Technical Information and Glossary

Technical information regarding the data and graphics on the U.S. Geological Survey National Water-Quality Assessment annual reporting Web site

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Background and Introduction

The U.S. Geological Survey (USGS) implemented the National Water-Quality Assessment (NAWQA) Project in 1991 to develop long-term consistent and comparable information on streams, rivers, groundwater, and aquatic systems in support of national, regional, state, and local information needs related to water-quality management and policy. A central goal of NAWQA since its inception is to assess the quality of the Nation's surface-water resources and to characterize how the quality of these resources changes over time.

Assessments of surface waters require consistent collection of data on the flow and quality of streams and rivers. The NAWQA Project and National Stream Quality Accounting Network (NASQAN) have been collecting stream-water-quality data in rivers across the United States since 1991 and 1973, respectively. At the beginning of the third decade (2013–2022) of the NAWQA Project, selected NAWQA, NASQAN, National Monitoring Network (NMN), and USGS Cooperative Water Program sites with historical streamflow and water-quality data were selected for inclusion in the USGS National Water Quality Network (NWQN) for Rivers and Streams which is operated by the USGS National Water Quality Program (NWQP). The NWQN is a network of 111 surface-water sites in which streamflow and water-quality data are collected in a consistent fashion, enabling long-term, consistent assessments of the quality of U.S. streams and rivers. The NWQN includes 20 large river coastal sites, 41 large river inland sites, 30 wadeable stream reference sites, 10 wadeable stream urban sites, and 10 wadeable stream agricultural sites (table 1). In addition to the 111 NWQP sites, 3 large inland river monitoring sites from the USGS Cooperative Water Program (table 1) are also included in this Web site to be consistent with previous USGS studies of nutrient transport in the Mississippi-Atchafalaya River Basin (Aulenbach and others, 2007).

The primary objectives of the NWQN are to:

- determine the status and trends in loads and concentrations of contaminants, nutrients, and sediment in the Nation's large rivers, including loads to selected major estuaries;
- determine the status and trends in concentrations of contaminants, nutrients, and sediment for wadeable streams in selected land-use and environmental settings; and
- determine trends in ecological condition in relation to trends in contaminants, nutrients, sediment, and streamflow alteration for wadeable streams in selected land-use and environmental settings.

The Water Quality Tracking Web site is the primary outlet for the reporting of NWQN data and findings. The current (2015) version of the Water Quality Tracking Web site provides information on the status of streamflow, nutrients, sediment, and pesticides at NWQN sites through 2015. Anticipated future updates to this Web site will expand the number of sites and constituents reported.

Table 1. National Water Quality Network sites

Table1.NWQN.sites.xlsx

Water-Quality Samples
The frequency of sample collection and the types of analyses obtained from samples have varied among NWQN sites through time. Beginning in 2013, the number of samples collected by NAWQA per year has varied by site type (Table 1). Fourteen water-quality samples are collected per year at the largest coastal and inland river sites, 6 of these samples are collected at bimonthly fixed intervals and the remaining 8 are collected at different fixed intervals during times of the year which have been historically characterized as having high-flow loads. This site-specific, seasonally weighted sampling scheme is designed to reduce the potential for introducing bias by specifically targeting high-flows. Slightly reduced sample collection (6 bimonthly samples and 6 seasonally weighted samples) is conducted at large river sites on the Rio Grande, the downstream Colorado River, and Columbia Rivers because fewer samples are needed from large river sites than from other sites to represent variability in constituent concentrations and loads. Additionally, only seven samples will be collected at the Yukon River because of seasonal access limitations. Eighteen samples are collected per year at other large inland river sites (6 at bimonthly intervals and 12 at seasonally weighted intervals), and 24 samples are collected per year at agricultural and urban indicator sites (12 fixed monthly samples and 12 seasonally weighted). With two exceptions, reference sites are sampled monthly with additional sample collection during periods in which sites are documented to have increased variability in constituent concentrations (Table 1). Andrews Creek near Mazama, WA and Talkeetna River near Talkeetna, AK reference sites have reduced sampling (approximately 7 and 8 samples collected per year respectively) because of difficulty accessing these sites during the cold season. Any samples collected by the USGS Cooperative Water Program or other USGS programs at NWQN sites are also presented on the Web site.

Methods of Sample Collection

Methods of sample collection used by the NWQN conform to the USGS National Field Manual for the Collection of Water-Quality Data. To the greatest extent possible, isokinetic, depth-integrated sampling techniques that provide samples representative of stream conditions are used. As of 2002, the US DH–2, US DH–81, US DH–95, US D–95, and US D–96 isokinetic samplers (Fig. 1) have been approved by the Interagency Technical Committee of the Subcommittee on Sedimentation and are used for water-quality and suspended-sediment sample collection. The report "A Guide to the Proper Selection and Use of Federally Approved Sediment and Water-Quality Samplers" discusses stream conditions suitable for the use of each sampler. Prior to 2002, the now superseded USGS Frame Bag, D–77, or D–77 bag samplers were commonly used (see section 2.1 of version 1 of USGS Techniques of Water-Resources Investigations, Book 9, Chapter A2 for details on these samplers).

Isokinetic depth-integrated samplers accumulate a representative water sample continuously and isokinetically—that is, stream water approaching and entering the sampler intake does not change in velocity—from a vertical section of a stream while transiting the section at a uniform rate (fig. 2).

Figure 2. Relation between intake velocity and sediment concentration for isokinetic and nonisokinetic collection of water samples that contain particulates greater than 0.062 millimeters; from Wilde (2006).

Collection of isokinetic, depth-integrated samples is done using either an equal-width-increment (EWI) or equal-discharge-increment (EDI) sampling method. The methods typically result in a composite sample that represents the streamflow-weighted concentrations of the stream cross section being sampled. The following material excerpted from Wilde and others (2014) describes these methods.

The EWI and EDI methods are used to divide a selected cross section of a stream into increments of a specified width. The term "vertical" refers to that location within the increment at which the sampler is lowered and raised through the water column. EWI verticals are located at the midpoint of each width increment. EDI verticals are located at the centroid, a point within each increment at which stream discharge is equal on either side of the vertical. If properly implemented, EDI and EWI methods should yield identical results.

For the EWI sampling method, the stream cross section is divided into a number of equal-width increments (fig. 3). Samples are collected by lowering and raising a sampler through the water column at the center of each increment. The combination of the same constant transit rate used to sample at each vertical and the isokinetic property of the sampler results in a discharge-weighted sample that is proportional to total streamflow.
The objective of the EDI method is to collect a discharge-weighted sample that represents the entire flow passing through the cross section by obtaining a series of samples, each representing an equal volume of stream discharge (Fig. 4). The EDI method requires that flow in the cross section be divided into increments of equal discharge.
Samples from small streams are commonly collected by means of a DH–81 sampler during wading in the stream (fig. 5). The DH–95 sampler is used to collect samples from shallow but nonwadeable streams and rivers (fig. 6). Both the DH–81 and DH–95 samplers collect water in a one liter fluorocarbon polymer (Teflon) bottle (fig. 6). [The use of firm, trade, and brand names is for identification purposes only and does not constitute endorsement by the U. S. Government.] A fluorocarbon polymer bottle is used to collect the sample because it is chemically inert to most chemicals occurring in water.

Currents in the large rivers sampled by the NWQN program require the use of heavy samplers (the D–96 sampler weighs 132 pounds and the D–99 weighs 275 pounds) to keep the sampler vertical in the current. Because of this weight, it is necessary to suspend the sampler from a crane assembly (fig. 7). Because of the large size of some of the rivers in the NWQN, samples can only be collected by boat (fig. 8). Because of the pressures involved at the greater depths sampled by the D–96 and D–99 samplers, a rigid bottle cannot be used with either of these samplers. To maintain the isokinetic properties of the sampler, a collapsible perfluoroalkoxy (Teflon-PFA) bag is used (fig. 9).

**Figure 4.** Equal-discharge-increment method for collection of water samples; from Wilde (2006).
See Rantz and others (1982) for a more complete description of cranes and associated equipment used to suspend water-sampling equipment. A more complete description of water-quality sampling by boat is available at U.S. Geological Survey (2003).

Figure 5. DH–81 water-quality sampler used to collect water samples from wadeable streams. Photograph from the U.S. Geological Survey Multimedia Gallery.
Figure 6. Teflon bottle (held by scientist) being prepared for insertion into DH–95 water-quality sampler (white object in lower center of photo) used for collecting a water sample from a boat in a shallow, slow-moving river. This sampler is suspended from a hand-held rope and can be used from either a boat or low bridge. Photograph from the U.S. Geological Survey Multimedia Gallery.
Figure 7. D–96 water-quality sampler suspended from crane used to collect water samples from nonwadeable rivers via a bridge. The crane is on wheels so that it can be easily moved between sampling verticals along the bridge. Photograph from the U.S. Geological Survey Multimedia Gallery.

