

# Annual Dissolved Nitrite Plus Nitrate and Total Phosphorous Loads for the Susquehanna, St. Lawrence, Mississippi—Atchafalaya, and Columbia River Basins, 1968—2004



Open-File Report 2006-1087

Cover photograph: Image from the Multi-angle Imaging SpectroRadiometer (MISR) highlights coastal areas of three states along the Gulf of Mexico: Louisiana, Mississippi, and Alabama—including the Mississippi River Delta.

Photograph credit: NASA/Goddard Space Flight Center/Langley Research Center/Jet Propulsion Laboratory, MISR Team, October 2001

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By Brent T. Aulenbach

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U.S. Department of the Interior U.S. Geological Survey

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## Annual Dissolved Nitrite Plus Nitrate and Total Phosphorous Loads for the Susquehanna, St. Lawrence, Mississippi—Atchafalaya, and Columbia River Basins, 1968–2004

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### **Abstract**

Annual stream-water loads were calculated near the outlet of four of the larger river basins (Susquehanna, St. Lawrence, Mississippi-Atchafalaya, and Columbia) in the United States for dissolved nitrite plus nitrate (NO<sub>2</sub> + NO<sub>3</sub>) and total phosphorus using LOADEST load estimation software. Loads were estimated for the period 1968-2004; although loads estimated for individual river basins and chemical constituent combinations typically were for shorter time periods due to limitations in data availability. Stream discharge and water-quality data for load estimates were obtained from the U.S. Geological Survey (USGS) with additional stream discharge data for the Mississippi-Atchafalaya River Basin from the U.S. Army Corps of Engineers. The loads were estimated to support national assessments of changes in stream nutrient loads that are periodically conducted by Federal agencies (for example, U.S. Environmental Protection Agency) and other water- and land-resource organizations. Data, methods, and results of load estimates are summarized herein; including World Wide Web links to electronic ASCII text files containing the raw data. The load estimates are compared to dissolved NO<sub>2</sub> + NO<sub>3</sub> loads for three of the large river basins from 1971 to 1998 that the USGS provided during 2001 to The H. John Heinz III Center for Science, Economics and the Environment (The Heinz Center) for a report The Heinz Center published during 2002. Differences in the load estimates are the result of using the most up-to-date monitoring data since the 2001 analysis, differences in how concentrations less than the reporting limit were handled by the load estimation models, and some errors and exclusions in the 2001 analysis datasets (which resulted in some inaccurate load estimates).

### Introduction

Stream-water constituent load, often referred to as mass flux, is the mass of a chemical constituent or sediment

transported past a point in a stream during a set period. From a watershed perspective, loads serve as an integrated measure of all processes within the watershed that affect water quality (Semkin and others, 1994). From a downstream perspective, loads quantify the transport of chemical constituents to a receiving water body such as a bay, an estuary, a lake, an ocean, or a reservoir. Loads can be used to assess the effectiveness of controls of nonpoint-source pollutants on water quality.

### **Stream-Water Nutrient Loads**

Nutrient loads such as nitrogen and phosphorus play an important role in ecosystems. While nutrients are vital for ecosystem functioning, increased nutrient loads have led to excessive algal growth and eutrophication of surface waters, resulting in reduced sunlight, loss of aquatic habitat, and the degradation of water quality for drinking and recreational use. When algae dies, it sinks to the bottom of the water column, decays, and consumes oxygen. If the water column is stratified, the oxygen levels at depth are not replenished, resulting in low oxygen conditions (hypoxia) or a complete lack of oxygen. Levels of oxygen can become too low to support fish and other aquatic species.

The effects of excess nutrients on ecosystems have been documented. One example is the eutrophication of many surface waters in the United States and Canada during the mid-1960s as the result of high phosphorus loads attributed largely to the use of phosphate detergents (Knud-Hansen, 1994). This resulted in the regulation and/or banning of phosphate in detergents in Canada and in many cities and states in the United States during the 1970s and 1980s, effectively reducing phosphorous loads in some surface waters. Another example is the development of a hypoxic zone in the Gulf of Mexico during some summers (for example, Committee on Environmental and Natural Resources, 2000; Rabalais and Turner, 2001). Scavia and others (2003) have shown that the areal extent of the hypoxic zone is related to the May–June total nitrogen loads for the Mississippi–Atchafalaya River Basin.

Tracking stream nutrient loads over time is an important task for assessing changes in loads in response to changes in natural and anthropogenic influences on water quality. Federal management (for example, U.S. Environmental Protection Agency, 2003) and water-resource agencies (for example, USGS; Smith and others, 1993) periodically have compiled information on the state of water quality in U.S. rivers to promote understanding of the state of water resources throughout the United States and to document changes over time. A previous report (The Heinz Center, 2002) identified four of the larger U.S. rivers with the intent of obtaining a representative perspective on changes in the status of stream nitrate loads over time in major U.S. rivers. This information is considered useful as an indicator of broad geographic changes that have occurred in nitrogen in streams of the United States.

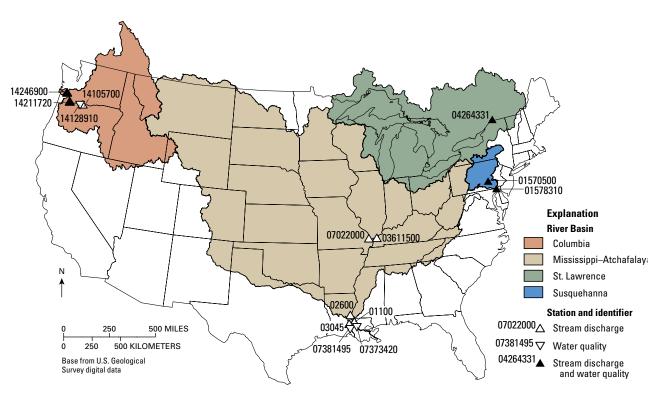
### **Purpose and Scope**

The purpose of this report is to estimate and document dissolved nitrite plus nitrate ( $\mathrm{NO_2} + \mathrm{NO_3}$ ) and total phosphorus (TP) loads on an annual basis for four of the larger river basins in the United States (Columbia, Mississippi–Atchafalaya, St. Lawrence, and Susquehanna; fig. 1) for data available for 1968 through 2004. The loads are useful to support national assessments of changes in stream nutrient loads that are conducted periodically by Federal agencies (for example, U.S. Environmental Protection Agency) and other water and landresource organizations. One such organization, The Heinz Center, is currently updating the estimates of nutrient loads

