1995 | 2.02 | 1.82 | 0.42 | 0.39 |
| MSSP-CL | 221,703 | 1996 | 2.18 | 1.75 | 0.55 | 0.38 |
| MSSP-CL | 221,703 | 1997 | 1.81 | 1.70 | 0.48 | 0.36 |
| MSSP-CL | 221,703 | 1998 | 1.67 | 1.66 | 0.35 | 0.35 |
| MSSP-CL | 221,703 | 1999 | 1.85 | 1.63 | 0.41 | 0.34 |
| MSSP-CL | 221,703 | 2000 | 1.46 | 1.61 | 0.24 | 0.34 |
| MSSP-CL | 221,703 | 2001 | 2.19 | 1.64 | 0.77 | 0.34 |
| MSSP-CL | 221,703 | 2002 | 1.85 | 1.70 | 0.39 | 0.36 |
| MSSP-CL | 221,703 | 2003 | 1.72 | 1.76 | 0.32 | 0.37 |
| MSSP-CL | 221,703 | 2004 | 2.03 | 1.82 | 0.50 | 0.38 |
| MSSP-CL | 221,703 | 2005 | 1.85 | 1.87 | 0.33 | 0.40 |
| MSSP-CL | 221,703 | 2006 | 1.88 | 1.93 | 0.35 | 0.41 |
| MSSP-CL | 221,703 | 2007 | 1.74 | 2.03 | 0.28 | 0.43 |
| MSSP-CL | 221,703 | 2008 | 2.85 | 2.18 | 0.85 | 0.46 |
| IOWA-WAP | 32,375 | 1980 | 4.51 | 5.74 | 0.098 | 0.25 |
| IOWA-WAP | 32,375 | 1981 | 4.08 | 5.68 | 0.069 | 0.25 |
| IOWA-WAP | 32,375 | 1982 | 6.81 | 5.73 | 0.30 | 0.25 |
| IOWA-WAP | 32,375 | 1983 | 6.85 | 5.69 | 0.36 | 0.25 |
| IOWA-WAP | 32,375 | 1984 | 7.10 | 5.70 | 0.35 | 0.25 |

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|---|---|---|---|---|---|---|
| IOWA-WAP | 32,375 | 1985 | 3.45 | 5.71 | 0.052 | 0.25 |
| IOWA-WAP | 32,375 | 1986 | 6.53 | 5.73 | 0.27 | 0.25 |
| IOWA-WAP | 32,375 | 1987 | 4.26 | 5.76 | 0.080 | 0.26 |
| IOWA-WAP | 32,375 | 1988 | 2.75 | 5.85 | 0.033 | 0.26 |
| IOWA-WAP | 32,375 | 1989 | 1.49 | 5.93 | 0.011 | 0.27 |
| IOWA-WAP | 32,375 | 1990 | 5.36 | 5.99 | 0.23 | 0.27 |
| IOWA-WAP | 32,375 | 1991 | 8.13 | 6.03 | 0.53 | 0.27 |
| IOWA-WAP | 32,375 | 1992 | 5.37 | 6.08 | 0.16 | 0.27 |
| IOWA-WAP | 32,375 | 1993 | 8.40 | 6.10 | 0.71 | 0.28 |
| IOWA-WAP | 32,375 | 1994 | 4.57 | 6.11 | 0.087 | 0.27 |
| IOWA-WAP | 32,375 | 1995 | 7.63 | 6.12 | 0.37 | 0.27 |
| IOWA-WAP | 32,375 | 1996 | 6.32 | 6.12 | 0.28 | 0.27 |
| IOWA-WAP | 32,375 | 1997 | 6.26 | 6.14 | 0.19 | 0.27 |
| IOWA-WAP | 32,375 | 1998 | 7.47 | 6.24 | 0.40 | 0.28 |
| IOWA-WAP | 32,375 | 1999 | 8.07 | 6.39 | 0.51 | 0.28 |
| IOWA-WAP | 32,375 | 2000 | 5.19 | 6.56 | 0.17 | 0.29 |
| IOWA-WAP | 32,375 | 2001 | 8.34 | 6.68 | 0.50 | 0.29 |
| IOWA-WAP | 32,375 | 2002 | 6.25 | 6.77 | 0.14 | 0.29 |
| IOWA-WAP | 32,375 | 2003 | 6.36 | 6.84 | 0.18 | 0.29 |
| IOWA-WAP | 32,375 | 2004 | 6.90 | 6.89 | 0.30 | 0.29 |
| IOWA-WAP | 32,375 | 2005 | 7.06 | 6.91 | 0.18 | 0.28 |
| IOWA-WAP | 32,375 | 2006 | 7.16 | 6.91 | 0.21 | 0.28 |
| IOWA-WAP | 32,375 | 2007 | 7.75 | 6.86 | 0.39 | 0.28 |
| IOWA-WAP | 32,375 | 2008 | 7.42 | 6.78 | 0.72 | 0.27 |
| ILLI-VC | 69,264 | 1980 | 4.89 | 4.85 | 0.38 | 0.43 |
| ILLI-VC | 69,264 | 1981 | 5.19 | 4.83 | 0.54 | 0.43 |
| ILLI-VC | 69,264 | 1982 | 5.12 | 4.82 | 0.54 | 0.43 |
| ILLI-VC | 69,264 | 1983 | 5.32 | 4.84 | 0.71 | 0.43 |
| ILLI-VC | 69,264 | 1984 | 5.36 | 4.84 | 0.58 | 0.43 |
| ILLI-VC | 69,264 | 1985 | 4.40 | 4.85 | 0.31 | 0.43 |
| ILLI-VC | 69,264 | 1986 | 4.60 | 4.86 | 0.24 | 0.43 |
| ILLI-VC | 69,264 | 1987 | 4.24 | 4.87 | 0.18 | 0.43 |
| ILLI-VC | 69,264 | 1988 | 3.54 | 4.85 | 0.16 | 0.43 |
| ILLI-VC | 69,264 | 1989 | 4.03 | 4.84 | 0.14 | 0.43 |
| ILLI-VC | 69,264 | 1990 | 5.32 | 4.82 | 0.52 | 0.42 |
| ILLI-VC | 69,264 | 1991 | 5.17 | 4.82 | 0.54 | 0.42 |
| ILLI-VC | 69,264 | 1992 | 3.99 | 4.82 | 0.16 | 0.42 |
| ILLI-VC | 69,264 | 1993 | 5.21 | 4.86 | 0.61 | 0.43 |
| ILLI-VC | 69,264 | 1994 | 4.88 | 4.91 | 0.40 | 0.43 |
| ILLI-VC | 69,264 | 1995 | 5.58 | 4.96 | 0.76 | 0.44 |
| ILLI-VC | 69,264 | 1996 | 5.33 | 5.00 | 0.57 | 0.44 |
| ILLI-VC | 69,264 | 1997 | 4.88 | 5.05 | 0.29 | 0.45 |
| ILLI-VC | 69,264 | 1998 | 5.93 | 5.11 | 0.75 | 0.46 |

