Load calculations

Discharge data used for load calculations were obtained via the Internet or electronic mail from the USGS/WRD and the USACE, St. Paul and Rock Island Districts. Whenever possible, data from the site nearest to the constituent monitoring location were used. When discharge data were not available from a location upstream of the constituent monitoring site, multiple-station regression equations and land-area ratios were used to estimate discharge (Gordon et al. 1992).

Discharge and constituent data were used to calculate mass transport (loads) in selected Mississippi River stations and tributaries. Software produced by the USGS (LOADEST2, Crawford 1998) was used to perform the loading calculations. This software was designed to accommodate missing values and measurements below constituent detection limits. The software produces daily loads from the following three rating curve methods: maximum likelihood parameter estimator, linear attribution parameter estimator, and least absolute deviation parameter estimator.

Rating curves are a statistically smoothed representation of empirical data. The rating curves relate discharge and day of the year to constituent concentration. The method used by LOADEST2 also incorporates any significant long-term trend in concentration. Once a curve is established, historical streamflow estimates are multiplied by the rating curve concentration for that given flow and date to give a daily load estimate. The rating curve approach works best with constituents that have strong relationships with flow and time of year, but is less successful for parameters such as NH_x-N and TSS that are less predictable. The rating curve approach does not directly use the instantaneous loads for days when constituents and discharge were both measured. In fact, the rating curve methods may give a result quite different from the instantaneous observed load depending on how well the constituent data fit the rating curve. This is reflected as residual variance, which is discussed later.

Daily load estimates were summed into monthly loads. In cases where some discharge estimates were missing, daily average load for a month was multiplied by the number of days in that month. Missing daily load estimates occurred when there was missing discharge data. Missing daily discharge could be estimated if there was a nearby station with a similar discharge regime as the target stream. If a target station had missing daily estimations, data from the nearby station were substituted using a regression-based conversion factor.

In addition to daily load estimates, LOADEST2 generates a single mean daily load estimate for the entire period of record using the Beale ratio estimator method (Crawford 1998). The Beale ratio estimator assumes a constant ratio between concentration and discharge and has been used to estimate nutrient loads entering the Great Lakes (Dolan et al. 1981, Richards and Holloway 1987, Preston et al. 1989). Average monthly load from the Beale ratio estimator is a single estimate for the entire period and cannot be used in time-series applications or in direct comparisons with monthly loads from the three rating curve methods. The three rating curve methods have high residual variance for NO_x-N and NH_x-N and tend to overestimate loads for streams where large discharge events were not sampled. In these situations, the Beale ratio estimator often results in lower load estimates for these two constituents. This does not mean that the Beale ratio estimator is superior, but that more data at large discharges need to be collected to improve the results of the rating curve methods (C. G. Crawford, U.S. Geological Survey, Indianapolis, Indiana; personal communication).

Additional outputs of LOADEST2 are useful for evaluating load estimates. For instance, the software generates the distribution of predicted concentrations used in load calculations. Differences between predicted and observed concentration distributions indicate a potential bias that can lead to erroneous load estimations. For example, there were several cases where the maximum predicted NO_x-N and NH_x-N concentration were higher than any measured concentration for a particular tributary or any monitored tributary. LOADEST2 also generates estimated residual variance for the maximum-likelihood estimate of best-fit model and the linear attribution estimate of best-fit model. The residual variance reflects lack of fit between the observed data and the rating curve equation (Table 1).

Data Screening

Some concentration data were determined to be erroneous or overly influential and were not used for generating the rating curves. This screening process was used with LTRMP and USGS/WRD data for the most part. In these cases, the available laboratory records were reviewed for any indication of problems. Additional outliers were identified by comparing the measured concentrations with the mean observed value for that level of river discharge. Values were designated as overly influential if they were more than double or less than a quarter of the next highest concentration at a given

Table 1. Residual variance expressed as upper and lower confidence intervals of LOADEST2 material load estimates. Upper and lower cutoffs listed are one standard error (log transformed) above and below the predicted value expressed as a percent of the predicted value. There is about a 67% probability that the actual value falls within one standard error of the predicted. Cutoffs were developed by Riggs (1968) and Hardison (1969).

Residual varianace (base e)	Upper cutoff (percent)	Lower cutoff (percent)
0.01	10.5	- 9.5
0.02	15.2	-13.8
0.05	25.1	-20.0
0.1	37.2	-27.1
0.2	56.4	-36.1
0.3	72.9	-42.2
0.4	88.2	-46.9
0.5	103.0	-50.7
0.6	117.0	-53.9
0.7	131.0	-56.7
0.8	145.0	-59.1
1.0	172.0	-63.2
1.2	199.0	-66.6
1.4	226.0	-69.4
1.6	254.0	-71.8
2.0	311.0	-75.7
2.5	386.0	-79.4
3.0	465.0	-82.3

discharge. All outliers were recorded in the "background information on load calculations" files. On average, less than one outlier per constituent per site was removed. Chloride concentrations were the most frequent outliers, often having values much greater than expected. The presence or removal of outliers significantly influenced rating curves, and consequently load estimates, only when few samples were available for a given discharge. Sufficient data availability at extreme high and low flow conditions mediated the potential influence of outliers, and presumably increased rating curve accuracy.

Results from the three rating curve methods should be compared to assess the uncertainty of the load estimates. Similarity of loading estimates generated by the three rating curve methods is one measurement of the accuracy for load estimations (C. G. Crawford, U.S. Geological Survey, Indianapolis, Indiana; personal communication). Concordance between the Beale ratio estimator and the other three methods further indicated that the load estimates were robust.

The floods of 1993 and 1997 in the UMR may have temporarily disturbed the nitrogen transport patterns of the river, and loads calculated from these years may not reflect the long-term average of the UMR. Annual discharge often varies over a much greater relative range than does the concentration of dissolved elements in large-order streams (Hill 1986). Consequently, yearly differences in discharge of tributaries can dramatically affect annual nutrient exports to the main river. We believe that the 1993 flood was the major cause of the negative trends for TN concentration that were observed for all LTRMP tributary sites monitored from 1991-1998. The flood of 1993 may have exported some of the stored TN out of the basin and lowered TN storage and transport. From 1997 through 1998, the TN concentrations in most tributaries appear to be steady or increasing. Because floods are a part of natural cycles, we included the data from 1993 and 1997 in load estimations.

Data for loads and concentrations generated from the LTRMP stations may not have an adequate period of record to use for average estimates. Hill (1986) discussed the sampling effort required to estimate mean springtime NO_3^--N loads in the Nottawasaga River and Duffin Creek in Ontario with an error less than 20%. Six to seven years of data was required at different sampling frequencies depending on discharge. Sampling was required every 3 - 4 d for high discharge periods and only once every 2 - 3 wk for low discharge periods. Data from the USGS/WRD used for tributary analysis have 2-3 times the period of record as the LTRMP sites. These sites should give approximate average annual loads that are not improperly influenced by single droughts and floods. Continued monitoring of LTRMP sites will be very useful for estimating average annual yields for tributaries that the USGS/WRD did not monitor and will be useful for comparative purposes for tributaries that the USGS/WRD has stopped monitoring. Monitoring programs should be designed to account for long-term oscillations rather than 1- to 6-yr programs where trends can be affected by short-term climatic variability.

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