Figure 8. D–96 water-quality sampler suspended from boat-mounted crane used to collect water samples from nonwadeable rivers by boat. Photograph by Timothy R. Lathrop, U.S. Geological Survey.
Water-Quality Analyses

Nutrients and Sediment

Samples collected from NWQN sites are analyzed for concentrations of suspended sediment, inorganic and organic carbon, and selected nutrients, pesticides, major ions, trace elements, and physical properties. Table 2 lists major ion, nutrient and sediment constituents reported in this (2017) version of the Water Quality Tracking Web site. A complete list of major ion, nutrient and sediment constituents collected at NWQN sites is provided as an attachment in table 3 below. Dissolved ammonia, dissolved orthophosphate, and dissolved silica are reported only for Mississippi-Atchafalaya River Basin sites because they have historically been reported as part of the NASQAN network (Aulenbach and others, 2007). Total and particulate analyses are not analyzed at reference sites.

Table 2. Constituents assessed through National Water-Quality Assessment annual reporting for water year 2013.
See for additional information about each constituent and parameter code. 

Total nitrogen can also be computed by using the sum of particulate nitrogen (USGS parameter code 49570) and dissolved total nitrogen as analyzed by alkaline persulfate digestion (USGS parameter code 62854) or by the sum of dissolved Kjeldahl nitrogen (USGS parameter code 00623) particulate nitrogen (USGS parameter code 49570), and dissolved nitrate plus nitrite (USGS parameter code 00631).

Table 3. Complete list of constituents collected at National Fixed Site Network sites

Data Preparation

Water-quality data have previously been screened, and loads have been computed for several NWQN sites in the Mississippi River Basin (table 1; Aulenbach and others, 2007) as part of the NASQAN program. These historical data have been prepared and computed through similar methods to those described herein, and thus these data are not recomputed so as to preserve historical records. Adjustments to NASQAN screening and load computations from 2013 forward are designed to simplify methods and improve the accuracy of load estimates. Data-preparation and load-computation methods described herein are applicable for all sites from 1993 forward, unless noted differently in table 1.

The USGS National Water Information System (NWIS) is the original repository for all streamflow and water-quality data served by the annual reporting Web site. Raw data from NWIS require preparation and screening to deal with inappropriate sample values, variation in analytical procedures through time, changes to the reporting of censoring levels for some water-quality parameters, and instances in which multiple samples were collected on the same day.

Removal of Inappropriate Samples

In addition to the standard water-quality samples used for load computation, NWIS contains (1) specialized water-quality samples such as composite samples, which are often collected over several days, and individual cross-section samples, which are obtained in sequence across a river; (2) other sample mediums, including analyses of bottom material and sediment; and (3) other sample types, including quality-assurance and -control samples, such as blanks, spikes, and reference samples. Initial water-quality data retrievals from NWIS include all data without regard to sampling approach, sample medium, or sample type. A sample screening process was developed to remove any samples not relevant to the computation of water-quality loads. Samples were removed if they were composite samples, were individual cross-sectional samples, or did not have the appropriate medium type or sample type code.

Samples were included in the analysis only if they had a medium code of WS or WSQ (surface-water sample), SS or SSQ (suspended sediment sample), ON (medium code not determined), or R (replicate). With regard to sample type, samples were included in the analysis only if they had a sample type code of 9 (regular sample), 5 (duplicate), 7 (replicate), or A (sample type code not determined). Sample types and mediums which are not known are retained because these fields occasionally are not defined with historical stream or river samples.

In some instances individual water-quality parameters had concentrations of zero. Two previous analyses for nutrient data in the Mississippi-Atchafalaya River Basin (Goolsby and others, 1999; Aulenbach and others, 2007) indicated that zero concentrations were most likely an indication of a missing value and were removed. More specifically, Aulenbach and others (2007) indicated that in some cases multiple parameter values were present for the same constituent on the same date with at least one parameter containing a zero value, but in about one-third of the cases, the other parameter value was above the detection limit. Because of the significant number of cases of uncensored values for similar parameters, it was unreasonable to assume that zero values always represent censored values. Therefore, zero concentrations in this analysis were assumed to be missing and were not used.

Quality-Control Procedures

[USGS, U.S. Geological Survey]
To properly interpret water-quality sampling data, it is necessary to have information about the sources of variability and possible contamination associated with sample collection, processing, and analysis. All analyses of NWQN water samples except for suspended-sediment concentration and particle size are provided by the USGS National Water Quality Laboratory (NWQL) in Lakewood, Colorado. Quality-control (QC) procedures for the NWQL are available at http://nwql.usgs.gov/quality.shtml. Suspended-sediment analyses are provided by several regional USGS sediment laboratories. Each regional laboratory has QC procedures specific to that laboratory. In addition to laboratory-specific QC programs, the quality of all NWQN analytical data is independently monitored by the USGS Branch of Quality Systems (BQS). Blind samples are made by BQS and submitted to the various laboratories as routine environmental samples. The bias and variability of analytical results are reported for suspended sediment, inorganic constituents, and organic constituents. The frequency and magnitude of contamination also is measured.

Field QC for the NWQN is based on that used previously by the USGS National Water-Quality Assessment Project (see Mueller and others, 1997). Field QC procedures require the collection and analysis of field blanks, field replicates, and field matrix spikes; the definitions in the Glossary are excerpted from Mueller and others (1997). Field QC samples are intended to measure sources of bias or variability attributed to field activities. Examples of USGS field QC data analyses are presented in numerous publications, including Mueller (1998), Martin (1999), Martin and others (1999), Kelly and others (2001), Martin (2002), and Mueller and Titus (2005).

Recensoring of Total Phosphorus Analyses

Total phosphorus analyses which used methods described in the Office of Water-Quality Technical Memorandum 92.10 (U.S. Geological Survey, 1992) from October 1, 1991, to September 30, 1998, and results from less than 0.01 to less than 0.03 milligram of phosphorus per liter (mg-P/L) were recensored to less than 0.03 because blank samples indicated a greater than 50-percent probability that the 0.01 reporting level would produce false negatives (Foreman and others, 1998).

Combining Multiple Parameters into One Constituent

Since the inception of the NAWQA Project in 1991, advancements in analytical techniques have resulted in changes to laboratory methods and to the manner in which analytical results are reported. Because of these developments results from different NWIS parameter codes must sometimes be combined to create long-term datasets for constituents identified in table 2.

A major change in analytical procedures is the change from total to dissolved analyses of nitrate plus nitrite (NO$\text{$_2$}^{+}$ NO$_3$), nitrate (NO$_3$), orthophosphate (OP) and ammonia (NH$_3$). Rickert (1992) supports the substitution of total analyses of these constituents with dissolved analyses because there was no difference in concentrations between filtered and unfiltered samples analyzed by the four-channel analyzer (which was used through 1993). This substitution is appropriate, in part, because "unfiltered" samples were analyzed from the supernatant of a well-settled sample, which may have been filtered at the analyst's discretion for turbid samples, though the samples were still coded as unfiltered. Furthermore, a digestion step is necessary in order to analyze these nutrients for total determinations, but this step was not included.

Historical analyses for NO$\text{$_2$}^{+}$ NO$_3$, total Kjehldahl nitrogen (TKN), OP, and TP can be obtained from multiple parameters (table 2). Rules for combining multiple parameters developed here are similar to the rules developed by Gooch and others (1999) and Aulenbach and others (2007).

For dissolved nitrate (NO$_3$) plus nitrite (NO$\text{$_2$}^{+}$), use:

- Dissolved NO$\text{$_2$}^{+}$ NO$_3$ (USGS parameter code 00631; in milligrams of nitrogen per liter)
- Total NO$\text{$_2$}^{+}$ NO$_3$ (parameter code 00630; in milligrams of nitrogen per liter)
- Dissolved NO$_3$ (parameter code 00618; in milligrams of nitrogen per liter)
- Total NO$_3$ (parameter code 00620; in milligrams of nitrogen per liter)
- Dissolved NO$_4$ (parameter code 71851; in milligrams of nitrate per liter; converted from milligrams of nitrate per liter to milligrams of nitrogen per liter by multiplying by 0.2259)
- Total NO$\text{$_4$}$ (parameter code 71850; in milligrams of nitrate per liter; converted from milligrams of nitrate per liter to milligrams of nitrogen per liter by multiplying by 0.2259)

If parameter codes 00620, 71851, or 71850 are used, then NO$_2$ is added to NO$_3$ values from the sources listed below, when available.

- Dissolved NO$_2$ (parameter code 00613; in milligrams of nitrogen per liter)
- Total NO$_2$ (parameter code 00615; in milligrams of nitrogen per liter)
- Dissolved NO$_3$ (parameter code 71856; in milligrams of nitrite per liter; converted from milligrams of nitrite per liter to milligrams of nitrogen per liter by multiplying by 0.3045)

For these cases, if both NO$_2$ and NO$_3$ are above or below the detection limit, they are added together (the less than remark is retained if both are below the detection limit). If one constituent is reported above the detection limit and the detected value is three times the detection limit of the undetected constituent, then only the value above the detection limit is used. If the detected value is less than three times the detection limit of the undetected constituent, then the values of both are added and reported as censored. If NO$_2$ is not reported, the value of NO$_3$ is used exclusively. NO$_3$ is used as an approximation for NO$\text{$_2$}^{+}$ NO$_3$ because NO$_2$ concentrations in surface waters are typically very low or are below analytical detection limits.