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|---|---|---|---|---|---|---|
| ILLI-VC | 69,264 | 1999 | 5.74 | 5.20 | 0.57 | 0.47 |
| ILLI-VC | 69,264 | 2000 | 4.51 | 5.26 | 0.21 | 0.47 |
| ILLI-VC | 69,264 | 2001 | 5.35 | 5.27 | 0.38 | 0.47 |
| ILLI-VC | 69,264 | 2002 | 5.85 | 5.25 | 0.75 | 0.46 |
| ILLI-VC | 69,264 | 2003 | 4.80 | 5.22 | 0.24 | 0.46 |
| ILLI-VC | 69,264 | 2004 | 5.22 | 5.15 | 0.39 | 0.45 |
| ILLI-VC | 69,264 | 2005 | 4.25 | 5.07 | 0.16 | 0.44 |
| ILLI-VC | 69,264 | 2006 | 4.76 | 4.98 | 0.25 | 0.43 |
| ILLI-VC | 69,264 | 2007 | 4.87 | 4.87 | 0.40 | 0.42 |
| ILLI-VC | 69,264 | 2008 | 5.01 | 4.70 | 0.47 | 0.41 |
| MSSP-GR | 443,665 | 1980 | 2.95 | 3.17 | 0.89 | 1.4 |
| MSSP-GR | 443,665 | 1981 | 3.05 | 3.19 | 1.1 | 1.5 |
| MSSP-GR | 443,665 | 1982 | 3.45 | 3.18 | 1.8 | 1.5 |
| MSSP-GR | 443,665 | 1983 | 3.53 | 3.16 | 2.1 | 1.5 |
| MSSP-GR | 443,665 | 1984 | 3.50 | 3.14 | 1.9 | 1.4 |
| MSSP-GR | 443,665 | 1985 | 2.87 | 3.12 | 1.0 | 1.4 |
| MSSP-GR | 443,665 | 1986 | 3.39 | 3.09 | 1.7 | 1.4 |
| MSSP-GR | 443,665 | 1987 | 2.43 | 3.06 | 0.59 | 1.4 |
| MSSP-GR | 443,665 | 1988 | 1.67 | 3.06 | 0.37 | 1.4 |
| MSSP-GR | 443,665 | 1989 | 1.98 | 3.06 | 0.41 | 1.4 |
| MSSP-GR | 443,665 | 1990 | 2.98 | 3.06 | 1.2 | 1.5 |
| MSSP-GR | 443,665 | 1991 | 3.58 | 3.08 | 1.9 | 1.5 |
| MSSP-GR | 443,665 | 1992 | 2.49 | 3.12 | 0.81 | 1.5 |
| MSSP-GR | 443,665 | 1993 | 3.83 | 3.16 | 2.6 | 1.5 |
| MSSP-GR | 443,665 | 1994 | 3.14 | 3.23 | 1.1 | 1.5 |
| MSSP-GR | 443,665 | 1995 | -- | -- | -- | -- |
| MSSP-GR | 443,665 | 1996 | 3.69 | 3.37 | 1.9 | 1.6 |
| MSSP-GR | 443,665 | 1997 | 3.54 | 3.44 | 1.5 | 1.6 |
| MSSP-GR | 443,665 | 1998 | 3.88 | 3.50 | 2.1 | 1.6 |
| MSSP-GR | 443,665 | 1999 | 3.92 | 3.56 | 2.1 | 1.6 |
| MSSP-GR | 443,665 | 2000 | 3.14 | 3.63 | 1.0 | 1.7 |
| MSSP-GR | 443,665 | 2001 | 4.12 | 3.70 | 2.6 | 1.7 |
| MSSP-GR | 443,665 | 2002 | 4.00 | 3.76 | 2.2 | 1.7 |
| MSSP-GR | 443,665 | 2003 | 3.59 | 3.77 | 1.2 | 1.7 |
| MSSP-GR | 443,665 | 2004 | 3.74 | 3.78 | 1.7 | 1.7 |
| MSSP-GR | 443,665 | 2005 | 3.75 | 3.77 | 1.2 | 1.7 |
| MSSP-GR | 443,665 | 2006 | 3.67 | 3.76 | 1.2 | 1.7 |
| MSSP-GR | 443,665 | 2007 | 3.88 | 3.78 | 1.5 | 1.7 |
| MSSP-GR | 443,665 | 2008 | 3.94 | 3.83 | 2.7 | 1.7 |
| MIZZ-HE | 1,353,269 | 1980 | 1.16 | 1.29 | 0.25 | 0.40 |
| MIZZ-HE | 1,353,269 | 1981 | 1.05 | 1.31 | 0.24 | 0.40 |
| MIZZ-HE | 1,353,269 | 1982 | 1.24 | 1.32 | 0.42 | 0.41 |
| MIZZ-HE | 1,353,269 | 1983 | 1.67 | 1.34 | 0.74 | 0.42 |

