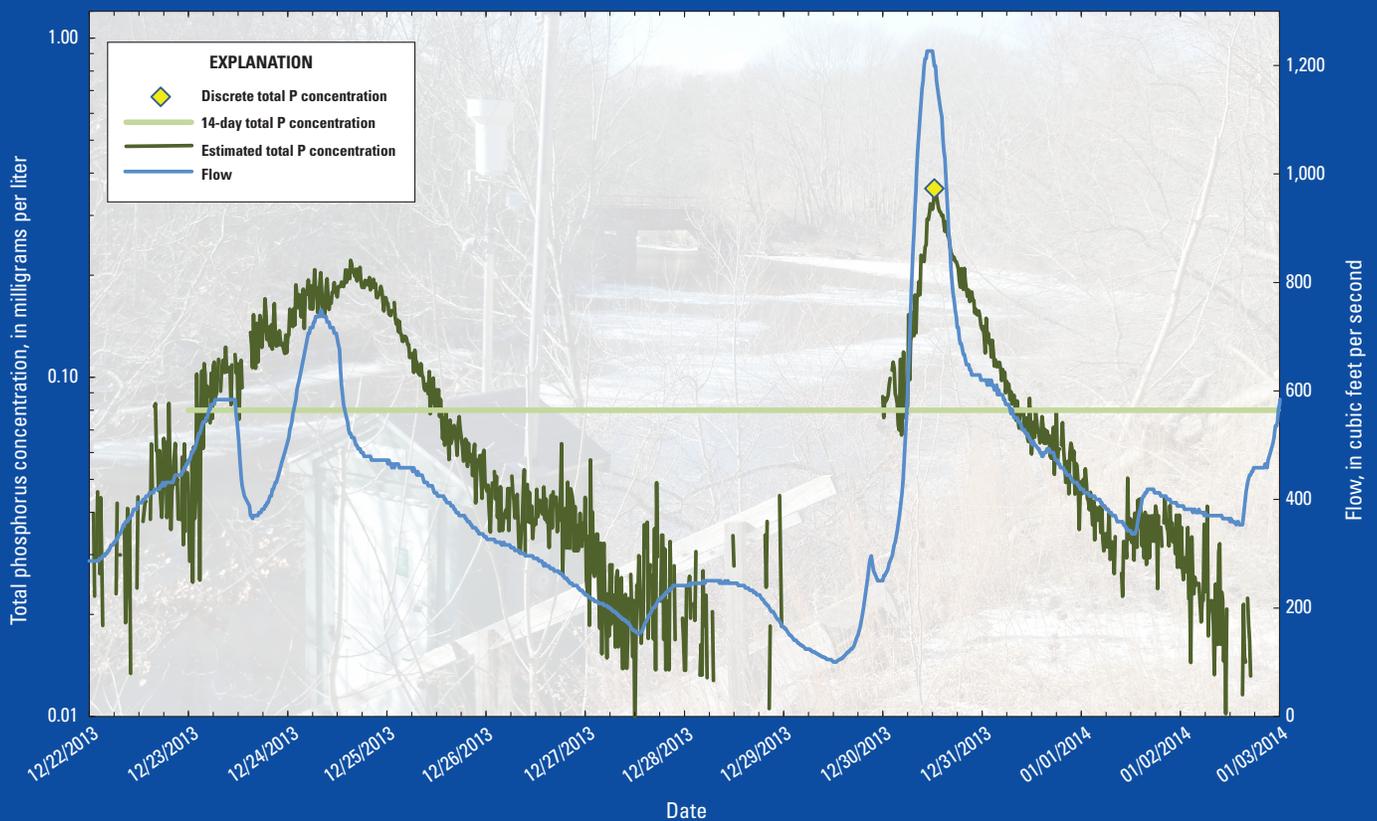


Prepared in cooperation with the Massachusetts Department of Environmental Protection

Nutrient and Metal Loads Estimated by Using Discrete, Automated, and Continuous Water-Quality Monitoring Techniques for the Blackstone River at the Massachusetts-Rhode Island State Line, Water Years 2013–14



Scientific Investigations Report 2017–5094

Cover. Monitoring station on the Blackstone River at Millville, Massachusetts, in winter 2014.

Banner photograph: Panoramic shot of the Blackstone River at Millville, Massachusetts, station (01111230).

Graph: Figure 9 from this report.

Back cover photograph: Blackstone River, looking downstream from the railroad bridge about 400 feet upstream from the Blackstone River at Millville, Massachusetts, station (01111230). Photographs by Jason Sorenson, U.S. Geological Survey.

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By Jason R. Sorenson, Gregory E. Granato, and Kirk P. Smith

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Scientific Investigations Report 2017–5094

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Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
square mile (mi ²)	2.590	square kilometer (km ²)
acre-foot (acre-ft)	1,233	cubic meter (m ³)
foot per second (ft/s)	0.3048	meter per second (m/s)
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)

International System of Units to U.S. customary units

Multiply	By	To obtain
micrometer (μm)	0.00003937	inch (in.)
milliliter (mL)	0.03381	ounce, fluid (fl. oz)
liter (L)	0.2642	gallon (gal)
cubic meter per second (m ³ /s)	35.31	cubic foot per second (ft ³ /s)
kilogram (kg)	2.205	pound avoirdupois (lb)
kilogram per year (kg/yr)	2.205	pound per year (lb/yr)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit as follows:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32.$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) / 1.8.$$

Datum

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

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μS/cm at 25 °C).

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

Abbreviations

ASEE	average standard error of the estimate
ASEP	average standard error of the prediction
DOC	dissolved organic carbon
EPA	U.S. Environmental Protection Agency
EWI	equal-width increment
FNU	formazin nephelometric unit
MassDEP	Massachusetts Department of Environmental Protection
NWQL	National Water Quality Laboratory
ppb	parts per billion
PRESS	prediction error sum of squares
R^2	coefficient of determination
RIDEM	Rhode Island Department of Environmental Management
RPD	relative percent difference
TSS	total suspended sediment
USGS	U.S. Geological Survey
WY	water year
VIF	variance inflation factor

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By Jason R. Sorenson, Gregory E. Granato, and Kirk P. Smith

Abstract

Flow-proportional composite water samples were collected in water years 2013 and 2014 by the U.S. Geological Survey, in cooperation with the Massachusetts Department of Environmental Protection, from the Blackstone River at Millville, Massachusetts (U.S. Geological Survey station 01111230), about 0.5 mile from the border with Rhode Island. Samples were collected in order to better understand the dynamics of selected nutrient and metal constituents, assist with planning, guide activities to meet water-quality goals, and provide real-time water-quality information to the public. An automated system collected the samples at 14-day intervals to determine total and dissolved nitrogen and phosphorus concentrations, to provide accurate monthly nutrient concentration data, and to calculate monthly load estimates. Concentrations of dissolved trace metals and total aluminum were determined from 4-day composite water samples that were collected twice monthly by the automated system. Results from 4-day composites provide stakeholders with information to evaluate trace metals on the basis of chronic 4-day exposure criteria for aquatic life, and the potential to use the biotic ligand model to evaluate copper concentrations. Nutrient, trace metal, suspended sediment, dissolved organic carbon, and chlorophyll *a* concentrations were determined from discrete samples collected at the Millville station and from across the stream transect at the upstream railroad bridge, and these concentrations served as a means to evaluate the representativeness of the Millville point location.

Analytical results from samples collected with the automated flow-proportional sampling system provided the means to calculate monthly and annual loading data. Total nitrogen and total phosphorus loads in water year (WY) 2013 were about 447,000 and 36,000 kilograms (kg), respectively. In WY 2014, annual loads of total nitrogen and total phosphorus were about 342,000 and 21,000 kg, respectively. Total nitrogen and total phosphorus loads from WYs 2013 and 2014

were about 56 and 65 percent lower than those reported for WYs 2008 and 2009. The higher loads in 2008 and 2009 may be explained by the higher than average flows in WY 2009 and by facility upgrades made by wastewater treatment facilities in the basin.

Median loads were determined from composite samples collected with the automated system between October 2012 and October 2014. Median dissolved cadmium and chromium 4-day loads were 0.55 and 0.84 kg, respectively. Dissolved copper and total lead median 4-day loads were 8.02 and 1.42 kg, respectively. The dissolved nickel median 4-day load was 5.45 kg, and the dissolved zinc median 4-day load was 36 kg. Median total aluminum 4-day loads were about 197 kg.

Spearman's rank correlation analyses were used with discrete sample concentrations and continuous records of temperature, specific conductance, turbidity, and chlorophyll *a* to identify correlations between variables that could be used to develop regression equations for estimating real-time concentrations of constituents. Correlation coefficients were generated for flow, precipitation, antecedent precipitation, physical parameters, and chemical constituents. A 95-percent confidence limit for each value of Spearman's rho was calculated, and multiple linear regression analysis using ordinary least squares regression techniques was used to develop regression equations for concentrations of total phosphorus, total nitrogen, suspended sediment concentration, total copper, and total aluminum. Although the correlations are based on the limited amount of data collected as part of this study, the potential to monitor water-quality changes in real time may be of value to resource managers and decision makers.

Introduction

Located in central Massachusetts and Rhode Island, the 475 square mile (mi²) Blackstone River Basin contains several urban centers and other major areas of development along the

48-mile course of the river, which discharges into Narragansett Bay (fig. 1). The Blackstone River was once referred to as “the hardest working river in America” (Massachusetts Executive Office of Energy and Environmental Affairs, 2013), and in recognition of being one of the birthplaces of the industrial revolution, the Blackstone River Valley National Heritage Corridor was established in December 2014. Detailed descriptions of the study area and industrial heritage are in earlier reports (Barbaro, 2007; Massachusetts Department of Environmental Protection [MassDEP], 2010; Zimmerman and others, 2015).

The Blackstone River and several of its tributaries are included on the State of Massachusetts’ list of impaired waters for recreational and aquatic uses (MassDEP, 2014). Impairment causes include flow and habitat alterations, pathogens, high phosphorus and nutrient concentrations, excess algal growth and eutrophication, lead (Pb), sedimentation, and several others (MassDEP, 2014). The Blackstone River is also listed as impaired on the State of Rhode Island’s list of impaired waters (Rhode Island Department of Environmental Management [RIDEM], 2015). Impairments reported by the State of Rhode Island include pathogens, high phosphorus and nutrient concentrations, excess algal and invasive macrophyte growth, and high lead and cadmium (Cd) concentrations (RIDEM, 2015). The State of Massachusetts has developed draft total maximum daily loads for pathogens and nutrients for the Blackstone River. The State of Rhode Island has established total maximum daily loads for pathogens, cadmium, copper, and lead for the Blackstone River (RIDEM, 2013).

Impaired waters from the Blackstone River drain into Narragansett Bay. High nitrogen levels have been identified as the trigger for algal blooms and dissolved oxygen deficits in the bay (RIDEM, 1998). Numerous infrastructure improvements have been carried out within the Blackstone River Basin by regulated dischargers, and data show a downward trend in nutrient concentrations (MassDEP, 2010; Massachusetts Executive Office of Energy and Environmental Affairs, 2015; Savoie and others, 2017). Durant and Raposa (2011) reported decreasing trends in concentrations of nitrogen species in Narragansett Bay; they also reported anoxic and hypoxic events still occurring during the time of their study (2008–9).

Excess phosphorus is linked to excess algal and rooted macrophyte growth in freshwater reaches (Carr and Chambers, 1998). Elevated trace metal concentrations may have adverse effects on an organism’s life expectancy, activity, growth, metabolism, or reproduction (Wright and Welbourn, 2002). Accurate load estimates are needed to support the allocation of allowable nitrogen and phosphorus loads among sources in the basin and to develop strategies for reducing nutrient loading. Dissolved trace metals data allow the surface-water quality of the river to be evaluated on the basis of 4-day exposure criteria for aquatic life (U.S. Environmental Protection Agency [EPA], 1994, 2009).

U.S. Geological Survey (USGS) has collected water-quality samples on the Blackstone River at the Millville, Massachusetts, station (USGS station 01111230, hereafter referred to as the Millville station) since 1971 (USGS, 2016).

The Millville station is about 1.3 miles (mi) upstream from the Massachusetts-Rhode Island State line. Monitoring nutrient concentrations near the State line is part of a comprehensive effort to improve water quality in the Blackstone River and Narragansett Bay. The potential to use automated measurements to estimate nutrient concentrations in real time was investigated in this study; this use could provide real-time monitoring of concentrations and loads and possibly reduce analytical costs.

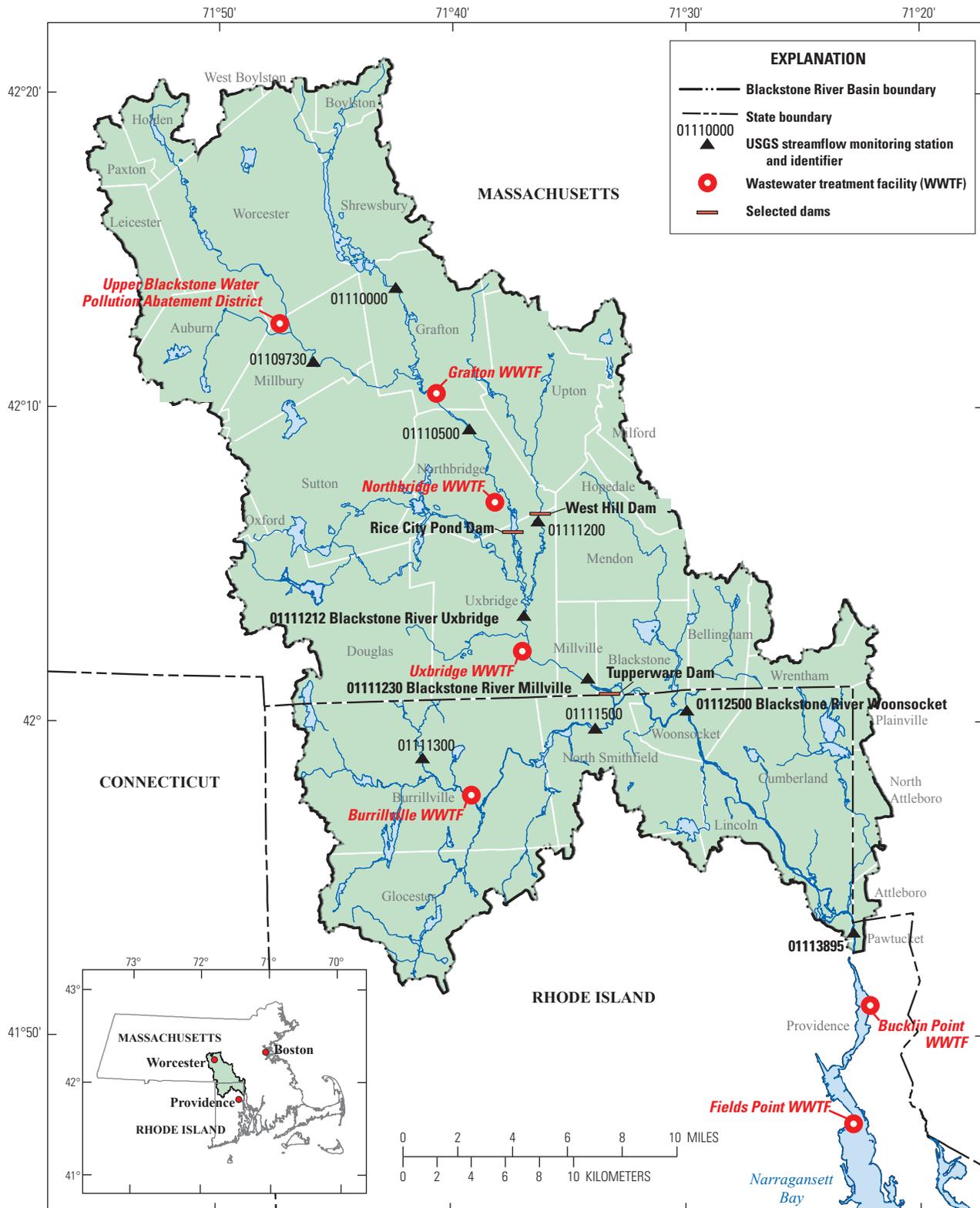
This study utilized similar sampling techniques to those used by Zimmerman and others (2015), except that composite samples were not separated into stormflow and base-flow components but, rather, collected as a single composite for each 14-day and 4-day sampling period. Collecting samples in this manner provided accurate monthly nutrient concentration data and two 4-day concentrations per month for dissolved trace metals and total aluminum (Al). The chronic 4-day exposure criteria for aquatic life were applied by using the biotic ligand model to evaluate copper. The biotic ligand model is a predictive tool that can account for variations in metal toxicity by using information on the chemistry of ambient water (Di Toro and others, 2001; HydroQual, Inc., 2005). The model incorporates metal speciation and the protective effects of competing cations into predictions of metal bioavailability and toxicity (Di Toro and others, 2001; Santore and others, 2001).

In October 2012, the MassDEP and the USGS re-established a cooperative study of nutrient, trace metal, and suspended sediment loads in the Blackstone River at the Massachusetts-Rhode Island State line. Continued monitoring of nutrient, trace metal, suspended sediment, and other constituent concentrations will improve the understanding of the dynamics of these constituents, assist with planning, guide activities to meet water-quality goals, and provide real-time water-quality information to the public (EPA, 2009; Upper Blackstone Water Pollution Abatement District, 2012, 2013; Massachusetts Executive Office of Energy and Environmental Affairs, 2015).

The primary objectives of this study were (1) to provide continuous, real-time (15-minute) water temperature, specific conductance, turbidity, and chlorophyll *a* data; (2) to continue data-collection activities sufficient to produce reliable estimates of nutrient and trace metal loads crossing the Massachusetts-Rhode Island State line; and (3) to use the data to develop regression models for estimating real-time concentrations and loads for nutrients and selected metals and to establish a basis for estimating constituent concentrations and loads and potentially displaying them on the USGS National Real-Time Water Quality website (USGS, 2010; <https://nrtwq.usgs.gov/>).

Purpose and Scope

This report presents the continuous and discrete measurements of physical parameters and the analytical results of water-quality samples, including quality-control samples, from manual and automated flow-proportional sample collection



Base from U.S. Geological Survey and Massachusetts Office of Geographic Information digital data, 2014
 Massachusetts State Plane Coordinate System, mainland zone

Figure 1. The Blackstone River Basin in Massachusetts and Rhode Island, U.S. Geological Survey (USGS) streamflow monitoring stations, and wastewater treatment facilities. Modified from Zimmerman and others (2015).

at the Blackstone River near the Massachusetts-Rhode Island border in Millville, Mass., primarily during water years¹ (WYs) 2013 and 2014.

Monthly and annual load estimates of nutrients, dissolved trace metals, and total aluminum are presented. Loads are based on 14-day and 4-day composite samples for nutrients and trace metals, respectively. The monthly loads are approximated as the sum of loads measured in the two consecutive 14-day composite sampling periods during each month. Point and equal-width-increment (EWI) (Wilde and others, 2002) sample results for nutrients, trace metals, and suspended sediment are also described.

The report includes a discussion of the approach used to develop regression equations that may be used to estimate near real-time (15-minute) concentrations and loads and describe the variability of selected constituents by using the continuously collected records of physical parameters. The uncertainty associated with this approach is also discussed. Regression models are intended to provide a means to estimate loads by using surrogate variables from automated data collection. The regression equations and discussion of them can be used for monitoring changes in concentrations and loads and for comparing concentrations and loads with water-quality standards.