that were published previously for these four river basins in its 2002 published report "The State of the Nation's Ecosystems." The Heinz Center is a nonprofit institution for improving the scientific and economic knowledge used for environmental policy. The USGS previously had provided The Heinz Center in a 2001 analysis with NO<sub>2</sub> + NO<sub>3</sub> loads for three of the river basins for 1971 through 1998. Additional data not used in the 2001 analysis and some corrections to the original dataset are used for the analysis in this report and a discussion is included on the effects on the load estimates.

### Data

Sampling stations were chosen as far downstream as possible from stations that had long-term stream discharge and water-quality data so that the load estimates best represent the delivery of nutrients to coastal waters. Sampling stations are summarized in table 1. In several cases, the reported nutrient loads result from combining records of water quality and stream discharge values from nearby stations on the same river. In these cases, stations were considered close enough to each other as to reflect similar chemical and flow conditions. For the Columbia River and Susquehanna River Basins, data were available at individual stations for only part of the period of interest; therefore, loads were calculated using different station configurations at different times. Data from the USGS were obtained from the National Water Information System (NWIS) Web-based data-base (NWISWeb) at <a href="http://waterdata.usgs.gov/usa/nwis/nwis.">http://waterdata.usgs.gov/usa/nwis/nwis.</a>



**Figure 1.** River basins and locations of stream-water flow stations. Stations are labeled with identifications from table 1.

Table 1. Summary of data sources used for load estimation.

[Station identifications (ID) are identifiers used by source agency. mi², square mile; NA, not applicable. Data type: QW, water quality; Q, stream discharge; Q\* indicates upstream discharge used for regression model load modeling. Source: USGS, U.S. Geological Survey; USACE, U.S. Army Corps of Engineers]

Station ID (see fig. 1)	Station name	River basin	Drainage area (mi²)	Data type	Source	Relational database daily discharge file name
01570500	Susquehanna River at Harrisburg, Pennsylvania	Susquehanna	24,100	QW, Q	USGS	Q.Susquehanna.Harrisburg.rdb (http://ga. water.usgs.gov/download/ofr061087/)
01578310	Susquehanna River at Conowingo, Maryland	Susquehanna	27,100	QW, Q	USGS	Q.Susquehanna.Conowingo.rdb (http://ga. water.usgs.gov/download/ofr061087/)
04264331	St. Lawrence River at Cornwall, Ontario near Massena, New York	St. Lawrence	298,800	QW, Q	USGS	Q.StLawrence.Cornwall.rdb (http://ga.water. usgs.gov/download/ofr061087/)
07373420	Mississippi River near St. Francisville, Louisiana	Mississippi– Atchafalaya	1,144,949	QW	USGS	NA
07381495	Atchafalaya River at Melville, Louisiana	Mississippi– Atchafalaya	93,316	QW	USGS	NA
01100	Mississippi River at Tarbert Landing, Mississippi	Mississippi– Atchafalaya	1,125,300	Q	USACE	Q.Mississippi.TarbertLanding.rdb (http://ga. water.usgs.gov/download/ofr061087/)
02600	Old River Outflow Channel near Knox Landing, Louisiana (total outflow)	Mississippi– Atchafalaya	na	Q	USACE	Q.OldRiver.KnoxLanding.rdb (http://ga.water. usgs.gov/download/ofr061087/)
03045	Atchafalaya River at Simmesport, Louisiana	Mississippi– Atchafalaya	87,570	Q	USACE	Q.Atchafalaya.Simmesport.rdb (http://ga. water.usgs.gov.download/ofr061087/)
03611500	Ohio River at Metropolis, Illinois	Mississippi– Atchafalaya	203,000	Q*	USGS	Q.Ohio.Metropolis.rdb (http://ga.water.usgs. gov/download/ofr061087/)
07022000	Mississippi River at Thebes, Illinois	Mississippi– Atchafalaya	713,200	Q*	USGS	Q.Mississippi.Thebes.rdb (http://ga.water. usgs.gov/download/ofr061087/)
14105700	Columbia River at The Dalles, Oregon	Columbia	237,000	Q	USGS	Q.Columbia.Dalles.rdb (http://ga.water.usgs. gov/download/ofr061087/)
14128910	Columbia River at Warrendale, Oregon	Columbia	240,400	QW	USGS	NA
14211720	Willamette River at Portland, Oregon	Columbia	11,200	QW, Q	USGS	Q.Willamette.Portland.rdb (http://ga.water. usgs.gov/download/ofr061087/)
14246900	Columbia River at Beaver Army Terminal near Quincy, Oregon	Columbia	256,900	QW, Q	USGS	Q.Columbia.Quincy.rdb (http://ga.water.usgs. gov/download/ofr061087/)

Stream discharge data for the lower part of the Mississippi–Atachfalaya River Basin were obtained from the U.S. Army Corps of Engineers (USACE) Web site at <a href="http://www.mvn.usace.army.mil/eng/edhd/Wcontrol/discharge.htm">http://www.mvn.usace.army.mil/eng/edhd/Wcontrol/discharge.htm</a>. The USACE verified its data (USACE, written commun., various dates).