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|---|---|---|---|---|---|---|
| MIZZ-HE | 1,353,269 | 1984 | 1.64 | 1.38 | 0.80 | 0.43 |
| MIZZ-HE | 1,353,269 | 1985 | 1.54 | 1.40 | 0.44 | 0.43 |
| MIZZ-HE | 1,353,269 | 1986 | 1.58 | 1.43 | 0.44 | 0.44 |
| MIZZ-HE | 1,353,269 | 1987 | 1.67 | 1.46 | 0.51 | 0.44 |
| MIZZ-HE | 1,353,269 | 1988 | 1.12 | 1.49 | 0.20 | 0.45 |
| MIZZ-HE | 1,353,269 | 1989 | 1.03 | 1.53 | 0.13 | 0.45 |
| MIZZ-HE | 1,353,269 | 1990 | 1.64 | 1.58 | 0.56 | 0.46 |
| MIZZ-HE | 1,353,269 | 1991 | 1.69 | 1.62 | 0.38 | 0.47 |
| MIZZ-HE | 1,353,269 | 1992 | 1.59 | 1.65 | 0.26 | 0.47 |
| MIZZ-HE | 1,353,269 | 1993 | 1.67 | 1.66 | 0.70 | 0.47 |
| MIZZ-HE | 1,353,269 | 1994 | 1.73 | 1.66 | 0.60 | 0.47 |
| MIZZ-HE | 1,353,269 | 1995 | 1.59 | 1.64 | 0.83 | 0.47 |
| MIZZ-HE | 1,353,269 | 1996 | 1.66 | 1.64 | 0.60 | 0.47 |
| MIZZ-HE | 1,353,269 | 1997 | 1.69 | 1.64 | 0.63 | 0.47 |
| MIZZ-HE | 1,353,269 | 1998 | 1.67 | 1.65 | 0.57 | 0.47 |
| MIZZ-HE | 1,353,269 | 1999 | 1.71 | 1.66 | 0.73 | 0.48 |
| MIZZ-HE | 1,353,269 | 2000 | 1.61 | 1.66 | 0.22 | 0.48 |
| MIZZ-HE | 1,353,269 | 2001 | 1.69 | 1.66 | 0.56 | 0.49 |
| MIZZ-HE | 1,353,269 | 2002 | 1.68 | 1.69 | 0.46 | 0.50 |
| MIZZ-HE | 1,353,269 | 2003 | 1.62 | 1.73 | 0.24 | 0.51 |
| MIZZ-HE | 1,353,269 | 2004 | 1.72 | 1.78 | 0.35 | 0.52 |
| MIZZ-HE | 1,353,269 | 2005 | 1.80 | 1.83 | 0.36 | 0.53 |
| MIZZ-HE | 1,353,269 | 2006 | 1.93 | 1.90 | 0.25 | 0.55 |
| MIZZ-HE | 1,353,269 | 2007 | 1.94 | 2.00 | 0.65 | 0.57 |
| MIZZ-HE | 1,353,269 | 2008 | 2.03 | 2.14 | 0.83 | 0.60 |
| MSSP-TH | 1,847,180 | 1980 | 2.02 | 2.50 | 1.1 | 2.1 |
| MSSP-TH | 1,847,180 | 1981 | 2.14 | 2.55 | 1.3 | 2.2 |
| MSSP-TH | 1,847,180 | 1982 | 2.95 | 2.61 | 2.6 | 2.2 |
| MSSP-TH | 1,847,180 | 1983 | 3.22 | 2.67 | 3.7 | 2.3 |
| MSSP-TH | 1,847,180 | 1984 | 3.29 | 2.73 | 3.5 | 2.3 |
| MSSP-TH | 1,847,180 | 1985 | 2.86 | 2.76 | 2.1 | 2.3 |
| MSSP-TH | 1,847,180 | 1986 | 3.06 | 2.79 | 2.4 | 2.3 |
| MSSP-TH | 1,847,180 | 1987 | 2.54 | 2.81 | 1.5 | 2.3 |
| MSSP-TH | 1,847,180 | 1988 | 2.05 | 2.84 | 0.83 | 2.3 |
| MSSP-TH | 1,847,180 | 1989 | 2.13 | 2.88 | 0.81 | 2.3 |
| MSSP-TH | 1,847,180 | 1990 | 2.96 | 2.91 | 2.4 | 2.3 |
| MSSP-TH | 1,847,180 | 1991 | 3.37 | 2.91 | 2.7 | 2.3 |
| MSSP-TH | 1,847,180 | 1992 | 2.57 | 2.91 | 1.3 | 2.3 |
| MSSP-TH | 1,847,180 | 1993 | 2.93 | 2.90 | 3.3 | 2.3 |
| MSSP-TH | 1,847,180 | 1994 | 2.99 | 2.87 | 2.2 | 2.3 |
| MSSP-TH | 1,847,180 | 1995 | 2.77 | 2.83 | 3.0 | 2.3 |
| MSSP-TH | 1,847,180 | 1996 | 2.89 | 2.79 | 2.8 | 2.2 |
| MSSP-TH | 1,847,180 | 1997 | 3.02 | 2.75 | 2.4 | 2.2 |

