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Nitrogen Concentrations and Loads for the Connecticut River at Middle Haddam, Connecticut, Computed With the Use of Autosampling and Continuous Measurements of Water Quality for Water Years 2009 to 2014

Scientific Investigations Report 2018–5006

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

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By John R. Mullaney, Joseph W. Martin, and Jonathan Morrison

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U.S. Department of the Interior
RYAN K. ZINKE, Secretary

U.S. Geological Survey
William H. Werkheiser, Deputy Director
    exercising the authority of the Director

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Acknowledgments

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Conversion Factors

International System of Units to U.S. customary units

Multiply	By	To obtain
meter (m)	3.281	foot (ft)
square kilometer (km^2)	0.3861	square mile (mi^2)
cubic meter (m^3)	0.0002642	million gallons (Mgal)
cubic meter per day (m^3/s)	0.0002642	million gallons per day (Mgal/d)
kilogram per hectare (kg/ha)	571.1	pounds per square mile (lb/mi^2)
metric ton	2,205	pound (lb)

U.S. customary units to International System of Units

Multiply	By	To obtain
inch (in.)	2.54	centimeter (cm)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m^3/s)

Datum

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Elevation, as used in this report, refers to distance above the vertical datum.

Supplemental Information

Concentrations of chemical constituents in water are given in milligrams per liter (mg/L).

Abbreviations

CDOM   colored dissolved organic matter

EPA   U.S. Environmental Protection Agency

USGS   U.S. Geological Survey

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Abstract

The daily and annual loads of nitrate plus nitrite and total nitrogen for the Connecticut River at Middle Haddam, Connecticut, were determined for water years 2009 to 2014. The analysis was done with a combination of methods, which included a predefined rating curve method for nitrate plus nitrite and total nitrogen for water years 2009 to 2011 and a custom rating curve method that included sensor measurements of nitrate plus nitrite nitrogen concentration and turbidity along with mean daily flow to determine total nitrogen loads for water years 2011 to 2014. Instantaneous concentrations of total nitrogen were estimated through the use of a regression model based on sensor measurements at 15-minute intervals of nitrate plus nitrite nitrogen and turbidity for water years 2011 to 2014.

Annual total nitrogen loads at the Connecticut River at Middle Haddam ranged from 12,900 to 19,200 metric tons, of which about 42 to 49 percent was in the form of nitrate plus nitrite. The mean 95-percent prediction intervals on daily total nitrogen load estimates were smaller from the custom model, which used sensor data, than those calculated by the predefined model.

Annual total nitrogen load estimates at the Connecticut River at Middle Haddam were compared with the upstream load estimates at the Connecticut River at Thompsonville, Conn. Annual gains in total nitrogen loads between the two stations ranged from 3,430 to 6,660 metric tons. These increases between the two stations were attributed to the effects of increased urbanization and to combined annual discharges of 1,540 to 2,090 metric tons of nitrogen from 24 wastewater treatment facilities in the drainage area between the two stations. The contribution of total nitrogen from wastewater discharge between the two stations had declined substantially before the beginning of this study and accounted for from 31 to 52 percent of the gain in nitrogen load between the Thompsonville and Middle Haddam sites.

Introduction

The Long Island Sound Study began in 1985 when Congress appropriated funds for the U.S. Environmental Protection Agency (EPA) to carry out a program to research, monitor, and assess the water quality of Long Island Sound as part of the National Estuary Program. This work has been undertaken in concert with the States of Connecticut and New York, forming a partnership consisting of Federal and State agencies, user groups, concerned organizations, and individuals dedicated to restoring and protecting Long Island Sound.

In 1994, the Long Island Sound Study completed a comprehensive conservation and management plan that identified problems that merit special attention, including low levels of dissolved oxygen (hypoxia), toxic contamination, pathogen contamination, the effects of habitat degradation and loss on the health of living resources, land use and development resulting in the habitat loss, and overall degradation of water quality (Long Island Sound Study, 1994). Hypoxia was identified as the highest priority water-quality problem for Long Island Sound. The Long Island Sound Study defined hypoxia as concentrations of dissolved oxygen of 3 milligrams per liter (mg/L) or less in the water column (Long Island Sound Study, 1994). Hypoxia occurs during the summer months in the bottom waters of western Long Island Sound and is believed to be caused by overenrichment of nitrogen.

A total maximum daily load (TMDL) was implemented in 2000 with the goal of reducing the point and nonpoint source nitrogen loads to Long Island Sound from New York and Connecticut by 58.5 percent by 2014 (New York State Department of Environmental Conservation and Connecticut Department of Environmental Protection, 2000). In 2010, the Long Island Sound Study formed a five-State committee (including representatives from the States of Connecticut, New York, Massachusetts, New Hampshire, and Vermont) to evaluate progress towards meeting the TMDL goals and to determine revised nitrogen loading targets. In addition, the comprehensive conservation and management plan was updated

and revised in 2014 (Long Island Sound Study, 2014), which involved reviewing program progress, soliciting stakeholder and public input, and developing a framework for updating this document. These efforts required information on tributary nitrogen loads to Long Island Sound in order to track progress toward management goals.

In 2016, the EPA created a new nitrogen strategy, organized by three customized watershed groups: embayments, large riverine systems, and priority western Long Island Sound point-source discharges to open water. For each group, there is the need to develop nitrogen thresholds that will translate the narrative water-quality standard into a numeric target, identify where watershed nitrogen loading results in threshold exceedances, and assess options for the load reductions from point and nonpoint sources that would be needed to remain below thresholds. An additional recommendation was to continue to pursue opportunities to monitor, model, and research the link between nitrogen load and bottom-water dissolved oxygen conditions in the open water of Long Island Sound (U.S. Environmental Protection Agency, 2015).

To address these issues, the U.S. Geological Survey (USGS), in cooperation with the Connecticut Department of Energy and Environmental Protection, has been quantifying nitrogen loads to Long Island Sound through analysis of streamflow and water-quality data collected in the Connecticut part of the watershed (Mullaney, 2016a,b). Historically, however, nitrogen loads from the Connecticut River have been calculated at Thompsonville, Conn., near the Massachusetts border, because this is the first location upstream from Long Island Sound where the river flows are not tidally affected. In addition, there are major nitrogen sources in the lower reaches of the Connecticut River below the Thompsonville monitoring station, including an additional 3,204 square kilometers (km^2) of drainage area (fig. 1) that includes 24 wastewater treatment facilities. As a result of management actions and wastewater facility upgrades, nitrogen loads from wastewater treatment plants in the lower Connecticut River Basin declined from about 2,600 metric tons (t) to about 1,540 t from 2002 to 2014 (fig. 2). Because the Connecticut River is the largest tributary of Long Island Sound, detailed characterization of nitrogen load from the lower Connecticut River is important for tracking of the overall nitrogen budget and understanding of hypoxia in Long Island Sound.

This report describes streamflow and the concentrations and loads of nitrate plus nitrite nitrogen and of total nitrogen at the Connecticut River at Middle Haddam and for comparison, those values for the upstream streamgage on the Connecticut River at Thompsonville from October 2008 to September 2014; the methods used to collect and process the water-quality and streamflow data at the Middle Haddam streamgage; and the uncertainties in the estimates of concentrations and loads.

The study area encompasses an area of 28,223 km^2, which covers about 97 percent of the Connecticut River Basin, and includes those parts of the basin where the river drains in Vermont, New Hampshire, Massachusetts, and Connecticut,

representing about 96.5 percent of the drainage area of the Connecticut River. The streamgaging station at Middle Haddam (USGS station 01193050) is approximately 39 kilometers (km) upstream from Long Island Sound and is characterized by freshwater tidal conditions. The major land uses and land covers of the upstream basin, based on a land use and land cover analysis for 2011 (Homer and others, 2015), are forested (73 percent), developed (9.4 percent), cultivated crops (6.4 percent), and wetlands (5.3 percent). The drainage basin above the Middle Haddam streamgage contains many small cities and towns, and the larger cities of Springfield, Mass., and Hartford, Conn. The headwaters of the Connecticut River begin in the mountainous regions of northern Vermont and northern New Hampshire, with elevations as high as 1,914 meters in the White Mountains of New Hampshire. The western side of the Connecticut River forms the border between Vermont and New Hampshire. As the river enters Massachusetts, it enters the Connecticut Valley Lowland, a broad lowland underlain by Mesozoic sedimentary bedrock, which it follows until Middletown, Conn., where the river enters the eastern uplands of Connecticut, just upstream from the streamgage at Middle Haddam.

Wastewater discharged to streams and rivers in the study area from 109 municipal facilities totals about 280 million gallons per day (Mgal/d; 1.06 million cubic meters per day [Mm^3/d]; Mullaney and others, 2002). The average annual air temperature ranges from less than 4 degrees Celsius (°C) in the northern mountainous areas to about 10 °C at Long Island Sound. Precipitation ranges from 86 centimeters per year (cm/yr) in the Connecticut Valley Lowland to more than 165 cm/yr in the northern mountainous areas (Bjerklie and others, 2011).

The Connecticut River is tidally influenced from the mouth of the river at Long Island Sound upstream to Windsor Locks, Conn. The streamgaging station at Thompsonville, Conn., (USGS station 01184000; drainage area 24,864 km^2) has typically been the farthest downstream water-quality monitoring site for which nitrogen loads have been estimated because of difficulties in the past with continuously monitoring the flow in the tidal reach of the river. The flow at the Middle Haddam site is tidally affected at all but the highest discharges. The water itself, however, is fresh at this site, and the salt wedge from the waters of Long Island Sound has never been observed upstream from Haddam, Conn., about 14 km downstream from the Middle Haddam streamgage (Meade, 1966).