Study Area

Water-quality samples were collected at the Millville station, about 1.3 mi upstream from the Massachusetts-Rhode Island border (fig. 1). The Millville station monitors continuous river stage and selected water-quality parameters representing flow from the upper portion of the basin, which drains about 263 mi² of the total basin area upstream from the State border (264 mi²), and contains parts or all of over 20 municipalities (fig. 1). The Blackstone River main-stem flow is joined by flows from three major tributaries (Quinsigamond, West, and Mumford Rivers), as well as by discharge from four wastewater treatment facilities, and travels over nine dams along its nearly 33-mi course toward the Millville station (fig. 1). Discharge from these various point and diffuse sources may cause water-quality conditions to change within hours.

Flow upstream and downstream from the Millville station is regulated by two dams. The Rice City Pond Dam in Uxbridge, Mass. (fig. 1, national identification number MA00935), is about 9 mi upstream from the Millville station and has a maximum height of 21 feet (ft). It has a maximum storage capacity of about 1,762 acre-feet (2.2 million cubic meters [m³]). About 1 mi downstream from the Millville station in Blackstone, Mass., is the Tupperware Dam, also known as the Stone Diversion Dam (fig. 1, Federal Energy Regulatory Commission number 3023; national

identification number MA00096) and the Blackstone Dam (MA01164). The Tupperware Dam is about 20 ft high and has an installed capacity of about 2,000 kilowatts. It retains between 790 and 1,762 acre-feet (between 974,450 and 2,173,392 m³). Stage and discharge at the Millville station are affected by backwater and regulation at the Tupperware Dam.

Data Collection

The water-quality monitoring station in Millville, reactivated in October 2012 after being shut down in 2009, was equipped to continuously collect stage, precipitation, air and water temperature, specific conductance, turbidity, and chlorophyll *a* measurements in 15-minute intervals. The stream discharge record from the upstream USGS station at Route 122 near Uxbridge, Mass. (01111212, referred to as the Rt. 122 station), was used to represent flow conditions at Millville. At the Millville station, an automated flow-proportional sampling system designed by the USGS was used to collect 14-day composite samples for nutrients and 4-day composite samples for total aluminum and dissolved trace metals. Samples were also collected manually at the Millville station to ensure that the automated point sampling location was representative of stream conditions of the Blackstone River.

Streamflow

Surface-water records from the Rt. 122 station were rated as fair (8-percent rating accuracy) for WYs 2013 and 2014 (USGS, 2015b). Flows at this station are affected at all flow levels by discharges from upstream wastewater treatment facilities and by power generation and dam maintenance at the Tupperware Dam about 4.5 mi downstream. Flow at the Rt. 122 station also is affected at high flows (greater than 5.66 cubic meters per second [m³/s] or 200 cubic feet per second [ft³/s]) by regulation at the U.S. Army Corps of Engineers Flood-Prevention Dam (or West Hill Dam) on the West River near Uxbridge, Mass. (fig. 1), and at extremely high flows (greater than 113.3 m³/s or 4,000 ft³/s) by flood bypass inflows from the Kettle Brook Diversion Weir in Auburn, Mass. (Wandle, 1984). Discharge records from the Rt. 122 station higher than about 5.66 m³/s (200 ft³/s) are considered good (5-percent rating accuracy); however, discharge measured at median to low flows (less than 5.66 m³/s or 200 ft³/s) are less accurate because of dam regulation at upstream and downstream locations. Streamflow was not measured at the Millville station in WYs 2013 and 2014 but was estimated by using data from the Rt. 122 station, located about 3.5 mi upstream (fig. 1), to trigger the flow-proportional sampling. This was the same method used by the sampling program reported by Zimmerman and others (2015).

A 19-mi² increase in drainage area between the Rt. 122 (244 mi²) station and Millville (263 mi²) station required estimating streamflow at the Millville station on the basis of

¹In 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.

the continuous streamflow data at the Rt. 122 station before loads could be calculated for this study. A drainage-area correction resulted in about a 7.2-percent increase in flow on average. Linear regression of 11 concurrent measurements collected at both the Route 122 and Millville stations between WYs 2006 and 2008 (USGS, 2015b, c) showed differences in flow ranging between about -12.7 to 9.5 percent and an average increase in flow of 1.6 percent (fig. 2). The equations for estimating streamflow at the Millville station covered a range from 1.7 to 53.2 m³/s (59 to 1,880 ft³/s), and flows estimated during WYs 2013 and 2014 ranged from 1.4 to 193.6 m³/s (50 to 6,836 ft³/s). Although some estimated low flows were slightly outside the range of measured streamflow, and some high flows were well outside the range of streamflow measurements used to develop the regression equations, the equations were extrapolated to more accurately estimate the extreme high flows at the Millville station. The linear regression equation was used to adjust the Rt. 122 flow record for use at the Millville station in this report. Mean annual flow estimated for the Millville station was 13.4 m³/s (472 ft³/s) for WY 2013 and 10.1 m³/s (356 ft³/s) for WY 2014. Mean annual flow in WY 2013 at the Millville station was 11 percent less than the 8-water year (2007–14) annual mean discharge at the Rt. 122 station (15.0 m³/s or 529 ft³/s). WY 2014 annual average flow at the Millville station was 33 percent less than the 8-year annual mean discharge at Route 122 and about 25 percent less than in WY 2013.

Automated, Flow-Proportional Water-Quality Sampling

Flow-proportional water-quality samples for chemical analysis were collected at the Millville station between October 2012 and October 2014. A modified automated sampling system based on a USGS design from a previous Blackstone River study was used (Zimmerman and others, 2015). The flow-proportional sampling at the Millville station was triggered by using the upstream flow measurements at the Rt. 122 station that were downloaded by the Millville datalogger. Stainless steel intake lines brought water from the river to the Millville shelter. Platinum-cured, flexible silicon tubing connected to the steel lines and routed sample water to the automated system by using three peristaltic pumps. The original system is fully described in Zimmerman and others (2015). Discharge at the Millville station was affected by backwater and regulation, so samples were collected as single composite samples rather than partitioned into base-flow and storm-flow components. A typical station visit included retrieving the previous 14-day nutrient samples and 4-day metal composite samples, documenting any errors or discrepancies, cleaning the system using 0.1-percent non-phosphate detergent and 5-percent hydrochloric acid solutions followed by thorough rinsing with deionized water, and replacing used capsule filters. Precleaned sampling bottles were installed, and the system was reset. Lastly, each 14-day sampling period

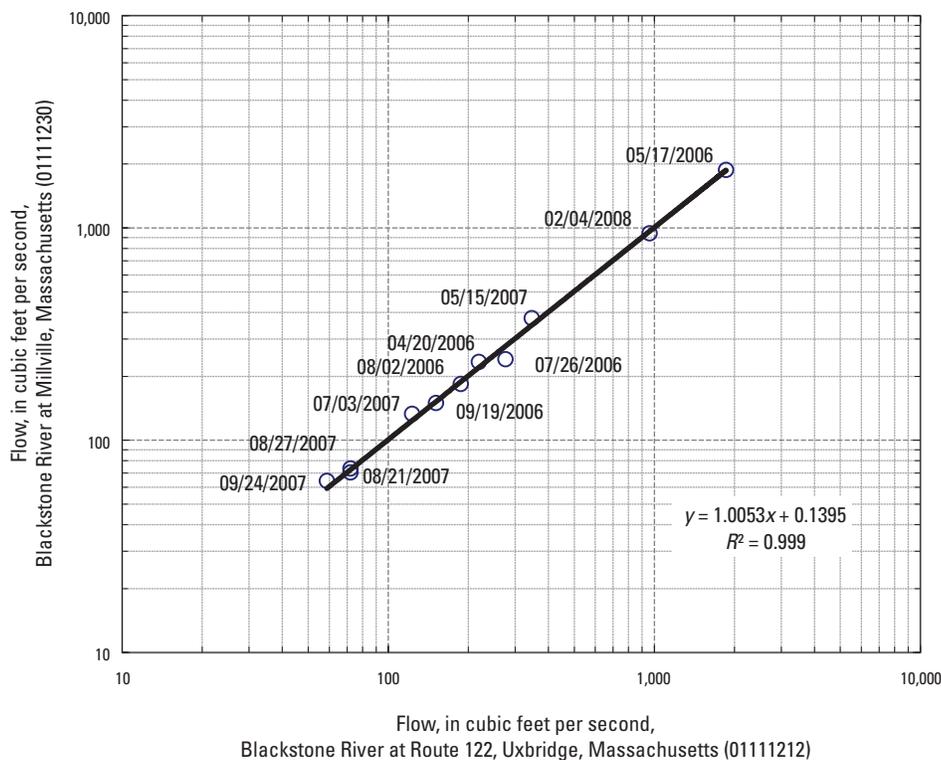


Figure 2. Linear regression of 11 concurrent measurements collected at the Blackstone River at Millville, Massachusetts (01111230), and the Blackstone River at Route 122, Uxbridge, Mass. (01111212), stations between water years 2006 and 2008.

required a new flow-proportional threshold to be entered into the datalogger. Thresholds were initially based on the mean 14-day flow multiplied by the number of seconds in 14 days and assuming a minimum number of 55 samples in the 14-day composite. This first-cut threshold value was then modified by field personnel on the basis of precipitation forecasts and expected changes in flow at the Millville station. The datalogger used the same first-cut threshold calculation on day 10 of the 14-day sampling period to establish a flow threshold for the 4-day metal sample composite. This flow threshold was based on a 12-sample metal composite. Field personnel could also adjust the threshold remotely if needed as a result of changes in flow or precipitation.

Samples for analysis of total and dissolved nitrogen and phosphorus were collected and composited throughout the year over periods of approximately 14 days. Samples for analysis of selected dissolved metals—cadmium, chromium (Cr), copper (Cu), lead, nickel (Ni), and zinc (Zn)—and total aluminum were collected and composited throughout the year over periods of approximately 4 days for comparison to 4-day exposure criteria for aquatic life. Table 1 lists all analytes investigated as part of this study.

Nutrient samples were composited in two precleaned, 14-liter (L) polyethylene bottles, one for whole-water samples and the second for dissolved samples, which was equipped with a single, in-line large-capacity capsule filter of 0.45 micrometer (μm) pore size attached to the sample bottle cap. The sample was pushed through the capsule filter by the system pumps. Bottles for collecting nutrient samples were preacidified with 20 milliliters (mL) of 4.5 normal sulfuric acid (H_2SO_4), sufficient to preserve a minimum sample volume of 2,500 mL. Nutrient sample volumes typically exceeded 10 L after the 14-day sampling period. Additional H_2SO_4 was added to the final sample volume as part of the collection and processing procedures to obtain a sample pH value between 1.6 and 1.9. Four-day composite samples of trace metals were distributed between three 2-L polyethylene bottles and were always processed after the nutrient samples. Two bottles contained the whole-water samples, and the third bottle contained the dissolved sample. One of the whole-water bottles was acidified with nitric acid (HNO_3) in the USGS laboratory in Northborough, Mass., and churn split for chemical analysis, and the second whole-water bottle was used for measuring the specific conductance and turbidity of the 4-day metals composite. Samples of dissolved trace metals were collected by using the automated system to pump through 0.45- μm capsule filters. Six capsule filters were installed within the pumping enclosure. A maximum of three samples were pulled through a single filter according to sampling protocols (Wilde and others, 2002). The system then switched to the next filter in line for collection of the next three samples. Trace metal sample bottles were not preacidified as the nutrient bottles were. All sample bottles and the filter used for nutrient composite samples were kept at 4 degrees Celsius ($^{\circ}\text{C}$) \pm 2 $^{\circ}$ in a small refrigerator installed in the station shelter during the sampling period.

About every 14 days, water-quality samples were retrieved by USGS personnel, stored on ice, and transported to the laboratory in Northborough, Mass. In WY 2013, a total of 56 days had no sample collection because of frozen sample lines during the winter, datalogger programming issues, or delayed sample retrievals. Programming modifications reduced the total number of days without sample collection to 12 days in WY 2014.

During routine station visits, sample bottles were retrieved and replaced with clean bottles, the automated sampling system was cleaned, and the 14- and 4-day sampling cycles were reactivated so that the 14-day nutrient sampling cycle would restart immediately and the 4-day metal sampling cycle would start on day 10. Composite nutrient samples were weighed, and the required amount of additional preservative acid was added to the sample containers. Trace metal samples were also weighed, and the necessary amount of preservative nitric acid (HNO_3) was added to one of the whole-water metal sample bottles. Acidified whole-water and dissolved samples were allowed to equilibrate within their respective sample containers for 24 to 48 hours before being processed. Specific conductance and turbidity measurements were collected from the second whole-water metal sample bottle. Filtered samples were processed first by decanting all water from the 14-L nutrient jug into a dedicated 14-L polyethylene churn splitter for nutrients and using it to distribute sample water into the appropriate sample bottles for laboratory analyses. Then whole-water samples were processed in the same way. Dissolved (filtered) and whole-water metal samples were then processed in the same way by a dedicated 4-L polyethylene churn splitter for metal samples. After processing, nutrient and trace metal samples were shipped overnight to the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado.

Manual Water-Quality Sampling

Isokinetic, equal-width-increment (EWI) samples were collected manually at the railroad bridge about 400 ft upstream from the Millville station over a wide range of flow and turbidity conditions (fig. 3) in accordance with USGS protocols (Wilde and others, 2002, 2004). The EWI samples were used to ensure that samples collected automatically at a single point were representative of the entire cross section of the river. Point samples were used to develop regression equations to estimate near real-time (15-minute) concentrations and loads of selected constituents. Point samples were collected at the intake for the automatic sampling system, the 15 EWI samples were collected concurrently, and samples were analyzed for all constituents to assess how the point samples compared to the EWI samples. Although EWI samples have been collected at this station for decades, only data from January 2012 to March 2015 were used for this study. Typical stream velocities at the Millville station (and at the railroad bridge 400 ft upstream)

Table 1. Constituents, U.S. Geological Survey (USGS) parameter codes, analytical methods, and method detection limits for the sampling program at the Blackstone River at Millville, Massachusetts, station (01111230), water years 2013 to 2014.

[USGS, U.S. Geological Survey; N, nitrogen; P, phosphorus; mg/L, milligram per liter; µg/L, microgram per liter; --, no data; ltmdl, long-term method detection limit; mdl, method detection limit; irl, interim reporting level; EPA, U.S. Environmental Protection Agency; Bridge, sample collected along bridge transect using equal-width-increment methods; Point, sample collected from Millville station intake point; Composite, sample collected using automated flow-proportional system at the Millville station intake point]

Constituent	USGS parameter code	Unit	Method reporting limit	Reporting limit type	Reference	Water-quality sample type
Total nitrogen, water, unfiltered	p00600	mg/L	--	--	Calculated	Bridge; Point
Total nitrogen, water, filtered	p00602	mg/L	--	--	Calculated	Bridge; Point
Organic nitrogen, water, unfiltered	p00605	mg/L	--	--	Calculated	Bridge; Point
Organic nitrogen, water, filtered	p00607	mg/L	--	--	Calculated	Bridge; Point
Ammonia, water, filtered, as N	p00608	mg/L	0.01	ltmdl	Zimmerman and others (1997)	Bridge; Point
Nitrite, water, filtered, as N	p00613	mg/L	0.001	mdl	Fishman (1993)	Bridge; Point
Nitrate, water, filtered, as N	p00618	mg/L	0.001	mdl	Fishman (1993)	Bridge; Point
Ammonia plus organic nitrogen, water, filtered, as N	p00623	mg/L	0.07	ltmdl	Patton and Truitt (2000)	Bridge; Point
Ammonia plus organic nitrogen, water, unfiltered, as N	p00625	mg/L	0.07	ltmdl	Patton and Truitt (2000)	Bridge; Point
Nitrate plus nitrite, water, filtered, as N	p00631	mg/L	0.04	ltmdl	Patton and Kryskalla (2011)	Bridge; Point
Particulate nitrogen, suspended in water	p49570	mg/L	0.03	ltmdl	Zimmerman and others (1997)	Bridge; Point
Total nitrogen (nitrate + nitrite + ammonia + organic N), water, filtered, analytically determined	p62854	mg/L	0.05	ltmdl	Patton and Kryskalla (2003)	Bridge; Point; Composite
Total nitrogen (nitrate + nitrite + ammonia + organic N), water, unfiltered, analytically determined	p62855	mg/L	0.05	ltmdl	Patton and Kryskalla (2003)	Bridge; Point; Composite
Phosphorus, water, unfiltered, as P	p00665	mg/L	0.004	ltmdl	EPA 365.1 (1993)	Bridge; Point
Phosphorus, water, filtered, as P	p00666	mg/L	0.003	ltmdl	EPA 365.1 (1993)	Bridge; Point
Orthophosphate, water, filtered, as P	p00671	mg/L	0.004	ltmdl	EPA 365.1 (1993)	Bridge; Point
Organic carbon, water, filtered	p00681	mg/L	0.23	ltmdl	Brenton and Arnett (1993)	Bridge; Point
Carbon (inorganic plus organic), suspended sediment, total	p00694	mg/L	0.05	ltmdl	Zimmerman and others (1997)	Bridge; Point
Hardness, water, as calcium carbonate	p00900	mg/L				Bridge; Point
Calcium, water, filtered	p00915	mg/L	0.022	ltmdl	Fishman (1993)	Bridge; Point; Composite
Magnesium, water, filtered	p00925	mg/L	0.011	ltmdl	Fishman (1993)	Bridge; Point; Composite
Sodium, water, filtered	p00930	mg/L	0.06	ltmdl	Fishman (1993)	Bridge; Point
Potassium, water, filtered	p00935	mg/L	0.03	ltmdl	Clesceri and others (1998)	Bridge; Point
Chloride, water, filtered	p00940	mg/L	0.02	ltmdl	Fishman and Friedman (1989)	Bridge; Point
Sulfate, water, filtered	p00945	mg/L	0.02	ltmdl	Fishman and Friedman (1989)	Bridge; Point
Cadmium, water, filtered	p01025	µg/L	0.03	ltmdl	Garbarino and others (2006)	Bridge; Point; Composite
Cadmium, water, unfiltered	p01027	µg/L	0.03	ltmdl	Garbarino and Struzeski (1998)	Bridge; Point
Chromium, water, filtered	p01030	µg/L	0.30	ltmdl	Garbarino and others (2006)	Bridge; Point; Composite

8 Nutrient and Metal Loads Estimated for the Blackstone River, Massachusetts and Rhode Island, Water Years 2013–14

Table 1. Constituents, U.S. Geological Survey (USGS) parameter codes, analytical methods, and method detection limits for the sampling program at the Blackstone River at Millville, Massachusetts, station (01111230), water years 2013 to 2014.—Continued

[USGS, U.S. Geological Survey; N, nitrogen; P, phosphorus; mg/L, milligram per liter; µg/L, microgram per liter; --, no data; ltmdl, long-term method detection limit; mdl, method detection limit; irl, interim reporting level; EPA, U.S. Environmental Protection Agency; Bridge, sample collected along bridge transect using equal-width-increment methods; Point, sample collected from Millville station intake point; Composite, sample collected using automated flow-proportional system at the Millville station intake point]