| | | | | | | |
|---|---|---|---|---|---|---|
| MSSP-TH | 1,847,180 | 1998 | 2.91 | 2.71 | 2.7 | 2.2 |
| MSSP-TH | 1,847,180 | 1999 | 2.92 | 2.68 | 2.8 | 2.1 |
| MSSP-TH | 1,847,180 | 2000 | 2.24 | 2.67 | 1.1 | 2.1 |
| MSSP-TH | 1,847,180 | 2001 | 2.97 | 2.69 | 2.8 | 2.2 |
| MSSP-TH | 1,847,180 | 2002 | 2.84 | 2.73 | 2.5 | 2.2 |
| MSSP-TH | 1,847,180 | 2003 | 2.67 | 2.77 | 1.5 | 2.2 |
| MSSP-TH | 1,847,180 | 2004 | 2.83 | 2.79 | 2.0 | 2.2 |
| MSSP-TH | 1,847,180 | 2005 | 2.83 | 2.80 | 1.5 | 2.2 |
| MSSP-TH | 1,847,180 | 2006 | 2.72 | 2.82 | 1.3 | 2.2 |
| MSSP-TH | 1,847,180 | 2007 | 3.04 | 2.86 | 2.3 | 2.2 |
| MSSP-TH | 1,847,180 | 2008 | 2.81 | 2.93 | 3.4 | 2.3 |
| OHIO-GRCH | 526,027 | 1980 | 1.20 | 1.12 | 1.1 | 0.92 |
| OHIO-GRCH | 526,027 | 1981 | 1.18 | 1.15 | 0.94 | 0.94 |
| OHIO-GRCH | 526,027 | 1982 | 1.22 | 1.16 | 0.76 | 0.95 |
| OHIO-GRCH | 526,027 | 1983 | 1.14 | 1.18 | 1.5 | 0.95 |
| OHIO-GRCH | 526,027 | 1984 | 1.14 | 1.18 | 1.4 | 0.94 |
| OHIO-GRCH | 526,027 | 1985 | 1.28 | 1.19 | 0.71 | 0.95 |
| OHIO-GRCH | 526,027 | 1986 | 1.18 | 1.21 | 0.39 | 0.97 |
| OHIO-GRCH | 526,027 | 1987 | 1.24 | 1.23 | 0.68 | 0.98 |
| OHIO-GRCH | 526,027 | 1988 | 1.08 | 1.24 | 0.41 | 0.98 |
| OHIO-GRCH | 526,027 | 1989 | 1.26 | 1.24 | 1.3 | 0.99 |
| OHIO-GRCH | 526,027 | 1990 | 1.29 | 1.23 | 1.1 | 0.99 |
| OHIO-GRCH | 526,027 | 1991 | 1.19 | 1.23 | 0.89 | 1.0 |
| OHIO-GRCH | 526,027 | 1992 | 1.27 | 1.23 | 0.58 | 0.99 |
| OHIO-GRCH | 526,027 | 1993 | 1.18 | 1.24 | 0.90 | 1.0 |
| OHIO-GRCH | 526,027 | 1994 | 1.17 | 1.25 | 1.2 | 1.0 |
| OHIO-GRCH | 526,027 | 1995 | 1.33 | 1.27 | 1.0 | 1.0 |
| OHIO-GRCH | 526,027 | 1996 | 1.33 | 1.29 | 1.7 | 1.0 |
| OHIO-GRCH | 526,027 | 1997 | 1.37 | 1.30 | 1.2 | 1.0 |
| OHIO-GRCH | 526,027 | 1998 | 1.32 | 1.30 | 1.6 | 1.0 |
| OHIO-GRCH | 526,027 | 1999 | 1.31 | 1.31 | 0.55 | 1.0 |
| OHIO-GRCH | 526,027 | 2000 | 1.33 | 1.30 | 0.71 | 1.0 |
| OHIO-GRCH | 526,027 | 2001 | 1.33 | 1.29 | 0.63 | 1.0 |
| OHIO-GRCH | 526,027 | 2002 | 1.23 | 1.27 | 1.3 | 1.0 |
| OHIO-GRCH | 526,027 | 2003 | 1.25 | 1.25 | 1.3 | 0.99 |
| OHIO-GRCH | 526,027 | 2004 | 1.26 | 1.23 | 1.1 | 0.96 |
| OHIO-GRCH | 526,027 | 2005 | 1.19 | 1.21 | 0.70 | 0.95 |
| OHIO-GRCH | 526,027 | 2006 | 1.21 | 1.18 | 0.62 | 0.93 |
| OHIO-GRCH | 526,027 | 2007 | 1.07 | 1.16 | 0.53 | 0.92 |
| OHIO-GRCH | 526,027 | 2008 | 1.16 | 1.14 | 1.1 | 0.90 |
| MSSP-OUT | 2,914,514 | 1980 | 1.58 | 1.54 | 3.1 | 3.2 |
| MSSP-OUT | 2,914,514 | 1981 | 1.54 | 1.61 | 2.3 | 3.4 |
| MSSP-OUT | 2,914,514 | 1982 | 1.72 | 1.67 | 3.4 | 3.6 |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| MSSP-OUT | 2,914,514 | 1983 | 1.77 | 1.70 | 5.9 | 3.7 |
| MSSP-OUT | 2,914,514 | 1984 | 1.80 | 1.71 | 5.2 | 3.7 |
| MSSP-OUT | 2,914,514 | 1985 | 1.76 | 1.71 | 3.4 | 3.7 |
| MSSP-OUT | 2,914,514 | 1986 | 1.76 | 1.71 | 2.8 | 3.7 |
| MSSP-OUT | 2,914,514 | 1987 | 1.60 | 1.71 | 2.4 | 3.7 |
| MSSP-OUT | 2,914,514 | 1988 | 1.18 | 1.70 | 1.6 | 3.6 |
| MSSP-OUT | 2,914,514 | 1989 | 1.73 | 1.68 | 3.4 | 3.6 |
| MSSP-OUT | 2,914,514 | 1990 | 1.71 | 1.65 | 4.3 | 3.5 |
| MSSP-OUT | 2,914,514 | 1991 | 1.68 | 1.62 | 4.0 | 3.4 |
| MSSP-OUT | 2,914,514 | 1992 | 1.57 | 1.61 | 2.1 | 3.4 |
| MSSP-OUT | 2,914,514 | 1993 | 1.63 | 1.61 | 4.6 | 3.4 |
| MSSP-OUT | 2,914,514 | 1994 | 1.63 | 1.63 | 3.8 | 3.4 |
| MSSP-OUT | 2,914,514 | 1995 | 1.67 | 1.65 | 3.8 | 3.5 |
| MSSP-OUT | 2,914,514 | 1996 | 1.69 | 1.67 | 4.2 | 3.5 |
| MSSP-OUT | 2,914,514 | 1997 | 1.71 | 1.68 | 4.1 | 3.5 |
| MSSP-OUT | 2,914,514 | 1998 | 1.68 | 1.68 | 4.2 | 3.5 |
| MSSP-OUT | 2,914,514 | 1999 | 1.74 | 1.68 | 3.5 | 3.5 |
| MSSP-OUT | 2,914,514 | 2000 | 1.74 | 1.70 | 2.3 | 3.5 |
| MSSP-OUT | 2,914,514 | 2001 | 1.79 | 1.71 | 3.1 | 3.5 |
| MSSP-OUT | 2,914,514 | 2002 | 1.67 | 1.73 | 4.3 | 3.5 |
| MSSP-OUT | 2,914,514 | 2003 | 1.77 | 1.74 | 3.5 | 3.5 |
| MSSP-OUT | 2,914,514 | 2004 | 1.81 | 1.76 | 3.5 | 3.5 |
| MSSP-OUT | 2,914,514 | 2005 | 1.92 | 1.76 | 2.7 | 3.5 |
| MSSP-OUT | 2,914,514 | 2006 | 1.97 | 1.76 | 2.4 | 3.5 |
| MSSP-OUT | 2,914,514 | 2007 | 1.93 | 1.78 | 3.1 | 3.5 |
| MSSP-OUT | 2,914,514 | 2008 | 1.49 | 1.83 | 4.6 | 3.6 |