For total organic nitrogen plus ammonia, use:

- Total organic nitrogen plus ammonia (TKN; parameter code 00625; in milligrams of nitrogen per liter)
- Total organic nitrogen (00605; in milligrams of nitrogen plus ammonia per liter (parameter codes 00608 or 00610; in milligrams of nitrogen per liter); both must be available and both must be above or below the detection limit; otherwise data are not used

For dissolved organic nitrogen plus ammonia, use:

- Dissolved organic nitrogen plus ammonia (DKN; parameter code 00623; in milligrams of nitrogen per liter)

For particulate nitrogen, use:
Particulate nitrogen, suspended in water (PN; parameter code 49570; in milligrams of nitrogen per liter)

For filtered total nitrogen, use:

- Total nitrogen (nitrate plus nitrite plus ammonia plus organic nitrogen), water, filtered (DN; parameter code 62854; in milligrams of nitrogen per liter)

For dissolved ammonia, use:

- Dissolved NH$_3$ (parameter code 00608; in milligrams of nitrogen per liter)
- Total NH$_3$ (parameter code 00610; in milligrams of nitrogen per liter)

For total phosphorus, use:

- TP (parameter code 00665; in milligrams of phosphorus per liter)
- TP (parameter code 71886; in milligrams of phosphate per liter; converted from milligrams of phosphate per liter to milligrams of phosphorus per liter by multiplying by 0.3261)

For dissolved orthophosphate, use:

- Dissolved OP (parameter code 00671; in milligrams of phosphorus per liter)
- Dissolved OP (parameter code 00660; in milligrams of phosphate per liter; converted from milligrams of phosphate per liter to milligrams of phosphorus per liter by multiplying by 0.3261)
- Total OP (parameter code 70507; in milligrams of phosphorus per liter)
- Total OP (parameter code 00650; in milligrams of phosphate per liter; converted from milligrams of phosphate per liter to milligrams of phosphorus per liter by multiplying by 0.3261)
- Dissolved OP (parameter code 00653; in milligrams of phosphate per liter; converted from milligrams of phosphate per liter to milligrams of phosphorus per liter by multiplying by 0.3261)

For total nitrogen, use the following methods (in order of preference in the presence of multiple analyses on the same date):

- Method 1: The sum of total organic nitrogen plus ammonia and dissolved nitrate plus nitrite
- Method 2: The sum of dissolved organic nitrogen plus ammonia, dissolved nitrate plus nitrite, and particulate nitrogen
- Method 3: The sum of filtered total nitrogen and particulate nitrogen

Rus and others (2013) evaluated three commonly used methods to compute total nitrogen, including methods 1 and 3 outlined above, as well as a method which utilized an alkaline persulfate digestion (parameter code 62855). The alkaline persulfate method exhibited persistent negative bias (median value of -13.2 percent), while method 1 had a slight positive bias (median value of 3.2 percent). Because of the persistent bias exhibited with the alkaline persulfate method, results under parameter code 62855 are not included on the annual reporting Web site and are not used, pending further evaluation, to compute total nitrogen loads. However, because method 1 is the only method consistently available from 1993 forward, and because observed biases were relatively small, it is used as the primary method for computing total nitrogen. Methods 2 and 3 are thought to have limited bias and are included with method 1 if not available for a given date. Methods 1 and 3 are being analyzed concurrently at most NWQN sites to evaluate the possibility of transitioning to using method 3 as the primary means of determining total nitrogen concentration and loads.

For discrete total nitrogen concentrations, the sum of reporting levels for the various constituents is used as the TN reporting level. As with nitrate and nitrate concentrations, constituents are summed if both are greater or less than detection limits (less than values are retained if both are below detection limits). If only one constituent is detected above the TN reporting level and the detected value is more than three times that of the undetected value, that value is designated as the TN concentration. If the detected value falls below the TN reporting level, or if the detected value is less than three times that of the undetected value, then the constituents are summed, and TN is designated as less than the detection level.

Reporting Levels

From October 1, 1998 to October 1, 2010, the USGS NWQL adapted multiple reporting-level conventions for selected water-quality parameters (Foreman and others, 1998; Oblinger and others, 1999). Prior to water year 1999, concentrations were censored to the minimum reporting level (MRL). These conventions determine a long-term method detection level (LT–MDL) and a laboratory reporting level (LRL, typically twice the LT–MDL). When concentrations are below the LRL but above the LT–MDL, values are qualified as "estimated." When concentrations are below the LT–MDL, values are set to less than the LRL (Oblinger and others, 1999). This reporting convention creates potential bias in statistical analyses because it improperly represents the proportions of the data below the LT–MDL and the LRL. In particular, any observations that are truly below the LT–MDL will be reported as censored at the higher LRL. Thus, the probability that an observation falls between the LT–MDL and the LRL may be exaggerated, and the probability that it falls below the LT–MDL may be underestimated (Helsel, 2005). Depending on the true proportion of data below the LT–MDL, this can cause an upward bias that will adversely affect statistical analyses. To prevent this problem, the LT–MDL is defined as the reporting limit, meaning that values reported as censored at the higher LRL are recensored to the lower LT–MDL while uncensored "estimated" values between the LT–MDL and the LRL are left as they are. Multiple reporting levels are no longer an issue after October 1, 2010, as the USGS redefined the LT–MDL as the reporting level for all inorganic constituents (Myers, 2010).

Selecting a Single Daily Sample for Computing Loads

Estimations of monthly and annual loads are conducted on a daily time step, meaning that only one sample per day is required for computing water-quality loads. The use of a daily time step is thought to be adequate for the calculation of annual and monthly fluxes of large rivers because constituent concentrations and discharge generally do not vary much within a given day in large rivers.

After samples are screened by using the process defined above, if multiple analyses are present for a given day, a single analysis is selected according to a specific selection hierarchy. The selection hierarchy gives priority to samples in the following order: those analyzed at the USGS National Water Quality Laboratory, those collected by the USGS, those collected for the NAWQA or NASQAN programs, those with a corresponding instantaneous streamflow value, those with a priority parameter code (table 4), and those in which the laboratory method code is known. If multiple samples are still present for a given day, a single sample is randomly selected. This procedure was adapted instead of that reported in Aulenbach and others (2007), in which samples were averaged, to ensure that the sample selection process does not influence variability in constituent concentrations.
Pesticides

Beginning in 2013, the NWQP began using a new analytical method developed by the USGS National Water Quality Laboratory (Sandstrom et al., 2015) to analyze water samples for current use pesticides and pesticide degradates. Before 2013, different analytical methods were used to measure many of these pesticides in water. To enable consistent comparisons of pesticide occurrence among NWQN sites through time, only those pesticides common to the new analytical method are presented on this website. A number of additional data preparation steps detailed below are implemented to ensure the consistency and comparability of pesticide data presented on this website.

Data Preparation

The following data preparation steps are taken with discrete water-quality data obtained from the USGS NWIS database:

1. An initial retrieval of water-quality data for NWQN sites from NWIS was limited to 227 pesticide compounds analyzed in Sandstrom et al., 2015, including compounds common to this method that were previously analyzed by other methods.
2. All internal or proprietary samples or results were removed.
3. Results duplicative among different USGS water science centers were narrowed to only one result.
4. Quality assurance data (i.e. spikes, blanks or duplicates) were removed.
5. Results that are identified as contaminated (with a REMARK code of "V") and results in which concentrations are equal to or less than zero were removed.
6. Only results from analyses conducted at the USGS National Water Quality Laboratory were retained.
7. Analyses with unknown or potentially incorrect laboratory method codes were removed.
8. Randomly selected among values collected at the same site within a single hour as these results were presumed to be from replicate sampling.
9. Units for pesticide concentrations were converted so that all results are reported in micrograms per liter.
10. Laboratory reporting level data provided by the USGS National Water Quality Laboratory were assigned to pesticide sample results.
11. Any pesticide concentrations that were more than 1.1 times the laboratory reporting level but are reported with a remark of "<" (less than) are removed to ensure consistent censoring levels among sample results. Removing such results with raised reporting levels is consistent with practices historically used by NAWQA for assessing pesticides in streams (Gilliom and others, 2006).
12. Pesticide sample results are only reported for Coastal River, Large Inland River, Urban Indicator, and Agricultural Indicator sites.
13. Pesticide sample results are only reported for sites in which a complete year of data were collected in 2015.