Methods

Streamflow was measured on a continuous basis, water samples were collected by an automated sampler, and continuous water-quality monitoring sensors were operated to be used as surrogates in a regression model. The statistical methods used to estimate nitrogen concentrations and loads

Figure 1. The Connecticut River Basin, encompassing Connecticut, Massachusetts, New Hampshire, and Vermont. U.S. Geological Survey streamgages used in the study of nitrogen loads in the Connecticut River Basin for water years 2009 to 2014 are shown.
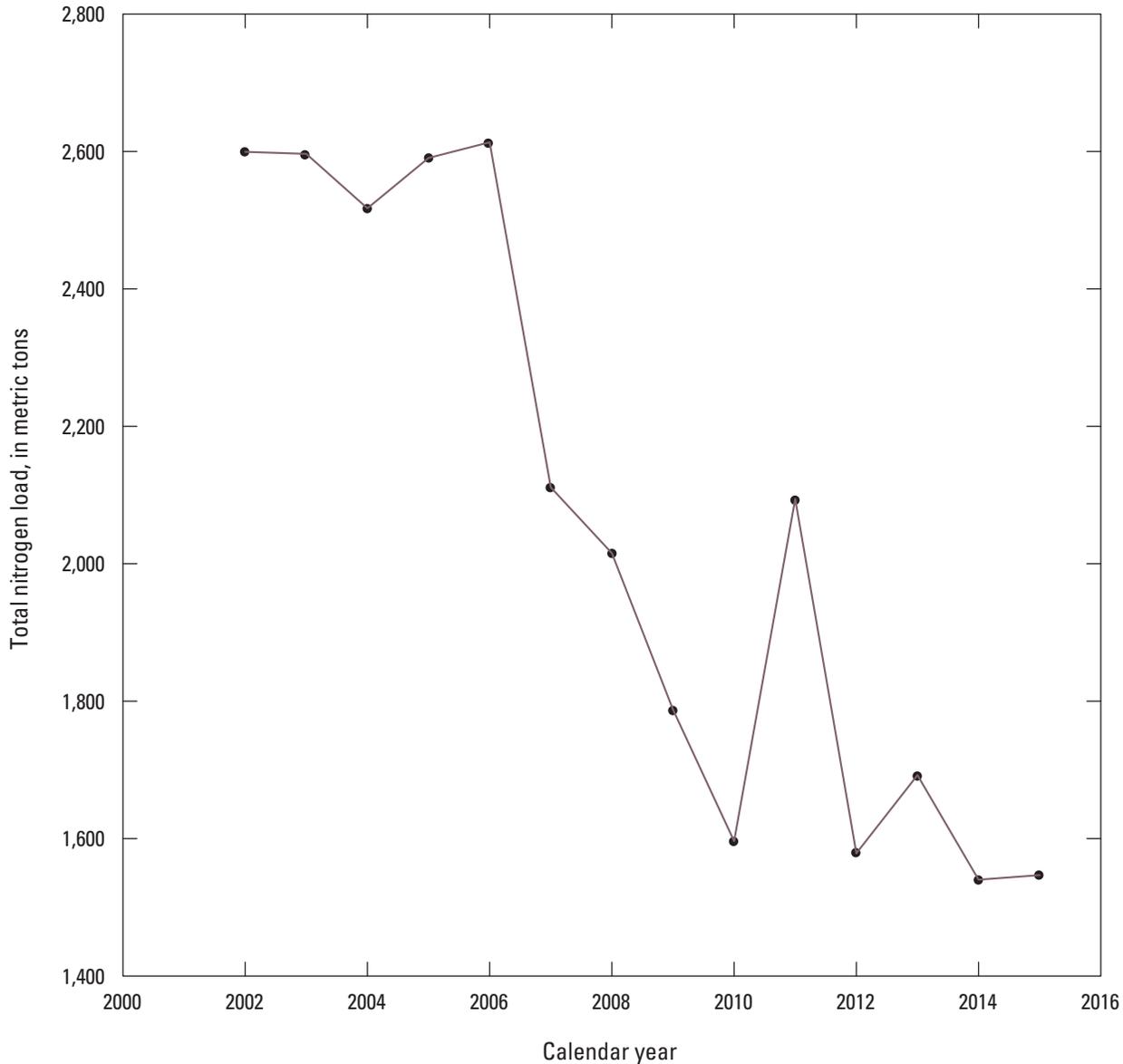
Figure 2.   Total nitrogen loads discharged from wastewater treatment facilities in the Connecticut River Basin in Connecticut for calendar years 2001 to 2015.

at the Middle Haddam streamgage included multiple regression modeling using continuously collected sensor data as a surrogate for total nitrogen and the use of a USGS rating curve method (LOADEST) for estimating nitrogen loads.

Continuous Streamflow Data Collection

The measurement of streamflow in the Connecticut River at Middle Haddam is complicated by tidal influence from Long Island Sound, including upstream flow in the river during low-flow conditions. A conventional streamgage, which relies on the relation between river stage and streamflow to compute discharge, could not be used at this location because of the upstream flow and inconsistent relation between river stage and streamflow caused by the interactions of flow volume and the tidal cycle. Continuous measurement of streamflow began in 2008 with the installation of a pressure transducer to measure river stage and a Sontek SL1500 "Side Looker" acoustic Doppler velocity meter (ADVM; fig. 3). The ADVM was installed on a vertical I-beam system on a fuel pier in the Connecticut River that intercepts the deepest part of the channel. Data on river stage and velocity are logged every 5 minutes and transmitted to the USGS National Water Information System (NWIS; https://nwis.waterdata.usgs.gov) by satellite.

Figure 3. The side of a fuel pier in the Connecticut River with an acoustic Doppler velocity current profiler and the rail system on which it was mounted. Photograph by Joseph Martin, U.S. Geological Survey.

In order to convert the ADVM data to streamflow, a stage-area rating and an index-velocity rating were established as described in Levesque and Oberg (2012). The stage-area rating was created by determining the cross-section characteristics at a location 500 feet upstream from the fuel pier. The index velocity rating was initially established by making 90 discharge measurements at the selected site from 2009 to 2010 using the moving boat method described in Mueller and others (2013). The index rating was developed by means of a regression technique in which the mean cross-sectional velocity for the standard section from measurements is related to the measured index velocity from the ADVM. An additional 75 measurements of discharge were made from 2011 to 2014 to update and verify the rating.

Discharge for each 5-minute observation was computed through the use of the resulting ratings. The daily mean discharge of a tidal river is subject to tidal aliasing, caused by a lunar day (24.84 hours) that is longer than the solar day (24 hours). Because of the differences, each 24-hour average includes a different portion of the lunar tidal cycle, resulting in a low frequency oscillation for some rivers (U.S. Geological Survey, 2011). Therefore, a low-pass filter is used to remove frequencies that have periods less than 30 hours. The most energetic variations removed in this process are the astronomical tides (typically with periods at or around 12 and 24 hours); however, other variations (meteorological, hydrologic, or operational) that have periods less than 30 hours also are removed (Ruhl and Simpson, 2005). To eliminate the tidal aliasing in the data, the daily mean discharge from the Middle Haddam streamgage (fig. 4) was extracted from the 5-minute data through the use of a low-pass Godin filter (Godin, 1972) as described by the U.S. Geological Survey (2011), (fig. 3).

Streamflow data from the Connecticut River at Thompsonville, Conn. (USGS station 01184000) also were used in calculating total nitrogen loads for the period of water years[1] 2009 to 2014 for comparison with downstream loads at Middle Haddam. Daily streamflow data from the Thompsonville streamgage were retrieved from the U.S. Geological Survey (2017).

Water-Quality Monitoring

Water samples collected primarily by an automated sampling system were analyzed for nutrients. Water-quality data also were collected by the use of sensors for the detection of values for nitrate plus nitrite nitrogen, turbidity, specific conductance, temperature, and colored dissolved organic matter (CDOM). All continuously collected data were transmitted to the USGS NWIS database (https://nwis.waterdata.usgs.gov) by satellite.

Collection and Analysis of Discrete Water Samples

Samples for laboratory analyses were collected primarily with an Isco model 4700 refrigerated automated sampler. The sampler's peristaltic pump collects a water sample from a selected point in the river through a flexible 3/8-inch vinyl tube. The sampler was fixed approximately 20 feet above

[1]In this report, years are given as water years. A water year is defined as the 12-month period from October 1 through September 30 and is designated by the calendar year in which it ends.