Loads were estimated for dissolved  $^{1}$  NO $_{2}$  + NO $_{3}$  and TP. For some time periods, dissolved NO $_{2}$  + NO $_{3}$  measurements were not available and other similar water-quality parameters were substituted (for example, "total" and "nitrate" only) so that loads could still be estimated (table 2). In other cases, additional samples analyzed only for the alternative water-quality parameters were used to supplement the existing dissolved NO $_{2}$  + NO $_{3}$  data. There was no significant difference between total and dissolved parameters (Rickert, 1992) and there was little difference between NO $_{2}$  + NO $_{3}$  versus just NO $_{3}$  as almost all of the NO $_{2}$  + NO $_{3}$  is in the form of NO $_{3}$ . Table 3 summarizes the number of water-quality samples used and which water-quality parameters were used for dissolved NO $_{2}$  + NO $_{3}$ .

 Table 2.
 Summary of water-quality parameters used.

[USGS, U.S. Geological Survey; mg/L milligram per liter; NO, nitrite; NO, nitrate; T, total; N, nitrogen; P, phosphorus]

Water-quality parameter name	Abbreviation	Unit	USGS parameter code
Nitrogen nitrite plus nitrate, dissolved	$NO_2 + NO_3$	mg/L as N	00631
Nitrogen nitrite plus nitrate, total	$T(NO_2 + NO_3)$	mg/L as N	00630
Nitrogen nitrate, dissolved	NO <sub>3</sub>	mg/L as N	00618
Nitrogen nitrate, total	TNO <sub>3</sub>	mg/L as N	00620
Phosphorus, total	TP	mg/L as P	00665

<sup>&</sup>lt;sup>1</sup>Dissolved is arbitrarily defined as the amount of material in the water after being passed through a 0.45-micrometer filter.

Table 3. Summary of water-quality data used for calibrating regression models.

[ID, identification; NO<sub>2</sub> + NO<sub>3</sub>, dissolved nitrite plus nitrate; TP, total phosphorous; USGS, U.S. Geological Survey; number of water-quality samples below the reporting limit are in parentheses]

Station ID (see fig. 1)	Station name	Number of NO <sub>2</sub> + NO <sub>3</sub> samples	Number of TP samples	USGS parameter code used for NO <sub>2</sub> + NO <sub>3</sub>	Periods of nitrate and nitrite data used
01570500	Susquehanna River at Harrisburg, Pennsylvania	337 (0)	453 (7)	00630 00631	2/74–8/79 9/79–8/95
01578310	Susquehanna River at Conowingo, Maryland	643 (0)	653 (23)	00631	1/79-12/02
04264331	St. Lawrence River at Cornwall, Ontario near Massena, New York	170 (1)	184 (27)	00630 00631	1/74–8/79 9/79–9/96
07373420	Mississippi River near St. Francisville, Louisiana	509 (2)	362 (1)	00620 00618 00618, 00620, 00631 00630, 00631 00631	10/67–5/72 1/73–8/73 8/73–9/74 10/74–9/79 10/79–9/93 11/93–6/04
07381495	Atchafalaya River at Melville, Louisiana	333 (0)	334 (0)	00630 00630 00631	8/78–9/79 10/79–9/93 11/93–6/04
14128910	Columbia River at Warrendale, Oregon	135 (23)	134 (2)	00630 00631	1/75–8/79 9/79–8/93
14211720	Willamette River at Portland, Oregon	156 (0)	156 (0)	00630 00631	2/75–8/79 9/79–12/93
14246900	Columbia River at Beaver Army Terminal near Quincy, Oregon	123 (8)	123 (8)	00631	1/92-12/02

When there was more than one, but fewer than four waterquality samples collected on the same day, the concentration for the first sample of the day was used. If there were four or more samples collected for a given day, that day was excluded from the calibration dataset because these cases typically indicate special-purpose sampling (e.g., cross-sectional, intensive storm hydrograph) was conducted, which is not representative of the daily average concentration of interest in this analysis.

Sample water-quality and daily stream-water data used in the analyses are available electronically for download from the Internet. The water-quality data file has the name QW.rdb and can be downloaded at the Internet address <a href="http://ga.water.uses.gov/download/ofr061087/">http://ga.water.uses.gov/download/ofr061087/</a>. Flow data file names and Internet addresses are listed in table 1. Data files are in RDB (relational database management system) format. RDB files are tab-delimited text (American Standard Code for Information Interchange, ASCII) files. In RDB format, comment lines begin with a #. The data start with a header line containing the variable names, followed by a line containing variable length and type information, followed by lines for each record with the data. Data are included only for years that have estimated loads even if data for other years are available.

### **Methods**

The regression-model method employed to estimate loads herein is described in the next section. Specific details about station configuration and data used to estimate loads within each river basin are found in the successive section.

### **Load Estimation**

Stream-water chemical constituent load  $(\Phi)$  is the product of constituent concentration (C) and discharge (Q) integrated over time (t):

$$\Phi = \int C(t)Q(t)dt \tag{1}$$

Load estimation using the integral in equation 1 requires a continuous record of concentration and discharge. Although discharge can be easily measured at a sufficiently high frequency, constituent concentration typically is measured less frequently due to the expense of collecting and analyzing samples for water-quality concentration. Therefore, concentration must be estimated between relatively infrequent samples.

The regression-model method, also known as the rating-curve method, is a standard statistical technique for estimating C(t) that uses a regression model relating concentration to continuous variables such as discharge and day of year (for example, Johnson, 1979; Cohn and others, 1992), thus enabling a direct calculation of equation 1. Consistent with many past studies, a seven-parameter regression model equation was fit with the form (Cohn and others, 1992; Runkel and others, 2004, LOADEST model number 9):

$$\begin{split} \ln(L_i) &= a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi dtime) + \\ &a_4 \cos(2\pi dtime) + a_5 dtime + a_6 dtime^2 + \varepsilon \end{split} \tag{2}$$

where

ln is the natural logarithm (log base e);

 $L_i$  is the calculated load for sample i;

lnQ is ln(daily average streamflow) – center of

ln(daily average streamflow);

dtime is decimal time – center of decimal time;

ε is error; and

 $a_0...a_6$  are the fitted parameters in the multiple regression model.