Load Estimation

Stream-water constituent mass flux, often referred to as load, is the mass of a chemical constituent or sediment transported past a stream cross-section over a defined period of time. Mass flux (\( \Phi \)) is the product of constituent concentration (\( C \)) and discharge (\( Q \)) integrated over time (\( t \)):

\[ \Phi = \int C(t)Q(t) \, dt \]

Flux calculations using the integral in equation 1 require a continuous record of concentration and discharge. Although discharge is computed at daily (and often finer) time steps at streamgages, time-series measurements of constituent concentrations are rarely available because of the expense and effort necessary to collect and analyze water-quality samples. Several approaches have been developed to estimate concentrations continuously through time; a regression-based methodology is employed for sampling sites within the NWQN.

After completion of the screening process, regression relations are developed among constituent concentrations and continuous information on streamflow, season, and time for the purpose of computing monthly and annual water-quality loads. As with historical NASQAN Mississippi River sites (Aul enbach and others, 2007), loads are computed for a particular site, constituent, and water year only if water-quality sampling was undertaken for the year in which loads are being computed and if 20 samples are present over a 5-year moving window. The 5-year moving window is used to capture enough samples while also adequately characterizing recent relations among observed and explanatory variables. For the first 5 years a site was sampled, annual and monthly loads are computed for each year from the first 5 years of water-quality data. For example, for sites in which data were collected during the first 5 years of NAWQA Project (1993-1997) loads for each of these years are computed using data collected from 1993-1997. For subsequent years, loads are computed using data collected during the previous four years and the year in which loads are being computed (i.e. for loads in 1998, loads are computed using data from 1994-1998). For sites and (or) constituents that were newly sampled in 2013, loads are computed after 20 samples are collected (in other words, 2013 and 2014 water-year loads may only be computed with 2013 and 2014 data), provided the regression conforms to model assumptions. In these cases, results will be flagged and loads will be recomputed annually until a full 5-year window is obtained. Additionally, the 5-year moving window may be reduced if model assumptions are not met, or if plots indicate that current water-year sample results are distinct from those from surrounding years.

The USGS LOADEST program is a regression-based FORTRAN program (Runkel and others, 2004) used to estimate water-quality constituent loads at NWQN sites. LOADEST defines regression relations through adjusted maximum likelihood estimation (AMLE). The log of load is used as the dependent variable; a variety of independent variables representative of past and current streamflow conditions, season, and time (table 4) are selected from to compute loads for each combination of site, constituent, and water year. A minimum variance unbiased estimate (MVUE) is used to correct for potential retransformation bias (Cohn and others, 1992). LOADEST is implemented by using the USGS rlodest package (Lorenz and others, 2014).
A variety of variables are considered for inclusion in load-computation regression relations (Table 4). Streamflow conditions are represented with the natural log of daily flow, daily flow squared, and daily flow cubed on the day of sampling. Flow variables are centered (as in Cohn and others, 1992) so as to reduce multicollinearity among independent variables. Fourier sine and cosine series are used to represent seasonal differences, and decimal time and decimal time-squared represent time. Four additional variables are included to represent short to long term histories of flow conditions (FA_1_10day, FA_1_30day, FA_30_365day, and FA_100day_all_minus_365day_all; Ryberg and Vecchia, 2012).

Table 4. Variables considered in load estimation models

<table>
<thead>
<tr>
<th>Independent variable abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ln(Q)</td>
<td>Natural log of daily streamflow (centered)</td>
</tr>
<tr>
<td>ln(Q)^2</td>
<td>Natural log of squared daily streamflow (centered)</td>
</tr>
<tr>
<td>ln(Q)^3</td>
<td>Natural log of cubed daily streamflow (centered)</td>
</tr>
<tr>
<td>T</td>
<td>Decimal time</td>
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<tr>
<td>T^2</td>
<td>Decimal time squared</td>
</tr>
<tr>
<td>sin(2πT); cos(2πT)</td>
<td>Fourier representations of season</td>
</tr>
<tr>
<td>FA_1_10day</td>
<td>Subtraction of the average daily flow (log-transformed) over the past 10 days from the natural log of flow on the day of sampling</td>
</tr>
<tr>
<td>FA_1_30day</td>
<td>Subtraction of the average daily flow (log-transformed) over the past 30 days from the natural log of flow on the day of sampling</td>
</tr>
<tr>
<td>FA_30_365day</td>
<td>Subtraction of the average daily flow (log-transformed) over the past 365 days from the average daily flow (log-transformed) over the past 30 days</td>
</tr>
<tr>
<td>FA_100day_all_minus_365day_all</td>
<td>A subtraction of the average daily flow (log-transformed) over the period of record is subtracted from a subtraction of the average daily flow (log-transformed) over the past 365 days from the average daily flow (log-transformed) over the period of record</td>
</tr>
</tbody>
</table>

A combined automated and manual process is used evaluate whether assumptions of the linear regression model are met. These assumptions are (1) that a log-log relation exists among load and explanatory variables, (2) that model errors are normally distributed, and that (3) model errors are independent of variables used in the regression model.

The automated process relates observed loads to all possible combinations of explanatory variables. Any model that has an explanatory variable with a variance inflation factor greater than 10 is removed from further consideration to reduce the potential for multicollinearity among independent variables. One to three models are then selected for further inspection. The model or models with the smallest Akaike information criteria (a measure of model error that includes penalties for additional explanatory variables; Helsel and Hirsch, 2002) and the model with the smallest p-value (a measure of the significance of the overall regression) are selected if these models are different. The regression relation from the previous water year (if loads were estimated) is selected for visual inspection as well.

Once a set of one to three models is identified, plots are made to check for outlying or incorrect data and to evaluate whether models conform to regression assumptions. Visual inspection of model residuals is necessary to confirm that model assumptions are met because single (or even multiple) model diagnostics have not necessarily been proven to bias model predictions (Helsel and Hirsch 2002; Hirsch, 2014).
Figure 10 is adapted from Weighted Regressions on Time, Discharge, and Season (WRTDS), an R package developed to predict water-quality loads (Hirsch and others, 2010). Eight plots are used to judge the degree to which models conform to regression assumptions:

- **A: Model residuals relative to model predictions, in log space**: Used to check that residual values are evenly distributed around zero across the range of load estimates. A locally weighted scatter plot fit (lowess) is used to approximate the relations among residual values and load estimates (lowess smooths are also used in assumptions B, C, F, and G).
- **B: Model residuals relative to streamflow, in log space**: Used to check that residual values are evenly distributed around zero across the range of flows.
- **C: Model residuals, in log space relative to date**: Used to check that residual values are evenly distributed around zero across the 5-year period.
- **D: Boxplots of model residuals, in log space, relative to month**: Used to check that residual values are evenly distributed around zero with respect to seasons.
- **E: Boxplots comparing sampled loads, estimated loads on sample days, and estimated loads over the entire 5-year estimation period**: Used to ensure that samples estimates approximate the range of sampled values and adequately represent the population of estimated days.
- F: Observed in relation to estimated concentrations in arithmetic space: Used to display the degree to which estimated concentrations represent observed concentrations across the range of values after retransformation to arithmetic space.
- G: Boxplots comparing sampled flows to flows over the entire 5-year estimation period: Used to ensure that samples were collected for a representative set of flow conditions over the 5-year period.
- H: Observed in relation to estimated loads in arithmetic space: Used to display the degree to which estimated concentrations represent observed concentrations across the range of values after retransformation to arithmetic space.

Additionally, summary statistics are computed for each model and are displayed in figure 10:

- AIC: Akaike’s information criterion (the smaller the value, the less error with respect to observed values while accounting for statistical power lost by adding more explanatory variables)
- MR: The mean value of residuals for samples within the upper half of observed loads (the closer the value to 0, the less bias for the highest loads)
- Flux Bias Statistic: The mean of the estimated flux on sampled days minus the mean of observed flux, divided the mean of observed flux (the closer the value to 0, the less bias among sampled values)

Additional plots are constructed to illustrate the influence of each sample on the regression model fit (Escobar and Meeker, 1992) and to indicate the degree to which potentially biased estimates of water-quality loads. Local influence plots are used, in part, to help identify whether outlying data exert undue influence on the model fit, biasing predictions for other more typically observed values. Outlying data are removed very rarely (less than 0.001 percent of the time) and only in cases in which analytical results are believed to be in error. In some cases, all of the models deviate from regression assumptions, requiring visual inspection of models not identified in the automated process. In these cases, typically the next smallest Akaike’s information criterion models are inspected until an appropriate model is identified. If an appropriate model cannot be specified from inspections of different combinations of explanatory variables, models may be reevaluated by using a smaller (2–4 year) window of observed data, or loads may not be computed.

Water quality loads may not be computed at NWQN sites for the following reasons:

1. Discrete water quality samples may not be collected or the amount of samples were deemed insufficient for a particular combination of site, constituent, and water year.
2. Diagnostic plots indicated that none of the possible LOADEST models considered could compute unbiased loads given observed values.