01193050, Connecticut River at Middle Haddam, Connecticut
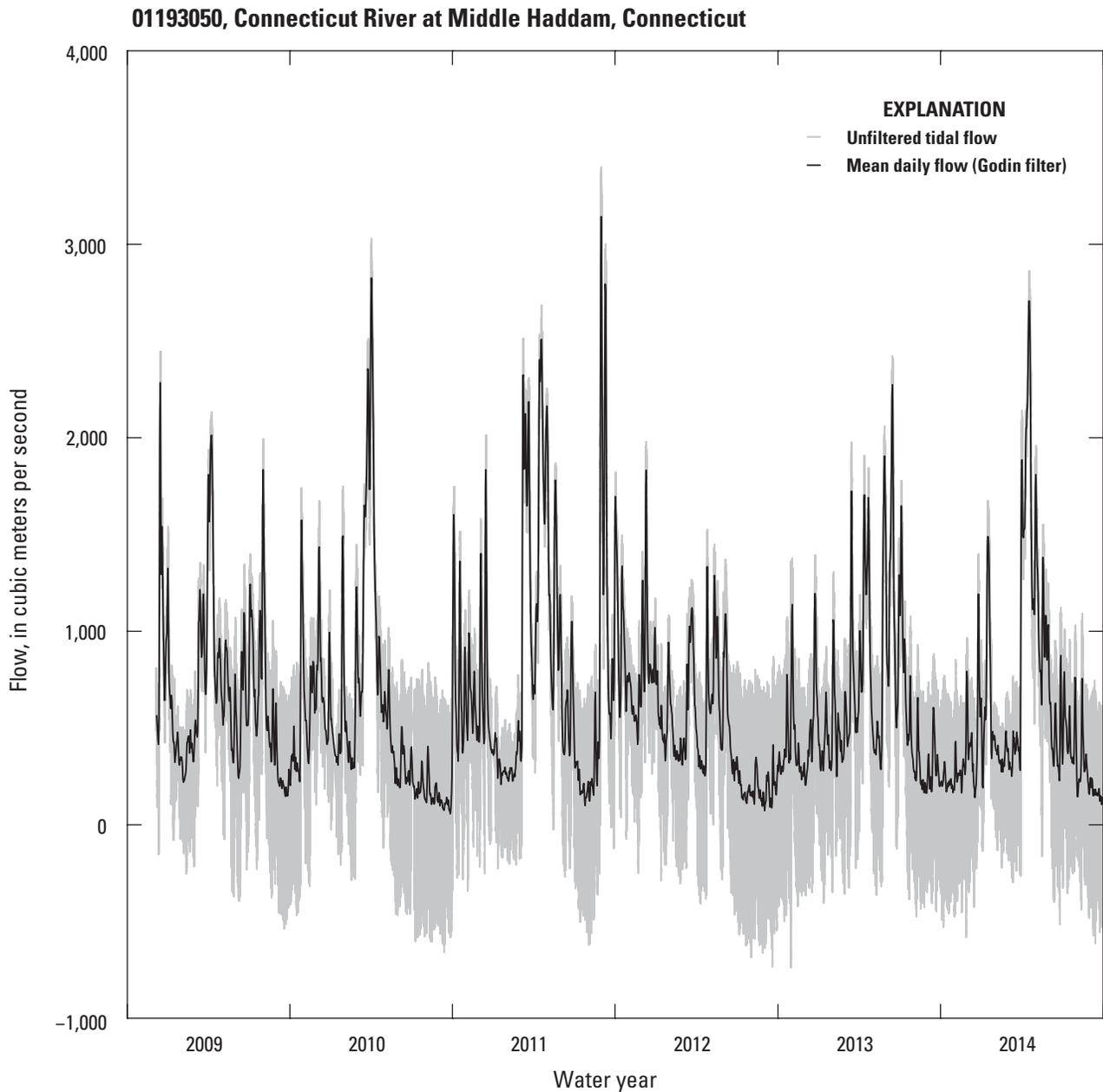
Figure 4.   Tidal discharge and filtered daily discharge at the Connecticut River at Middle Haddam, Conn., for water years 2009 to 2014.

the water, with the tube intake set at a fixed height of 10 feet above the river bottom and adjacent to the nitrate plus nitrite sensor on the end of the fuel pier. The tubing was replaced twice yearly, in the spring and the fall. Heating tape was used to keep the intake tubing from freezing during the winter. Before collecting each sample, the sampler automatically conditioned the tubing by rinsing it with river water and then reversing the pumping direction to empty the line. The sample was then pumped into a bottle in the refrigerated section of the sampler and kept chilled for preservation. The tubing was purged of water after each sample and air was kept in the tubing until the next sample interval.

From 2009 to 2011, the sampler was programmed to collect routine water samples as well as multiple samples at increased frequency during storm events to capture samples that would represent the entire range of total nitrogen concentrations. From the end of 2011 to 2014, the automated sampler was programmed on a more regular, approximately weekly schedule. Additional samples were collected manually over the course of the study using a weighted bottle sampler.

From 2009 to 2014, a total of 315 samples were collected and analyzed for nitrate plus nitrite nitrogen (USGS parameter code 00631) and total ammonia plus organic nitrogen (total Kjeldahl nitrogen; USGS parameter code 00625). These

two parameters are summed to compute total nitrogen (Mullaney, 2016b). Samples also were collected and analyzed for total nitrogen by persulfate digestion (USGS parameter code 62855). These samples were used for comparison with other total nitrogen results, but were not used in nitrogen load calculations. Both of the above methods are considered to have some slight bias as determined by Rus and others (2012), and the USGS has started transitioning to a new method for determining total nitrogen (though not used in this study) that combines total particulate nitrogen, and a filtered persulfate digestion (U.S. Geological Survey, 2013).

Water-quality data were collected at the Connecticut River at Thompsonville, Conn. (station 01184000) using sampling methods and equipment described in U.S. Geological Survey (2006). Data from 113 water samples collected during water years 2007 to 2015 were used to estimate total nitrogen loads. As with samples collected at the Middle Haddam streamgage, analyses for nitrite plus nitrate nitrogen (USGS parameter code 00631) and total ammonia plus organic nitrogen (USGS parameter code 00625) were combined to determine total nitrogen. All samples were analyzed at the USGS National Water-Quality Laboratory in Denver, Colorado.

Continuous Water-Quality Data Collection

A series of sensors were deployed from the fuel pier at the Middle Haddam site to continuously monitor water quality. These included sensors for the concentrations of nitrate plus nitrite nitrogen, dissolved oxygen, and CDOM; as well as those to measure values of specific conductance, water temperature, turbidity, and pH. Data from these sensors were recorded at 15-minute intervals and were processed in accordance with USGS methods, including those described by Wagner and others (2006) and Pellerin and others (2013). Data collected by these sensors from December 2011 to September 2014 were used in the analyses in this report. Each sensor had periods of missing data because of instrument failure during the study period. More details are given below on selected sensor data that were used to calculate nitrate plus nitrite and total nitrogen loads at the Connecticut River at Middle Haddam.

Nitrate plus nitrite nitrogen data were collected with a Satlantic submersible ultraviolet (UV) nitrate analyzer V1 sensor with a 10-millimeter optical path length. The measurements were made using a direct spectrophotometric determination of nitrate concentration, in which the magnitude of the absorbance at a peak wavelength of 220 nanometers is proportional to the concentration of nitrate ions in solution. A detailed description of the operation of UV nitrate sensors is given in Pellerin and others (2013).

The nitrate plus nitrite sensor was mounted horizontally at a fixed depth on the fuel pier near the center of the Connecticut River near the Middle Haddam streamgage (fig. 5). The sampling interval was set to 15 minutes, and an external wiper system cleaned the sensor face before each reading. The sensor was checked and cleaned manually using deionized water during regular site visits at intervals that typically ranged between 1 and 6 weeks, depending on field conditions. Beginning in March 2014, periodic linearity performance checks of the sensor with nitrate standards were made (Pellerin and others, 2013).

Figure 5. The sensor array to measure nitrate plus nitrite nitrogen mounted to a fuel pier in the center of the Connecticut River at Middle Haddam, Conn. Photograph by Joseph Martin, U.S. Geological Survey.

Sensor readings and the results of analyses of concurrent discrete water samples for nitrate plus nitrite nitrogen (USGS parameter code 00631) had a strong correlation (fig. 6*A*). The concentration of nitrite nitrogen is considered negligible, with the highest value in the study period of 0.025 mg/L. Data from the sensor were corrected to nitrate plus nitrite nitrogen (fig. 6*B*); therefore, all results are reported as nitrate plus nitrite nitrogen. Intermittent instrument failures resulted in the use of four different nitrate plus nitrite sensors between December 2011 and September 2014. Because swapping factory calibrated instruments resulted in instrument-specific bias, for each period when a specific sensor was deployed or recalibrated, an average correction for bias was calculated for that sensor based on the difference between the sensor readings and the concentrations nitrate plus nitrite from laboratory analyses of concurrent discrete samples. The bias corrections were applied if the correction exceeded the calibration criteria of the sensor of 0.03 mg/L of nitrate plus nitrite nitrogen (Pellerin and others, 2013). No fouling corrections were applied to the nitrate plus nitrite data because the external wiper and the additional maintenance during site visits kept the sensor face clean. The sensor data did not exceed the recommended fouling correction criterion of 0.03 mg/L, or 10 percent, as recommended by Pellerin and others (2013).

Data for turbidity, specific conductance, temperature, pH, and dissolved oxygen were collected initially using a multiparameter YSI–6600 sonde from 2011 to 2013. This instrument was replaced in October 2013 with a multiparameter YSI–6920V2 sonde. Site visit intervals for maintenance and calibration ranged from 1 to 6 weeks, depending on site conditions and if problems were visible from the real-time data collection. During each visit, measurement probes were cleaned and checked for biofouling and electronic drift and recalibrated as necessary, according to USGS methods (Wagner and others, 2006).

Nitrogen Concentration and Load Estimation

In order to calculate continuous concentrations and loads of nitrate plus nitrite nitrogen and total nitrogen, several techniques were used. For nitrate plus nitrite nitrogen, concentration data were summarized as measured and adjusted (as described in the "Continuous Water-Quality Data Collection" section) at 15-minute intervals from December 2011 to September 2014. The nitrate plus nitrite sensor had multiple periods of missing record because of sensor malfunction.

For concentration of total nitrogen, data for discrete samples collected from December 2011 to September 2014 (summing data from parameter codes 00631 and 00625) were used as the dependent variable in an ordinary least-squares linear regression model that used continuously collected sensor data as independent variables to describe the variability in total nitrogen concentration. Continuously collected sensor data that were evaluated for use in the regression model included nitrate plus nitrite probe values, specific conductance, turbidity, pH, dissolved oxygen, temperature, and CDOM. The goal of the regression modeling for total nitrogen concentration was to be able to predict nitrogen concentrations and loads in near real time for display on the USGS NWIS website (https://nwis.waterdata.usgs.gov).

Sensor datasets are prone to periods of missing record because of environmental conditions and instrument failure; therefore, minimizing the number of sensors used in estimating total nitrogen concentration is likely to decrease the number of periods of missing record for a particular sensor and maximize the number of laboratory observations used as the dependent variable. Although many regression models commonly use the natural log of the instantaneous flow as one of the variables to estimate concentration and loads, it was not used to estimate total nitrogen concentrations in this study because of the negative values that occur during periods of tidally influenced upstream flow (negative) of the Connecticut River at Middle Haddam.