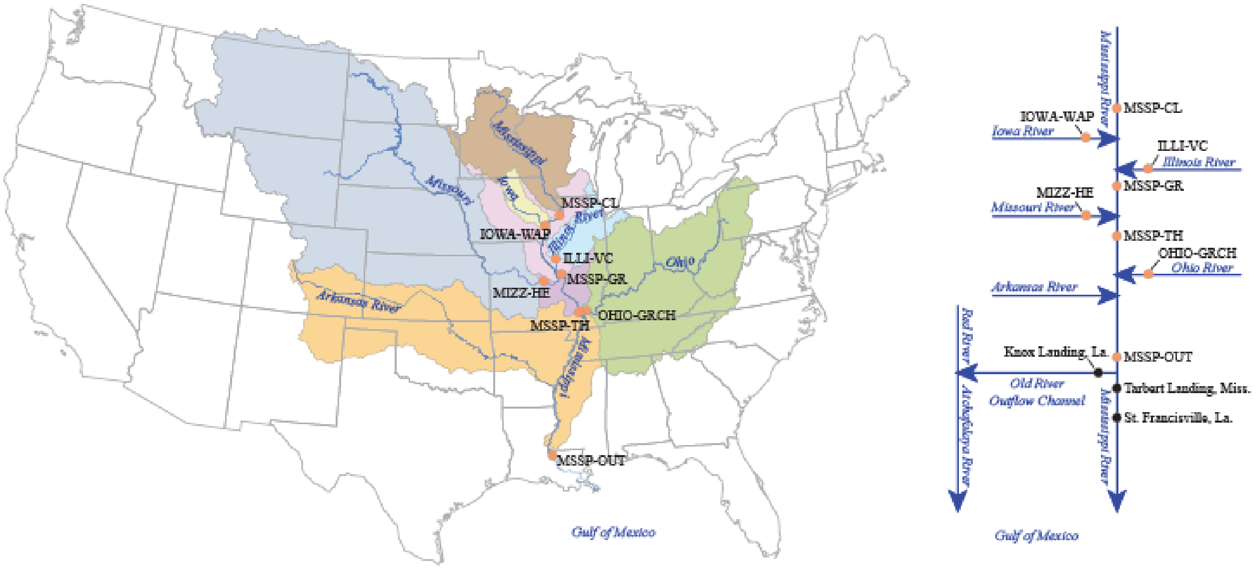

Figure SI-S1. Location of sampling sites in the Mississippi River basin.