Constituent	USGS parameter code	Unit	Method reporting limit	Reporting limit type	Reference	Water-quality sample type
Chromium, water, unfiltered, recoverable	p01034	µg/L	0.40	ltmdl	Garbarino and others (2006)	Bridge; Point
Copper, water, filtered	p01040	µg/L	0.80	ltmdl	Garbarino and others (2006)	Bridge; Point; Composite
Copper, water, unfiltered, recoverable	p01042	µg/L	0.80	ltmdl	Garbarino and others (2006)	Bridge; Point
Lead, water, filtered	p01049	µg/L	0.04	ltmdl	Garbarino and others (2006)	Bridge; Point; Composite
Lead, water, unfiltered, recoverable	p01051	µg/L	0.04	ltmdl	Garbarino and Struzeski (1998)	Bridge; Point
Nickel, water, filtered	p01065	µg/L	0.20	ltmdl	Garbarino and others (2006)	Bridge; Point; Composite
Nickel, water, unfiltered, recoverable	p01067	µg/L	0.20	ltmdl	Garbarino and others (2006)	Bridge; Point
Zinc, water, filtered	p01090	µg/L	2.00	ltmdl	Garbarino and others (2006)	Bridge; Point; Composite
Zinc, water, unfiltered, recoverable	p01092	µg/L	1.90	ltmdl	Garbarino and others (2006)	Bridge; Point
Aluminum, water, unfiltered, recoverable	p01105	µg/L	3.80	ltmdl	Garbarino and Struzeski (1998)	Bridge; Point; Composite
Pheophytin <i>a</i> , phytoplankton	p62360	µg/L	0.10	irl	Arar and Collins (1997)	Bridge; Point
Chlorophyll <i>a</i> , phytoplankton, chromatographic-fluorometric	p70953	µg/L	0.10	irl	Arar and Collins (1997)	Bridge; Point
Dissolved solids, water, filtered, sum of constituents	p70301	mg/L	--	--	Calculated	Bridge; Point

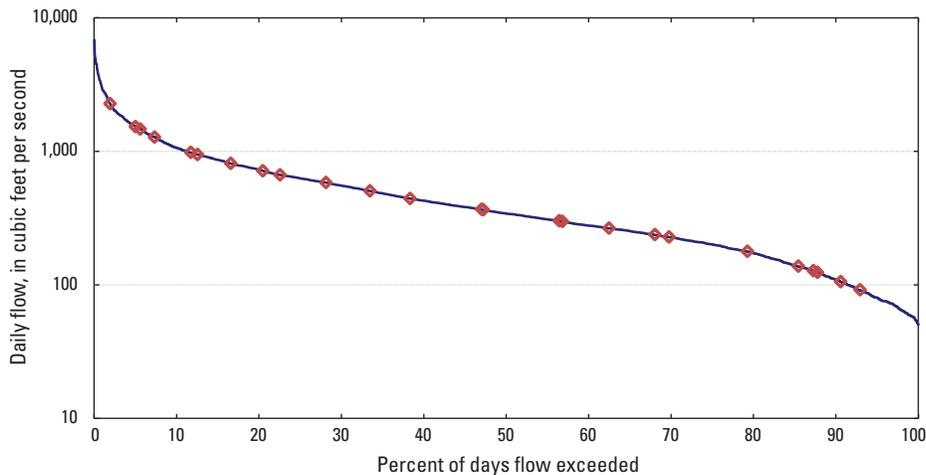
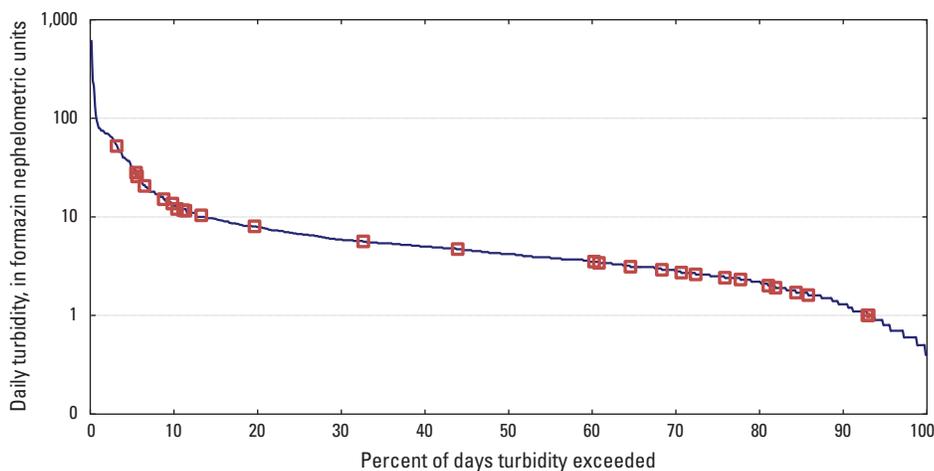
A**B**

Figure 3. A, Flow and B, turbidity duration curves, Blackstone River at Millville, Massachusetts, station (0111230), 2012 to 2014. Manual sampling events are shown as red markers.

were less than the 1.5 feet per second (ft/s) minimum needed to use isokinetic techniques, so a weighted bottle sampler was the appropriate approach (Wilde and others, 2002). The EWV subsamples, collected from across the stream transect, were composited into a churn splitter and then processed and analyzed, as previously described for samples collected by the automated sampling system. Manual samples were submitted for analysis of total (whole-water) and dissolved (filtered) concentrations of total and dissolved nitrogen and phosphorus, orthophosphate phosphorus, ammonia nitrogen, nitrate nitrogen, and nitrite nitrogen, total and dissolved organic carbon (DOC), common ions (calcium, magnesium, sodium, chloride, potassium, and sulfate), dissolved and total trace metals (cadmium, chromium, copper, lead, nickel, and zinc), and total aluminum concentrations (table 1). Additional constituents included suspended sediment concentration and turbidity (table 1). Suspended sediment concentrations were measured by using standard gravimetric techniques (American

Society for Testing and Materials, 2002). DOC was measured by ultraviolet light-promoted persulfate oxidation and infrared spectrometry (Brenton and Arnett, 1993). Nutrient, common ion, DOC, and trace metal samples were shipped overnight to the USGS NWQL in Denver, Colo., and suspended sediment samples were shipped to the USGS Kentucky Water Science Center Sediment Laboratory in Louisville, Kentucky.

Continuous Water-Quality Parameter Measurements

Continuous water temperature, specific conductance, turbidity, and chlorophyll *a* measurements were collected at 15-minute intervals by a Eureka Manta 2 multiparameter probe and posted online in real time. The period of record included WYs 2013 and 2014, and the accuracies of all data were evaluated and adjusted on the basis of sensor fouling and

calibration drift. Minor data gaps exist in the records as the result of programming issues or deletion of very poor quality periods of record (Wagner and others, 2006). An extended gap in the continuous record occurred from September 2 to October 30, 2014, following a lightning strike at the station, requiring the damaged sensor to be returned to the manufacturer for repair. Continuous water-quality data are available through the National Water Information System at <https://nwis.waterdata.usgs.gov/nwis>.

All water temperature records at the station were rated excellent (less than ± 0.2 degrees Celsius ($^{\circ}\text{C}$) (Wagner and others, 2006). Specific conductance records were also rated excellent (less than ± 3 percent), except for several daily values that were rated good (± 3 to 10 percent; Wagner and others, 2006).

Optical sensors such as those used for turbidity and chlorophyll *a* are sensitive to fouling compared to temperature and specific conductance sensors, especially in a slow-moving section of the river such as at the Millville station. The turbidity and chlorophyll *a* sensors were equipped with wipers and were regularly maintained by personnel. Although the accuracy of turbidity records was generally good (± 0.5 to 1.0 turbidity units), the precision of the measurements was rated fair to poor (Wagner and others, 2006). Records for chlorophyll *a* were not rated; however, continuous chlorophyll *a* concentration data were two to five times greater than laboratory concentrations and ranged to nearly an order of magnitude beyond the high-end calibration point.

Quality-Control Sampling

Blank and replicate samples were collected to assure that manual and composite sampling equipment was not a source of contamination and that sampling and laboratory procedures resulted in reproducible samples of the Blackstone River at the Millville station. All blank and replicate samples were processed in the USGS laboratory in Northborough, Mass., and shipped to the USGS NWQL and the USGS Kentucky Water Science Center Sediment Laboratory for analysis.

Blank Samples

A total of six equipment blank samples were collected from the automated sampling system. Blank water produced by a Millipore Elix Advantage 10 water system in the Northborough laboratory was run through the newly constructed automated sampling system before being deployed. System components were thoroughly cleaned according to USGS guidelines for the preparation of sampling equipment (Wilde, 2004). Initial results from equipment blank samples collected from the system before deployment in September 2012 had detectable concentrations of chromium, lead, and nickel that were attributed to the milling of plastic components (table 2). After additional cleaning, a second set of blank samples was submitted, and resulting concentrations had smaller detections

of the same three analytes. The remaining three system blank samples were all at or below detection limits, except for a single detection of aluminum, which indicated a potential contamination bias. The blank sample was collected on October 15, 2014. The resulting total aluminum concentration (9.6 micrograms per liter [$\mu\text{g/L}$]) was about 10 times less than the average concentration in samples collected by the automated system (94.7 $\mu\text{g/L}$), about 25 times less than the average concentration in manually collected samples (241.0 $\mu\text{g/L}$), and about 6 times less than the average concentration in samples collected by the system in October 2014 (56.9 $\mu\text{g/L}$), indicating the potential contamination bias is small.

A total of five blank samples were submitted for nutrient analysis. All results were less than detection limits for total and dissolved nitrogen and phosphorus. Blank water was decanted into the manual sampling equipment used to collect EWI samples at the railroad bridge, about 400 ft upstream from the Millville station's point location, and from the point location itself. After 15 minutes of exposure to sampling equipment, blank water was poured from the sampling equipment into churn splitters and then decanted into sample bottles for shipping and analysis. Analytical results from these samples were all at or below detection limits (table 2).

Capsule Filter Blank Samples

The disposable Pall GWV high capacity in-line capsule filters (0.45 μm) that were used to process filtered samples in this study were found to be a source of organic nitrogen contamination when used in the automated sampling system and possibly for the collection of manual samples as well. Low-levels of dissolved organic nitrogen (less than [$<$] 0.1 milligram per liter [mg/L]) were detected in blank samples used to test the quality of the capsule filters by the USGS NWQL quality-assurance program for sampling supplies (USGS, 2015a). Preconditioning the capsule filters by passing 2 L of water through the filter prior to use was shown to reduce the level of contamination to below reporting limits and is the currently (2016) recommended procedure (USGS, 2009, 2012). However, when filters were preconditioned but not used immediately, such as occurred in the automated sampling system and possibly for some manually collected samples, the level of nitrogen contamination was substantially greater.

Field blanks collected during the sampling period used for load calculations (WYs 2013–14) showed no detections of nitrogen in filtered or unfiltered samples. However, these field blanks did not represent the additional potential for contamination that could have resulted from keeping the filters installed in the automated sampling system housing prior to use. There was evidence of organic contamination from capsule filters in instances when measured concentrations of dissolved total nitrogen were found to be substantially greater than concentrations of unfiltered total nitrogen. This evidence was in manually collected samples and samples collected by the automated sampling system. Concentrations of dissolved nitrogen greater than total nitrogen could result from analytical uncertainty,

from contamination in dissolved (filtered) samples, or from underestimation of total nitrogen in whole-water (unfiltered) samples. Historical evidence shows that total nitrogen in whole-water samples could be underestimated by the alkaline persulfate digestion method in samples with suspended sediment concentrations higher than 500 mg/L. However, concentrations of suspended sediment in all samples were less than 10 mg/L (most were less than 4 mg/L), making it unlikely that the unfiltered samples were biased low as a result of incomplete oxidation of all nitrogen species to nitrate (Patton and Kryskalla, 2003, 2011; Mohrman, 2009). Overacidification with preservative also could result in underestimation of nitrogen in whole-water samples (Patton and Kryskalla, 2003), but samples were not overacidified in the present study.

The automatic sampling system employed in the present study used an automatic filtration process; the capsule filters used in the automated sampling system were preconditioned before being deployed in the field. A single capsule filter was deployed to filter the composite sample aliquots collected over a 14-day period for nutrients. Thus, the remaining six filters installed in line for use to filter samples for trace metal composite sampling typically remained in the monitoring shelter for more than a week before use. During this time, the protective effects of preconditioning may have been lost. However, the contamination effects are substantially minimized for trace

metal constituents. In cases where water samples are composited into a single filtered bottle, such as used in the 14-day automated sampling routine for nutrients, only small amounts of water (<200 mL) are typically passed through a preconditioned filter in the field for analysis. This may not have been sufficient to rinse any contamination from the filter that was generated in it after preconditioning. For manual sample collection, in most cases, capsule filters are preconditioned the day they are to be used; in some cases, preconditioned filters may have been held in refrigerated storage for more than 24 hours before use, and this hold time, or even a shorter hold time (<24 hours), may have resulted in sample contamination.

In December 2015, nine filters were tested in an effort to characterize potential contamination of water samples from organic nitrogen associated with the capsule filters. In this test, filters were preconditioned by following USGS National Field Manual recommended procedures: 2 L of deionized water was passed through each filter at several different time periods before the filter was used to collect test samples (table 3). One filter was preconditioned about 4 weeks prior to collecting test samples and was stored in the laboratory refrigerator. Six filters also were preconditioned about 4 weeks prior to collecting test samples and were installed in the field as part of the automatic sampling system. To serve as a control, two filters from a different manufacturer's lot were not preconditioned

Table 3. Test results from capsule filter experiments.

[Unless noted otherwise, all filters were prerinsed (conditioned) by flushing with 2 liters (L) of deionized water (DIW) at a rate less than or equal to 1 L per minute before samples were collected. Disposable Pall GWV high-capacity in-line capsule filters (0.45 micrometer) were used. NWIS, National Water Information System; N, nitrogen; mg/L, milligram per liter; mL, milliliter; --, no data; <, less than]

Sample	Sample identification	Water sampled	NWIS capsule filter lot number	Ammonia + organic N (mg/L)	Alkaline persulfate N (mg/L)
1	Source water	Direct from Millipore Elix Advantage 10 water system	--	<0.07	<0.05
2	Filter 1 (installed about 4 weeks in the field before testing)	First 125 mL passed through filter	10027	4.35	5.2
3	Filter 1 (installed about 4 weeks in the field before testing)	125 mL after 875 mL passed through filter	10027	<0.07	0.089
4	Filter 2 (installed about 4 weeks in the field before testing)	First 125 mL passed through filter	10027	6.33	7
5	Filter 3 (installed about 4 weeks in the field before testing)	First 125 mL passed through filter	10027	14.9	17.3
6	Filter 3 (installed about 4 weeks in the field before testing)	125 mL after 875 mL passed through filter	10027	0.184	0.241
7	Filter 4 (installed about 4 weeks in the field before testing)	First 125 mL passed through filter	10027	9.08	11.9
8	Filter 5 (installed about 4 weeks in the field before testing)	First 125 mL passed through filter	10027	6.11	9.3
9	Filter 5 (installed about 4 weeks in the field before testing)	125 mL after 875 mL passed through filter	10027	<0.07	0.09
10	Filter 6 (installed about 4 weeks in the field before testing)	First 125 mL passed through filter	10027	7.93	10.3
11	Filter 7 (not prerinsed, not conditioned)	First 125 mL passed through filter	10033	0.108	0.127
12	Filter 8 (not prerinsed, not conditioned)	First 125 mL passed through filter	10033	0.245	0.282
13	Filter 9 (stored about 4 weeks in refrigerator before testing)	First 125 mL passed through filter	10027	<0.07	<0.05

at all. Source water was provided from the Millipore water system. Concentrations of all nitrogen species in the source water were below detection limits (table 3). The capsule filters, except for the control filters, were tested by collecting the first 125 mL of water that passed through the filter after the holding period; the control filters were tested with no preconditioning or holding period. For three filters that were previously installed in the field, a second sample was collected representing the terminal part of 1 L of filter water; that is, about 875 mL of source water was passed through the filter to the sink, and the final 125 mL of source water was collected in the sample bottle. All samples were analyzed for unacidified dissolved ammonia plus organic nitrogen and for total dissolved nitrogen (table 3).

Concentrations of dissolved ammonia plus organic nitrogen and total dissolved nitrogen in water collected from capsule filters that were preconditioned and stored at ambient temperatures for several weeks were high, ranging from 4 to 15 mg/L and 5 to 17 mg/L, respectively (table 3). Nitrogen concentrations were lower (about 80 times lower on average) when flushed with less than a liter of deionized water. Nitrogen concentrations for the blank samples collected through the preconditioned filters stored in the refrigerator in the filter test were less than detection limits. However, concentrations of dissolved ammonia plus organic nitrogen and total dissolved nitrogen in a USGS field blank sample collected in July 2015 were 0.195 and 0.23 mg/L, respectively (USGS, unpub. data). The time of filter conditioning and (or) storage duration for the filter used to prepare the July 2015 field blank was not recorded, but storage in the refrigerator after preconditioning could have been a factor in the detections of ammonia plus organic nitrogen and total dissolved nitrogen.

Results from the tests described in the present study, as well as results from recent, similar testing of capsule filters and holding times by the NWQL (unpub. data, USGS, Office of Water Quality Information Note 2017.03), indicate that the organic nitrogen originating as contamination within the capsule filter is rapidly flushed from the filters. However, the filters in the automated system sit for 10 to 13 days, and detections under the conditions seen in the automated system make all dissolved total nitrogen results in filtered samples questionable. For this reason, loading calculations for dissolved total nitrogen in filtered samples based on automatically collected composite samples are not included in this report.²

Equal-Width-Increment and Point Sample Comparisons

Fifteen EWI and point sample pairs were collected concurrently from the upstream railroad bridge and at the Millville station intake point to evaluate the representativeness

of the station's single intake point for the entire cross section of the river. The timing of sampling events was chosen to cover as wide a range of flow and turbidity conditions as possible (fig. 2). EWI samples were collected from 9 to 12 locations across the river on the downstream side of the railroad bridge and emptied into a precleaned polyethylene churn as a single composite sample. At the point location at the Millville station, 12 point samples were collected on a timed program into a precleaned polyethylene churn with an ISCO 6700 automated sampler equipped with a peristaltic pump. Table 4 shows the relative percent differences (RPDs) between these samples. About 11 percent of all constituents had an incidence or incidences where RPDs were greater than the established performance criterion of 20 percent (quality assurance project plan, Robert F. Breault and Kim W. Campo, U.S. Geological Survey, written commun., 2007). Suspended sediment concentration and particulate nitrogen had the highest number of values greater than established performance criteria. Dissolved copper, total and dissolved zinc, and ammonia had fewer 20-percent exceedances, and total aluminum and some trace metals had the least number of performance criteria exceedances (table 4). Of the three samples associated with the most RPDs greater than the performance criteria, two were collected during two low-flow periods, and one was collected during the highest flow of all sampling events between WYs 2013 and 2014. Only one of these three sampling events was associated with substantial rainfall prior to sampling.

Table 4. Concentrations of nutrients, trace metals, and suspended sediment in sample pairs collected from the upstream railroad bridge and from the point location at the Blackstone River at Millville, Massachusetts, station (01111230).

[Table available for download at <https://doi.org/10.3133/sir20175094>]

Many constituents had no or few RPD values greater than the performance criterion. These include water temperature, specific conductance, pH, dissolved oxygen, and alkalinity, as well as all major ions and several trace metals (table 4). The primary components of the study, total nitrogen (and almost all nitrogen species) and total phosphorus, showed agreement between point and EWI samples (table 4). All water-quality parameters were measured in situ by using multiple vertical measurements for the EWI/bridge samples and a single point measurement of water-quality parameters at the Millville station intake point. Overall the point location is considered representative of the Blackstone River.

Data Analysis

Data collected by this project were analyzed in multiple ways. Loads of constituents were calculated by using the concentrations provided by laboratory analysis and the average flow of the river during each respective sampling period.

²Contamination of organic nitrogen from capsule filters may have affected concentrations of total dissolved nitrogen in samples collected with the automated system in the previous Blackstone River loads study, Zimmerman and others (2015), but the extent of that potential effect is undetermined.

Explanatory variables are defined as those that can be measured continuously at a station by using automated sensors. Correlation analysis showed which of the possible predictive relations had the most potential to be used to estimate selected constituent concentrations, versus the generally more expensive option of collecting representative samples and submitting them for laboratory analysis.