Loads of nitrate plus nitrite nitrogen and of total nitrogen at the Connecticut River at Middle Haddam from December 2008 to September 2014 were calculated using the computer program LOADEST (Runkel and others, 2004). Given a time series of daily streamflow and instantaneous constituent concentration, LOADEST assists the user in developing a regression model for the estimation of constituent load (flux). Explanatory variables in the regression model may include various functions of streamflow, decimal time, seasonal terms, and additional user-specified data. The formulated regression model then is used to estimate loads over a user-specified time interval. The LOADEST program also was used to estimate total nitrogen loads at the Connecticut River at Thompsonville from October 2008 to September 2014.

The calculations in this report were done using a version of LOADEST adapted to the R statistical package (RLoadest; Runkel, 2013; U.S. Geological Survey, 2015). The water discharge data used in the RLoadest models for the Connecticut River at Middle Haddam were mean daily discharge (fig. 4) computed using a Godin filter as described in the "Continuous Streamflow Data Collection" section.

Predefined RLoadest models for total nitrogen and nitrate plus nitrite nitrogen were used to estimate the daily loads from December 2008 to December 2011 and intermittently from December 2011 to September 2014. For the period of intermittent measurements at the Middle Haddam streamgage, a custom RLoadest model was used with additional daily aggregated sensor data to calculate the daily load of total nitrogen (fig. 7). Additionally, the original predefined RLoadest model was used as a substitute model during periods of sensor malfunction for the period of December 2011 to September 2014. Data on daily model outputs are in Mullaney and others (2017).

Nitrate plus nitrite nitrogen loads from December 2011 to September 2014 at the Connecticut River at Middle Haddam were calculated using the 15-minute nitrate plus nitrite

A. 01193050, Connecticut River at Middle Haddam, Connecticut

B. 01193050, Connecticut River at Middle Haddam, Connecticut
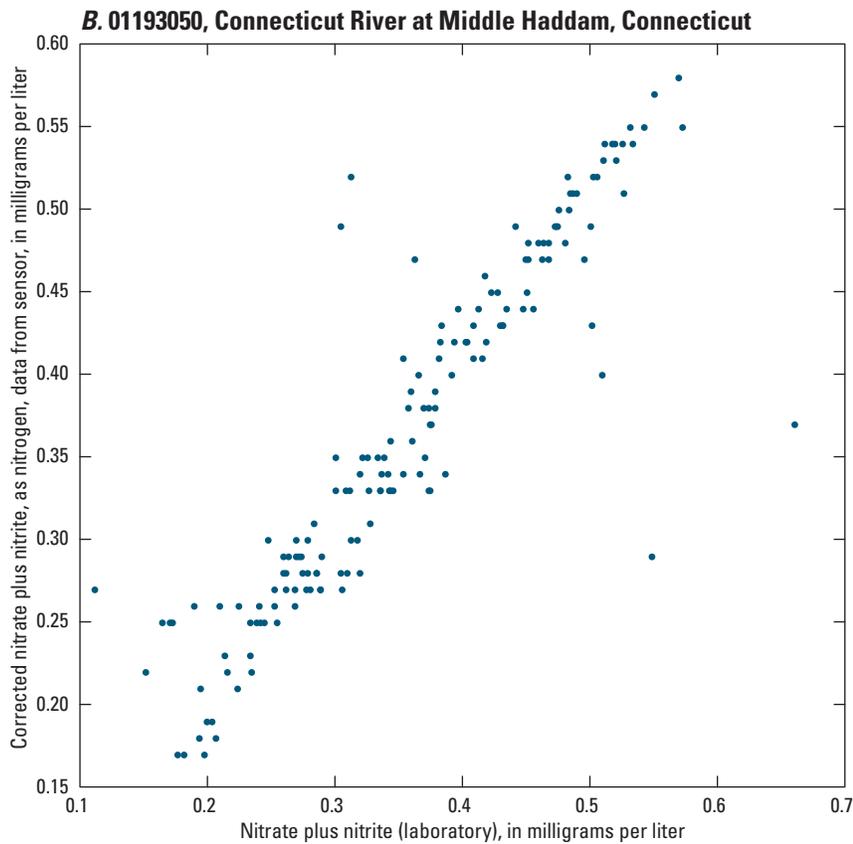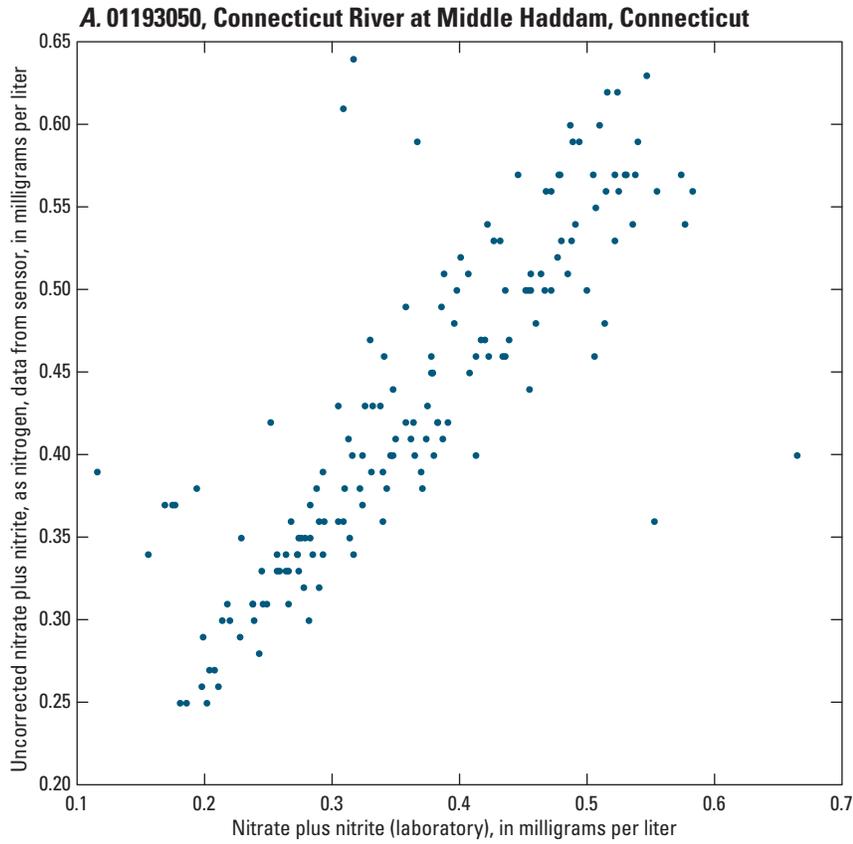
**Figure 6.**   Comparison of laboratory and sensor data for nitrate plus nitrite, as *A*, uncorrected and *B*, adjusted to unique instrument characteristics, for the Connecticut River at Middle Haddam, Conn.
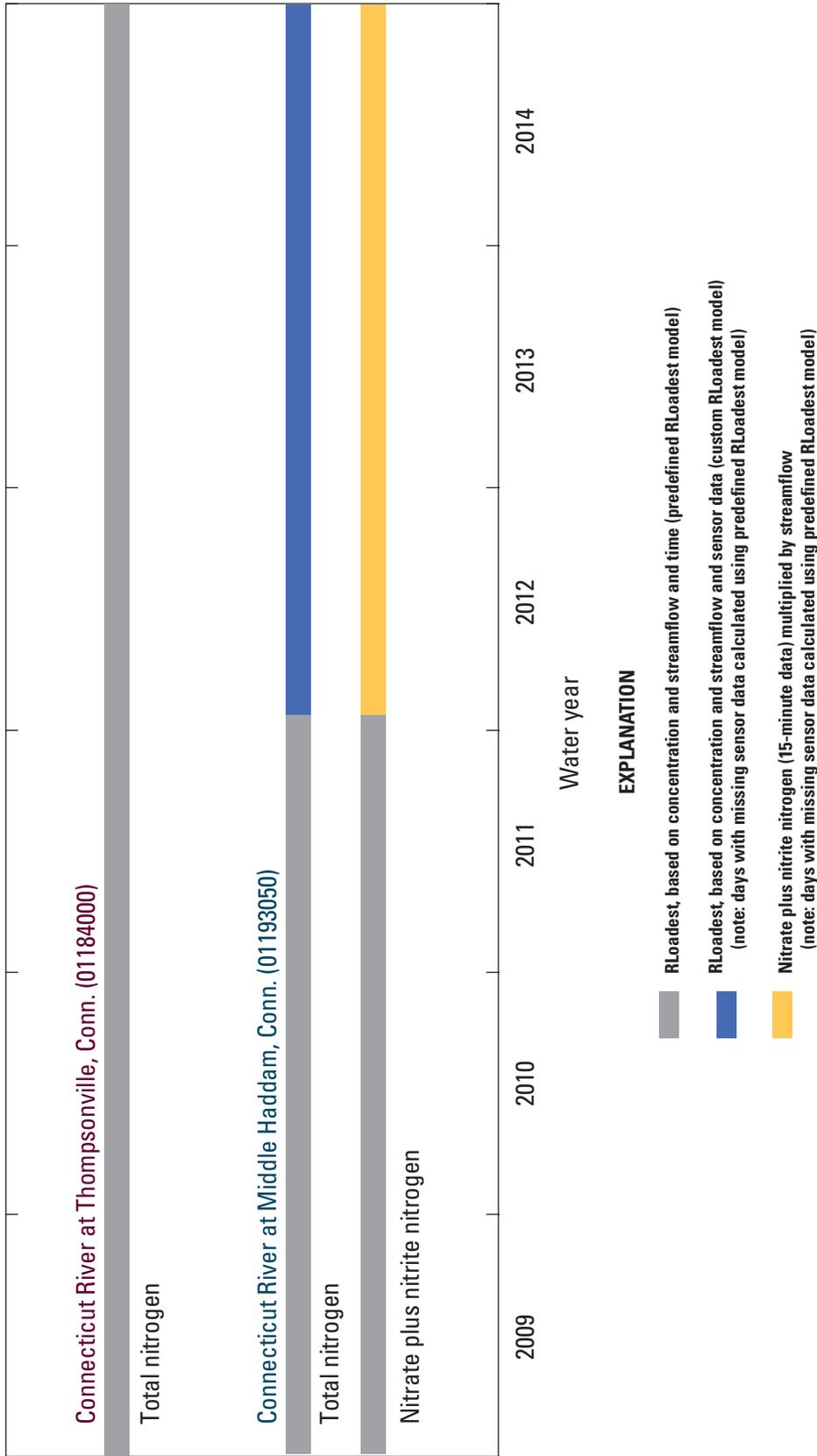
Figure 7.   Timeline of methods of daily load calculation for nitrate plus nitrite nitrogen and of total nitrogen for the Connecticut River at Middle Haddam and Thompsonville, Conn., for water years 2009 to 2014.

nitrogen sensor measurements multiplied by the corresponding 15-minute flow value to determine an instantaneous load. The daily load values were then determined by calculating the mean value of instantaneous load for each day. Periods of missing record were backfilled using the daily predefined RLoadest model for nitrate plus nitrite nitrogen loads described earlier in this section.