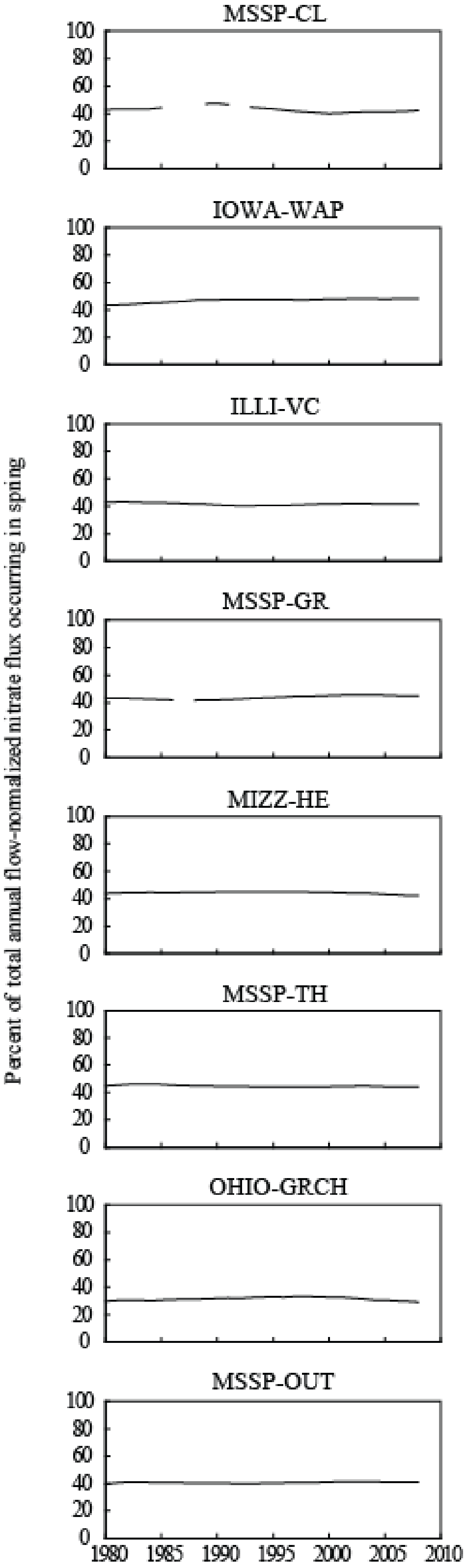

Figure SI-S2. Percent of total annual flow-normalized nitrate flux occurring in the spring (April, May, and June).

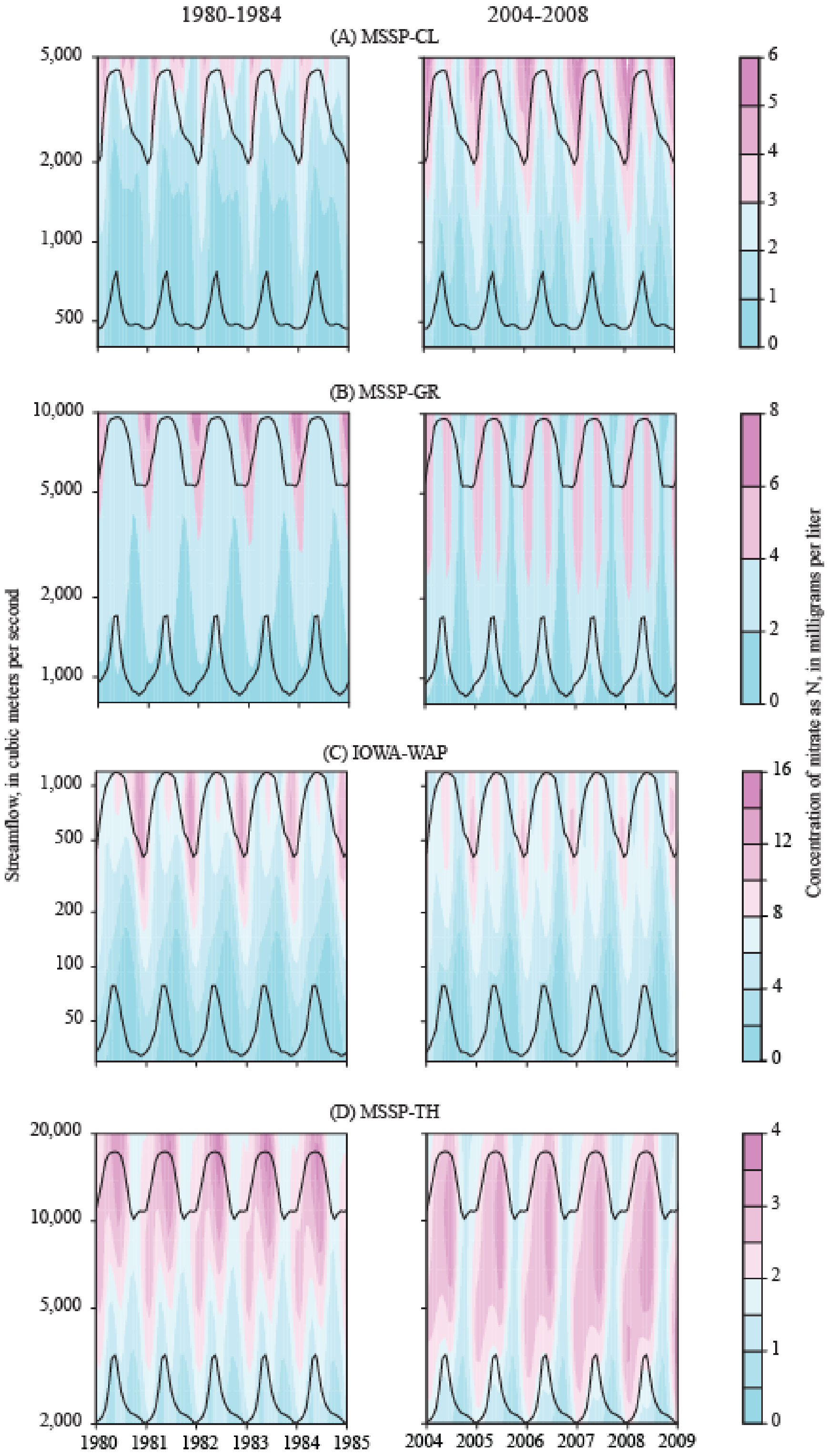

Figure SI-S3. Contour plots of expected nitrate concentration, in milligrams per liter. Upper black line represents the 95th percentile of streamflows; lower black line represents the 5th percentile of streamflows.