Selected explanatory variables are related to selected water-quality constituents by using ordinary least squares regression techniques. Regression models were developed by using multiple linear regression analysis and one or more of the explanatory variables from the near real-time record to estimate the concentration of selected water-quality constituents in near real-time.

Load Calculation

Loads were calculated by multiplying 14-day nutrient and 4-day metal composite sample concentrations, collected with the automated flow-proportional system, by the average flow of their respective time periods (table 5). When flow data were missing, the average flow was based on the available data for the time period of interest, including data from the following sampling period. Two sets of 14-day nutrient loads were summed to approximate monthly loads, and all 14-day composite loads were combined to provide annual load values. All 15-minute streamflow values at the Millville station were estimated with the linear regression equation, using the 15-minute streamflow at the Rt. 122 station.

Table 5. Concentrations of nutrients, total aluminum, and dissolved trace metals in 14-day nutrient composite samples and 4-day metal composite samples collected by the automated sampling system from the point location at the Blackstone River at Millville, Massachusetts, station (01111230) during water years 2013 and 2014.

[Table available for download at <https://doi.org/10.3133/sir20175094>]

Correlation Analysis

Correlation analysis is a method to quantify the type and strength of relations between two variables (Haan, 1977; Press and others, 1992; Helsel and Hirsch, 2002; Granato, 2013, 2014). Correlation coefficients were calculated for all of the water-quality variables collected during the monitoring period, as well as for the estimated streamflow and the precipitation variables (precipitation during the sampling event and precipitation recorded during the preceding 24, 48, and 72 hours). Rank correlations were calculated by using Spearman's rho (ρ) (Haan, 1977; Helsel and Hirsch, 2002), and censored data were treated by using one-half of the detection limit. These correlation coefficients are dimensionless and are scaled to be in the range of -1 to 1 , inclusive. The strength of relations between pairs of variables is indicated by the values of the

correlation coefficients. The relation between two variables ranges from random association (no relation) to monotonic covariance (perfect correlation) as the absolute value of the correlation coefficient increases from 0 to 1 . The sign of the correlation coefficient indicates the type of relation. A positive sign indicates that one variable generally increases as the other increases; a negative sign indicates that one variable generally decreases as the other increases; and a value of 0 indicates that variations in the two variables are totally unrelated. The statistical significance of the correlation coefficient is a function of the absolute value of the coefficient and the sample size.

The correlation coefficient is not a measure of a causal relation between variables. Variation in one variable may cause changes in another. For example, antecedent precipitation may be one factor causing increases in streamflow; another factor would be the streamflow that occurred before the precipitation event, or prestorm flow (Granato, 2010). Both variables may be affected by a third. For example, a positive correlation between specific conductance and pH may be affected by the negative correlations between these constituents and increasing streamflow. In this case, the positive correlation between the water-quality variables may be attributed to dilution from precipitation as well as chemical processes that affect both pH and conductance. An apparent correlation also may occur purely by chance. Confidence intervals for correlation coefficients indicate the likelihood that the value of a calculated correlation coefficient is due to chance.

Correlation coefficients, the associated 95-percent confidence intervals, and statistical-significance probability values for the coefficients were calculated by use of standard methods (Fisher, 1924; Haan, 1977; Press and others, 1992; Caruso and Cliff, 1997; Helsel and Hirsch, 2002; Granato, 2013, 2014). Paired sample sizes of five or more values were used to estimate correlation coefficients because Abdel-Megeed (1984) determined that at least five data pairs were necessary to begin to quantify the correlation. To compute Spearman's rho, the data for the two selected variables x and y are ranked independently, and the correlation of the ranks is computed (Haan, 1977; Press and others, 1992; Helsel and Hirsch, 2002). To calculate the ranks, the data are sorted and ranked from 1 to the number of data points (N). Tied data values are assigned a midrank, which is the average of the preceding and following ranks. The confidence interval is calculated from the sample size and the value of rho by using the Fisher's Z transformation method (Fisher, 1924; Haan, 1977; Caruso and Cliff, 1997). If the 95-percent confidence interval does not include a correlation value of 0 , then the calculated correlation value is statistically significant. Spearman's rho was calculated on the basis of the approaches described by Press and others (1992). The 95-percent confidence limits of each value of Spearman's rho were calculated to determine the range of likely values of the actual rank correlation coefficient and to determine if the calculated value is significantly different from 0 .

The rank correlations on the arithmetic and logarithmic values were calculated to help inform the development of predictive equations among variables. Analysis of the correlation

coefficients indicates the potential for developing quantitative regression equations between variables or the potential for multicollinearity among predictor variables if multiple linear regression equations are developed (Helsel and Hirsch, 2002). Spearman's rho is a robust estimator of a monotonic relation between two variables that is resistant to outliers; the rho value is not dependent on the linearity of the relation between variables (Haan, 1977; Press and others, 1992; Helsel and Hirsch, 2002; Granato, 2014).

Correlations Among Potential Explanatory Variables

Analysis of correlations among potential explanatory variables indicates possible causal relations between selected variables, possible predictive relations between variables, and the potential for relations that may cause multicollinearity if used. Strong correlations between variables also may provide an opportunity to substitute an expensive or difficult measurement with a less expensive and (or) more robust alternative. In this study, potential explanatory variables are defined as those variables that can be measured automatically by sensors at field monitoring stations. These variables include streamflow, water temperature, specific conductance, dissolved oxygen, pH, chlorophyll *a*, turbidity, and current or antecedent precipitation volumes.

Multicollinearity is of concern because strong correlations among predictor variables could adversely affect the development and interpretation of multiple linear regression equations between these explanatory variables and the water-quality constituents that are of interest to water-resource managers (Helsel and Hirsch, 2002). The effect of multicollinearity is quantified by using the variance inflation factor (VIF). The VIF increases the width of the confidence interval for the regression coefficient compared to a perfectly independent set of explanatory variables. Helsel and Hirsch (2002, p. 306) indicate that "serious problems" may occur if the VIF for a given predictor is greater than 10. The VIF for a variable is equal to the reciprocal of one minus the coefficient of determination (R^2) between predictors. Therefore, a VIF of 10 would equal a correlation coefficient (R) value of about 0.9486. A VIF value of 5 is the boundary between moderately and highly correlated variables and is equivalent to an R value of about 0.894 (Minitab Inc., 2015).

Regression Model Development

Regression models were developed to provide the means for estimating near real-time values of concentrations and loads of water-quality constituents of interest, such as dissolved and total nitrogen and phosphorus, from the explanatory variables that, in theory, can be measured throughout the year by continuous monitoring stations. The correlation analyses were used to evaluate the potential for

developing regression equations for use with available near real-time measurements. Regression equations were developed for concentrations but not for loads. Because loads are the product of concentration and streamflow, regression equations developed for loads with the highest predictive power will by necessity include streamflow as an explanatory variable. The use of streamflow in this way, however, causes problems in the development and interpretation of the resulting regression equations and adversely affects regression statistics that are used to estimate prediction intervals for the equations; these problems are described as spurious self-correlation (Kenney, 1982; Vogel and others, 2007; Shivers and Moglen, 2008). The problems associated with spurious self-correlations are made worse if logarithmic transformations are used to develop the regression equations (Kenney, 1982). This is not to say, however, that measured flow is not an important variable for consideration in the development of regression equations for estimating concentrations. Equations that use streamflow to estimate concentration, known as water-quality transport curves, can be the best way to accurately estimate concentrations if the relations are strong and other near real-time measurements are not readily available (O'Connor, 1976; Glysson, 1987; Granato, 2006; Granato and others, 2009). Therefore, measured flows and estimated concentrations provide the best possible load estimates with meaningful prediction-interval estimates.

Analytical Procedures for Regression Analysis

Ordinary least squares regression techniques were used to relate the selected explanatory variables to the selected water-quality constituents. Multiple linear regression analysis was used to develop regression models that incorporated one or more automated measurements to represent the concentration of constituents of concern in the near real-time record. Multiple linear regression analysis using ordinary least squares techniques provides a systematic method for estimating the coefficients of a mathematical equation of the relation between a response variable and two or more explanatory variables (Haan, 1977; Tasker and Granato, 2000; Helsel and Hirsch, 2002). In this regression analysis, concentration (the dependent variable) is statistically related to one or more automated hydrologic or water-quality variables recorded at the monitoring station (the independent variables). This results in equations that can be used to estimate the water quality when water-quality sample analyses are not available. The multiple linear regression equations commonly are developed in the following form:

$$Y_p = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \dots + \beta_n X_n + \varepsilon, \quad (1)$$

or, if equations are developed by using the logarithms of data,

$$\log(Y_p) = \beta_0 + \beta_1 \log(X_1) + \beta_2 \log(X_2) + \dots + \beta_n \log(X_n) + \varepsilon, \quad (2)$$

where

- Y_p is the predicted water-quality value,
- β_0 is the estimated value of the linear intercept,
- n is the number of explanatory variables used in the equation,
- X_1 to X_n are the values of each of the n explanatory variables,
- β_1 to β_n are the slopes associated with each of the n explanatory variables, and
- ϵ is the random error component (scatter of measured points around the regression estimates).

The concentrations and the potential explanatory variables were transformed to their common (base 10) logarithms to develop the regression models. The precipitation variables, however, were not readily transformable to logarithms. The precipitation variables have many 0 values, and the logarithm of 0 is undefined; therefore, a value of 1 inch (half the minimum reporting limit of the precipitation gage) was added to all precipitation values to enable use of the logarithms of precipitation variables. The value of 1 was selected because the common logarithm of 1 is equal to 0. Transforming the variables to logarithms increased the linearity of relations and reduced heteroscedasticity (nonconstant variance of residuals). Once the coefficients are calculated, equation 2 is transformed to a power equation in arithmetic space because the estimated concentrations (rather than the logarithms of the estimated concentrations) are of interest and because the arithmetic values of the explanatory variables are more intuitive to use. Addition in log space is equivalent to multiplication in arithmetic space, and multiplication in log space is equivalent to exponentiation in arithmetic space. If retransformed from the common (base 10) logarithms, equation 2 becomes

$$Y_p = 10^{\beta_0} \times X_1^{\beta_1} \times X_2^{\beta_2} \times \dots \times X_n^{\beta_n} \times 10^\epsilon. \quad (3)$$

In regression analysis, the mean of the errors (ϵ) should be 0 in log space; when transformed, this term would equal 1. However, the mean of the errors in logarithmic space is the geometric mean of errors in arithmetic space. As a consequence, the best-fit line in logarithmic space tends to provide a biased estimate of the dependent variable in arithmetic space, and a bias correction factor is needed to compensate. The nonparametric smearing estimator (the average of the retransformed log-regression residuals) proposed by Duan (1983) was selected as a bias correction factor for the regression equations developed in this study because it performs reasonably well and is not sensitive to statistical assumptions regarding residual-population characteristics (Gilroy and others, 1990; Crawford, 1991; Hirsch and others, 1993; Tasker and Granato, 2000; Helsel and Hirsch, 2002; Granato, 2012). The Duan (1983) bias correction factor is called the smearing estimator because the method applies or “smears” the average retransformed error over all measurements. A generalized

expression of the smearing estimator, applicable for any log-based transformation, is the following:

$$BCF = \frac{\sum_{i=1}^n G(e_i)}{N_{xy}}, \quad (4)$$

where

- BCF is the bias correction factor,
- G is the retransformation function,
- e_i is the residual error, which is calculated by subtracting the regression estimate from the data value for each data point (Y_i), and
- N_{xy} is the number of XY data pairs.

For the common logarithms, G is:

$$G(e_i) = 10^{e_i}. \quad (5)$$

A number of statistics are commonly used to assess the strength of a regression equation (Haan, 1977; Gilroy and Tasker, 1990; Tasker and Granato, 2000; Helsel and Hirsch, 2002; Granato, 2012). The coefficient of determination, commonly known as the R -squared (R^2), indicates the fraction of the variance explained by explanatory variables in the model. The adjusted R^2 also indicates the fraction of the variance explained by the explanatory variables in the model; however, in contrast to R^2 , the adjusted R^2 is adjusted for the number of variables in the model and the size of the sample. In general, larger R^2 values indicate a better fit to the available data; a perfect linear fit would have an R^2 value of 1. The prediction error sum of squares ($PRESS$) statistic is the sum of the squared errors calculated for each value (i) by using a version of the regression equation developed with all the other $N_{xy} - 1$ values. In theory, the equation with the minimum $PRESS$ value will produce the least error when making predictions with new data. The average standard error of the estimate ($ASEE$) is also known as the mean-square error and as the variance of the residuals (σ^2); it is the sum of squared residual errors divided by $N_{xy} - 2$. In this case, it is a measure of the variation between the concentration estimates and the observed predictive variables. The square root of the $ASEE$ is known as the root mean-square error or the standard deviation of residuals (σ). In general, regression models with small $ASEE$ values will produce the least error among the available data. $ASEE$ values are calculated within log space and are commonly converted to percent errors to facilitate model evaluation and comparison. The $ASEE$ statistic is converted from a logarithm to a percent error by using the following equation:

$$ASEE_{percent} = 100 \times \left(e^{\left(\sigma^2 \times (\ln(10))^2 \right)} - 1 \right)^{0.5}. \quad (6)$$

Theoretically, about two-thirds of the estimates obtained from the equations in the regression analysis will have errors less

than the calculated standard errors of estimate. The average standard error of the prediction (*ASEP*) is similar to the *ASEE* but is a measure of the predictive ability of the regression model. The *ASEP* can be estimated by using the *PRESS* statistic (Gilroy and Tasker, 1990; Koltun and Whitehead, 2002; Granato, 2012), as described in the following equation:

$$ASEP_{est} = \sqrt{\frac{PRESS}{N_{xy}}} \quad (7)$$

The *ASEP* can be converted from a logarithm to a percent error by using the method shown in equation 7. In theory, regression models with small *ASEP* values will produce the least error for predictions using new data. Theoretically, about two-thirds of the concentration estimates obtained from automated measurements will have errors less than the calculated standard errors of prediction.

Continuous and Manual Water-Quality Data

This section of the report examines the range and quality of continuous water-quality measurements and discusses analytical results from samples collected by the automated sampling system at the Millville station, as well as samples collected manually from the intake point at the station and from upstream bridge.

Continuous Water-Quality Data

Temperature generally followed seasonal patterns, except during runoff events, and was warmest during summer months and coldest in winter months over the period of record (WYs 2013 and 2014). The median water temperature recorded at the Millville station was about 11.5 °C over the period of record. The lowest temperature was 0.0 °C on December 15, 2013, and many other days in winter, and the highest was 29.3 °C on July 3, 2014.

Changes in specific conductance also followed a typical seasonal pattern. Specific conductance was highest in winter months, and large peaks in the record were associated with the runoff of winter deicing and maintenance materials from impervious surfaces. Runoff from meltwater and spring rains begin to clear impervious surfaces and decrease specific conductance. Late spring and early summer are typically associated with the lowest specific conductance values. Although runoff events during the summer and fall cause short-term decreases in specific conductance observed until winter road maintenance activities begin again, the specific conductance gradually increases during the summer and fall. Median conductance was 476 microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C). The lowest recorded

specific conductance was 202 $\mu\text{S}/\text{cm}$ in April 2014, and the highest was 1,550 $\mu\text{S}/\text{cm}$ in January 2014.

The lowest turbidity was 0.4 formazin nephelometric units (FNU), and the highest turbidity, which followed sediment-laden winter runoff events, was 67 FNU. The median turbidity for the period of record was 2.5 FNU.

Median chlorophyll *a* was 8.1 parts per billion (ppb). The lowest measured chlorophyll *a* was 0.07 ppb, and the highest was 268 ppb. Diurnal fluctuations of chlorophyll *a* were also observed throughout the record during peak growing months (June through September). Chlorophyll *a* values have been used as a measure of algal concentrations in lakes (Vollenweider and Kerekes, 1982; Kreakie and others, 2015). Oligotrophic conditions, or low algal concentrations, are associated with chlorophyll *a* concentrations less than 2.0 ppb, whereas hypereutrophic conditions, or very high algal concentrations, are considered to be those chlorophyll *a* concentrations greater than 35 ppb.

Automated and Manually Collected Concentration Data

Analytical results from samples collected by the automated flow-proportional sampling system and manual sampling techniques are listed in tables 5 and 6, respectively. At the Millville station, fifty 14-day composite samples were collected by the automated flow-proportional system for nutrients, and fifty-two 4-day composite samples were collected by the automated system for dissolved trace metals and total aluminum. Over 30 manually collected samples were collected either at the Millville station (as point samples) or at the upstream railroad bridge (with the EWI method). A subset of these EWI and point samples were collected as pairs to evaluate representativeness of the Millville station intake point, discussed in the section “Equal-Width-Increment and Point Sample Comparisons.”

Table 6. Concentrations of nutrients, trace metals, and suspended sediment in manually collected samples from the upstream railroad bridge and from the collection point at the Blackstone River at Millville, Massachusetts, station (01111230) during water years 2013 and 2014.

[Table available for download at <https://doi.org/10.3133/sir20175094>]

Suspended Sediment

Excessive suspended sediment concentration limits light penetration and covers habitat in sediment, which can have negative ecological effects on fish, invertebrates, and aquatic vegetation (EPA, 2003). Suspended sediment guidelines are not established for the Blackstone River. However, the highest maximum daily concentration of total suspended sediment (TSS) in 24-hour composite samples of treated effluent, as specified in the 2010 Upper Blackstone Pollution

Abatement District, National Pollutant Discharge Elimination System (NPDES) permit, is 55 mg/L TSS. Therefore, for this study, concentrations greater than 55 mg/L TSS may be informally considered representative of poor water quality in the Blackstone and other northeastern U.S. streams (Kimberly Groff, MassDEP, written commun., 2011). Samples collected by the automated system were not submitted for suspended sediment analysis. Suspended sediment concentration in manually collected samples ranged from 1.0 to 75 mg/L during WYs 2013–14 (table 6).

Nitrogen and Phosphorus

Total and dissolved nitrogen concentrations in composite samples collected with the automated system ranged from 0.77 to 2.71 mg/L and 0.69 to 2.65 mg/L, respectively, during WYs 2013 and 2014 (table 5). It is unclear how much contamination from the 0.45- μ m capsule filters may have affected dissolved nitrogen concentrations in composite samples collected by the automated system. However, manually sampled concentrations of total and dissolved nitrogen were similar, ranging from 0.88 to 2.83 mg/L and 0.78 to 2.80 mg/L, respectively (table 6). Concentrations for each method of sample collection are shown as boxplots in figure 4A.

Total and dissolved phosphorus concentrations are also shown in boxplot form (figs. 4B and C). Composite samples collected with the automated system ranged from 0.030 to 0.200 mg/L for total phosphorus and 0.010 to 0.150 mg/L for dissolved phosphorus (table 5). Manually sampled concentrations of total and dissolved phosphorus ranged from 0.040 to 0.356 mg/L and 0.015 to 0.124 mg/L, respectively (table 6).

Trace Metals

Unlike manually collected samples, which were analyzed for both total and dissolved trace metals, samples collected by the automated system were submitted for analysis of dissolved trace metals and total aluminum. Boxplots of dissolved metal and total aluminum concentrations from all three sampling methods are shown in figure 5. All other total metal concentrations and chloride concentrations from only manual sampling methods are shown in figure 6.

Dissolved cadmium and chromium concentrations in samples collected by the automated system ranged from 0.11 to 0.75 and 0.19 to 2.5 μ g/L, respectively, during WYs 2013–14 (table 5 and figs. 5A and B). Manually sampled concentrations of dissolved cadmium and chromium ranged from 0.13 to 0.46 and 0.14 to 0.70 μ g/L, respectively (table 6 and figs. 5A and B). Dissolved copper concentrations in composite samples collected with the automated system ranged from 2.1 to 9.2 μ g/L (table 5 and fig. 5C). Manually sampled concentrations of total and dissolved copper ranged

from 3.0 to 25.4 and 2.0 to 10.4 μ g/L, respectively (table 6 and fig. 5C).