Load estimates for total nitrogen for the Connecticut River at Thompsonville also were computed with a predefined RLoadest using data from water years 2007 to 2015. A longer record was available for this streamgage and thus was used to improve the model calibration.

Nitrogen Concentrations and Loads

Nitrate Plus Nitrite Nitrogen

Concentrations of nitrate plus nitrite nitrogen in discrete, periodic samples and concentrations in the data collected by the nitrate plus nitrite sensor had similar distributions from 2011 to 2014. The mean and median concentrations in both datasets were similar (table 1), and the interquartile ranges (75th percentile minus the 25th percentile) were 0.185 mg/L for the samples and 0.15 mg/L for the nitrate sensor measurements, indicating that the typical range of concentration over the sampling period and the sensor-data period was narrow and the statistics were similar.

The instantaneous load of nitrate plus nitrite nitrogen was calculated for each sensor measurement. Instantaneous load data were filtered to remove data from partial days, those with fewer than 82 measurements. The daily (net) load was then calculated by computing the mean of the instantaneous values for each day that had sufficient measurements.

Daily nitrate plus nitrite nitrogen loads for the entire study period (water years 2009–14) also were calculated using RLoadest based on the results of analyses of 239 samples and the daily mean discharge for the streamgage that was calculated using the Godin filter (fig. 4) as described in the "Continuous Streamflow Data Collection" section. On sample dates when more than one sample was collected for nitrate

plus nitrite nitrogen, the average concentration for that day was used. The predefined RLoadest model selected was model number 9 from Runkel and others (2004), also known as LOADEST–7 (Hirsch, 2014; Lee and others, 2016). The model was selected on the basis of the lowest Akaike information criterion. This can be done by automatic selection in the LOADEST model. It was noted in Lee and others (2016) that this method of selection can have a high mean percent error, particularly for nitrate plus nitrite nitrogen. As a check on model selection, LOADEST models 1 to 9 (Runkel and others, 2004) were run, and the outputs and model diagnostics were compared. In comparison to the other models, model 9 had the highest coefficient of determination (R^2), the lowest serial correlation of residuals, and the lowest percent load bias (Runkel, 2013). Model 9 is of the following form:

$$\ln C = a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi dtime) + a_4 \cos(2\pi dtime) + a_5\, dtime + a_6\, dtime^2 + e, \quad (1)$$

where

C	is the constituent concentration (mean value used if more than one sample per day);
a_0, a_1, a_2, etc.	is the model coefficient for each variable;
$\ln Q$	is ln(*streamflow*) – center of ln(*streamflow*);
streamflow	is a daily filtered tidal discharge value;
dtime	decimal time – center of decimal time; and
e	is a model residual, assumed to be independent across observations and identically normally distributed.

At the Connecticut River at Middle Haddam streamgage, daily load estimates for nitrate plus nitrite nitrogen from the RLoadest output were used to fill periods of missing data from nitrate plus nitrite sensor malfunctions from December 2011 to September 2014 and for the period before sensor installation (2008–11). The two records together were used to create a composite daily load record for nitrate plus nitrite nitrogen (fig. 8). The daily load record from 2011 to 2014 (excluding days with missing data because of sensor malfunction) for nitrate plus nitrite nitrogen from the nitrate sensor data does not have a 95-percent prediction interval because the calculation is based on use of adjusted sensor measurements. The summary of the daily 95-percent prediction intervals for water

Table 1. Statistics on nitrate plus nitrite concentrations from periodic samples collected from December 2011 to September 2014 and from nitrate sensor measurements, Connecticut River at Middle Haddam, Conn.

[Concentrations are in milligrams per liter]

| Nitrate plus nitrite nitrogen method	Number of samples	Mean	Minimum	25th percentile	Median	75th percentile	Maximum
Laboratory analyzed samples	177	0.374	0.117	0.284	0.371	0.469	0.666
Sensor measurement	87,263	0.388	0.160	0.310	0.390	0.460	0.630
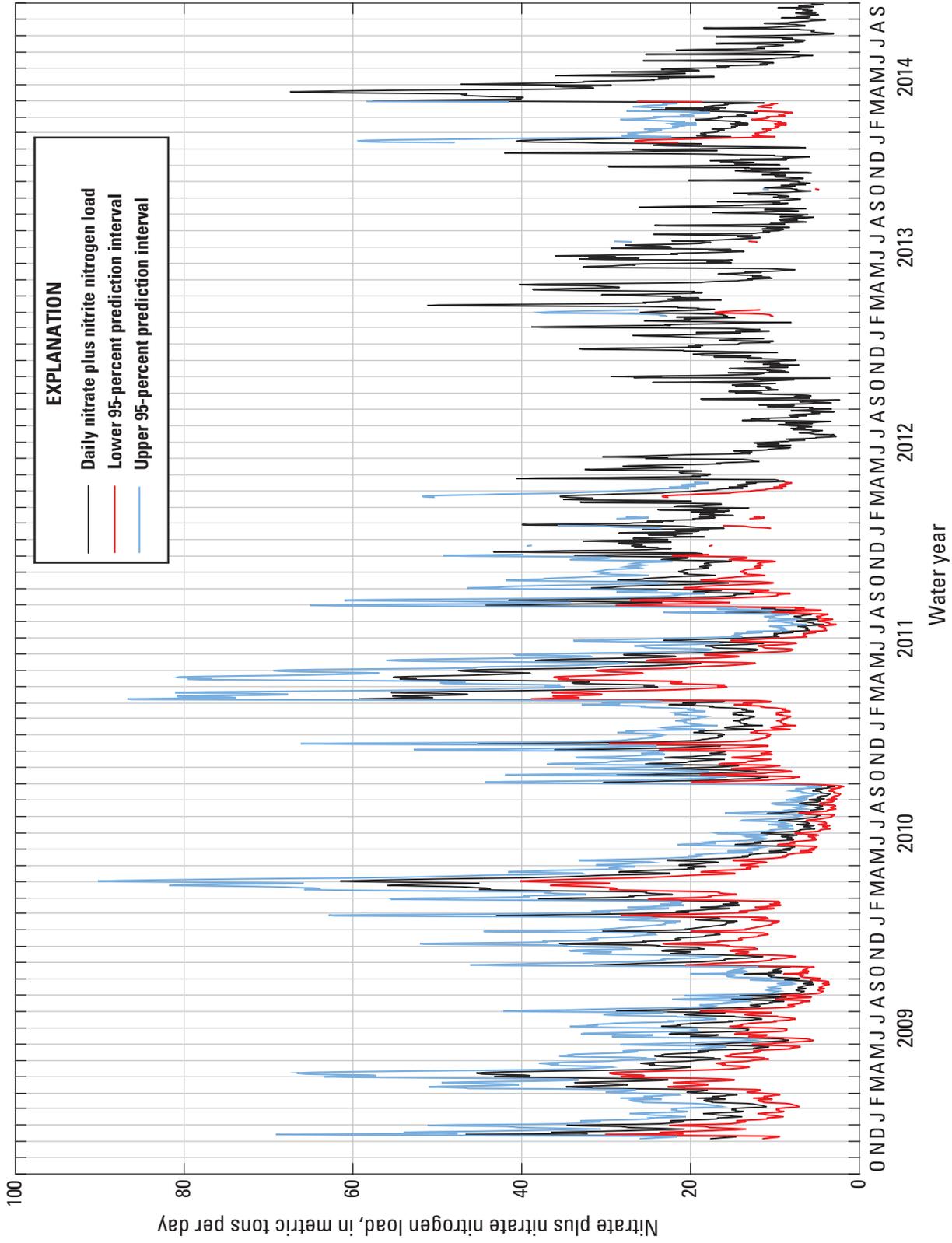
Figure 8. Daily nitrate plus nitrite nitrogen loads at the Connecticut River at Middle Haddam, Conn., and associated prediction intervals for RLoadest results for water years 2009 to 2014.

years 2009 to 2014 for the days with RLoadest results is listed in table 2. The mean daily 95-percent prediction interval on the daily nitrate plus nitrite nitrogen load calculated on the days where RLoadest was used was 6.8 metric tons per day (t/d) below and 9.1 t/d above the estimated mean daily value of 19.6 (table 2*A*). The annual loads of nitrate plus nitrite as nitrogen for water years 2010 to 2014 ranged from 6,240 to 8,000 t. The estimated load for water year 2009 is about 6,920 t based on the average mean of 18.96 t/d (table 2*A*). The daily load estimates are published in Mullaney and others (2017).

For comparison, annual loads of nitrate plus nitrite nitrogen computed using only the RLoadest model (no sensor data used) were calculated along with the annual aggregated confidence intervals. Loads estimated by this method for water years 2012 to 2014 (the years for which values were estimated using sensor data in the above described results) are similar to those estimated using sensor data (table 2*B*). Mean annual prediction intervals ranged from -4.80 to +4.98 percent.