Note that the sample concentration has been multiplied by the daily average discharge so that equation 2 is a function of load instead of concentration, and that this modification has no effect on the resulting load estimates. The model in equation 2 captures the dependence of concentration on discharge and season (the sine and cosine terms) and any long-term trend. The load estimates are sensitive to the accuracy of the fitted model. All model terms were retained in the models, even when the model parameters were not significant, to simplify calculation of models across all sites and constituents. Inclusion of the insignificant terms does not change the load estimates appreciably, and the estimation of any additional parameters caused only a small proportional decrease in the degrees of freedom in the regression because of the large number of observations available. Average daily discharge was used instead of the instantaneous discharge when the sample was collected because instantaneous discharge was typically not available.

The integral in equation 1 for load was estimated in a discrete manner using the model in equation 2 with a daily time step, which was then summed for the period of interest:

$$L_T = \Delta t \sum_{i=1}^{n} L_i \tag{3}$$

where

 $L_r$  is the total load;

 $L_i$  is the predicted load for day i from equation 2;

*n* is the number of days;

 $\Delta t$  is the daily time step; and

 $\Sigma$  is a summation.

The average daily discharge was used to estimate  $L_i$ . The use of a daily time-step should be adequate for the calculation of annual loads of large rivers because stream-water concentration and discharge do not change radically within a given day.

Loads were estimated using Load Estimator (LOADEST), a FORTRAN based load estimation program (Runkel and others, 2004). LOADEST estimates loads using various algorithms for different statistical distributions of the data and correction factors for back-transformation bias corrections from a log model back to linear space. Results from the adjusted maximum likelihood estimates (AMLE) are used in this report, which modifies equation 2 to correct for transformation bias. LOAD-EST also handles censored (concentrations below the reporting limit) water-quality data by inferring the censored sample concentrations from the statistical distribution of sample concentrations above the reporting limit.

### **River Basin Specific Load Methodology**

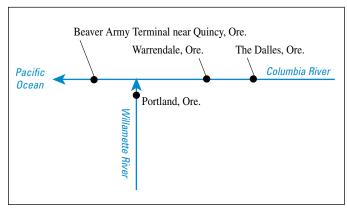
Details on station data and time periods used for each river basin are summarized in table 4. Due to changes in the availability of water-quality sampling and streamflow measurements from different stations, two different combinations of water quality and stream discharge stations are used during different time periods in the Susquehanna and Columbia River Basins. These periods overlap by 17 years for the Susquehanna River and 2 years for the Columbia River, providing two annual load estimates for each overlapping year which can be used for comparisons. In the Susquehanna River Basin, the drainage area of the downstream station at Conowingo, Maryland, was 12.4 percent larger than the upstream station at Harrisburg, Pennsylvania. Flows were 16.7 percent higher at Conowingo than at Harrisburg for the 17-year overlapping period. In the Columbia River Basin (fig. 2), the drainage area of the downstream station at Beaver Army Terminal near Quincy, Oregon, was 3.5 percent larger than the upstream stations Columbia River at The Dalles and Willamette River at Portland, Oregon. Flows were 12.7 percent higher at Beaver Army Terminal than at the upstream stations for the 2-year overlapping period. If yields (loads per unit area) in these river basins are similar for the upstream basin and the intervening drainage area between the upstream and downstream stations, one would expect loads from the downstream stations to be proportionally higher due to the increase in drainage areas.

The model structure in equation 2 was modified for the Mississippi–Atchafalaya River Basin. These models used only a linear decimal time term (Runkel and others, 2004, LOADEST model number 8). The Mississippi River models also included flow terms (both flow and flow-squared terms) from two upstream stations (Mississippi River at Thebes and Ohio River at Metropolis, Illinois; tables 1 and 4) in addition to the flow from the sampling station. Upstream flows were lagged 10 days to account for travel time between the streamflow stations and the sampling station. These upstream flow terms improved model predictions because of the different nutrient characteristics that exist between the Ohio River and the Upper Mississippi River Basins.

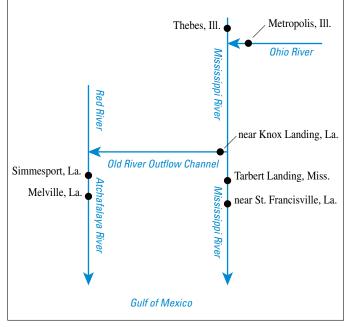
**Table 4.** Summary of station data and time periods used for load estimation.

River basin	Time period	Water-quality station name and identification (see fig. 1)	Discharge station name and identification (see fig. 1)
Susquehanna	1971–1995¹	Susquehanna River at Harrisburg, Pennsylvania (01570500)	Susquehanna River at Harrisburg, Pennsylvania (01570500)
Susquehanna	1979–2002	Susquehanna River at Conowingo, Maryland (01578310)	Susquehanna River at Conowingo, Maryland (01578310)
St. Lawrence	1974–1996	St. Lawrence River at Cornwall, Ontario near Massena, New York (04264331)	St. Lawrence River at Cornwall, Ontario near Massena, New York (04264331)
Mississippi– Atchafalaya	1968–2004 <sup>2</sup>	Mississippi River near St. Francisville, Louisiana (07373420) Atchafalaya River at Melville, Louisiana (07381495)	Mississippi River at Tarbert Landing, Mississippi (01100) Old River Outflow Channel near Knox Landing, Louisiana (total outflow) (02600) Atchafalaya River at Simmesport, Louisiana (03045) Ohio River at Metropolis, Illinois³ (03611500) Mississippi River at Thebes, Illinois³ (07022000)
Columbia	1975–1993	Columbia River at Warrendale, Oregon (14128910)	Columbia River at The Dalles, Oregon (14105700)
Columbia	1975–1993	Willamette River at Portland, Oregon (14211720)	Willamette River at Portland, Oregon (14211720)
Columbia	1992–2002	Columbia River at Beaver Army Terminal near Quincy, Oregon (14246900)	Columbia River at Beaver Army Terminal near Quincy, Oregon (14246900)

<sup>&</sup>lt;sup>1</sup>NO<sub>2</sub> + NO<sub>3</sub> (nitrite plus nitrate); loads 1974–1995.