Dissolved lead and nickel concentrations in automated samples ranged from 0.19 to 5.9 and 1.4 to 3.6 μ g/L, respectively (table 5 and figs. 5D and E). Dissolved lead concentrations in manual samples ranged from 0.3 to 20.6 μ g/L (table 6 and fig. 5D). Dissolved nickel concentrations in manual samples ranged from 1.3 to 4.4 μ g/L (table 6 and fig. 5E). Dissolved zinc concentrations in the automated 4-day composite samples ranged from 6.9 to 19.7 μ g/L, and dissolved zinc concentrations in samples collected manually ranged from 5.9 to 37.8 μ g/L (tables 5 and 6 and fig. 5F).

Total aluminum concentrations in samples collected by the automated system ranged from 12.8 to 395 μ g/L; concentrations ranged from 35.8 to 1,080 μ g/L in samples collected manually (tables 5 and 6 and fig. 5G). Manual sampling captured samples with much higher concentrations of aluminum. Manually collected samples with the largest concentrations of aluminum appear to be associated with storm runoff, particularly during the winter and spring. Composite samples collected by the automated system over 4 days were less sensitive to maximum and minimum concentrations than manually collected samples were.

Total cadmium concentrations in manually collected samples ranged from 0.23 to 1.18 μ g/L, and total chromium concentrations ranged from 0.43 to 12.4 μ g/L (table 6 and figs. 6A and B). Manually sampled concentrations of total copper ranged from 3.0 to 25.4 μ g/L (table 6 and fig. 6C). Total lead concentrations in manual samples ranged from 0.70 to 49.4 μ g/L (table 6 and fig. 6D). Total nickel concentrations in manual samples ranged from 1.3 to 4.8 μ g/L (table 6 and fig. 6E). Total zinc concentrations in manually collected samples ranged from 9.5 to 55.2 μ g/L (table 6 and fig. 6F).

Samples collected by both automated and manual techniques were also analyzed for selected major ions (tables 5 and 6). Samples collected with the automated system were only analyzed for calcium and magnesium; however, manually collected samples were analyzed for calcium, chloride, magnesium, sodium, potassium, and sulfate concentrations, and results can be seen in tables 5 and 6. Two major ions are of particular interest are chloride and magnesium. Concentrations of chloride from manual samples ranged from 52.3 to 201 mg/L (table 6 and fig. 6G). These data support the identification of upward trends in chloride identified in the Blackstone River by Savoie and others (2017). Concentrations of magnesium from samples collected by both methods ranged from 1.5 to 13.4 mg/L (tables 5 and 6). Magnesium concentrations from samples collected manually during WY13 were about 2.45 mg/L on average and in WY14 were about two times greater at 4.78 mg/L (table 6).

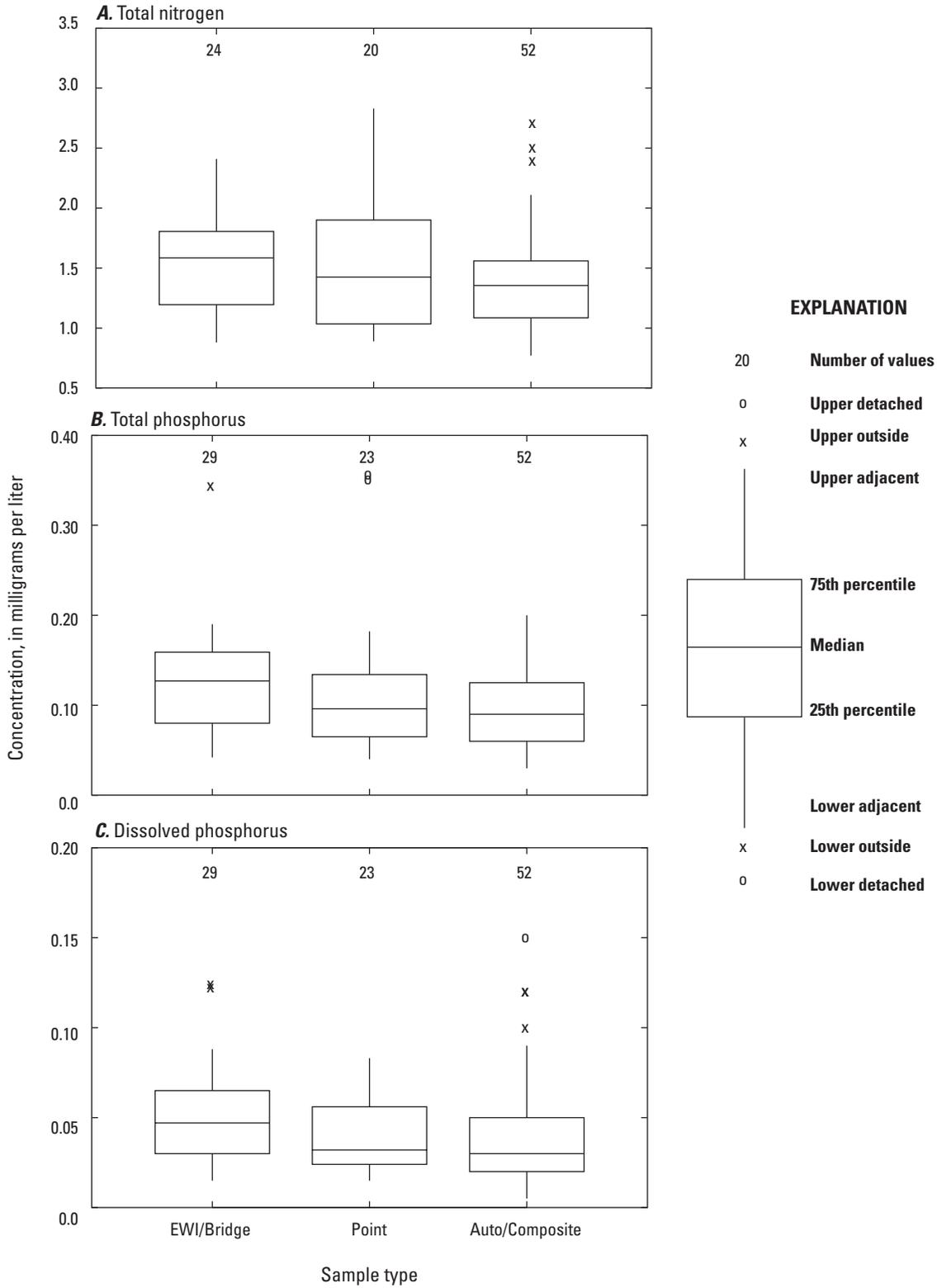


Figure 4. A, Total nitrogen, B, total phosphorus, and C, dissolved phosphorus concentrations collected from the upstream train bridge (EWI/Bridge), the Millville station intake point (Point), and the automated system (Auto/Composite) from the Blackstone River at Millville, Massachusetts, station (01111230), water years 2013 and 2014.

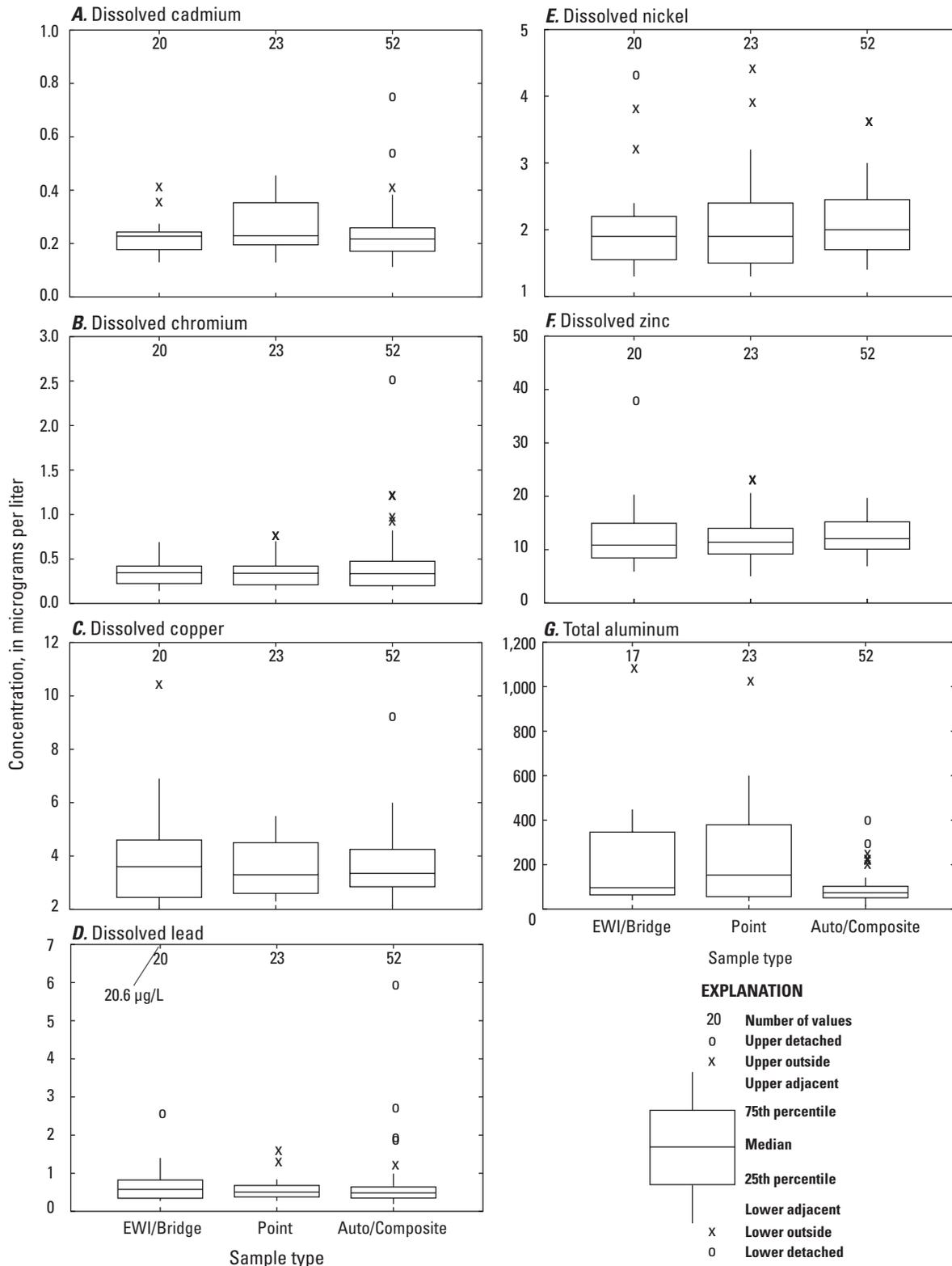


Figure 5. Concentrations of dissolved trace metals *A*, cadmium, *B*, chromium, *C*, copper, *D*, lead, *E*, nickel, and *F*, zinc, and of *G*, total aluminum collected from the upstream train bridge (EWI/Bridge), the Millville station intake point (Point), and the automated system (Auto/Composite) from the Blackstone River at Millville, Massachusetts, station (01111230), water years 2013 and 2014.

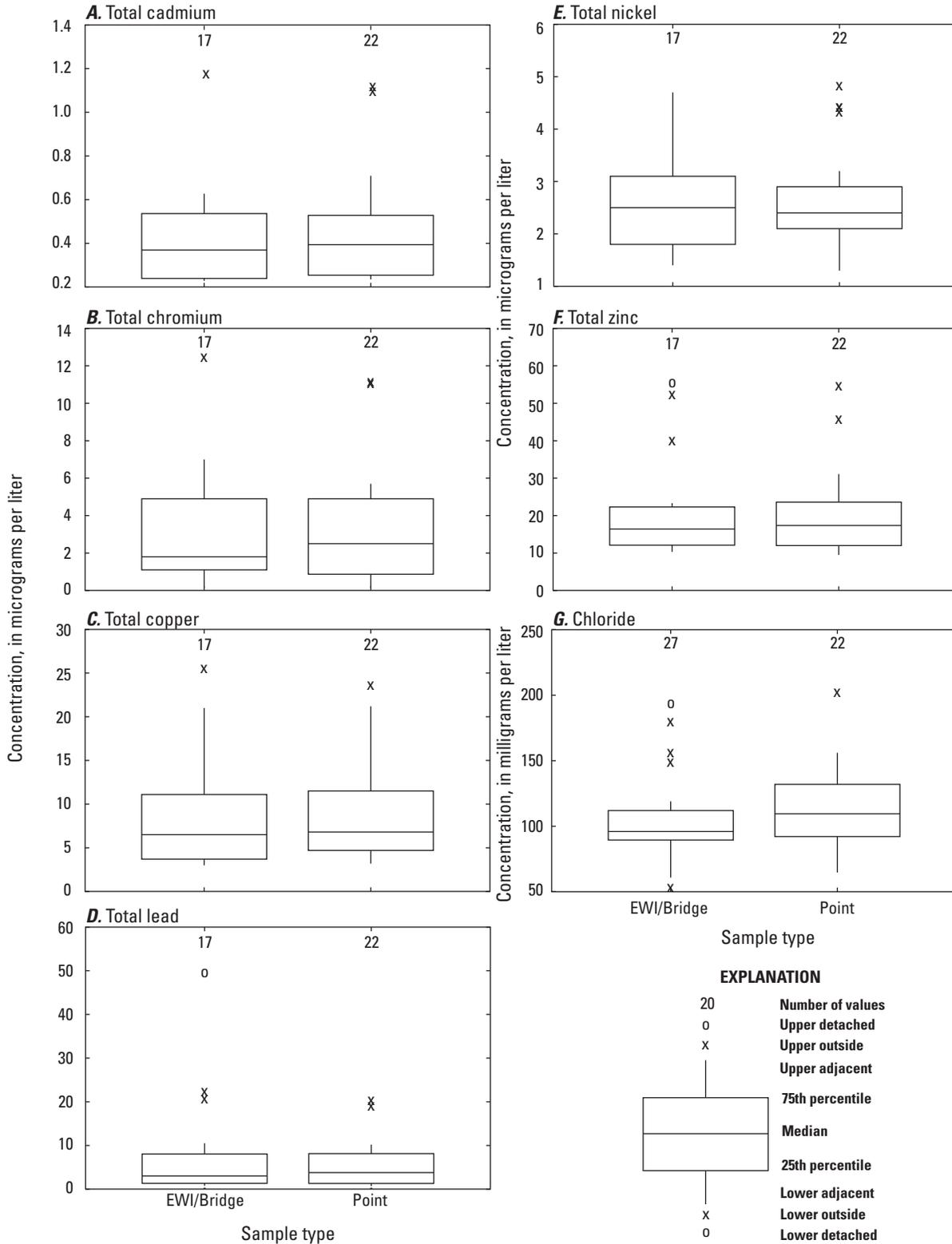


Figure 6. Concentrations of total trace metals *A*, cadmium, *B*, chromium, *C*, copper, *D*, lead, *E*, nickel, and *F*, zinc, and of *G*, chloride collected from the upstream train bridge (EWI/Bridge) and the Millville station intake point (Point) from the Blackstone River at Millville, Massachusetts, station (01111230), water years 2013 and 2014.

Constituent Loads in the Blackstone River Crossing the Massachusetts-Rhode Island State Line, Water Years 2013–2014

Concentrations of nutrients from the 14-day composite samples and metals from the 4-day composite samples collected by the automated system were individually multiplied by the average flow of their respective time periods to calculate loads. To compensate for missed days of sampling, the load per day times the number of missed sampling days within its time period was added to the load without missing days. Monthly, seasonal, and annual loading values for nutrients and metals are discussed on the basis of these adjusted values and are compared to previously published loads for the Blackstone River for WYs 2008 and 2009.

Nitrogen and Phosphorus

Fourteen-day loads of total nitrogen and total and dissolved phosphorus are listed in table 7. The maximum and minimum total nitrogen loads of the fifty 14-day composites collected during WYs 2013 and 2014 were 46,170 and 1,932 kg, respectively. The ranges of total and dissolved phosphorus loads based on the 14-day composites were 5,397 to 120 kg and 1,799 to 15 kg, respectively.

Table 7. Loads of nutrients based on 14-day nutrient composite samples, and loads of dissolved trace metals and total aluminum based on 4-day metal composite samples collected by the automated sampling system from the point location at the Blackstone River at Millville, Massachusetts, station (0111230) during water years 2013 and 2014.

[Table available for download at <https://doi.org/10.3133/sir20175094>]

Two 14-day composite loads were summed to approximate monthly total nitrogen loads and total and dissolved phosphorus loads, as shown in figure 7. The largest 28-day loads of total nitrogen were in April of 2014, followed by March and June of 2013 (fig. 7A). The largest 28-day loads of total phosphorus were in June 2013, followed by April 2014 (fig. 7B). However, the largest 28-day dissolved phosphorus loads were observed in October 2012, followed by June 2013 and April 2014 (fig. 7B). Seasonally, the largest nitrogen loads appeared in the spring and winter during WYs 2013 and 2014, and the largest phosphorus loads were seen in the spring and summer and associated with major storm events.

The annual load of total nitrogen in WY 2013 was about 447,000 kg. Estimated flows at Millville in WY 2014 were about 25 percent lower than in WY 2013, and the annual load of total nitrogen in WY 2014 was about 342,000 kg. The annual loads of total and dissolved phosphorus in WY 2013 were about 35,900 and 12,000 kg, respectively. In WY 2014,

the annual loads of total and dissolved phosphorus were about 20,700 and 8,220 kg, respectively. The lower flows seen in WY14 are a possible explanation for the 42-percent decrease in total phosphorus loading.

Zimmerman and others (2015) used a similar sampling system and reported the following estimated annual loads in the Blackstone River at Millville. The estimated annual load of total nitrogen was 936,000 kg in WY 2008 and 878,000 kg in WY 2009. The estimated annual load of total phosphorus was 81,400 kg in WY 2008 and 80,900 kg in WY 2009. Total nitrogen and total phosphorus annual loads from WYs 2013 and 2014 were about 56 and 65 percent lower than those reported for WYs 2008 and 2009. The higher loads in 2008 and 2009 may be explained by the higher than average flows in WY 2009 and by facility upgrades made by wastewater treatment facilities in the basin.

The estimated annual load of suspended sediment was 4,940,000 kg in WY 2008 and 7,040,000 kg in WY 2009. As a point of comparison, the flows in WYs 2008 and 2009 were about 38 and 25 percent less, respectively, than the long-term (WYs 1929–2012) mean annual flow of 22.5 m³/s (793 ft³/s) at the Blackstone River at Woonsocket, Rhode Island, gage (USGS station 01112500). During WYs 2013 and 2014, flows were about 50 and 76 percent less, respectively, than the Woonsocket mean annual flow. Downward trends in nutrient concentrations in both the Blackstone River and Narragansett Bay have been reported (Savoie and others, 2017; Durant and Raposa, 2011).

Trace Metals

Four-day loads of magnesium, dissolved trace metals, and total aluminum, based on composite sample concentrations collected by the automated station multiplied by the average 4-day flows, are listed in table 7 and shown as a function of time in figure 8 (except magnesium).