Total Nitrogen

Connecticut River at Middle Haddam

Concentrations of total nitrogen were predicted through the use of a regression model for 15-minute sensor values from December 2011 to September 2014. The final regression model inputs included the variables nitrate plus nitrite nitrogen and turbidity sensor data (fig. 9; table 3). Streamflow data were not used in the regression to estimate concentration because the flow becomes negative (upstream flow) during incoming tides at times of the year when flows are low. Negative values cannot be used for a model with natural log of streamflow. The dependent variable was total nitrogen concentration. Total nitrogen concentrations for the prediction dataset were then computed by applying the regression model to the 15-minute sensor data. A summary of predicted total nitrogen concentrations is listed in table 4. Total nitrogen concentration

Table 2.   Nitrate plus nitrite loads for the Connecticut River at Middle Haddam, Conn., for water years 2009 to 2014.

[*A*, Composite summary from sensor measurements and with the use of RLoadest model 9, including mean daily prediction intervals, for periods using RLoadest, for water years 2009 to 2014. *B*, Annual loads and prediction intervals calculated using only the RLoadest model for water years 2010 to 2014. All statistical values are shown unrounded. —, no data]

			A, Sensor measurements plus RLoadest model 9			
Water year[1]	**Mean daily load, in metric tons**	**Number of days**	**Number of days load calculated using RLoadest**	**95-percent prediction interval of the mean daily nitrate plus nitrite nitrogen load for days calculated with RLoadest (model 9), in metric tons per day**		**Annual load, combining two methods, in metric tons**
				Lower limit	**Upper limit**	
2009	18.97	299	299	12.37	27.86	6,924[2]
2010	17.47	365	365	11.46	25.56	6,377
2011	21.91	365	365	14.39	32.03	7,999
2012	17.83	366	107	14.02	31.20	6,526
2013	17.51	365	16	12.78	28.36	6,390
2014	17.10	365	75	12.55	27.94	6,242

		B, RLoadest model 9 only			
Water year[1]	**Annual load, in metric tons**	**95-percent prediction interval of the annual nitrate plus nitrite nitrogen load, in metric tons**		**95-percent prediction interval of the annual nitrate plus nitrite nitrogen load, in percent**	
		Lower limit	**Upper limit**	**Lower limit**	**Upper limit**
2010	6,377	6,023	6,746	5.55	5.79
2011	7,999	7,630	8,380	4.60	4.77
2012	6,518	6,217	6,830	4.62	4.79
2013	6,569	6,307	6,840	3.99	4.11
2014	5,923	5,614	6,245	5.23	5.44
Mean				4.80	4.98

[1]Data for water year 2009 are incomplete because the sampling period began after the start of water year 2009.

[2]Estimate for water year 2009, based on mean value for available data.
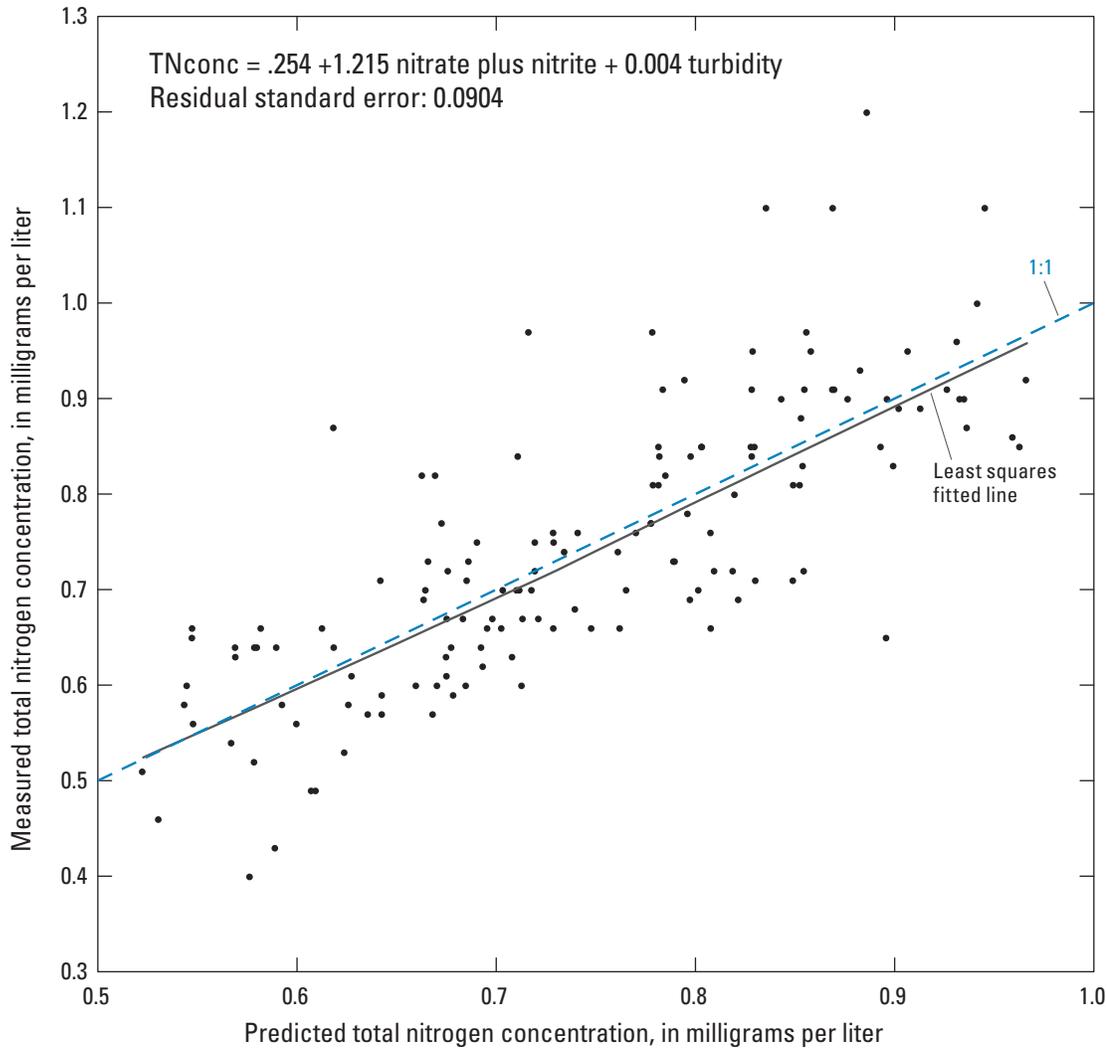
Figure 9. Predicted versus measured total nitrogen concentrations at the Connecticut River at Middle Haddam, Conn., streamgage based on data from 2011 to 2014. TNconc, total nitrogen concentration.

Table 3. Regression estimates of model coefficients, standard errors, with *t*-statistics and *p*-values to describe the variability of total nitrogen concentrations at the Connecticut River at Middle Haddam, Conn., for water years 2011 to 2014.

[Adjusted coefficient of determination (R^2) is 0.608; residual standard error is 0.0904 on 140 degrees of freedom. <, less than, no data for water years 2009–10, as sensors were not installed during this period.]

Variable	Coefficient estimates	Standard error	*t*-statistic	*p*-value
Intercept (dimensionless)	0.253806	0.033934	7.48	<0.001
Nitrate plus nitrite nitrogen from sensor, in milligrams per liter	1.214782	0.08158	14.89	<0.001
Turbidity, in formazin nephelometric units	0.004463	0.000594	7.52	<0.001

Table 4.   Statistics on total nitrogen concentrations from periodic samples collected from December 2011 to September 2014, and from regression model estimates, Connecticut River at Middle Haddam, Conn.

[Concentrations are in milligrams per liter. NA, not applicable]

Nitrate plus nitrite nitrogen method	Number of samples	Mean lower 95-percent prediction interval	Mean	Mean upper 95-percent prediction interval	Minimum	25th percentile	Median	75th percentile	Maximum
Laboratory analyzed samples	177	NA	0.752	NA	0.400	0.640	0.730	0.850	1.200
Regression model	81,067	0.571	0.751	0.931	0.504	0.665	0.750	0.830	1.514

estimates from December 2011 to September 2014 are published in Mullaney and others (2017). The concentration estimates included periods of missing record because of sensor malfunction. A total of 44 laboratory analyses of total nitrogen were eliminated because of missing associated values for nitrate plus nitrite nitrogen or turbidity sensor data.

Daily total nitrogen load at the Connecticut River at Middle Haddam from December 2011 to September 2014 was calculated using RLoadest with the addition of the following variables: mean daily nitrate plus nitrite nitrogen and turbidity sensor data. This method was chosen over the other method that used the regression for concentration described in this section (fig. 9; table 3) based on 15-minute values of nitrate plus nitrite nitrogen sensor data and turbidity. The method that employs 15-minute values is capable of producing an estimate of the daily load; however, there are no methods suitable for describing the uncertainty (prediction interval) when aggregated at the daily scale (Gregory Schwarz, U.S. Geological Survey, written commun., 2017). Therefore, a custom RLoadest model (Lorenz, 2015) was created using the variables described in the following equation:

$$\ln C = a_0 + a_1 \ln Q + a_2 \, (\text{UV–NO}_3\text{NO}_2) + a_3 \, (Turb) + e, \quad (2)$$

where

$\text{UV–NO}_3\text{NO}_2$ is the mean daily nitrate plus nitrite, from sensor measurements, and

$Turb$ is mean daily turbidity, from turbidity sensor measurements.

In order to fill gaps in the record from sensor malfunction, daily total nitrogen loads for the entire study period also were calculated using RLoadest, based on the use of 239 observations of total nitrogen for samples analyzed at the laboratory along with the daily mean discharge for the station calculated using the Godin filter (fig. 4) as described in the "Continuous Streamflow Data Collection" section. The RLoadest model selected was also model number 9 (eq. 1; Runkel and others, 2004). The two records together were used to create a composite daily load record for total nitrogen (fig. 10; table 5A). The summary of the 95-percent prediction intervals for water years 2009 to 2014 for both load estimation

methods is listed in table 5. The mean daily prediction intervals were smallest for water years 2013 and 2014, for which the custom RLoadest model based on sensor data was primarily used (table 5).