**Modifications to Flux Estimation Procedures**

**Modifications at small stream sites (agricultural, urban, and reference streams)**

Runoff reaches and exits headwater stream sites more quickly than in larger rivers, and thus smaller agricultural, urban, and reference NWQN fixed sites experience more sub-daily variability in flow conditions as compared to large-inland river or coastal river sites. Because flow conditions are the principal data used to estimate water-quality flux, inaccurate representation of relations among water quality concentrations and flow conditions may result in more variable and (or) potentially biased estimates of water-quality loads. Preliminary tests conducted comparing loads computed using daily versus hourly flows indicate that the primary differences occur for total phosphorus and suspended-sediment loads (constituents typically transported primarily during high flow conditions) and in situations where relatively few high-flow samples are collected.

In an attempt to improve load computations at small stream sites, instantaneous flow values assigned by sample collectors at the time of water quality sampling are used to develop regression relations with water-quality concentrations and loads. These relations are applied to hourly flows obtained from the USGS Instantaneous Data Archive (IDA: [http://ida.water.usgs.gov/ida/index_usgs.cfm](http://ida.water.usgs.gov/ida/index_usgs.cfm)) and from NWIS. Hourly flows are used because some sites do not have flows recorded at finer time scales and because hourly is the minimum time-step utilized by LOADEST. In cases in which instantaneous flows are not entered by water-quality sampling teams, hourly flows from the streamflow record nearest the time of sample collection are used to develop regression relations.

Two additional steps were necessary to utilize hourly flows to compute water-quality loads. First, if subdaily flows not recorded on the hour, they were rounded to the nearest to the hour. Second, sub-hourly flow time series often have extended gaps because these data were not traditionally estimated during periods in which gages were inoperable (e.g. because of equipment malfunction, ice, etc). In these cases, daily flows are utilized to compute flows on days in which a complete hourly flow record is not available using the same explanatory variables selected in the regression utilizing instantaneous flows. Water year loads are then computed by adding partial loads computed from daily and hourly flows. Confidence intervals for loads are estimated by addding the size of the confidence interval above or below the load estimate of each of the two fluxes in quadrature (as is done to compute loads to the Gulf of Mexico in Aulenbach, 2007).

Although it is sometimes not possible to identify suitable regression relations at large river sites, these difficulties are often amplified at smaller stream sites. This may be because it is more difficult to collect samples during rapidly changing high flow conditions, because different source area contributions (that may be averaged out in larger basins) lead to variable concentration/discharge relations, or other reasons. Figure 11 illustrates relation in which (A) no loads were computed because too much extrapolation from observed values was required and, (B) loads were computed because a model fit was identified that could compute relatively unbiased loads among the range of observed and estimated conditions.
Figure 11. Plots used to evaluate load estimates. TP, total phosphorus; NO23, nitrate plus nitrite; AIC, Akaike’s information criterion; MR, mean value of residuals in the upper half of observed load; m3/s, cubic meters per second; kg/d, kilograms per day; Est., estimated; Obs., observed; Conc., concentration.

Modifications to Lower Mississippi River Sites

Flux estimation methods for the four most downstream Mississippi River stations (Vicksburg, MS; St. Francisville, LA; Baton Rouge, LA; and Belle Chase, LA) require modification to account for changing sources of streamflow and the diversion of the main stem Mississippi River. A portion of flows from the lower Mississippi River (an average of 23.2 percent from 1967 to 2008) is diverted to the Atchafalaya River just upstream from the St. Francisville sampling site. The proportion of diverted flow varies daily, but because the concentrations of water-quality constituents at downstream sites are more indicative of natural Mississippi River flows upstream from the diversion, flows upstream from the diversion are used for the development of load regression relations at St. Francisville. Discharges upstream from the diversion (the sum of daily flows from Tarbert Landing and the Old River Outflow Channel) are used to develop regression relations for the St. Francisville site. Resulting daily loads are then multiplied by the percentage of flows that remain in the main stem Mississippi River and are summed to obtain monthly/annual loads. Streamflow and flux diverted by the Old River Diversion are accounted for by the fluxes estimated at Atchafalaya River at Melville, La. (which also includes the fluxes from the upstream Red and Black River Basins).

Confidence intervals for the Mississippi River stations downstream from Tarbert Landing are also adjusted for the proportion of streamflow diverted from the lower Mississippi River. Monthly and water-year confidence intervals computed for these sites are multiplied by the average percentage of flows remaining in the Mississippi River. This adjustment should be adequate because the proportion of flow diverted from the Mississippi River does not vary greatly on a daily basis.
The transport of water-quality constituents in the downstream Mississippi River Basin are influenced by the contribution of streamflows and fluxes from the upper Mississippi, Missouri, and Ohio/Tennessee River Basins. Additional independent variables indicative of flows from the Mississippi River upstream from the Ohio (Mississippi River at Thebes) and from the combined Ohio/Tennessee River Basins (Ohio River at Metropolis, Illinois) are included as potential explanatory variables. The logs of daily flows and squared daily flows from these sites are considered, among other explanatory variables from these sites. River at Melville, LA) used to predict constituent flux to the Gulf of Mexico (Aulenbach and others, 2007) because of interest in the relation between nutrient delivery and the development of the hypoxic zone.

Composite Method

The composite method is a hybrid flux estimation approach that combines the regression-model method with a period-weighted approach used to adjust for structure present in residual concentrations over time (Aulenbach and Hooper, 2006). The composite method adjusts the concentration predicted by the regression model to the observed concentration on days when samples are collected and applies the residuals to the fluxes between samples in a piecewise linear fashion. This approach improves flux estimates when there is serial autocorrelation in the residual concentrations, which indicates unmodeled structure in the residuals that was not captured by the regression model. Serial autocorrelation in residual concentrations typically increases as sampling frequency increases. Assessments of the composite method indicate that when serial autocorrelation is about 0.2 or greater, the composite method may improve flux estimates at monthly or annual time scales. Serial autocorrelations of this level have been observed for monthly or greater sampling frequencies. The composite method is employed using a modified version of LOADEST based on the AMLE estimates with a routine for period-weighting the residual concentrations.

The composite method is provided as an alternate methodology for load computation at sites (Mississippi River at St. Francisville, LA., and Atchafalaya River at Melville, LA) used to predict constituent flux to the Gulf of Mexico (Aulenbach and others, 2007) because of interest in the relation between nutrient delivery and the development of the hypoxic zone.

The composite method uses the same 5-year moving window approach used for the regression-model method. The calibration datasets were modified slightly because the composite method requires a sample either on the first day or before the beginning of the estimation period, and a sample either on the last day or after the end of the estimation period. Hence, two additional samples (the last sample before the 5-year calibration window and the first sample after the calibration window) are included in the calibration dataset. Also, it was occasionally necessary to extrapolate sample concentrations at the beginning or end of the entire flux estimation period when there were no samples available. In these cases, daily loads for the extrapolation period were computed without adjusting the residuals and were additional composite-method loads used for the majority of the estimation period.

Composite-method fluxes are reported on annual (water year) and monthly time steps but only for water years that have at least 10 samples. This is the sampling frequency at which the serial autocorrelation in the residual concentrations generally was high enough that the composite method would improve the flux estimates. Occasionally, negative daily fluxes were estimated from the LOADEST composite method routine. These fluxes were set to zero before fluxes were summed by month or water year.

Error estimates cannot be calculated for the composite method. It can be assumed that the error estimates for the composite method are similar to or better than those for the AMLE method because the composite method should generally be improving the flux estimates toward the observed water-quality concentrations. Occasionally, the composite method estimates were observed to fall outside the AMLE 95-percent confidence limits.

Use of continuous nitrate data for load estimation

Continuous nitrate sensors have been installed at locations throughout the United States and at selected NWQN sites (see Table 1) in part to improve the accuracy of computed nitrate loads. To begin to evaluate these potential improvements, nitrate loads are computed alongside streamflow-based estimates at NWQN sites when adequate data are available. Methods used to compute nitrate loads using continuous nitrate are performed in a similar manner as with streamflow-based loads. Regression relations are established between discrete nitrate loads and mean-daily streamflow and sensor-based nitrate concentrations through the roadiest package. Residual plots (shown in figure 10) are evaluated to verify that regression assumptions are being met prior to computing loads. Continuous nitrate loads are not currently displayed in the website graphics, but are available via data download by filtering to a model type (MODTYPE) of “CONTIN.” There are two differences in the load estimation process when using continuous nitrate data versus streamflow-based estimates:

1. In contrast to streamflow data, sensor malfunctions, environmental fouling, and other factors often make it difficult to obtain a complete record of daily nitrate concentrations for an entire water year. Thus in cases where 1-7 days of sensor data are missing during relatively stable flow conditions, daily nitrate concentrations may be linearly interpolated among measured values in order to obtain a complete record for the water year. Loads are not estimated for sites and water years with longer periods of missing record or in which there is missing record during rapidly changing or extreme conditions. Currently, missing sensor records have only allowed for loads to be computed using continuous nitrate data at the Illinois River at Valley City, IL and Mississippi River at Baton Rouge sites for water years 2013 and 2014.