(Streamflow and concentration scales differ among sites.)

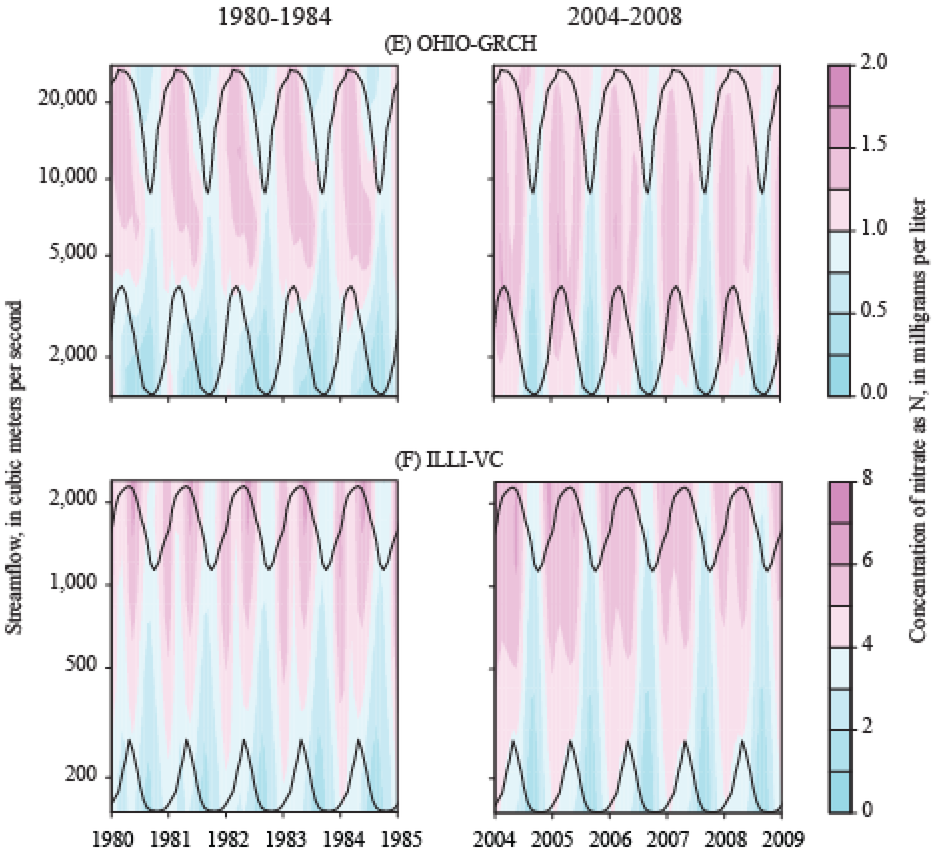

Figure SI-S3 Continued. Contour plots of expected nitrate concentration, in milligrams per liter. Upper black line represents the 95th percentile of streamflows; lower black line represents the 5th percentile of streamflows.

(Streamflow and concentration scales differ among sites.)