The annual loads of total nitrogen for water years 2010 to 2014 ranged from 12,900 to 19,200 t, of which about 42 to 49 percent was in the form of nitrate plus nitrite. The estimated load for water year 2009, for which data were incomplete, is 13,980 t based on the daily mean of 38.3 t/d (table 5). Daily load estimates are published in Mullaney and others (2017).

For comparison, annual loads calculated using only the RLoadest model 9 (no sensor data used in the regression) ranged from 12,333 t in water year 2014 to 19,201 t in water year 2011. For the years where use of the two methods overlap, the loads developed using the RLoadest model were similar to those computed using the custom RLoadest model. The mean prediction intervals on the RLoadest model (number 9) for water years 2010 to 2014 ranged from -4.28 to +4.42 of the annual load predicted by this method.

Connecticut River at Thompsonville

Total nitrogen loads at the Thompsonville station for water years 2009 to 2014 were calculated with a predefined RLoadest model, using the analyses of 113 samples for total nitrogen (fig. 11). Because this streamgage has a long-term record, additional water-quality data from water years 2008 and 2015 were used to improve the calibration for the load estimation. The data for total nitrogen were used along with daily mean flow data as input to the model.

The predefined RLoadest model selected was model number 4 (Runkel and others, 2004). This model is of the following form:

$$\ln C = a_0 + a_1 \ln Q + a_3 \sin(2\pi dtime) + a_4 \cos(2\pi dtime) + e, \quad (3)$$

where

$\ln Q$ is ln(*streamflow*) – center of ln(*streamflow*) and

*streamflow*   is a daily mean discharge value.
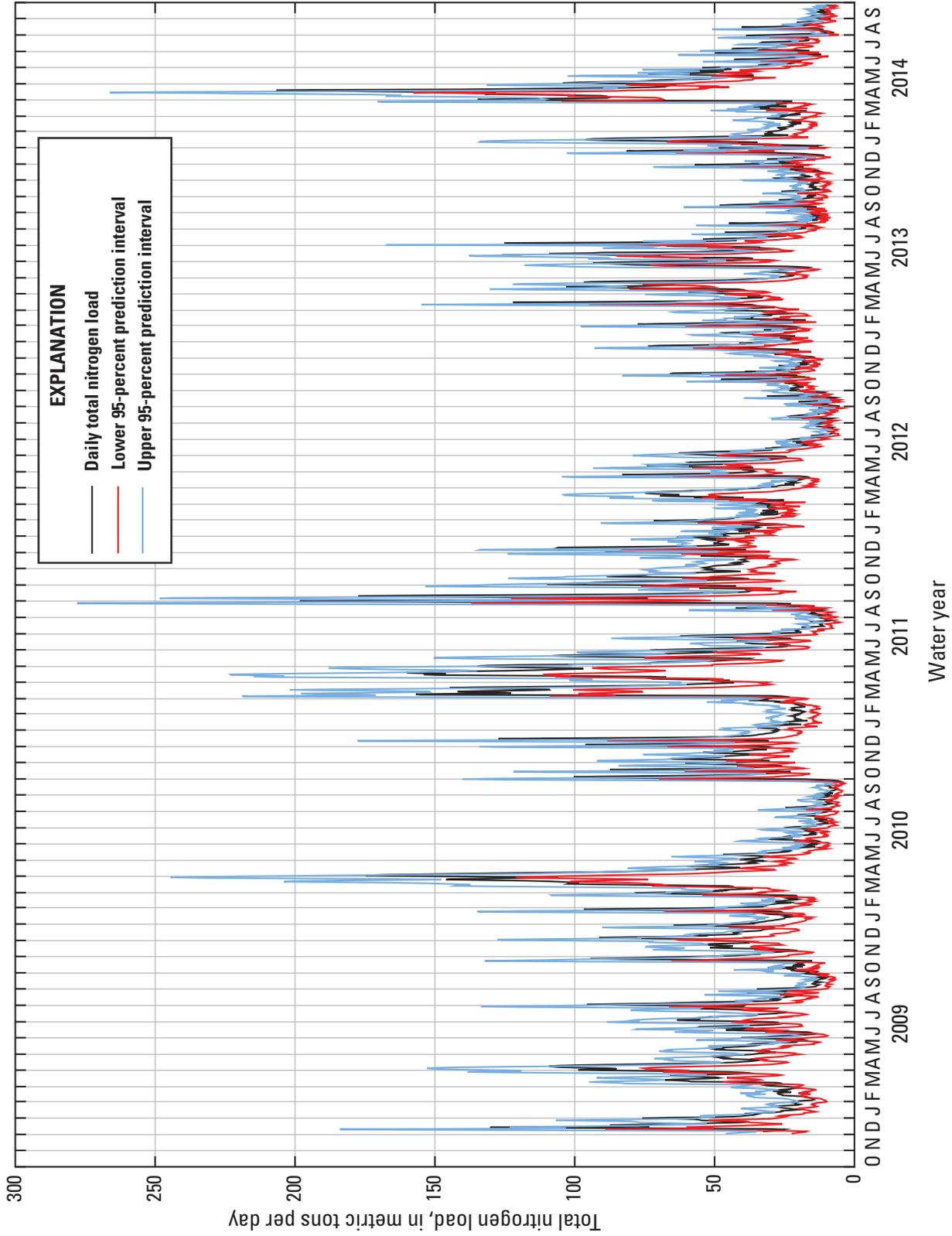
Figure 10.   Daily total nitrogen loads at the Connecticut River at Middle Haddam, Conn., and associated 95-percent prediction intervals for water years 2009 to 2014.

Table 5.   Total nitrogen loads and prediction intervals for the Connecticut River at Middle Haddam, Conn., for water years 2009 to 2014.

[*A*, Composite summary from predefined RLoadest model and custom RLoadest model and *B*, annual values calculated using only the predefined RLoadest model. All values are unrounded. —, data not available]

A, Composite, daily, and annual loads								
Water year	Mean daily load, in metric tons	Number of days[1]	Number of days load calculated using RLoadest		Limits of mean daily 95-percent prediction interval, in metric tons[1]		Annual load, in metric tons[1]	
			Model 9	Custom model[2]	Lower	Upper		
2009	38.31	299	299	0	26.50	53.65	13,983[3]	
2010	35.80	365	365	0	24.86	49.95	13,065	
2011	52.61	365	365	0	36.57	73.35	19,201	
2012	36.78	366	104	262	27.55	48.22	13,461	
2013	36.69	365	23	342	28.47	46.59	13,393	
2014	35.33	365	124	241	26.71	45.94	12,895	

B, Annual loads, RLoadest model 9					
Water year[1]	Annual load, in metric tons	95-percent prediction interval of the annual total nitrogen load, in metric tons		95-percent prediction interval of the annual total nitrogen load, in percent	
		Lower limit	Upper limit	Lower limit	Upper limit
2009	—	—	—	—	—
2010	13,065	12,424	13,730	4.91	5.09
2011	19,201	18,398	20,030	4.18	4.31
2012	13,866	13,300	14,451	4.09	4.21
2013	14,136	13,636	14,649	3.53	3.63
2014	12,333	11,756	12,930	4.68	4.84
Mean				4.28	4.42

[1]Data for water year 2009 are incomplete because the sampling period began after the start of water year 2009.

[2]Custom RLoadest model includes log of flow, mean daily nitrate plus nitrite sensor measurements, and mean daily turbidity sensor measurements (equation 2).

[3]Estimate for water year 2009, based on mean daily value for available data.
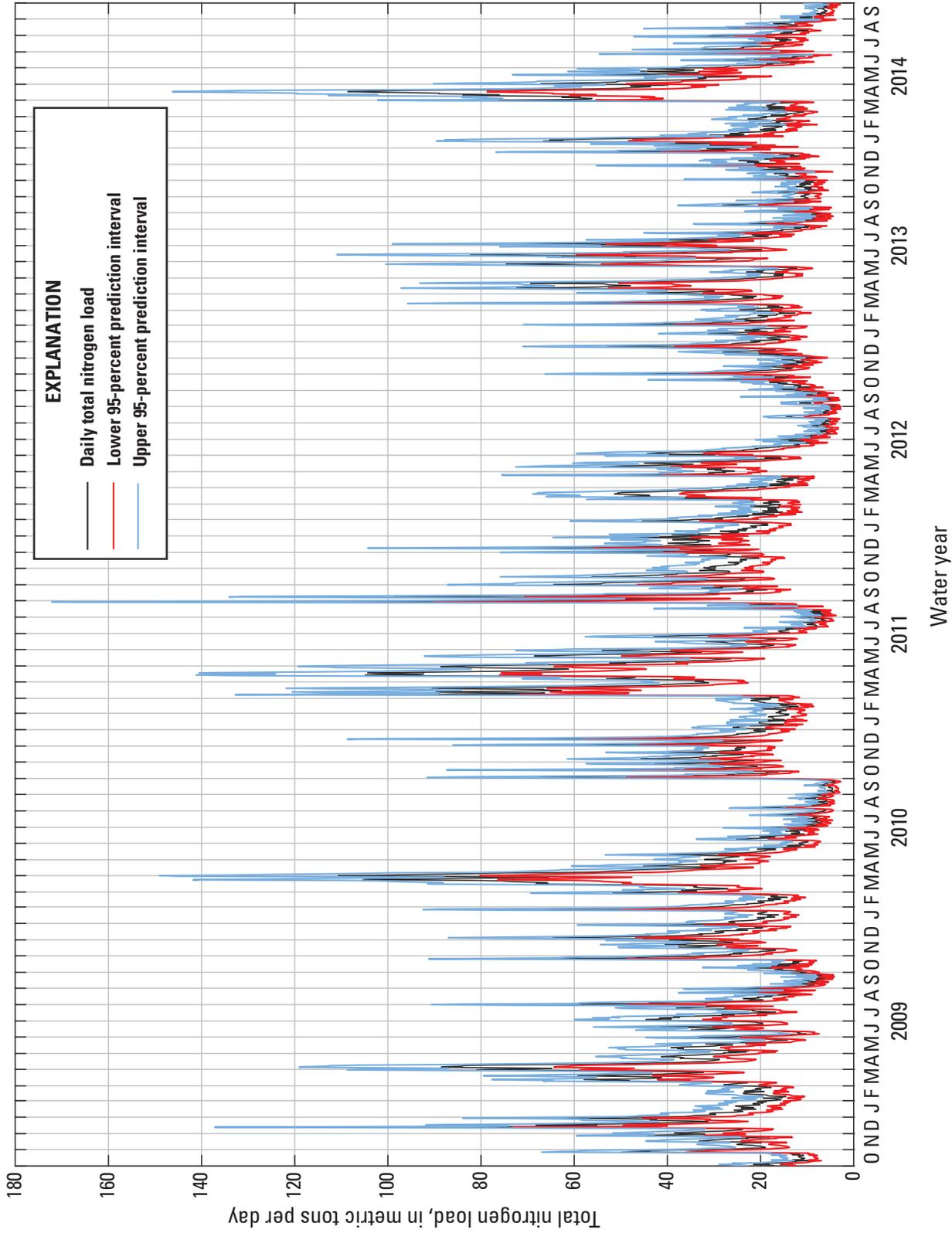
Figure 11.   Daily total nitrogen loads at the Connecticut River at Thompsonville, Conn., and associated prediction intervals for results for water years 2009 to 2014.