**Figure 2.** Schematic diagram of Columbia River Basin and sampling stations.



**Figure 3.** Schematic diagram of Mississippi–Atchafalaya River Basin and sampling stations.

<sup>&</sup>lt;sup>2</sup>Total phosphorus loads for Mississippi River 1975–2004; Atchafalaya River loads 1979–2004.

<sup>&</sup>lt;sup>3</sup>Indicates an upstream stream discharge that is included in the regression model for modeling load.

For modeling purposes, the at-site flow used for the Mississippi River models was a combination of flows from the Mississippi River at Tarbert Landing, Mississippi, and the Mississippi River flows diverted upstream of Tarbert Landing by the Old River Diversion to the Atchafalaya, because this combined flow would be the natural flow associated with the variations in nutrient concentrations (fig. 3). After the Mississippi River load was estimated using this combined at-site flow, the portion of the load transported in the Mississippi River at Tarbert Landing to the Gulf of Mexico is determined by multiplying the load by the portion of flow transported in the Mississippi River at Tarbert Landing. This partitioning was done on a daily basis. The flow and loads diverted by the Old River Diversion are included in the Atchafalaya River load estimates.

For the Columbia, St. Lawrence, and Susquehanna River Basins, all water-quality samples were included to calibrate the regression models for the entire period of estimation. A different sample/model calibration scheme was used for the Mississippi-Atchafalaya River Basin. The first 10 years of loads are calculated using the first 10 years of available waterquality data. Each subsequent year of load estimates were calculated using samples from the current year and the previous 9 years. This "moving window" approach allows a sufficient number of samples in each model run to represent the full range of flow and nutrient concentration conditions. A July through June annual calculation period was used for Mississippi-Atchafalaya River Basin loads to coordinate with surveys of the Gulf of Mexico hypoxic zone (Rabalais and others, 2001), which annually requires spring loads to be estimated by mid-July; but calendar year load estimates are reported herein.

### **Results**

Annual loads are summarized in table 5 for  $NO_2 + NO_3$  and in table 6 for TP. Note that a dominant factor in controlling year-to-year variability in loads is the amount of annual runoff. Annual average concentrations can be computed using the annual loads with the annual average stream discharges reported in table 7. Basin yields, loads per unit area, also can be computed using the basin drainage areas in table 1.

### **Discussion**

Comparisons of loads from different station configurations for periods with overlapping annual loads are discussed in the next section. Comparisons of  $NO_2 + NO_3$  annual loads estimated herein with previously estimated  $NO_2 + NO_3$  loads are found in the successive section.

## Comparison of Overlapping Annual Loads from Different Station Configurations

On the Susquehanna River, the downstream station at Conowingo, Maryland, had lower TP loads (14 percent) and higher  $NO_2 + NO_3$  loads (26 percent) than the upstream station at Harrisburg, Pennsylvania, for the 17 overlapping years (1979–1995). The decrease in TP loads indicates a loss of TP between these stations. The increase in  $NO_2 + NO_3$  is greater than the increase in drainage area (12 percent) and flows (17 percent) along this stream segment, indicating that yields of  $NO_2 + NO_3$  are higher for this intervening basin than for the basin upstream of the upstream station.

On the Columbia River, the downstream station at Beaver Army Terminal near Quincy, Oregon, had much greater TP loads (57 percent) and higher NO<sub>2</sub> + NO<sub>3</sub> loads (8.6 percent) than the upstream station configuration (Columbia River at Warrendale and The Dalles, and Willamette River at Portland, Oregon) for the two overlapping years (1992 and 1993). These differences cannot be explained fully from the increase in drainage area of the downstream station (3.5 percent). The increase in NO<sub>2</sub> + NO<sub>3</sub> loads is not too different compared to the increase in flow between the upstream stations and the downstream station of 12.7 percent. The much larger increase TP loads indicates a much higher yield of TP in the intervening basin between the upstream and downstream stations.

The above observations need to be considered when choosing how to combine load estimates from different stations to make a longer time series of loads; scaling would be necessary. For years in which multiple loads are estimated within a single basin, the downstream loads generally are preferable because these better represent the entire transport of nutrients from that basin. A recommendation for use of loads for the Susquehanna River is to use the loads from Harrisburg through 1978 and then use the loads from the downstream station at Conowingo from 1979 through 2002. A recommendation for use of loads for the Columbia River is to use the loads from the upstream station configuration (Columbia River at Warrendale and The Dalles, and Willamette River at Portland) through 1993 and then use the loads from the downstream station at Beaver Army Terminal for 1994 through 2002. The upstream station configuration was chosen for the two overlapping years (1992 and 1993) because the record was so much longer for that station configuration. Note that the differences in the loads between stations also may be indicative of the possible differences one might expect to observe between the stations used to estimate loads and the actual bay, gulf, or ocean.