2. Because laboratory analyses of discrete nitrate samples and nitrate sensor values have been observed to have near 1:1 relations with little variability, only 10 samples are required to compute loads (as opposed to 20 sample for streamflow-based estimates). Thus nitrate loads may be computed at continuously monitored sites for the first water-year in which data are available (provided 10 samples have been collected). As with streamflow-based estimates, data collected over subsequent years are added to the regression relations for estimates produced for the following water years until 5 years of data have been collected. At this point loads will be computed using a 5 year moving window as done with streamflow-based estimates.

Methods Used to Produce Graphics

The Water Quality Tracking Web site is designed to provide visualizations and context to data and loads computed at NWQN sites. The following is a description of the methods used to create these graphics.

Water-Quality Benchmark Information
Measured concentrations in water samples collected from rivers and streams at NWQN sites are compared to human-health or aquatic-life benchmarks, when available, to place the data in context. The following section details the sources and application of benchmark information displayed on the summary and detailed graph pages.

**Human-Health Benchmarks**

One of three general types of human-health benchmarks is used:

- U.S. Environmental Protection Agency (EPA) Maximum Contaminant Levels (MCLs) are used for contaminants that are regulated in drinking water by the EPA under the Safe Drinking Water Act.
- EPA Human Health Benchmarks for Pesticides (HHBPs) are used for pesticides that EPA does not regulate in drinking water. EPA computes HHBPs for pesticide active ingredients that are registered for use on food crops and for which Health Advisories or enforceable MCLs have not been developed.
- USGS Health-Based Screening Levels (HBSLs) are used for contaminants that EPA does not regulate in drinking water. USGS computes HBSLs for contaminants for which MCLs or HHBPs have not been developed.

Table 5 summarizes each type of human-health benchmark and how these benchmarks are compared to sample concentration data.

### Table 5. Description of human-health benchmarks and how environmental concentrations are compared to them on the Tracking Water Quality Page

<table>
<thead>
<tr>
<th>Type of human-health benchmark</th>
<th>Benchmark description</th>
<th>Concentration to compare against benchmark¹</th>
<th>Example use</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA MCLs</td>
<td>Legally enforceable drinking-water standards that are set as close as feasible to the maximum level at which no known or anticipated adverse effects on human health would occur.</td>
<td>Time-weighted annual mean²</td>
<td>Discrete data from each individual sample</td>
</tr>
<tr>
<td>EPA HHBPs – acute</td>
<td>Nonenforceable advisory values protective of acute noncancer effects.</td>
<td>Discrete data from each individual sample</td>
<td></td>
</tr>
<tr>
<td>EPA HHBPs – chronic noncancer³</td>
<td>Nonenforceable advisory values protective of chronic noncancer effects.</td>
<td>Time-weighted annual mean</td>
<td></td>
</tr>
<tr>
<td>EPA HHBPs – carcinogenic³</td>
<td>Nonenforceable advisory values protective of carcinogenic effects.</td>
<td>Time-weighted annual mean</td>
<td></td>
</tr>
<tr>
<td>USGS HBSLs – chronic noncancer⁴</td>
<td>Nonenforceable benchmarks protective of chronic noncancer effects.</td>
<td>Time-weighted annual mean</td>
<td></td>
</tr>
<tr>
<td>USGS HBSLs – cancer⁴</td>
<td>Nonenforceable benchmarks protective of cancer effects.</td>
<td>Time-weighted annual mean</td>
<td></td>
</tr>
</tbody>
</table>

¹ Gilliom et al., 2006, Toccalino, 2007

² Unlike most MCLs, the MCL for nitrate is based on acute (short-term) health effects for infants (U.S. Environmental Protection Agency, 2012), so it is appropriate to compare discrete nitrate data from individual samples to the nitrate MCL.

³ The lower of the chronic noncancer or carcinogenic HHBP is used in the calculations and graphs on this website.

⁴ The lower of the chronic noncancer or cancer HBSL is used in the calculations and graphs on this website.

Several of the human-health benchmarks (MCLs, chronic and carcinogenic HHBPs, and HBSLs) are typically based on chronic (long-term) health effects. As a result, concentrations above a benchmark indicate a potential human-health concern if the water were to be consumed without treatment for many years. None of the NWQN samples were collected from drinking-water intakes. Because concentrations in surface water can change substantially over time and have strong seasonal patterns, it is generally most appropriate to compare annual or long-term mean (average) concentrations to human-health benchmarks because mean concentrations provide a more reliable indication of long-term exposure than concentrations from individual samples. Comparisons of concentrations from discrete individual samples to benchmarks can be a useful first step, however, for evaluating the potential relevance of measured concentrations to human health (Toccalino, 2007). More details about how human-health benchmarks are compared to sample data can be viewed in the Summary and Detailed Graphs sections below.

**Aquatic-life benchmarks**

EPA Office of Pesticide Programs (OPP) Aquatic Life Benchmarks are benchmarks for freshwater organisms that are based on the most sensitive toxicity value for a given pesticide, taxon, and exposure duration. Benchmarks incorporate the EPA ecological level of concern (LOC) and are equal to the Toxicity value x LOC (U.S. Environmental Protection Agency, 2016a). Table 6 summarizes how the various types of OPP Aquatic Life Benchmarks are compared to sample concentration data.
### Table 6. Description of aquatic-life benchmarks and how environmental concentrations are compared to them on the Tracking Water Quality Page

<table>
<thead>
<tr>
<th>Type of EPA OPP Aquatic Life Benchmark</th>
<th>Benchmark description</th>
<th>Concentration to compare against benchmark¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acute fish</td>
<td>Concentrations below which pesticides are not expected to harm fish species after acute (short-term) exposure</td>
<td>Discrete data from each individual sample</td>
</tr>
<tr>
<td>Chronic fish</td>
<td>Concentrations below which pesticides are not expected to harm fish species after chronic (long-term) exposure</td>
<td>60-day moving average</td>
</tr>
<tr>
<td>Acute invertebrate</td>
<td>Concentrations below which pesticides are not expected to harm aquatic invertebrate species after acute (short-term) exposure</td>
<td>Discrete data from each individual sample</td>
</tr>
<tr>
<td>Chronic invertebrate</td>
<td>Concentrations below which pesticides are not expected to harm aquatic invertebrate species after chronic (long-term) exposure</td>
<td>21-day moving average</td>
</tr>
<tr>
<td>Acute nonvascular plant</td>
<td>Concentrations below which pesticides are not expected to harm aquatic nonvascular plants after acute (short-term) exposure²</td>
<td>Discrete data from each individual sample</td>
</tr>
<tr>
<td>Acute vascular plant</td>
<td>Concentrations below which pesticides are not expected to harm aquatic vascular plants after acute (short-term) exposure²</td>
<td>Discrete data from each individual sample</td>
</tr>
</tbody>
</table>

¹ U.S. Environmental Protection Agency 2016b
² The lower of the acute nonvascular and vascular plant benchmarks is used in the calculations and graphs on this website.

### Summary Graphs

Two primary summary graphs are provided for each non-reference site. The “Streamflow and Water Quality” graph on the left-hand pane shows the annual mean streamflow and annual loads of nitrate, total phosphorus, and suspended-sediment for the most recent year in which data were collected. These data are compared with the mean of historical annual streamflows and the means of historical annual loads of nitrate, total phosphorus, and suspended-sediment. Because sites vary in terms of the length of historical records, the period over which historical flow and loads are averaged will vary on a site-to-site basis (table 1). However, other than for Mississippi River sites in which loads have previously been published, 1993 (the onset of NAWQA) is the first possible year in which loads were published.

The Pesticides flow chart on the right-hand pane is displayed for non-reference sites with at least a full year of pesticide sampling in current water year (currently 2015). This chart summarizes pesticide analysis and occurrence, and compares concentrations to applicable benchmarks for the most recent water year in which analyses are complete. The flowchart provides information about the numbers of compounds at each site (1) that were analyzed, (2) that were detected in one or more samples, (3) with human-health or aquatic-life benchmarks, and (4) with concentrations that are greater than those benchmarks. If there are any exceedances, the user can hover over the number of exceedances shown in the flow chart to view which compounds had an exceedance in the most current water year.

### Benchmark summary graphs

In addition to the two primary summary graphs, four additional bar graphs provide additional information about (1) the percentage of samples and (2) the number of pesticide compounds with human-health or aquatic-life benchmark exceedances (if any) at each site. A description of how environmental concentrations were compared to the benchmarks is provided below.

Bars for three time periods are shown on each graph:

- One bar for the most recent year (currently 2015)
- One bar showing the average annual exceedances during the period between 2013 and one year prior to the most recent year (currently 2014). This represents the time period after NAWQA began using the new pesticide analytical method (Sandstrom and others, 2015).
- One bar showing the annual average of exceedances during 1993-2012. This represents the time period since the inception of the NAWQA Project, but before NAWQA began using the new pesticide method.