The annual loads of total nitrogen for water years 2009 to 2014 at the Thompsonville station ranged from 8,720 to 12,540 t (table 6). The mean prediction intervals on the annual loads from RLoadest (model 4) for water years 2009 to 2014 ranged from -3.79 to +3.90 percent of the annual load. To obtain the annual loads, daily load estimates (Mullaney and others, 2017) were summed for each water year.

Gain in Total Nitrogen Load From Thompsonville to Middle Haddam

The increase in drainage area from the Connecticut River at Thompsonville streamgage to the Connecticut River at Middle Haddam streamgage is 3,204 km², or about 11.4 percent of the total upstream drainage area. The gain in total nitrogen load between the two stations ranged from an estimated 3,430 t in water year 2009 to 6,660 t in water year 2011 (table 7), indicating an increase in total nitrogen yield by three to five times. The total nitrogen yield from the drainage area between the two stations ranged from about 10.7 to 20.8 kilograms per hectare (kg/ha). This compares with the yields at the Thompsonville station that ranged from 3.5 to 4.2 kg/ha, indicating a substantial gain in total nitrogen concentrations between the two stations.

Gains in total nitrogen are related to the increased drainage area and to the increased urbanization of the land in the drainage basin between the two streamgages. Forested land represents 51.2 percent of the drainage area, developed land represents about 31 percent of the drainage area, agricultural land (pasture, hay, and cultivated crops) represents about 7.9 percent, and wetlands represent 7.8 percent (Homer and others, 2015). Wastewater from 24 treatment facilities totaling

Table 6. Total nitrogen loads and prediction intervals for the Connecticut River at Thompsonville, Conn., for water years 2009 to 2014.

[All values are unrounded.]

Water year	Mean daily load, in metric tons	Daily 95-percent prediction interval, in metric tons		Annual load, in metric tons	95-percent prediction interval of the annual total nitrogen load, in metric tons		95-percent prediction interval of the annual total nitrogen load, in percent	
		Lower limit	Upper limit		Lower limit	Upper limit	Lower limit	Upper limit
2009	28.93	21.04	38.82	10,558	10,167	10,959	3.70	3.80
2010	25.27	18.38	33.91	9,222	8,868	9,587	3.84	3.95
2011	34.36	24.95	46.18	12,540	11,988	13,111	4.41	4.55
2012	23.82	17.33	31.98	8,719	8,408	9,039	3.57	3.67
2013	25.10	18.26	33.69	9,162	8,840	9,493	3.52	3.61
2014	24.78	18.03	33.26	9,046	8,712	9,390	3.70	3.80
Mean							3.79	3.90

Table 7. Summary of annual total nitrogen loads, differences between stations, and calendar year total nitrogen loads from wastewater treatment facilities between the Connecticut River at Thompsonville, Conn., and the Connecticut River at Middle Haddam, Conn., for water years 2009 to 2014.

[All values are unrounded.]

Water year	Annual total nitrogen at Middle Haddam, in metric tons	Annual total nitrogen load at Thompsonville, in metric tons	Gain in total nitrogen load, in metric tons	Calendar year nitrogen loads from wastewater treatment facilities between the stations, in metric tons[2]
2009	13,983[1]	10,558	3,425[1]	1,788
2010	13,065	9,222	3,843	1,596
2011	19,201	12,540	6,661	2,094
2012	13,461	8,719	4,742	1,579
2013	13,393	9,162	4,231	1,692
2014	12,895	9,046	3,849	1,540

[1]Estimate for water year 2009, based on mean daily value for available data.

[2]Connecticut Department of Energy and Environmental Protection, 2016.

about 140 Mgal/d (530,000 m³/d) is discharged to rivers (Mullaney and others, 2002), representing about half of the wastewater discharge volume for the entire basin upstream from the Middle Haddam streamgage. The annual contribution of total nitrogen from wastewater discharge from the drainage area between the two streamgages ranged from 1,540 to 2,094 t for calendar years 2009 to 2014 (fig. 2; table 7), or about 31 percent (2011) to an estimated 52 percent (2009) of the gain in nitrogen load between the Thompsonville and Middle Haddam streamgages.

Summary

In 2009, the U.S. Geological Survey, in cooperation with the Connecticut Department of Energy and Environmental Protection, began streamflow and water-quality monitoring for nitrogen concentrations at the Connecticut River at Middle Haddam, Connecticut. At the end of 2011, sensors were installed at the Middle Haddam streamgage to collect data at 15-minute intervals on the concentrations of nitrate plus nitrite nitrogen, colored dissolved organic matter, and dissolved oxygen and on specific conductance, temperature, turbidity, and pH of the water. Sensor data on concentrations of nitrate plus nitrite nitrogen were corrected on the basis of laboratory analyses of samples collected during the earlier monitoring period. It was determined that the relations between nitrate plus nitrite nitrogen concentrations measured by the sensor and by the laboratory were not consistent among different instruments; therefore, sensor data were adjusted separately for each instrument used.

Nitrate plus nitrite nitrogen loads were computed by multiplying the 15-minute adjusted nitrate plus nitrite nitrogen sensor concentrations by instantaneous values of flow. The daily load was calculated by taking the mean of the 15-minute loads for the day. Before sensor installation in 2011 and for periods of missing record from instrument malfunction, the daily loads were calculated using a predefined RLoadest regression model, which required the use of mean laboratory values of the nitrate plus nitrite nitrogen concentrations for a given day and the mean daily flow at the streamgage. Daily mean flow for this tidally affected streamgage was determined using a Godin filter applied to the 5-minute flow data.

In order to calculate concentrations of total nitrogen for the sensor period, a regression model was developed to describe the variability in laboratory measurements of total nitrogen, using nitrate plus nitrite nitrogen sensor data and turbidity data. Predictions of total nitrogen concentrations were made using this model for 15-minute sensor data from the end of 2011 to 2014. Daily loads of total nitrogen during the sensor period were computed using a custom RLoadest model, which used mean daily sensor values of nitrate plus nitrite nitrogen and turbidity, along with mean daily streamflow.

Daily total nitrogen loads before sensor installation in 2011 and during subsequent periods of missing record were calculated using a predefined RLoadest model, using laboratory measurements of total nitrogen and the mean daily flow for this tidal streamgage. In addition to these load analyses, a predefined RLoadest model also was used to compute total nitrogen loads using data from the upstream Connecticut River at Thompsonville streamgage. This estimate of load provided information on the increases in total nitrogen loads from the drainage basin between the Thompsonville streamgage and the downstream Middle Haddam streamgage.

Composite total nitrogen loads from the Middle Haddam streamgage ranged from 12,900 metric tons (t) in water year 2015 to 19,200 t in water year 2011. The mean daily prediction intervals were smallest for water years 2013 and 2014 where the custom RLoadest model based on sensor data was primarily used, indicating that the sensor data provided an improved method for calculating daily total nitrogen loads at this streamgage with reduced uncertainty. Prediction intervals would likely be smaller with fewer missing days of sensor record because of malfunction.

The annual mean prediction interval on the annual loads of total nitrogen calculated using the predefined RLoadest model (with no sensor data) was -4.28 to +4.42 percent at the Middle Haddam streamgage and -3.79 to +3.90 percent at the Thompsonville streamgage.

Nitrate plus nitrite nitrogen loads ranged from 6,240 t in water year 2014 to 8,000 t in water year 2011. Nitrate plus nitrite nitrogen ranged from about 42 to 49 percent of the annual daily mean load of total nitrogen.

The total nitrogen loads at the Connecticut River at Thompsonville ranged from 8,720 t in water year 2014 to 12,540 t in water year 2011. The gain in annual total nitrogen load in the intervening drainage basin between the Thompsonville and Middle Haddam streamgages ranged from 3,430 to 6,660 t, indicating an increase in total nitrogen yield by three to five times.

Gains in total nitrogen are related to the increased drainage area and to the increased urbanization of the land in the drainage basin between the two streamgages. The contribution of total nitrogen from wastewater discharge between the two sites decreased substantially before the beginning of this study and ranged from about 31 to 52 percent of the gain in nitrogen load between Thompsonville and Middle Haddam.

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