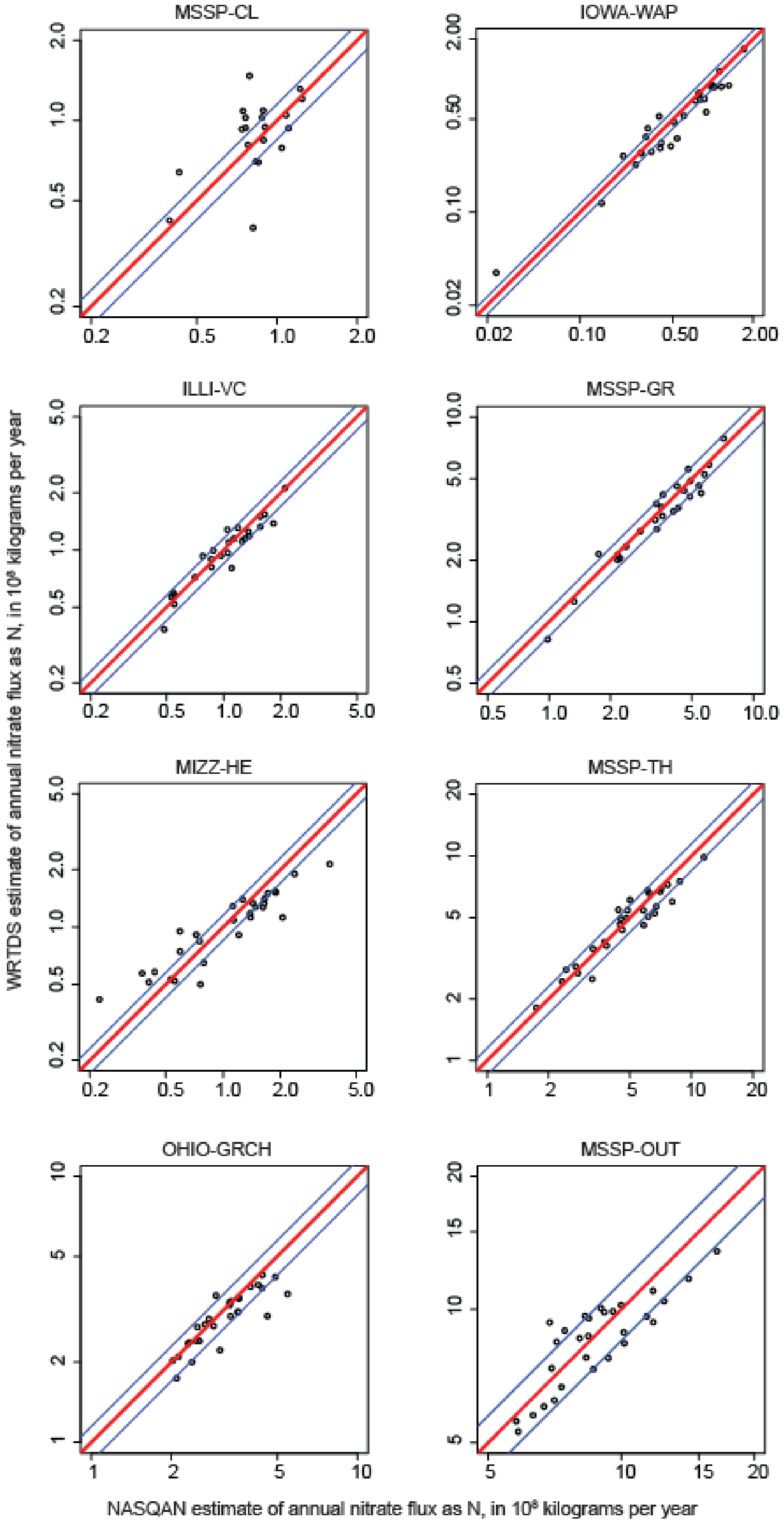

Figure SI-S4. WRTDS estimates versus NASQAN estimates of annual nitrate flux from 1980 to 2008. The red line represents perfect agreement; the blue lines represent differences of + or – 15%.

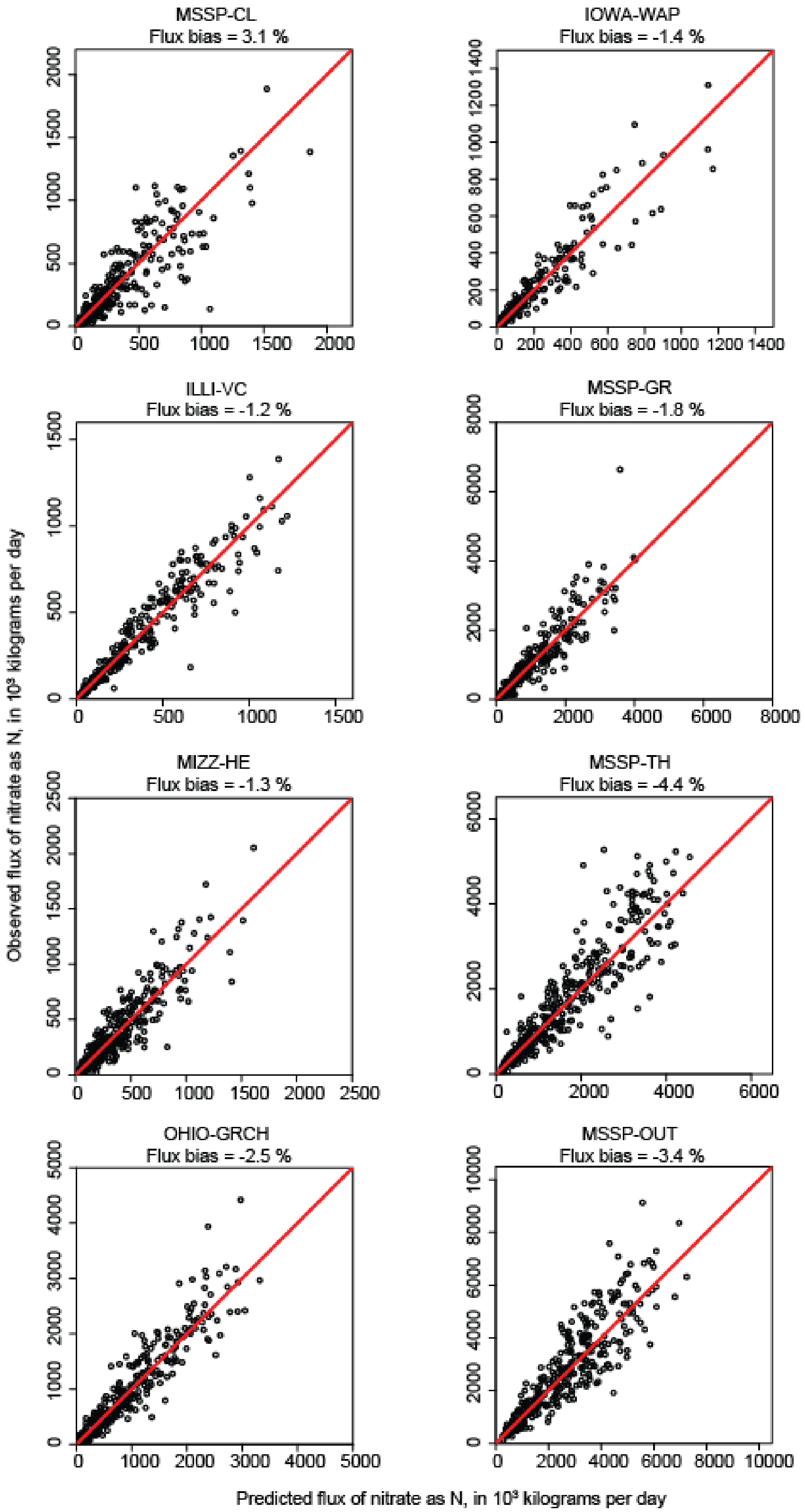

Figure SI-S5. Observed versus predicted daily nitrate flux on all sampled days from 1980 to 2008. The red line represents perfect agreement. Points plotted above the line indicate that the prediction was too low; those below the line indicate that the prediction was too high.