Dissolved cadmium 4-day loads collected by the automated system during WYs 2013 and 2014 (fig. 8A) ranged from 0.16 to 12.2 kg, and dissolved chromium loads (fig. 8B) ranged from 0.21 to 56.7 kg, and the largest cadmium and chromium loads were associated with flows following a storm event on June 6, 2013. Dissolved copper loads (fig. 8C) ranged from 2.90 to 208.8 kg, and dissolved lead loads (fig. 8D) ranged from 0.19 to 134.1 kg. Dissolved nickel loads (fig. 8E) ranged from 1.59 to 49.9 kg, and dissolved zinc loads (fig. 8F) ranged from 6.67 to 419.8 kg. Individual total aluminum 4-day loads (fig. 8G) ranged from 10 to 7,015 kg, and the largest aluminum load was during the March 29, 2014, event. Median dissolved cadmium and chromium 4-day loads were 0.55 and 0.84 kg, respectively, during WYs 2013 and 2014. Dissolved copper and lead median loads were 1.42 and 8.02 kg, respectively. The dissolved nickel median load was 5.45 kg, and the dissolved zinc median load was 36 kg. Median total aluminum 4-day loads were about 197 kg.

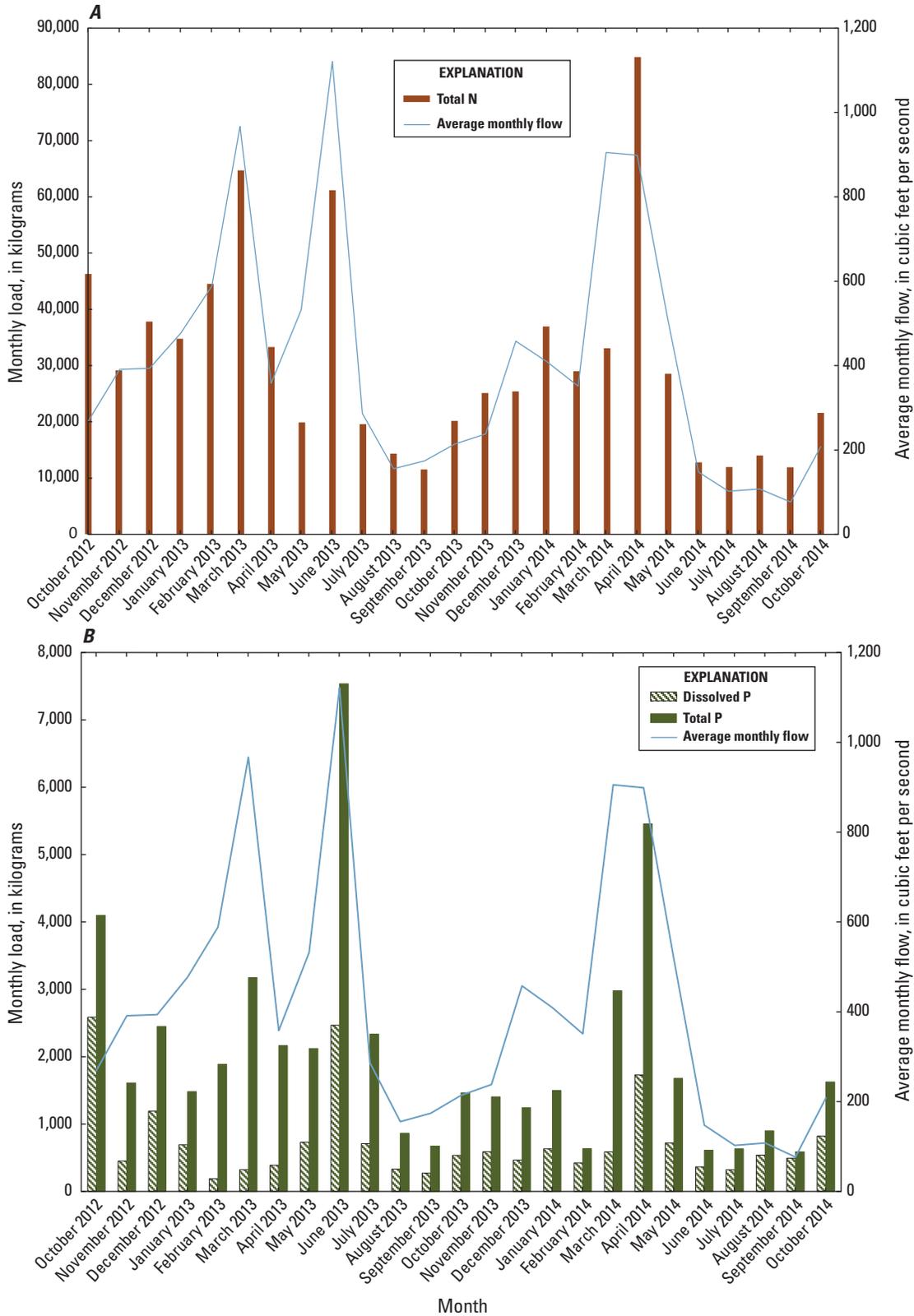


Figure 7. Monthly loads of A, total nitrogen (N) and B, total and dissolved phosphorus (P) based on 14-day composite samples from the Blackstone River at Millville, Massachusetts, station (01111230), water years 2013 and 2014. Monthly loads are approximated as the sum of loads measured from the consecutive 14-day composite samples during the month indicated.

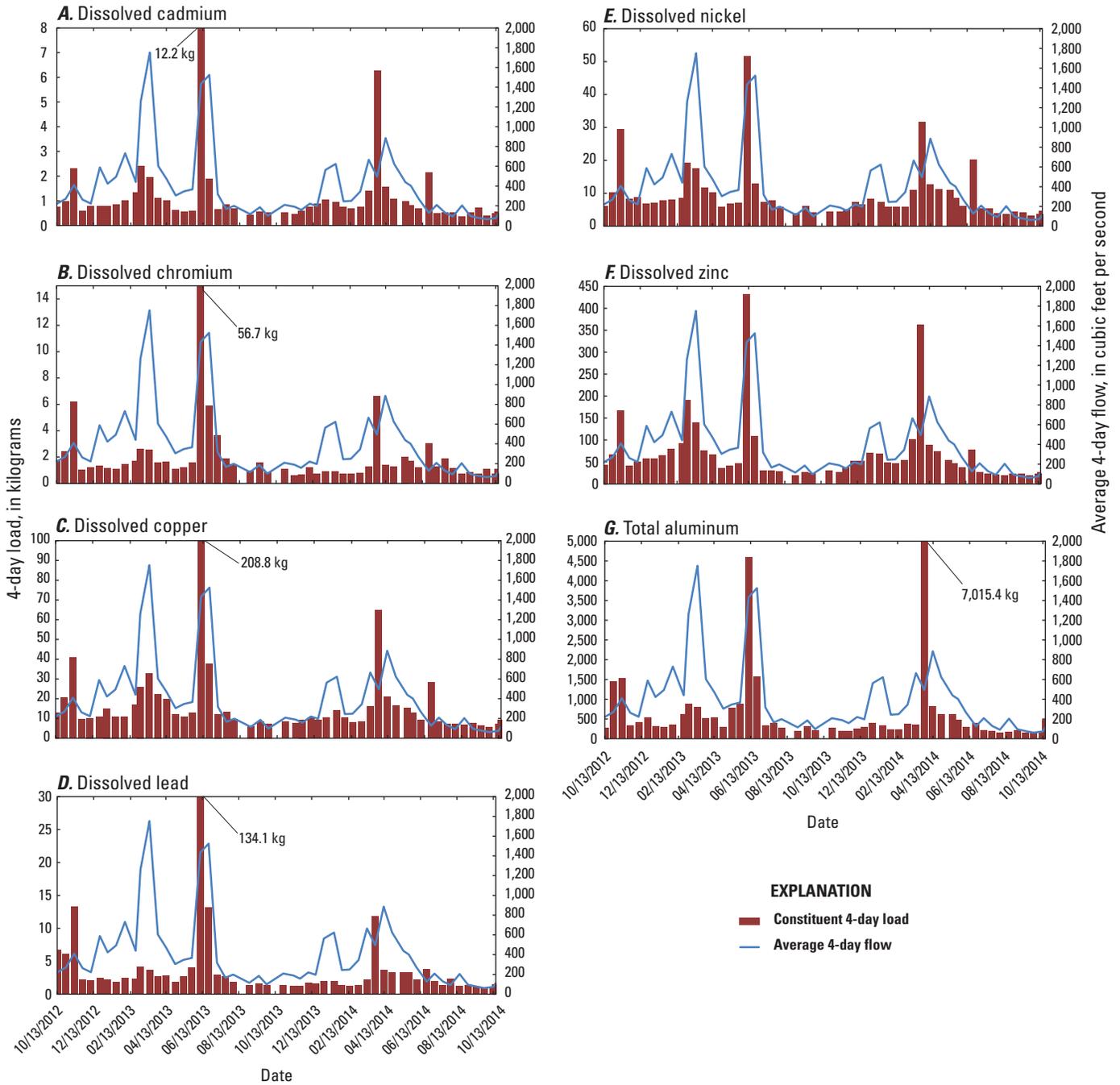


Figure 8. 4-day loads of *A*, dissolved cadmium, *B*, dissolved chromium, *C*, dissolved copper, *D*, dissolved lead, *E*, dissolved nickel, *F*, dissolved zinc, and *G*, total aluminum, based on composite samples collected by the automated system from the Blackstone River at Millville, Massachusetts, station (0111230), water years 2013 and 2014. kg, kilogram.

Various peak loads exist in the individual records for metals, but in general two large loads can be seen in figure 8. These two extremes are associated with major storm events that occurred during the 4-day sampling periods or within 72 hours of their start times. During the first of these two periods, which began on June 6, 2013, sampled flows included runoff from 0.54 inches (in.) of rain in the previous 72 hours. The second sampling period, which began on March 29, 2014, followed a storm event with 3.78 in. of precipitation, as recorded by the Millville station.

Correlation Among Variables

Correlation coefficients among the potential explanatory variables taken from the discrete point samples and their associated water-quality parameter readings are shown in table 8. Many of these water-quality and hydrologic variables have statistically significant correlations with one another; however, only temperature and dissolved oxygen are highly correlated. This relationship is expected because the solubility of oxygen in water is a function of atmospheric pressure and temperature (Hem, 1992). Temperature sensors are less expensive, require less maintenance, are more robust, and are more reliable than dissolved oxygen sensors, which commonly need temperature compensation (Wagner and others, 2006). Thus, correlation analysis and monitoring logistics indicate that temperature is a good predictor for dissolved oxygen and may be selected as one of the explanatory variables for other constituents of interest, even if the correlation to temperature is slightly less than the correlation to dissolved oxygen (table 8).

The rank correlations among the precipitation variables are strong, but only the linear correlation between the 48- and 72-hour precipitation totals is strong; logarithmic transformations for these variables are not applicable because logarithms are limited to nonzero, positive values. In table 8, the magnitudes and signs of the various correlation coefficients are, by and large, consistent with theoretical relations between measured variables (Hem, 1992).

Nutrient-Concentration Correlations

The use of automated measurements to estimate constituent concentrations can provide valuable information to help monitor abrupt changes in quality or short-term signals missed by fixed-frequency measurement. Analytical results from manually collected samples and water-quality parameter measurements were used in the following correlation analysis discussions.

Correlations Between Potential Explanatory Variables and Nutrient Concentrations

The values of correlations between selected explanatory variables and nutrient constituents of interest indicate the

potential for developing quantitative, single or multiple linear regression equations to relate values of one or more automated measurements to concentrations of the constituents of interest (table 9). For this study, a $\rho \geq 0.90$ is considered strong, a $\rho \geq 0.80$ to < 0.90 is semistrong, a $\rho \geq 0.75$ to < 0.80 is moderate, and a $\rho < 0.75$ is weak. The only semistrong correlations between the potential explanatory variables and nutrients are between discharge and dissolved nitrate ($\rho = -0.866$), specific conductance and total nitrogen ($\rho = 0.844$), specific conductance and dissolved nitrogen ($\rho = 0.806$), turbidity and particulate carbon ($\rho = 0.864$), and turbidity and particulate phosphorus ($\rho = 0.834$). The remaining correlations are weak to moderate, indicating that two or more explanatory variables are needed to produce nutrient concentration estimates.

Correlations Among Nutrient Concentrations

Analysis of correlations among nutrient concentrations indicates possible causal relations between selected variables, possible predictive relations between variables, and the potential for substituting a constituent that is less expensive to collect, process, and analyze for a more expensive constituent. Identification of possible causal relations between selected variables may provide information that decision makers can use to identify potential sources of a nutrient and therefore the most effective mitigation measures. The ability to substitute a constituent that is less expensive to collect could result in greater efficiency in field operations by potentially reducing time spent in the field while simultaneously providing estimated data at a greater frequency. Cost savings from reduced work hours in the field could be shifted towards helping to increase the number of sampling events, and thereby increase the confidence in the representativeness of data.

Strong correlation coefficients for the nitrogen and phosphorus species indicate potential sources and transport mechanisms. Strong and semistrong correlation coefficients are shown as bold values in table 10. Correlation coefficients for the nitrogen species indicate that the total nitrogen and dissolved nitrogen are highly correlated (exceeding 0.96 for ρ), and both are strongly correlated to nitrate (0.921 or greater); this indicates either that the sources and processes that contribute nitrogen to the river produce dissolved nitrogen or that the sources are predominantly nitrate. Furthermore, moderate to semistrong negative correlations between the explanatory variable of discharge and total nitrogen ($\rho = -0.662$), dissolved nitrogen ($\rho = -0.759$), and nitrate ($\rho = -0.866$) indicate dilution with increasing flow (table 9). These negative correlations indicate that the primary source of nitrogen may be from groundwater discharge or a relatively constant point source (O'Connor, 1976; Albek, 2003; Granato, 2006; Granato and others, 2009). Total organic nitrogen, particulate nitrogen, and particulate carbon have semistrong to strong relations with each other (table 10). Although suspended sediment has a semistrong correlation with the explanatory variable of discharge ($\rho = 0.724$), only the total organic nitrogen constituent has

Table 8. Correlation coefficients among potential explanatory variables.

[Correlation coefficients that are statistically significant at the 95th percentile are shown as italic numbers. Correlation coefficients that are greater than 0.8 are shown as bold italic numbers. Water-quality parameters: p00010, temperature, water, degrees Celsius; p00060, discharge, cubic feet per second; p00095, specific conductance, water, unfiltered, microsiemens per centimeter at 25 degrees Celsius; p00300, dissolved oxygen, water, unfiltered, milligrams per liter; p00400, pH, water, unfiltered, field, standard units; p32209, chlorophyll *a*, fluorometric method, corrected, water, micrograms per liter; p63676, turbidity, water, unfiltered, broadband light source (400–680 nanometers), detectors at multiple angles including 90 ± 30 degrees, ratiometric correction, nephelometric turbidity ratio unit; p7977a, precipitation, total, in inches; p7977b, antecedent precipitation, total, (24-hour), in inches; p7977c, antecedent precipitation, total, (48-hour), in inches; p7977d, antecedent precipitation, total, (72-hour), in inches]

Water-quality parameter	Spearman's rho										
	Discharge (Q); p00060	Temperature (Tmp); p00010	Specific conductance (SC); p00095	Dissolved oxygen (DO); p00300	pH; p00400	Chlorophyll <i>a</i> (CA); p32209	Turbidity (Trb); p63676	Precipitation (P); p7977a	24-hour precipitation (24P); p7977b	48-hour precipitation (48P); p7977c	72-hour precipitation (72P); p7977d
Discharge (Q)	1										
Temperature (Tmp)	-0.370	1									
Specific conductance (SC)	-0.436	0.032	1								
Dissolved oxygen (DO)	0.027	-0.951	-0.217	1							
pH	-0.327	-0.091	0.063	0.184	1						
Chlorophyll <i>a</i> (CA)	-0.205	0.506	0.159	-0.789	-0.097	1					
Turbidity (Trb)	0.491	-0.101	0.009	-0.379	-0.517	0.287	1				
Precipitation (P)	0.111	-0.199	-0.075	0.000	0.000	-0.034	0.061	1			
24-hour precipitation (24P)	0.484	-0.216	0.032	0.007	-0.619	0.171	0.395	0.441	1		
48-hour precipitation (48P)	0.481	-0.154	0.004	-0.021	-0.570	0.192	0.497	0.456	0.933	1	
72-hour precipitation (72P)	0.481	-0.135	0.000	-0.071	-0.584	0.200	0.495	0.425	0.990	0.993	1

Table 9. Correlation coefficients between potential explanatory variables and nutrient concentrations.

[Correlation coefficients that are statistically significant at the 95th percentile are shown as italic numbers. Correlation coefficients that are greater than 0.8 are shown as bold italic numbers. Water-quality parameters for potential explanatory variables: temperature, water, degrees Celsius (p00010); discharge, cubic feet per second (p00060); specific conductance, water, unfiltered, microsiemens per centimeter at 25 degrees Celsius (p00095); dissolved oxygen, water, unfiltered, milligrams per liter (mg/L) (p00300); pH, water, unfiltered, field, standard units (p00400); chlorophyll *a*, fluorometric method, corrected, water, micrograms per liter (p32209); turbidity, water, unfiltered, broadband light source (400–680 nanometers), detectors at multiple angles including 90 ± 30 degrees, radiometric correction, nephelometric turbidity ratio unit (p63676); precipitation, total, in inches (p7977a); antecedent precipitation, total, (48-hour), in inches (p7977b); antecedent precipitation, total, (72-hour), in inches (p7977d). Water-quality parameters for nutrient concentrations: p00600 fTN, total nitrogen, water, filtered, mg/L; p00605 fON, organic nitrogen (organic N), water, unfiltered, mg/L; p00607 fON, organic N, water, filtered, mg/L; p00608 fNH3, ammonia, water, filtered, mg/L as nitrogen (mg/L as N); p00613 fNO2, nitrite, water, filtered, mg/L as N; p00618 fNO3, nitrate, water, filtered, mg/L as N; p00665 fTP, phosphorus (P), water, unfiltered, mg/L; p00671 fOP, orthophosphate, water, filtered, mg/L as P; p00681 fOC, organic carbon, water, filtered, mg/L; p00694 pC, carbon (inorganic plus organic), suspended sediment, total, mg/L; p49570 pN, particulate nitrogen, suspended in water, mg/L; p62854 fSN, total nitrogen (nitrate + nitrite + ammonia + organic N), water, filtered, analytically determined, mg/L as N; p62855 fSN, total nitrogen (nitrate + nitrite + ammonia + organic N), water, filtered, analytically determined, mg/L as N]

Water-quality parameter	Spearman's rho												
	Total nitrogen, water, unfiltered (mg/L); p00600 fTN	Total nitrogen, water, filtered (mg/L); p00602 fTN	Organic nitrogen, water, unfiltered (mg/L); p00605 fON	Organic nitrogen, water, filtered (mg/L); p00607 fON	Ammonia, water, filtered (mg/L as N); p00608 fNH3	Nitrite, water, filtered (mg/L as N); p00613 fNO2	Nitrate, water, filtered (mg/L as N); p00618 fNO3	Phosphorus, water, unfiltered (mg/L as P); p00665 fTP	Orthophosphate, water, filtered (mg/L as P); p00671 fOP	Organic carbon, water, filtered (mg/L); p00681 fOC	Carbon (inorganic, plus organic), suspended sediment, total (mg/L); p00694 pC	Particulate nitrogen, suspended in water, filtered, water, unfiltered, analytically determined (mg/L); p49570 pN	Total nitrogen (nitrate + nitrite + ammonia + organic N), water, filtered, analytically determined (mg/L); p62854 fSN
Discharge (Q)	-0.662	-0.759	0.528	0.323	0.483	-0.866	0.234	-0.507	0.074	0.336	0.2	-0.741	-0.619
Temperature (Temp)	0.212	0.221	-0.004	-0.313	-0.675	0.261	0.438	0.495	0.195	-0.036	0.169	0.204	0.344
Specific conductance (SC)	0.844	0.806	0.018	0.016	-0.112	0.71	0.169	0.318	0.054	-0.002	0.181	0.828	0.871
Dissolved oxygen (DO)	-0.27	-0.152	-0.436	-0.181	0.486	-0.156	-0.801	-0.457	-0.562	-0.409	-0.789	-0.13	-0.64
pH	0.112	0.252	-0.434	-0.497	-0.304	0.28	-0.030	-0.106	-0.248	-0.310	-0.224	0.345	-0.248
Chlorophyll <i>a</i> (CA)	0.310	0.322	0.135	-0.331	-0.243	0.313	0.551	0.238	0.013	0.268	0.542	0.390	0.463
Turbidity (Trb)	0.072	-0.046	0.783	0.323	0.314	-0.165	0.834	0.109	0.285	0.864	0.770	-0.045	0.171
Precipitation (P)	-0.102	-0.074	-0.063	0.046	0.071	-0.074	-0.112	-0.046	0.253	-0.021	-0.042	-0.126	-0.170
24-hour precipitation (24P)	-0.263	-0.368	0.451	0.137	0.470	-0.444	0.324	-0.416	0.245	0.562	0.412	-0.464	-0.269
48-hour precipitation (48P)	-0.243	-0.345	0.531	0.135	0.374	-0.410	0.416	-0.275	0.308	0.631	0.461	-0.434	-0.218
72-hour precipitation (72P)	-0.247	-0.344	0.523	0.285	0.351	-0.405	0.426	-0.305	0.306	0.614	0.456	-0.437	-0.222

Table 10. Correlation coefficients among nutrient concentrations.