Graphs on the left hand side illustrate the percentage (or average percentage) of samples in a given year or set of years that exceeded human-health or aquatic life benchmarks. For human health benchmarks (upper-left hand pane of the benchmark summary graph), the percentage of samples is evaluated only with respect to acute benchmarks because chronic benchmarks can only be evaluated on a time-weighted, annual mean concentration. The percentage of samples exceeding aquatic-life benchmarks (lower-left hand pane of the benchmark summary graph) is evaluated relative to both acute and chronic benchmarks. Acute aquatic-life benchmarks are compared directly to sample values, while chronic aquatic-life benchmarks are compared to applicable 21 or 60-day moving average values on the day of sample collection. However because chronic aquatic-life benchmarks are only applicable to 21 and 60-day moving average pesticide concentrations over time, computations indicating the percentage of samples exceeding aquatic-life benchmarks are not strictly accurate. This computation is provided to give an estimate of the amount of time a benchmark is exceeded based on individual samples.
Clicking on the respective time periods allows users to view the number (or average number) of samples analyzed and the number (or average number) of pesticides with human-health or aquatic-life benchmarks. Clicking on the number of pesticides exceeding a benchmark identifies which pesticides (if any) had benchmark exceedances.

**Nutrient and Sediment graphs**

For each site, detailed graphs display daily streamflow data, discrete water-quality concentrations, annual flows and water-quality loads. Additional computations based on these data include flow-normalized concentrations of water-quality and baseline concentrations designed to provide context to year-to-year variability in flow and water-quality results. Flow-normalized constituent concentrations are computed by dividing the annual load by the annual volume of streamflow transported past a particular site, multiplied by a conversion factor to facilitate display in milligrams per liter.

**Pesticide graphs**

These graphs show all discrete (individual) sample concentrations for the most commonly detected herbicide and non- herbicide in the most current water year (currently 2015). Herbicide and non-herbicide classes were obtained from the following website: [http://www.alanwood.net/pesticides/](http://www.alanwood.net/pesticides/)

**Constituent Transport in the Mississippi/Atchafalaya River Basin**

Nitrate, total nitrogen, and total phosphorus loads computed at NWQN sites in the Mississippi-Atchafalaya River Basin are the basis for figures which use river width to display the relative contributions of different rivers to loading nutrient to the Gulf of Mexico. Users have the option to display the relative contributions of rivers for individual water years from 1993 to 2015, for May loads from 1993 to 2015, and mean (water-year or May) loads from 1980 to 1996 and 1993 to 2014. May loads are displayed in addition to water-year loads because May nitrate plus nitrite (Turner and others, 2006; 2008) and total nitrogen (Scavia and others, 2003; Scavia and others, 2004) loading to the Gulf of Mexico is used to predict the extent of the summer Gulf hypoxic zone. Mean annual loads from 1980 to 1996 are displayed because this period is used as a baseline for comparison to future loads (Mississippi River Gulf of Mexico Watershed Nutrient Task Force, 2008). Mean annual loads from 1993 to 2014 are provided to characterize average loading since the inception of the USGS NAWQA Project.

The relative contributions of various rivers are determined by creating a stream network of monitored rivers within the Mississippi-Atchafalaya River Basin. Then rivers are broken into a series of small segments to allow the linear interpolation (or extrapolation in the case of headwater streams) of estimated NWQN loads throughout the river network. After annual and May loads are computed for NWQN sites with the requisite data, interpolated loads are assigned to small stream segments among sites and are extrapolated to 0 from NWQN locations to the locations nearest the headwater streams. Water-year and May loads for each stream segment are then assigned one of 24 bins using Jenks natural breaks (Jenks, 1967). The smallest of these bins is assigned a minimum line thickness of 0.5 pixels, the second smallest bin is assigned a line width of 1.0 pixels, and so forth, up to a maximum of 12 pixels. Thus at each NWQN site, the stream width corresponds to the load that passed that site relative to the load entering the Gulf of Mexico. Line thickness is linearly interpolated among or upstream from NWQN sites, except where other monitored rivers enter the network.

It is important to note that this methodology does not account for inputs from any streams or rivers not displayed on the figures. If a particular headwater NWQN site does not have data necessary to compute loads for a particular nutrient and (or) time period, stream lines are displayed as a black line with the minimum width level. If loads aren’t available at downstream NWQN sites, loads are linearly interpolated between the upstream and the next downstream NWQN site. Mean water-year and May loads are computed regardless of any missing data during the period of interest.

These figures also allow users the ability to select individual NWQN sites; selecting a site will open a new browser window allowing a user to select Summary Graphs or Detailed Graphs (as described earlier) or Annual Load or May Load. Selecting Annual Loads displays the times series for the nutrient in the underlying map. Baseline values displayed on bar charts for the Mississippi-Atchafalaya Delta site (defined as the sum of loads from the Mississippi River at St. Francisville and the Atchafalaya River at Melville) include the 1980–1996 averages, a 45-percent reduction line from this value (as identified by Mississippi River Gulf of Mexico Watershed Nutrient Task Force, 2008), and a 5-year moving average. Users also have the option to view loads contributed to the Gulf of Mexico (Mississippi-Atchafalaya Delta). Upon selection of the Mississippi-Atchafalaya Delta site May Loads option, a bar chart displaying loads relative to the observed extent of the Gulf hypoxic zone is shown; this hypoxic zone data is obtained from the Louisiana Universities Marine Consortium.

**Nitrate in Coastal Rivers**

Data at coastal NWQN sites are used to display nitrate plus nitrite loads to U.S. estuaries and rivers from upstream watersheds. U.S. estuaries are grouped into four regions: North and Middle Atlantic, South Atlantic, Gulf of Mexico, and Pacific. When a particular region is selected, loads and yields are displayed for the 2015 water year and the mean annual values from 1993 to 2014. For mean annual values, all available data is taken regardless of any missing water years. Loads for individual previous water years can be viewed by clicking on the site location and selecting the "detailed graphs" option. Note that loads and yields from the Mississippi River are taken from the Mississippi River at St. Francisville site, and loads and yields from the Atchafalaya River are taken from the Atchafalaya River at Melville site, as these sites have the longest historical water-quality records.

**Data Download**

In 2015, data retrievals from U.S. Geological Survey Water Quality Tracking Web site migrated to being hosted by the USGS ScienceBase Catalog. Users have the option of downloading various data types from all sites in the NWQN or from specific sites of interest. Data download buttons located on individual site pages in the Water Quality Tracking Web site link to data only from that specific site. Data download buttons located on the home page, the Rivers and Streams page, the Mississippi River Basin page, of the Coastal Rivers page send users to data for all sites in the NWQN.

Ten files are available for all sites in the USGS Tracking Water Quality page. A smaller set of these files are available for specific sites depending upon the type and amount of data collected at the site. Listed below are the file names and a brief description:
1. Nutrient_and_pesticide_data_collected_from_the_USGS_National_Water_Quality_Network_and_previous_networks_1980_2015.xml - Metadata file describing the source of all data files
2. NWQI_sites.csv - Information on site identifiers, site names, drainage area, etc.
3. aflow.csv - Annual flow data, in acre-feet.
4. aloads.csv - Annual water-quality load data for nutrients and sediment, in tons.
5. discqw.csv - Discrete water quality results for nutrients and sediment, in mg/L.
6. dflow.csv - Daily flow data, in cubic feet per second.
7. mflow.csv - May flow data, in acre-feet. This data is only provided for sites historically published in the Mississippi River basin.
8. mlloads.csv - Monthly water-quality load data for nutrients and sediment, in tons. This data is only provided for sites historically published in the Mississippi River basin.
9. pestlong.csv - Information on the pesticides analyzed, including abbreviated and long pesticide names, USGS parameter codes, and chemical abstract service (CAS) numbers.
10. pestsamp.csv - Discrete pesticide results in micrograms per liter.

Glossary

**Annual flow-normalized concentration:** Annual loads divided by the total volume of streamflow transported over the water year. Annual loads, measured in tons, are converted to milligrams (multiplied by 907,184,740), and the annual flow volume, measured in acre-feet, is converted to liters (multiplied by 1,233,481.84).

**Annual load:** The mass of a particular constituent passing a stream cross section over a water year.

**Aquatic Life Benchmarks:** Benchmarks for freshwater aquatic species based on toxicity values used in EPA risk assessments for pesticide registration. EPA Office of Pesticide Programs Aquatic Life Benchmarks are available for fish (acute and chronic), invertebrates (acute and chronic), and nonvascular and vascular plants (acute) and are based on the most sensitive, scientifically acceptable toxicity endpoint available to EPA for a given taxon.

**Censored value:** A value reported as less than the laboratory reporting level.

**Daily mean streamflow:** The average streamflow for a particular day, measured in cubic feet per second.

**Discrete sample:** Samples collected from the National Fixed Site Network for the purpose of characterizing water-quality conditions and computing loads. These samples have undergone a series of screening steps to facilitate unbiased computation of loads.