**Table 5.** Annual (calendar year) stream-water dissolved nitrite plus nitrate loads in metric tons in four major United States river basins. [—, data unavailable; see figure 1 for locations]

	Susquehanna River Basin		St. Lawrence River Basin		sippi–Atcha River Basin	falaya		Columbi	a River Basin	
Year	Susquehanna River at Harrisburg, Pennsylvania	Susquehanna River at Conowingo, Maryland	St. Lawrence River at Cornwall, Ontario near Massena, New York	Mississippi River near St. Francisville, Louisiana	Atchafalaya River at Melville, Louisiana	Total Mississippi– Atchafalaya River Basin	Columbia River at Warrendale, Oregon	Willamette River at Portland, Oregon	Total Columbia River at Warrendale and Willamette River at Portland, Oregon	Columbia River at Beaver Army Terminal near Quincy, Oregon
1968	_	_	_	204,000	_	_	_	_	_	_
1969	_	_	_	256,000	_	_	_	_	_	_
1970	_	_	_	268,000	_	_	_	_	_	_
1971	_	_	_	255,000	_	_	_	_	_	_
1972	_	_	_	395,000	_	_	_	_	_	
1973	_	_	_	573,000	_	_	_	_	_	_
1974	29,600	_	46,800	560,000	_	_	_	_	_	_
1975	36,600	_	45,000	593,000	_	_	25,400	22,700	48,100	_
1976	34,500	_	51,200	368,000	_	_	30,800	16,600	47,500	
1977	41,000	_	44,200	429,000	_	_	21,500	16,700	38,200	_
1978	35,400	_	49,800	579,000	_	_	31,900	12,200	44,000	_
1979	44,200	50,600	49,600	867,000	336,000	1,200,000	31,500	15,000	46,500	_
1980	23,000	27,500	51,300	638,000	193,000	831,000	34,300	19,100	53,500	
1981	27,200	31,500	51,200	621,000	161,000	781,000	42,100	17,300	59,400	_
1982	31,300	36,600	53,000	1,010,000	235,000	1,240,000	53,800	25,400	79,200	_
1983	38,400	46,200	54,700	1,190,000	310,000	1,500,000	57,100	25,400	82,500	_
1984	43,800	55,200	59,500	1,070,000	269,000	1,340,000	53,200	20,300	73,500	
1985	31,500	37,400	61,500	926,000	241,000	1,170,000	48,700	9,890	58,600	_
1986	41,400	50,500	75,000	774,000	205,000	980,000	49,600	19,500	69,100	_
1987	31,800	39,700	71,700	508,000	159,000	666,000	38,100	13,800	51,900	_
1988	26,500	33,800	58,100	420,000	130,000	550,000	36,000	14,800	50,800	
1989	33,900	45,700	59,500	494,000	183,000	677,000	38,700	14,100	52,800	_
1990	49,000	61,100	64,900	700,000	183,000	882,000	42,800	16,300	59,000	_
1991	30,300	38,900	69,500	817,000	191,000	1,010,000	42,700	15,400	58,100	_
1992	33,900	43,900	67,300	710,000	150,000	860,000	28,500	11,600	40,100	41,700
1993	43,300	62,200	80,900	1,390,000	292,000	1,680,000	25,700	18,100	43,800	49,500
1994	43,900	59,800	69,500	801,000	201,000	1,000,000	_	_	_	46,500
1995	26,200	34,200	67,700	770,000	206,000	976,000	_	_	_	77,000
1996		73,000	76,600	712,000	248,000	960,000				117,000
1997	_	34,300	_	699,000	250,000	949,000	_	_	_	103,000
1998	_	45,000	_	788,000	285,000	1,070,000	_	_	_	69,400
1999	_	29,000	_	657,000	230,000	887,000	_	_	_	88,800
2000		33,600		359,000	145,000	504,000				53,600
2001	_	22,300	_	704,000	216,000	920,000	_	_	_	31,900
2002	_	29,500	_	653,000	213,000	866,000	_	_	_	40,000
2003	_	_	_	530,000	193,000	723,000	_	_	_	_
2004	_	_		734,000	235,000	969,000	_	_	_	

**Table 6.** Annual (calendar year) stream-water total phosphorous loads in metric tons in four major United States river basins.

[—, data unavailable; see figure 1 for locations]

	Susquehanna River Basin		St. Lawrence River Basin		sippi–Atcha River Basin			Columbi	ia River Basin	
Year	Susquehanna River at Harrisburg, Pennsylvania	Susquehanna River at Conowingo, Maryland	St. Lawrence River at Cornwall, Ontario near Massena, New York	Mississippi River at St. Francisville, Louisiana	Atchafalaya River at Melville, Louisiana	Total Mississippi– Atchafalaya River Basin	Columbia River at Warrendale, Oregon	Willamette River at Portland, Oregon	Total Columbia River at Warrendale and Willamette River at Portland, Oregon	Columbia River at Beaver Army Terminal near Quincy, Oregon
1971	2,410	_	_	_	_	_	_	_	_	_
1972	8,310	_	_	_	_	_	_	_	_	_
1973	3,220	_	_	_	_	_	_	_	_	_
1974	2,820	_	7,630	_	_	_	_	_	_	_
1975	5,000	_	7,410	96,300	_	_	7,530	2,920	10,400	_
1976	3,630	_	7,040	70,300	_	_	9,300	2,210	11,500	_
1977	4,740	_	6,490	73,600	_	_	4,060	2,830	6,880	_
1978	4,100	_	6,530	89,800	_	_	7,270	1,810	9,080	_
1979	4,610	4,450	6,360	123,000	62,200	185,000	6,090	2,170	8,260	_
1980	2,200	1,830	6,140	82,500	34,500	117,000	6,950	2,950	9,900	_
1981	2,440	1,900	5,790	74,000	28,500	102,000	8,780	2,830	11,600	_
1982	2,650	1,990	5,620	109,000	45,200	155,000	12,600	3,760	16,300	_
1983	3,620	2,770	5,410	112,000	56,300	169,000	11,400	3,720	15,100	
1984	4,340	3,440	5,310	102,000	50,300	153,000	10,200	3,150	13,400	_
1985	1,960	1,470	5,090	83,600	47,400	131,000	6,960	1,580	8,540	_
1986	3,010	2,290	4,870	83,500	41,300	125,000	8,040	2,770	10,800	_
1987	1,930	1,450	4,640	57,100	29,100	86,200	4,820	1,950	6,770	
1988	1,490	1,130	4,070	57,100	26,200	83,300	4,270	2,070	6,350	_
1989	2,580	2,020	3,750	98,400	46,400	145,000	4,830	1,810	6,640	_
1990	2,820	2,390	4,020	97,600	51,600	149,000	5,620	2,010	7,620	_
1991	1,400	1,240	3,690	115,000	51,900	167,000	5,640	1,840	7,480	_
1992	1,540	1,420	3,580	98,700	37,300	136,000	2,980	1,360	4,340	6,530
1993	3,420	3,630	3,520	160,000	61,700	222,000	3,090	1,860	4,950	8,090
1994	2,860	2,990	3,320	114,000	36,600	150,000	_	_	_	5,970
1995	965	1,090	2,900	96,400	31,500	128,000	_	_	_	11,100
1996	_	4,160	3,100	97,800	36,600	134,000	_	_	_	18,300
1997	_	1,110	_	94,300	36,300	131,000	_	_	_	17,400
1998	_	2,080	_	103,000	38,800	142,000	_	_	_	10,100
1999		1,050		91,900	34,600	127,000				14,200
2000	_	1,440	_	65,700	25,300	91,000	_	_	_	8,270
2001	_	884	_	110,000	44,400	155,000	_	_	_	5,210
2002	_	1,460	_	116,000	48,200	164,000	_	_	_	8,730
2003		_		109,000	46,100	155,000				_
2004	_	_	_	137,000	56,900	194,000	_	_	_	_