[Correlation coefficients that are statistically significant at the 95th percentile are shown as italic numbers. Correlation coefficients that are greater than or equal to 0.8 are shown as bold italic numbers. Water-quality parameters: p00600 tTN, total nitrogen, water, unfiltered, milligrams per liter (mg/L); p00602 fTN, total nitrogen, water, filtered, mg/L; p00605 tON, organic nitrogen (organic N), water, unfiltered, mg/L; p00607 fON, organic N, water, filtered, mg/L; p00608 fNH3, ammonia, water, filtered, mg/L as nitrogen (mg/L as N); p00613 fNO2, nitrite, water, filtered, mg/L as N; p00618 fNO3, nitrate, water, filtered, mg/L as N; p00665 tTP, phosphorus (P), water, unfiltered, mg/L; p00671 fOP, orthophosphate, water, filtered, mg/L as P; p00681 fOC, organic carbon, water, filtered, mg/L; p00694 pC, carbon (inorganic plus organic), suspended sediment, total, mg/L; p49570 pN, particulate nitrogen, suspended in water, mg/L; p62854 fSN, total nitrogen (nitrate + nitrite + ammonia + organic N), water, filtered, analytically determined, mg/L as N; p62855 tSN, total nitrogen (nitrate + nitrite + ammonia + organic N), water, unfiltered, analytically determined, milligrams per liter as N]

Water-quality parameter	Spearman's rho													
	Total nitrogen, water, unfiltered (mg/L); p00600 tTN	Total nitrogen, water, filtered (mg/L); p00602 fTN	Organic nitrogen, water, unfiltered (mg/L); p00605 tON	Organic nitrogen, water, filtered (mg/L); p00607 fON	Ammonia, water, filtered (mg/L as N); p00608 fNH3	Nitrite, water, filtered (mg/L as N); p00613 fNO2	Nitrate, water, filtered (mg/L as N); p00618 fNO3	Phosphorus, water, unfiltered (mg/L as P); p00665 tTP	Ortho-phosphate, water, filtered (mg/L as P); p00671 fOP	Organic carbon, water, filtered (mg/L); p00681 fOC	Carbon (inorganic plus organic), suspended sediment, total (mg/L); p00694 pC	Particulate nitrogen, suspended in water (mg/L); p49570 pN	Total nitrogen (nitrate + nitrite + ammonia + organic N), water, filtered, analytically determined (mg/L); p62854 fSN	Total nitrogen (nitrate + nitrite + ammonia + organic N), water, unfiltered, analytically determined (mg/L); p62855 tSN
p00600 tTN	1													
p00602 fTN	<i>0.975</i>	1												
p00605 tON	0.052	-0.119	1											
p00607 fON	0.109	0.018	<i>0.685</i>	1										
p00608 fNH3	-0.204	-0.272	0.326	0.302	1									
p00613 fNO2	-0.088	-0.171	0.284	0.120	0.415	1								
p00618 fNO3	<i>0.921</i>	<i>0.962</i>	-0.24	-0.105	-0.435	-0.257	1							
p00665 tTP	0.255	0.148	<i>0.746</i>	0.255	-0.050	0.028	0.045	1						
p00671 fOP	<i>0.549</i>	<i>0.556</i>	0.047	0.138	-0.495	-0.091	<i>0.539</i>	0.345	1					
p00681 fOC	-0.001	-0.061	0.220	0.227	-0.129	0.284	-0.114	0.248	0.395	1				
p00694 pC	0.052	-0.125	<i>0.863</i>	0.435	0.303	<i>0.496</i>	-0.211	<i>0.845</i>	0.228	0.414	1			
p49570 pN	0.234	0.122	<i>0.741</i>	0.322	0.129	0.465	0.056	<i>0.860</i>	0.255	0.294	<i>0.892</i>	1		
p62854 fSN	<i>0.963</i>	<i>0.997</i>	-0.081	-0.006	-0.312	-0.184	<i>0.963</i>	0.145	0.560	-0.147	-0.141	0.109	1	
p62855 tSN	<i>0.993</i>	<i>0.927</i>	0.212	0.097	-0.247	-0.046	<i>0.900</i>	0.378	0.687	0.012	0.191	0.363	<i>0.929</i>	1

a statistically significant positive correlation to discharge ($\rho = 0.528$; table 9). Total phosphorus has weak and statistically insignificant relations with total and dissolved nitrogen but has a moderate and statistically significant correlation to total organic nitrogen ($\rho = 0.746$) and semistrong correlations with particulate nitrogen ($\rho = 0.860$) and particulate carbon ($\rho = 0.845$; table 10). Orthophosphate has a weak but statistically significant correlation with the total and dissolved nitrogen constituents, nitrate, and total phosphorus (table 10). Thus, correlations among nutrients are suggestive but not definitive (the correlations seem logical given a knowledge of sources, transport, and fate, but insufficient to form quantitative relations), probably indicating various sources, variable geochemical effects, and the effect of seasonality on discharge and sources of nutrients.

Trace Metal Concentration Correlations

Composite samples were collected from the Blackstone River in 4-day increments and provide data that support biotic ligand model analysis. Similar to the potential to use automated measurements to estimate nutrient concentrations, if real-time monitoring of metal concentrations and loads is feasible, it would support faster recognition of conditions toxic to aquatic organism health and could reduce analytical costs.

Correlations Between Potential Explanatory Variables and Metal Concentrations

The values of correlations between selected explanatory variables and concentrations of metal constituents of interest indicate potential sources and transport mechanisms and the potential for developing quantitative, single or multiple linear regression equations to relate values of one or more automated measurements to concentrations of the constituents of interest (table 11). The only semistrong correlations between the potential explanatory variables and metals are between turbidity and total Cd, total Cr, total Cu, total Pb, total Zn, and total Al. There also are semistrong correlations between dissolved oxygen and dissolved copper and between temperature and dissolved zinc. The remaining correlations are weak to moderate, indicating that two or more explanatory variables are needed to describe the variability in estimates of trace metal concentration. Several dissolved trace metals have negative correlations to discharge and (or) antecedent precipitation, which may indicate that the dissolved species are from point sources that are diluted by runoff (O'Connor, 1976) or perhaps from groundwater discharge. Many of these correlations are weak, however, and many of the correlations to antecedent precipitation are not statistically significant at the 95-percent confidence limit. In comparison, with the exception of total nickel, correlations between discharge and total metals, and between antecedent precipitation totals and total metals, are positive and statistically significant at the 95-percent confidence interval. These values indicate that

rainfall-washoff processes may be a substantial contributor to total metal concentrations.

Correlations Among Metal Concentrations

Analysis of correlations among metal concentrations indicates possible causal relations between selected variables, possible predictive relations between variables, and the potential for using whole-water values to predict dissolved (filtered) concentrations. Identification of possible causal relations between selected variables may provide information that decision makers can use to identify potential sources of a metal and therefore the most effective mitigation measures. Correlations among the total metals are generally positive, statistically significant, and semistrong to strong, and these characteristics indicate common sources (table 12). Correlations between total and dissolved concentrations for Cu, Pb, and Ni are positive, statistically significant, and moderate to strong. Correlations between total and dissolved concentrations for Cd, Cr, and Zn are positive but are not statistically significant and are weak. Negative correlations between dissolved Cr and dissolved Zn, dissolved Ni and dissolved Zn, and dissolved Ni and total Al are statistically significant but weak.

There are a number of nondetect concentration values for each metal, and these nondetect values may affect correlations. For example, the correlation between total and dissolved copper (0.452) is more than twice that of total and dissolved chromium (0.18), and total and dissolved lead concentrations (0.711) are about four times total and dissolved chromium. Chromium correlations that are unusually low may result from ties caused by using one-half detection limits.

Development of Water-Quality Regression Equations

The objective of this analysis was to provide regression equations that can be used to estimate concentrations of water-quality constituents of interest from automated monitoring measurements and to estimate instantaneous loads by multiplying estimated concentration times discharge. A multiple stepwise regression was done in which independent variables were added one at a time to obtain the final equation. In stepwise regression, the automated selection program finds the explanatory variable with the highest correlation (R^2) with the response variable; it then tries each of the remaining variables until it finds the two explanatory variables with the highest R^2 ; then it tries all of them again until it finds the three variables with the highest R^2 , and so on. The goal of the stepwise procedure is to ensure that only statistically significant independent variables are added to an equation and to exclude the variables that account for a very small part of the variance in the dependent variable. Correlation matrices with Spearman's rank correlation coefficients (ρ) (tables 10 and 12) were used to assess relations between explanatory variables and the selected constituents collected manually from the

Table 11. Correlation coefficients between potential explanatory variables and metal concentrations.

[Correlation coefficients that are statistically significant at the 95th percentile are shown as italic numbers. Correlation coefficients that are greater than 0.8 are shown as bold italic numbers. Water-quality parameters: Temp, temperature, water, degrees Celsius (p00010); Q, discharge, cubic feet per second (p00060); SC, specific conductance, water, unfiltered, corrected, water, micrograms per liter (µg/L) (p32209); Trb, turbidity, water, unfiltered, broadband light source (400–680 nanometers), detectors at multiple angles including 90 ± 30 degrees, radiometric correction, nephelometric turbidity ratio unit (p63676); P, precipitation, total, in inches (p7977a); DO, dissolved oxygen, water, unfiltered, field, standard units (p00300); pH, water, unfiltered, field, standard units (p00400); CA, chlorophyll *a*, fluorometric method, 24P, antecedent precipitation, total, (24-hour), in inches (p7977b); 48P, antecedent precipitation, total, (48-hour), in inches (p7977c); 72P, antecedent precipitation, total, (72-hour), in inches (p7977d). Metal concentrations: p00925 fMg, magnesium, water, filtered, mg/L; p01025 fCd, cadmium, water, filtered, µg/L; p01027 tCd, cadmium, water, unfiltered, recoverable, µg/L; p01030 fCr, chromium, water, unfiltered, recoverable, µg/L; p01040 fCu, copper, water, filtered, µg/L; p01042 tCu, copper, water, unfiltered, recoverable, µg/L; p01049 fPb, lead, water, filtered, µg/L; p01051 tPb, lead, water, unfiltered, recoverable, µg/L; p01065 fNi, nickel, water, filtered, µg/L; p01067 tNi, nickel, water, unfiltered, recoverable, µg/L; p01090 fZn, zinc, water, filtered, µg/L; p01092 tZn, zinc, water, unfiltered, recoverable, µg/L; p01105 tAl, aluminum, water, unfiltered, recoverable, µg/L]

Water-quality parameter	Spearman's rho													
	Magnesium, water, filtered (mg/L); p00925 fMg	Cadmium, water, filtered (µg/L); p01025 fCd	Cadmium, water, unfiltered (µg/L); p01027 tCd	Chromium, water, filtered (µg/L); p01030 fCr	Chromium, water, unfiltered (µg/L); p01034 tCr	Copper, water, filtered (µg/L); p01040 fCu	Copper, water, unfiltered (µg/L); p01042 tCu	Lead, water, filtered (µg/L); p01049 fPb	Lead, water, unfiltered (µg/L); p01051 tPb	Nickel, water, filtered (µg/L); p01065 fNi	Nickel, water, unfiltered (µg/L); p01067 tNi	Zinc, water, filtered (µg/L); p01090 fZn	Zinc, water, unfiltered (µg/L); p01092 tZn	Aluminum, water, unfiltered, recoverable (µg/L); p01105 tAl
Discharge (Q)	-0.535	-0.224	0.503	-0.26	0.565	-0.3	0.49	0.38	0.567	-0.685	-0.11	0.219	0.696	0.871
Temperature (Temp)	0.305	-0.208	0.125	0.53	0.087	0.523	0.267	0.257	0.092	0.301	0.333	-0.807	-0.258	-0.292
Specific conductance (SC)	0.783	0.591	0.13	0.05	-0.029	0.523	0.106	-0.025	-0.042	0.663	0.632	0.134	-0.064	-0.127
Dissolved oxygen (DO)	-0.156	0.149	-0.489	-0.73	-0.475	-0.918	-0.613	-0.638	-0.383	-0.447	-0.691	0.468	-0.184	-0.121
pH	-0.168	0.259	-0.126	-0.189	-0.524	-0.105	-0.346	-0.573	-0.49	-0.147	-0.199	0.161	-0.301	-0.42
Chlorophyll <i>a</i> (CA)	0.406	0.302	0.345	0.073	0.251	0.462	0.378	0.086	0.313	0.245	0.184	-0.203	0.125	0.141
Turbidity (Trb)	0.194	0.253	0.837	0.099	0.886	0.316	0.871	0.523	0.870	-0.081	0.376	0.170	0.829	0.828
Precipitation (P)	-0.152	0.118	0.09	-0.145	0.064	-0.069	0.029	-0.034	0.037	-0.003	0.104	0.203	0.119	0.094
24-hour precipitation (24P)	0.005	-0.025	0.503	-0.365	0.581	-0.189	0.477	0.186	0.466	-0.211	0.235	0.142	0.531	0.495
48-hour precipitation (48P)	0.025	0.044	0.645	-0.177	0.7	-0.091	0.591	0.302	0.571	-0.191	0.284	0.011	0.651	0.604
72-hour precipitation (72P)	0.017	0.021	0.626	-0.16	0.689	-0.067	0.585	0.32	0.557	-0.189	0.273	0.014	0.638	0.594

Table 12. Correlation coefficients among metal concentrations.

[Correlation coefficients that are statistically significant at the 95th percentile are shown as italic numbers. Correlation coefficients that are greater than or equal to 0.8 are shown as bold italic numbers. Water-quality parameters: p00925 fMg, magnesium, water, filtered, milligrams per liter (mg/L); p01025 fCd, cadmium, water, filtered, micrograms per liter (µg/L); p01027 tCd, cadmium, water, unfiltered, µg/L; p01030 fCr, chromium, water, filtered, µg/L; p01034 tCr, chromium, water, unfiltered, recoverable, µg/L; p01040 fCu, copper, water, filtered, µg/L; p01042 tCu, copper, water, unfiltered, recoverable, µg/L; p01049 fPb, lead, water, filtered, µg/L; p01051 tPb, lead, water, unfiltered, recoverable, µg/L; p01065 fNi, nickel, water, filtered, µg/L; p01067 tNi, nickel, water, unfiltered, recoverable, µg/L; p01090 fZn, zinc, water, filtered, µg/L; p01092 tZn, zinc, water, unfiltered, recoverable, µg/L; p01105 tAl, aluminum, water, unfiltered, recoverable, µg/L]

Water-quality parameter	Spearman's rho												
	Magnesium, water, filtered (mg/L); p00925 fMg	Cadmium, water, filtered (µg/L); p01025 fCd	Cadmium, water, unfiltered (µg/L); p01027 tCd	Chromium, water, filtered (µg/L); p01030 fCr	Chromium, water, unfiltered, recoverable (µg/L); p01034 tCr	Copper, water, filtered (µg/L); p01040 fCu	Copper, water, unfiltered, recoverable (µg/L); p01042 tCu	Lead, water, unfiltered, recoverable (µg/L); p01051 tPb	Nickel, water, filtered (µg/L); p01065 fNi	Nickel, water, unfiltered, recoverable (µg/L); p01067 tNi	Zinc, water, filtered (µg/L); p01090 fZn	Zinc, water, unfiltered, recoverable (µg/L); p01092 tZn	Aluminum, water, unfiltered, recoverable (µg/L); p01105 tAl
p00925 fMg	1												
p01025 fCd	0.537	1											
p01027 tCd	0.153	0.367	1										
p01030 fCr	0.202	0.239	0.18	1									
p01034 tCr	0.059	-0.014	0.842	0.093	1								
p01040 fCu	0.503	0.562	0.446	0.664	0.182	1							
p01042 tCu	0.124	0.149	0.932	0.209	0.905	0.452	1						
p01049 fPb	-0.173	-0.01	0.569	0.435	0.631	0.48	0.686	1					
p01051 tPb	-0.013	-0.02	0.816	0.065	0.918	0.245	0.908	0.711	1				
p01065 fNi	0.635	0.445	-0.077	0.289	-0.11	0.538	-0.096	0.03	-0.153	1			
p01067 tNi	0.514	0.392	0.495	0.181	0.465	0.527	0.484	0.303	0.69	1			
p01090 fZn	-0.17	0.447	0.042	-0.344	-0.123	-0.097	-0.148	-0.121	-0.109	-0.172	1		
p01092 tZn	-0.129	0.159	0.855	-0.1	0.821	0.136	0.806	0.538	-0.309	0.261	0.304	1	
p01105 tAl	-0.218	0.078	0.746	-0.084	0.818	0.022	0.767	0.552	-0.404	0.115	0.227	0.906	1

upstream railroad bridge near the Millville station. This was done to guide variable selection and minimize use of highly correlated variables in the same regression model. Coefficients of the regression equations, regression statistics, and the resulting equations for estimating the constituent concentrations from automated monitoring measurements are shown in table 13. The regression equations and regression statistics were calculated by using Minitab software (version 15). For this study, only the strongest regressions based on the limited data available are presented: total nitrogen, total phosphorus, suspended sediment concentration, total copper, and total aluminum. With additional data, additional relationships could be developed. Plots of the equation values and residuals were made and examined to ensure that predicted values were reasonable and that residuals were unbiased and had constant variance. The following section contains a detailed example of the calculations needed to obtain estimated concentrations of total phosphorus.

Application of Water-Quality Regression Equations

Each regression equation produces a value of the concentration for a unique combination of the values of the explanatory variables, but there is uncertainty associated with each estimate (Driver and Tasker, 1990). Prediction-interval estimates commonly are used to define the degree of uncertainty for estimating the concentrations for any given set of explanatory variables. The prediction interval for equations developed in logarithmic space by transforming data to the common (base 10) logarithms can be calculated by

$$\frac{1}{T} \frac{C_i}{BCF} < C_i < \frac{C_i}{BCF} T, \tag{8}$$

where C_i is the prediction interval for true concentration. Because the regression equations were developed by using the common (base 10) logarithms of the input variables, the value of T is calculated as follows:

$$T = 10^{\left[t_{(\alpha/2, n-p)} \times (V_{pi})^{0.5} \right]}, \tag{9}$$

where $t_{(\alpha/2, n-p)}$ is the critical value of the Student's t distribution for the selected confidence interval for $n-p$ degrees of freedom with n data points in the regression analysis dataset and p parameters in the regression equation. In both cases, V_{pi} is the variance of prediction for concentration i and is calculated as follows:

$$V_{pi} = \sigma^2 \times (1 + x_i U x_i'), \tag{10}$$

where σ is the standard error of the estimate for the selected regression equation,
 U is the variance-covariance matrix for the regression equation, and
 x_i and x_i' are the row and column vector of the predictor variables for concentration i , respectively.