**Dissolved and total concentrations:** Constituent concentrations listed in the accompanying figures and tables refer to dissolved concentrations unless it is specifically stated otherwise. Dissolved constituent concentrations are derived from laboratory analysis of water samples passed through a filter with 0.45 micrometer pore size, whereas total constituent concentrations are determined from laboratory analysis of unfiltered water samples.

**Field blank:** A field blank is prepared in the field and used to demonstrate that (1) equipment has been adequately cleaned to remove contamination introduced by samples obtained at previous sites, (2) sample collection and processing have not resulted in contamination, and (3) sample handling and transport have not introduced contamination. In addition, because the field blank is treated like an environmental sample at the laboratory, it includes potential contamination introduced during laboratory handling and analysis.

**Field matrix spike:** A field matrix spike is a specific type of spiked sample that is fortified in the field prior to shipping. These samples are used to assess the potential bias for analytes in a particular sample matrix. This bias also might include analyte degradation during shipping and handling. Bias is estimated from spiked samples by calculating the percentage of the added analyte that is measured (recovered) in the sample. Recovery can be either greater than or less than 100 percent, so the bias can be either positive or negative; however, matrix interference and analyte degradation generally result in a negative bias.

**Health-Based Screening Levels (HBSLs):** Nonenforceable water-quality benchmark concentrations of contaminants in water that were developed by the USGS using (1) the latest EPA policies for establishing drinking-water benchmarks and (2) the most recent EPA peer-reviewed publicly available toxicity information. Noncancer HBSLs are concentrations below which adverse noncancerous health effects are not expected over a lifetime of exposure. Cancer HBSLs are concentrations that correspond to a range in excess estimated lifetime cancer risk of one-in-one million (10^{-6}) to one-in-ten thousand (10^{-4}).

**Human-health benchmarks:** Used in this site as a collective term that includes drinking-water standards (MCLs) and guidelines (human-health benchmarks for pesticides (HHBPs)) established by the EPA and HBSLs calculated by the USGS. For each constituent, measured concentrations are compared to the appropriate human-health benchmark, when available, to provide a human-health context for the data.

**Human Health Benchmarks for Pesticides (HHBP):** Nonenforceable advisory values in water established by the EPA for selected pesticides registered for use on food crops. Acute and chronic noncancer HHBPs are protective of acute and chronic noncancer effects, respectively. Carcinogenic HHBPs are protective of cancer effects and represent a one-in-one-million (10^{-6}) to one-in-ten-thousand (10^{-4}) cancer-risk range.

**Laboratory reporting level (LRL):** Generally is equal to twice the yearly determined long-term method detection level (LT–MDL). The LRL controls false-negative error. The probability of falsely reporting a nondetection for a sample that contained an analyte at a concentration equal to or greater than the LRL is predicted to be less than or equal to 1 percent. The value of the LRL will be reported with a less than (<) remark code for samples in which the analyte was not detected. The National Water Quality Laboratory collects quality-control data about selected analytical methods on a continuing basis to determine LT–MDLs and to establish LRLs. These values are reevaluated annually on the basis of the most current quality-control data and therefore may change. (Note: Previously, the LRL has been called the nondetection value or NDV, a term that is no longer used.)

**Level of Concern (LOC):** Criteria used by EPA Office of Pesticide Programs to indicate potential risk to non-target organisms and the need to consider regulatory action. The LOC is 0.5 for acute fish and invertebrates and 1 for chronic fish and invertebrates and for acute nonvascular and vascular plants.

**Long-term mean:** Mathematical average of the constituent concentration or load for the period of record.
Lowess line: Lowess lines (Helsel and Hirsch, 2002) are provided to characterize changes in discrete water-quality samples over time. Lowess lines are displayed when at least four samples were collected per year and when less than 25 percent of the data were censored. A span of 0.4 was used.

Maximum Contaminant Level (MCL): An MCL is a legally enforceable drinking-water standard established by the EPA that sets the maximum permissible level of a contaminant in water that is delivered to any user of a public water system. MCLs are set as close as feasible to the maximum level of a contaminant at which no known or anticipated adverse effects on human health would occur, taking into account the best available analytical and treatment technologies and cost considerations.

May load: The mass of a particular constituent passing a stream cross section during the month of May.

Period of record: Defined for the annual reporting Web site as the period of time (in water years) included in the summary graphs. The period of record may not include all historic records available.

Replicate: The second of two samples, collected at the same time, undergoing identical sample-collection and analytical procedures. Replicates are used to determine the variability of reported constituent concentrations.

Water-quality constituent: One of a group of analytes currently selected for inclusion on the annual reporting Web site. Water-quality constituents for 2013 include ammonia, nitrate plus nitrite, total nitrogen, total phosphorus, suspended sediment, and silica.

Water-quality load: The mass of a particular constituent passing a stream cross section over a specified time span. Water-quality loads on the annual reporting Web site are reported for months and water years in tons or thousands of tons.

Water-quality yield: The mass of a particular constituent passing a stream cross section over a specified time span, normalized by upstream drainage area. Yield is a valuable way to compare the relative contribution of monitoring sites with different upstream drainage areas. Water-quality yields on the annual reporting Web site are reported for months and water years in tons per square mile or thousands of tons per square mile.

Water year: A 12-month period beginning on October 1 for any given year and lasting through September 30 of the following year. The water year is designated by the calendar year in which it ends.

Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AIC</td>
<td>Akaike's information criterion</td>
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<tr>
<td>AMLE</td>
<td>adjusted maximum likelihood estimation</td>
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<tr>
<td>BQS</td>
<td>USGS Branch of Quality Systems</td>
</tr>
<tr>
<td>DKN</td>
<td>dissolved organic nitrogen plus ammonia</td>
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<tr>
<td>EDI</td>
<td>equal-discharge increment</td>
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<tr>
<td>EPA</td>
<td>U.S. Environmental Protection Agency</td>
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<tr>
<td>EWI</td>
<td>equal-width increment</td>
</tr>
<tr>
<td>HBSL</td>
<td>USGS Health-Based Screening Levels</td>
</tr>
<tr>
<td>HHBP</td>
<td>EPA Human Health Benchmarks for Pesticides</td>
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<tr>
<td>LOADEST</td>
<td>USGS Load Estimator software</td>
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<tr>
<td>LRL</td>
<td>laboratory reporting level</td>
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<tr>
<td>LT–MDL</td>
<td>long-term method detection level</td>
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<tr>
<td>MCL</td>
<td>EPA Maximum Contaminant Level</td>
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<tr>
<td>mg/L</td>
<td>milligrams per liter</td>
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<tr>
<td>MR</td>
<td>mean value of residuals</td>
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<tr>
<td>MRL</td>
<td>minimum reporting level</td>
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<tr>
<td>MVUE</td>
<td>minimum variance unbiased estimate</td>
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<tr>
<td>NASQAN</td>
<td>USGS National Stream Quality Accounting Network</td>
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<tr>
<td>NAWQA</td>
<td>USGS National Water-Quality Assessment Project</td>
</tr>
<tr>
<td>NWQN</td>
<td>USGS National Water Quality Network</td>
</tr>
<tr>
<td>NH₃</td>
<td>dissolved ammonia as nitrogen</td>
</tr>
<tr>
<td>NMN</td>
<td>National Monitoring Network</td>
</tr>
<tr>
<td>NO₂+NO₃</td>
<td>dissolved nitrate plus nitrite as nitrogen</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>--------</td>
<td>------------</td>
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<tr>
<td>NO₃</td>
<td>nitrate</td>
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<tr>
<td>NWIS</td>
<td>USGS National Water Information System</td>
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<tr>
<td>NWQL</td>
<td>USGS National Water Quality Laboratory</td>
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<tr>
<td>OP</td>
<td>dissolved orthophosphate as phosphorus</td>
</tr>
<tr>
<td>PN</td>
<td>particulate nitrogen suspended in water</td>
</tr>
<tr>
<td>Q</td>
<td>streamflow</td>
</tr>
<tr>
<td>SI</td>
<td>dissolved silica as silicon dioxide</td>
</tr>
<tr>
<td>SSC</td>
<td>suspended sediment</td>
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<tr>
<td>T</td>
<td>time</td>
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<tr>
<td>TKN</td>
<td>Kjeldahl nitrogen (total organic nitrogen plus ammonia as nitrogen)</td>
</tr>
<tr>
<td>TN</td>
<td>total nitrogen as nitrogen</td>
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</tbody>
</table>

### References Cited


Analytical methods—Discontinuation of the National Water Quality Laboratory determinations for “total” nitrate, “total” nitrite plus nitric oxide, and “total” nitrite plus nitric oxide plus nitrous oxide, and the load estimator (LOADEST)—A FORTRAN program for estimating constituent loads in streams and surface waters.