 Table 7.
 Annual (calendar year) average streamflow in cubic feet per second in four major United States river basins.

[—, data unavailable; see figure 1 for locations]

	Susquehann	a River Basin	St. Lawrence River Basin	Miss	issippi–Atcl River Basi			Columbia	ı River Basin	
Year	Susquehanna River at Harrisburg, Pennsylvania	Susquehanna River at Conowingo, Maryland	St. Lawrence River at Cornwall, Ontario near Massena, New York	Mississippi River at Tarbet Landing, Mississippi	Atchafalaya River at Simmesport, Louisiana	Total Mississippi— Atchafalaya River Basin	Columbia River at Warrendale, Oregon	Willamette River at Portland, Oregon	Total Columbia River at Warrendale and Willamette River at Portland, Oregon	Columbia River at Beaver Army Terminal near Quincy, Oregon
1968	_	_	_	433,000	_	_	_	_	_	_
1969	_	_	_	457,000	_	_	_	_	_	_
1970	_	_	_	437,000	_	_	_	_	_	_
1971	33,200	_	_	388,000	_	_	_	_	_	_
1972	59,500	_	_	481,000		_	_	_	_	
1973	40,200	_	_	720,000	_	_	_	_	_	_
1974	36,000	_	300,000	586,000	_	_	_	_	_	_
1975	45,800	_	284,000	563,000	_	_	193,000	39,800	233,000	_
1976	39,400	_	300,000	364,000	_	_	215,000	28,400	244,000	
1977	45,200	_	262,000	379,000	_	_	117,000	27,300	144,000	_
1978	39,300	_	277,000	469,000	_	_	174,000	25,100	199,000	_
1979	44,300	52,300	276,000	708,000	304,000	1,010,000	150,000	29,800	179,000	_
1980	24,400	28,400	277,000	437,000	186,000	623,000	161,000	31,700	193,000	_
1981	27,100	30,400	270,000	363,000	156,000	519,000	188,000	32,600	220,000	_
1982	29,900	34,600	270,000	544,000	235,000	779,000	231,000	41,700	273,000	_
1983	36,200	41,900	270,000	682,000	293,000	975,000	218,000	43,100	261,000	_
1984	41,800	49,800	282,000	616,000	264,000	879,000	210,000	41,700	251,000	
1985	26,300	30,500	284,000	591,000	254,000	845,000	167,000	23,500	191,000	_
1986	35,400	41,200	316,000	519,000	223,000	741,000	187,000	32,400	220,000	_
1987	27,600	32,300	292,000	406,000	175,000	581,000	142,000	24,200	166,000	_
1988	23,000	27,200	246,000	375,000	160,000	535,000	138,000	29,100	167,000	_
1989	33,600	39,900	243,000	573,000	246,000	818,000	155,000	26,700	182,000	_
1990	41,400	48,300	266,000	614,000	263,000	878,000	184,000	30,200	215,000	_
1991	24,800	29,700	264,000	647,000	278,000	925,000	197,000	29,500	226,000	_
1992	30,300	35,500	264,000	470,000	201,000	671,000	139,000	21,200	160,000	179,000
1993	44,200	52,500	292,000	773,000	331,000	1,100,000	154,000	32,400	186,000	211,000
1994	45,500	51,700	264,000	556,000	238,000	794,000	_	_	_	178,000
1995	24,600	28,000	244,000	513,000	220,000	732,000	_	_	_	251,000
1996	_	63,500	278,000	562,000	241,000	803,000	_	_	_	323,000
1997	_	29,700	_	600,000	257,000	857,000	_	_	_	330,000
1998	_	41,300	_	604,000	259,000	862,000	_	_	_	248,000
1999	_	26,800	_	496,000	212,000	708,000	_	_	_	296,000
2000		34,300		337,000	144,000	481,000				216,000
2001	_	23,600	_	499,000	214,000	714,000	_	_	_	145,000
2002	_	33,400	_	532,000	228,000	760,000	_	_	_	214,000
2003	_	_	_	492,000	211,000	703,000	_	_	_	_
2004	_	_	_	581,000	249,000	831,000	_	_	_	

### Previous NO<sub>2</sub> + NO<sub>3</sub> Loads

During 2001, the USGS provided dissolved  $NO_2 + NO_3$  loads for the Columbia, St. Lawrence, and Susquehanna River Basins from 1971 through 1998 to The Heinz Center, which it used the 2002 report "The State of the Nation's Ecosystems." These loads are compared to the loads contained herein, whereas some of the differences in loads are minor, with the previous loads being sufficiently accurate, other loads are significantly different. Note that the loads from the 2001 analysis are not included in this report.