For example, the row vector (x_i) for the logarithmic total phosphorus equation (TP p00665) in table 13 would be the following:

$$x_i = [1, \log(p00010), \log(p00095), \log(p63676), \log(p7977c+1)], \tag{11}$$

which includes the constant 1 and the terms p00010 (temperature), p00095 (specific conductance), p63676 (turbidity) and p7977c (48-hour antecedent precipitation). The column vector is made up of the same four values transposed. The variable U in equation 10 is the variance-covariance matrix for the regression equation. For example, the arithmetic total phosphorus equation (TP p00665) in table 13 would be the following:

$$U = \begin{pmatrix} 31.6928 & 0.107122 & -11.8779 & 0.616279 & -2.78013 \\ 0.107122 & 0.482042 & -0.205842 & -0.056612 & 0.141424 \\ -11.8779 & -0.205842 & 4.5342 & -0.283495 & 1.0218 \\ 0.616279 & -0.056612 & -0.283495 & 0.448842 & -0.753287 \\ -2.7801 & 0.141424 & 1.0218 & -0.753287 & 2.64014 \end{pmatrix}. \tag{12}$$

The values needed to calculate the 90-percent confidence interval, the model error variance, and the variance-covariance matrix for selected regression equations are shown in table 14.

The procedure to estimate the total phosphorus concentration is explained by an example computation following the method of Driver and Tasker (1990). On December 30, 2013, at noon, values of explanatory variables were as follows: temperature, 3.3 degrees Celsius; specific conductance, 783 μ S/cm; turbidity, 52 FNU; and 48-hour antecedent precipitation, 1.01 in. The estimated total phosphorus concentration is calculated from the TP p00665 equation as follows:

$$TP\ p00665 = 0.003 \times 3.3^{0.18934} \times 783^{0.3897} \times 52^{0.5115} \times (1.01 + 1)^{-0.2329} \times 1.01 = 0.327, \tag{13}$$

given the following:

- $n-p$ is $18 - 4 = 14$ (degrees of freedom);
- α is 0.1 (90-percent confidence interval);
- $t_{(\alpha/2, n-p)}$ is 1.761 (from table 14, or a statistical text);
- x_i is $[1, \log(3.3), \log(783), \log(52), \log(1.01 + 1)]$, vector of basin characteristics (equation 11);
- U is equivalent to equation 7 (provided for the other regression equations in table 13);
- σ^2 is 0.00375, the variance of the regression model (from table 14); and
- BCF is 1.01 (from table 13)

Table 14. Values needed to determine 90-percent prediction intervals for selected regression equations for estimating selected water-quality constituent concentrations from continuous monitoring data at the Blackstone River at Millville, Massachusetts, station (01111230).

[The degrees of freedom is the number of samples minus the number of predictor variables. Water-quality parameters: p00010, temperature, water, degrees Celsius; p00060, discharge, cubic feet per second; p00095, specific conductance, water, unfiltered, microsiemens per centimeter at 25 degrees Celsius; p63676, turbidity, water, unfiltered, broadband light source (400–680 nanometers), detectors at multiple angles including 90 ± 30 degrees, ratiometric correction, nephelometric turbidity ratio unit; p7977c, antecedent precipitation, total, (48-hour), in inches. CI, confidence interval]

Regression equation	Count	Degrees of freedom	Critical Student's t for 90-percent CI	Model error variance	Variance-covariance matrix							
Total phosphorus (p00665)	18	14	1.761	0.061	Constant	log ₁₀ (p00010)	log ₁₀ (p00095)	log ₁₀ (p63676)	log ₁₀ (p7977c+1)	log ₁₀ (p0005)	log ₁₀ (p63676)	log ₁₀ (p7977c+1)
					31.7	0.107	-11.9	0.616	-2.78	0.616	-2.78	
					0.107	0.482	-0.206	-0.057	0.141	-0.057	0.141	
					-11.9	-0.206	4.53	-0.283	1.022	-0.283	1.022	
					0.616	-0.057	-0.283	0.449	-0.753	0.449	-0.753	
-2.78	0.141	1.02	-0.753	2.64	-0.753	2.64						
Total nitrogen (p62855)	16	14	1.761	0.077	Constant	log ₁₀ (p00060)	log ₁₀ (p00095)					
					55.1	-3.37	-17.2					
					-3.37	0.425	0.829					
-17.2	0.829	5.581										
Suspended sediment concentration (p80154)	19	17	1.740	0.204	Constant	log ₁₀ (p00060)	log ₁₀ (p63676)					
					2.319	-0.900	0.215					
					-0.900	0.375	-0.151					
					0.215	-0.151	0.262					
Total copper (p01042)	22	20	1.725	0.094	Constant	log ₁₀ (p63676)						
					0.148	-0.143						
-0.143	0.199											
Total aluminum (p01105)	22	20	1.725	0.085	Constant	log ₁₀ (p00060)	log ₁₀ (p63676)					
					2.26	-0.885	0.226					
					-0.885	0.372	-0.154					
					0.226	-0.154	0.255					

Determine the variance of the concentration estimate and prediction interval by calculating as follows:

$$V_{pi} = 0.0613 \times (1 + x_i U x_i') = 0.0613 \times (1 + 0.6719) = 0.1025 \text{ [eq. 10];}$$

$$T = 10[1.761(0.1025)^{0.5}] = 3.66 \text{ [eq. 9]; and}$$

$$\frac{1}{3.66} \times \frac{0.327}{1.01} < 0.327 < 1.044 \times \frac{0.327}{3.66} \text{ or } 0.088 < 0.327 < 1.18 \text{ [eq. 8]}$$

Thus, the estimated phosphorus concentration is 0.327 mg/L, with a 90-percent confidence interval from 0.088 to 1.18, as calculated from the TP p00665 equation (table 13). In comparison, the measured concentration in the water sample was 0.351 mg/L. Regression equations developed with the logarithms of data produce confidence intervals that are proportional to the predicted value (Driver and Tasker, 1990; Granato, 2012).

Figure 9 shows a comparison of concentrations from manual and automated samples and estimated concentrations calculated from the regression equation. The date range of

figure 9 reflects the 14-day sampling period for the automated system beginning on December 23, 2013, and ending on January 7, 2014.

Limitations of the Analysis

The major limitation of this regression analysis is that it is based on the limited number of samples. A longer term of data collection would narrow prediction intervals of concentration estimates. The 4-day composite sampling approach provided accurate information relative to the chronic exposure guidelines and biotic ligand model analysis, but it also resulted in missing data for large portions of WYs 2013 and 2014. The explanatory variables in the regression models are mainly automated monitoring data; these hydrologic and water-quality measurements are limited in range and subject to errors in measurement and interpretation. Streamflow at the Millville station was estimated by using a relation with the upstream continuous streamgage at the Rt. 122 station and thus inherently has more error than if streamflow were measured at the Millville station. In addition, stream velocities were often less than 1.5 ft/s and too slow for the use of isokinetic sampling

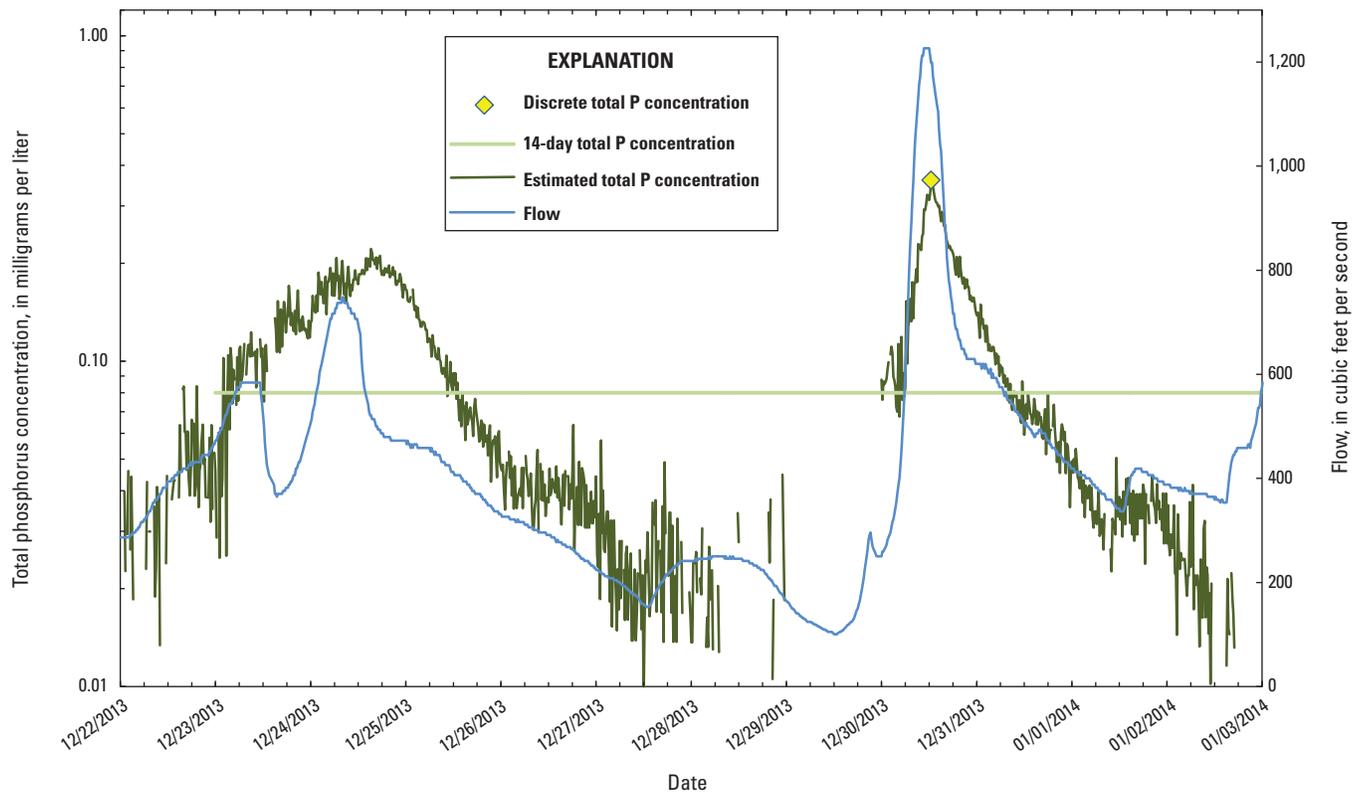


Figure 9. Estimated 15-minute total phosphorus (P) concentrations (dark green line) from the Blackstone River at Millville, Massachusetts, station (0111230), December 22, 2013, to January 1, 2014. The total phosphorus concentration from the 14-day composite sample collected by the automated system (light green line) and the discrete multiple vertical sample collected manually from the upstream railroad bridge (yellow diamond) are shown for comparison.

techniques. Extrapolation of regression equations beyond the range of explanatory variables used to formulate the regression may result in faulty estimates, and the confidence and prediction intervals are not valid beyond these ranges (Helsel and Hirsch, 2002; Rasmussen and others, 2009).

Potential effects of misspecification of explanatory variables were assessed by using standardized beta coefficients (Driver and Tasker, 1990; Granato, 2012). Sensitivity tests indicate the effects of measurement and interpretive errors on estimation of the response variables in regression models. Standardized beta coefficients for all the variables in the regression models are listed in table 15 to facilitate sensitivity testing. The standardized beta coefficient is the standard deviation of the response variable divided by the standard deviation of the explanatory variable. This coefficient (table 15)

reflects the change in the mean response per unit change in the explanatory variable (in units of standard deviations of both variables) when all other explanatory variables are held constant. Therefore, misspecification of a variable with a high standardized beta coefficient is likely to introduce more error than an equivalent error in a variable with a smaller beta coefficient. Some explanatory variables have more natural variance than others. Spacing of the observations on the explanatory variables, which may be somewhat arbitrary, also affects the standardized beta coefficients (Driver and Tasker, 1990). These equations could be used as a reconnaissance-level monitoring tool until new data are added and their respective correlations made more robust. Collecting new data could also allow development of new relationships for other constituents of concern, such as dissolved nutrient and metal species.

Table 15. Ranges of values, population statistics, and standardized beta coefficients for the variables used in each regression model.

[Water-quality parameters: p00010, temperature, water, degrees Celsius; p00060, discharge, cubic feet per second; p00095, specific conductance, water, unfiltered, microsiemens per centimeter at 25 degrees Celsius; p63676, turbidity, water, unfiltered, broadband light source (400–680 nanometers), detectors at multiple angles including 90 ± 30 degrees, ratiometric correction, nephelometric turbidity ratio unit; p7977c+1, antecedent precipitation, total, (48-hour), in inches]

Equation	Variable	Minimum	Maximum	Mean		Median	Standard deviation		Standardized beta coefficient
				Arithmetic	Geometric		Arithmetic	Logarithm	
Total phosphorus (p00665)	p00665	0.040	0.356	0.128	0.107	0.110	0.090	0.259	1.00
	p00010	2.24	25.3	11.9	8.93	9.85	8.2	0.359	1.39
	p00095	274	783	438	466	445	134	0.121	0.468
	p63676	1.00	52	9.91	5.38	6.33	12.5	0.502	1.94
	p7977c +1	1.00	4.61	1.71	1.51	1.19	1.00	0.213	0.824
Total nitrogen (p62855)	p62855	0.890	2.83	1.56	1.46	1.48	0.619	0.168	1.00
	p00060	90.6	2,262	807	533	666	640	0.455	2.71
	p00095	274	783	486	467	442	138	0.126	0.746
Suspended sediment concentration (p80154)	p80154	1.00	67.0	23.3	11.5	22.0	22.6	0.604	1.00
	p00060	90.6	2,262	747	494	583	628	0.439	0.727
	p63676	1.00	52.0	10.3	5.42	7.95	12.5	0.525	0.869
Total copper (p01042)	p01042	3.20	23.5	8.55	7.15	6.80	5.57	0.262	1.00
	p63676	1.00	52.0	9.49	5.24	5.15	11.8	0.490	1.87
Total aluminum (p01105)	p01105	35.8	1,020	256	150	164	252	0.486	1.00
	p00060	90.6	2,262	693	460	583	601	0.429	0.883
	p63676	1.00	52.0	9.92	5.48	6.33	11.8	0.499	1.03

Summary and Conclusions

The main-stem Blackstone River and several of its tributaries continue to be designated as impaired for recreational and aquatic uses. Nutrients (total and dissolved nitrogen and phosphorus), trace metals, and suspended sediment are some of the constituents of concern. Impaired water draining into Narragansett Bay from the Blackstone River contributes to decreased clarity, seasonal eutrophication, and degraded habitat seen in Narragansett Bay. However, downward trends in nutrient concentrations in both the Blackstone River and Narragansett Bay have been reported.

To continue to assess the water quality of the Blackstone River, which drains central Massachusetts before crossing the State line into Rhode Island, the U.S. Geological Survey (USGS), in cooperation with the Massachusetts Department of Environmental Protection, reactivated the automated monitoring station on the Blackstone River at Millville, Massachusetts, near the State line with Rhode Island (USGS station 01111230) in October 2012.

The Millville monitoring station was used to provide continuous water-quality monitoring, monthly and annual loading information for nutrients, and 4-day loadings of trace metals for water years 2013–14. These data were used to evaluate the potential to use surrogate measurements of physical parameters to estimate real-time (15-minute) constituent concentrations in the Blackstone River as it enters Rhode Island from Massachusetts.

The Millville station was equipped with an automated flow-proportional sampling system that collected fifty 14-day composite samples for total and dissolved nitrogen and phosphorus and fifty-two 4-day composite samples for dissolved trace metals and total aluminum. Temperature, specific conductance, turbidity, and chlorophyll *a* were also measured every 15 minutes. The point sampling location used by the automated system was determined to be representative over a wide range of flow conditions. Concentrations from composite samples collected by the automated system provide the basis to determine monthly and annual loads. Concentrations from discrete point samples from the point location were used to evaluate the potential to develop regression models to estimate constituent concentrations and allow for real-time load estimation.

The annual load of total nitrogen as collected by the automated system in water year (WY) 2013 was about 447,000 kilograms per year (kg/yr). Flows in WY 2014 were about 25 percent lower than in the previous year, and the annual load of total nitrogen was about 342,000 kg/yr. The annual loads of total and dissolved phosphorus in WY 2013 were about 35,900 and 12,000 kg/yr, respectively. In WY 2014, the annual load of total phosphorus was 20,700 kg/yr, and dissolved P was about 8,220 kg/yr. The lower flows seen in WY 2014 are a possible explanation for the 42-percent decrease in total phosphorus loading.

Median dissolved cadmium and chromium 4-day loads were 0.55 and 0.84 kilograms (kg), respectively, during

WYs 2013 and 2014. Dissolved copper and lead median loads were 8.02 and 1.42 kg, respectively. The dissolved nickel median load was 5.45 kg, and the dissolved zinc median load was 36 kg. Median total aluminum 4-days loads were about 200 kg.

Correlation coefficients were generated among flow, precipitation, antecedent precipitation, physical parameters, and chemical constituents. Spearman's rho rank correlations were calculated. A 95-percent confidence limit for each value of Spearman's rho was also calculated. These data allowed for the development of quantitative regression equations for selected constituents and determined the likelihood of multicollinearity between predictor variables.

Multiple linear regression analysis using ordinary least squares regression techniques was used to develop regression equations for the strongest correlations (total nitrogen, total phosphorus, total suspended solids, total copper, and total aluminum) from samples collected manually from the Millville point location during WYs 2013 and 2014. The independent variables with the greatest explanatory power were isolated in a stepwise manner to develop equations for the five selected constituents of concern. Each regression equation yields a unique value of constituent concentration that can therefore be estimated at the sampling point at the Millville station. Although the uncertainty associated with each estimate is greater than the uncertainty associated with an actual sample result from an analytical lab, the ability to estimate reconnaissance-level concentrations every 15 minutes is useful to monitor changes in concentrations and loads that may not be easily captured by traditional sampling techniques.

Concentrations from manually collected water-quality samples are sensitive to temporal changes, and in a heavily industrialized and urbanized basin such as the Blackstone River, concentrations can vary greatly from hour to hour. Concentrations from the automated flow-proportional system are less sensitive to environmental extremes (such as high-flow and low-flow conditions) than those from manually collected samples. The automated flow-proportional sampling approach captures daily variations and provides the high resolution needed to develop accurate monthly and annual loading information. Near real-time (15-minute) concentrations estimated by regression equations provide the greatest temporal resolution but also the greatest uncertainty. Continued monitoring and collecting of constituent concentration data would reduce uncertainties in these regression equations over time and improve their predictive power. Maintenance of instruments needed to provide the data for calculating real-time constituent concentrations and yielding real-time load estimates in a heavily impacted basin is labor intensive, but even in challenging environments, the continuous concentration data can contribute to critical knowledge of extreme events and enable event-based sampling and management strategies. This combination of traditional manual sampling and flow-proportional automated sampling provides accurate loading information. Although the data used to develop regression equations were limited to those collected in this study, by using the real-time

load-estimation capabilities from these data, regulators and stakeholders would have the information necessary to make time-sensitive and cost-effective decisions to improve impaired water resources and provide tools for monitoring the effectiveness of implemented management strategies.

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