There were several reasons for minor differences in the loads. Changes in the water-quality sample datasets used to calibrate the regression model caused some minor differences. Changes in the water-quality datasets were caused by (1) slight changes in the sample selection included in the analysis; (2) additional samples which had similar water-quality parameters available to augment the dissolved NO<sub>2</sub> + NO<sub>3</sub> dataset, and; (3) additional samples related to the extension in the length of period analyzed for this most current analysis. The updated loads reflect the most up-to-date retrievals (data retrieved May 19-20, 2005) and selection of observations from the NWIS records and the use of the most current load estimation methods, though the loads estimated from the 2001 analysis are not considered to be in error except for the specific years noted below. The load estimation method used here was based on the AMLE procedure, which differs from the method used to calculate the 2001 load estimates. The 2001 analysis used the minimum variance unbiased estimator (Cohn and others, 1989), which is equivalent to the maximum likelihood estimation and the AMLE methods in LOADEST when there are no censored (concentrations less than the detection limit) data. The 2001 analysis estimated values below the detection limit by using one-half the detection limit, whereas the AMLE method, used in the analysis for this report, determines an expected distribution of sample concentrations below the detection limit when calculating the loads. Most stations had very few NO<sub>2</sub> + NO<sub>3</sub> concentrations below the detection limit, less than (<)1 percent, with the exception of the Columbia River at Beaver Army Terminal near Quincy, Oregon (6.5 percent), and the Columbia River at Warrendale, Oregon (17 percent; table 3). Hence, only the Columbia River loads were significantly affected by the one-half detection limit simplification.

For the Susquehanna River at Harrisburg, Pennsylvania, there were only minor differences between the 2001 and current load estimates, with differences always being less than 3 percent on an annual basis. One cause for the difference was that the 2001 calibration dataset had no available dissolved  $\mathrm{NO_2} + \mathrm{NO_3}$  concentrations from March 1974 through September 1979. For the current load estimates, an additional 101 samples were added to the calibration dataset for this missing period using data from the alternative parameter code 00630 (tables 2 and 3). Furthermore, the 2001  $\mathrm{NO_2} + \mathrm{NO_3}$  dataset had no water-quality data for 1973, although loads were estimated from 1971 through 1994. Because of this data

gap, the loads in this report were only estimated for 1974 through 1994.

For the Susquehanna River at Conowingo, Maryland, 90 percent of the annual loads differed by <5 percent, and 10 percent of the annual loads differed between 5 and 10 percent. The reason for the difference in annual loads was the length of the period of the calibration dataset; the 2001 load estimates spanning the period from 1979 to 1998, whereas the current load estimates were extended through 2002.

For the St. Lawrence River, the differences in annual load estimates from 1974 through 1987 were small, with only one year being greater than (>) 5 percent different. But starting with 1988, the differences are progressively larger, with the earlier load estimates underestimated by as much as 49 percent during 1996. These large differences in loads occurred because of the lack of any NO<sub>2</sub> + NO<sub>3</sub> concentrations at the end of the calibration period, from November 1985 through 1996, for the 2001 analysis. Regression models generally cannot accurately predict values outside the period of the calibration dataset. Furthermore, the inclusion of the time-squared term in the model allowed the errors to become much larger as one gets farther out from the calibration period. The current load estimates include an additional 51 samples in the calibration dataset, and provide a more accurate description of the annual loads during this period than those based on the 2001 report. Load estimates from the 2001 analysis should not be used from 1988 through 1996.

For the Columbia River at Warrendale, there were significant differences between the 2001 and current annual load estimates from 1975 to 1993; 5 percent of the loads differed by < 5 percent; 47 percent of the loads differed between 5 and 10 percent, and; 47 percent, of the loads differed by > 10 percent. One reason for the difference was the length of the period of the calibration dataset; the 2001 load estimates used data from 1975 to 1993, whereas the current load estimates were extended through 1998. The effect of using the simplification of setting censored values to one-half the detection limit in the 2001 analysis likely caused much of the differences observed. The Columbia River at Warrendale NO<sub>2</sub> + NO<sub>3</sub> dataset had 17 percent censored values along with much larger differences in loads compared to the differences in the Susquehanna River at Conowingo loads for which NO<sub>2</sub> + NO<sub>3</sub> dataset had no censored values.

For the Willamette River at Portland, Oregon, the differences in annual load estimates from 1975 through 1993 were generally small, with 74 percent of the loads differing by <5 percent and 26 percent of the loads differing by between 5 and 10 percent. However, the load estimates reported herein are recommended for use in place of those published in the 2001 analysis. Loads estimated in the 2001 analysis for 1994 through 1997 are incorrect—the flow data from water years (WY; defined as October 1 of previous year through September 30 of water year) 1996 to 1999 were mistakenly assigned the dates of WYs 1995 through 1998. This affected all load estimates from the 2001 analysis because the regression model calibration had the wrong flows assigned to the water-

quality samples from October 1994 through December 1997. Therefore, the 2001 analysis loads should not be used for the Willamette River. The Willamette River accounted for a significant portion (31 percent) of the total load from the sum of the Columbia River at The Dalles and the Willamette River at Portland for the period 1975–1993. Flow data were not available for the Willamette River at Portland for WY 1995; hence, the current analysis loads are for the 1975–1993 period. Loads for the Columbia River at Beaver Army Terminal from 1992 through 2002 in the current analysis were estimated for and can be used to extend the time period of loads for the Columbia River Basin.

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