

Prepared in cooperation with Cambridge [Massachusetts] Water Department

Loads and Yields of Deicing Compounds and Total Phosphorus in the Cambridge Drinking-Water Source Area, Massachusetts, Water Years 2009–15



Scientific Investigations Report 2017–5047

Cover. Photograph of upper Cambridge Reservoir and Trapelo Road gatehouse (looking south).

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By Kirk P. Smith

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Scientific Investigations Report 2017–5047

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Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
square mile (mi ²)	2.590	square kilometer (km ²)
gallon (gal)	3.785	liter (L)
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)
ton, short (2,000 lb)	0.9072	metric ton (t)

International System of Units to U.S. customary units

Multiply	By	To obtain
metric ton per square kilometer (t/km ²)	2.85497	short ton per square mile (ton/mi ²)

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

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

Datum

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

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C).

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$).

Abbreviations

CCC	criterion continuous concentration
CMC	criterion maximum concentration
CWD	Cambridge [Massachusetts] Water Department
EPA	U.S. Environmental Protection Agency
FNU	formazin nephelometric unit
MassDEP	Massachusetts Department of Environmental Protection
MassDOT	Massachusetts Department of Transportation
NTRU	nephelometric turbidity ratio unit
NTU	nephelometric turbidity unit
p	attained significance level
RPD	relative percent difference
SDWR	secondary drinking-water regulation
USGS	U.S. Geological Survey

Loads and Yields of Deicing Compounds and Total Phosphorus in the Cambridge Drinking-Water Source Area, Massachusetts, Water Years 2009–15

By Kirk P. Smith

Abstract

The source water area for the drinking-water supply of the city of Cambridge, Massachusetts, encompasses major transportation corridors, as well as large areas of light industrial, commercial, and residential land use. Because of the large amount of roadway in the drinking-water source area, the Cambridge water supply is affected by the usage of deicing compounds and by other constituents that are flushed from such impervious areas. The U.S. Geological Survey (USGS) has monitored surface-water quality in the Cambridge Reservoir and Stony Brook Reservoir Basins, which compose the drinking-water source area, since 1997 (water year 1998) through continuous monitoring and the collection of stream-flow samples.

In a study conducted by the USGS, in cooperation with the City of Cambridge Water Department, concentrations and loads of calcium (Ca), chloride (Cl), magnesium (Mg), sodium (Na), and sulfate (SO_4) were estimated from continuous records of specific conductance and streamflow for streams and tributaries at 10 continuous water-quality monitoring stations. These data were used to characterize current (2015) water-quality conditions, estimate loads and yields, and describe trends in Cl and Na in the tributaries and main-stem streams in the Cambridge Reservoir and Stony Brook Reservoir Basins. These data also were used to describe how stream-water quality is related to various basin characteristics and provide information to guide future management of the drinking-water source area.

Water samples from 2009–15 were analyzed for physical properties and concentrations of Ca, Cl, Mg, Na, potassium (K), SO_4 , and total phosphorus (TP). Values of physical properties and constituent concentrations varied widely, particularly in composite samples of stormflow from tributaries that have high percentages of constructed impervious areas. Median concentrations of Ca, Cl, Mg, Na, and K in samples collected from the tributaries in the Cambridge Reservoir Basin (27.2, 273, 4.7, 154.5, and 2.8 milligrams per liter (mg/L), respectively) were higher than those for the Stony Brook Reservoir Basin (22.2, 128, 4.3, 77.1, and 2.5, respectively). Differences between tributary samples for concentrations of Cl and Na were related to the percentage of developed land and constructed impervious area

in the drinking-water source area. Median concentrations of SO_4 in samples collected from the tributaries in the Cambridge Reservoir Basin (10.7 mg/L) were lower than those for the Stony Brook Reservoir Basin (18.0 mg/L).

Concentrations of dissolved Cl and Na in samples and those concentrations estimated from continuous records of specific conductance (particularly during base flow) often were greater than the U.S. Environmental Protection Agency (EPA) secondary drinking-water standard for Cl (250 mg/L), the chronic aquatic-life guideline for Cl (230 mg/L), and the Massachusetts Department of Environmental Protection drinking-water guideline for Na (20 mg/L). Concentrations of TP (range from 0.008 to 0.69 mg/L in all subbasins) in tributary samples did not differ substantially between the Cambridge Reservoir and Stony Brook Reservoir Basins. About one-half of the concentrations of TP in samples collected during water years 2013–15 exceeded the EPA proposed reference concentration of 0.024 mg/L.

For most tributaries, about 70 percent of the annual loads of Ca, Cl, Mg, Na, and SO_4 were associated with base flow. Concentrations of major ions were negatively correlated with streamflow, indicating that these constituents were diluted during stormflow and tend to increase during the summer when streamflow is low. In contrast, between 57 and 92 percent of the annual load for TP was transported during stormflows.

Mean annual yields of Ca, Cl, Mg, Na, and SO_4 in the drinking-water source area were 13, 75, 2.6, 40, and 6.9 metric tons per square kilometer, respectively, for water years 2009–15. The mean annual yield of TP in the drinking-water source area for water years 2013–15 was 0.012 metric tons per square kilometer. Yields for major ions and TP were highest in tributary subbasins adjacent to Interstate 95.

Temporal trends in mean annual concentrations for Cl and Na were not significant for water years 1998–2015 (period of record by the USGS) for the outlet of the Cambridge Reservoir and for the main stem of Stony Brook downstream from the reservoir. Median values of base-flow concentrations of TP at three stations were higher for samples collected during base-flow conditions during water years 2005–7 than for samples collected during water years 2013–15. However, the results were not significant for statistical tests between concentrations in samples collected during storms for the same periods, indicating that the quality of stormwater remains similar.

Introduction

The City of Cambridge, Massachusetts, supplies approximately 14 million gallons per day of drinking water to more than 100,000 customers (David Kaplan, Cambridge [Mass.] Water Department, written commun., 2016). The Cambridge Water Department (CWD) obtains raw water from a serial system of three primary storage reservoirs. These reservoirs receive inflow from a drainage area of 23.7 square miles (mi²; 61.4 square kilometers; henceforth, the drinking-water source area) that is outside Cambridge; in parts of the towns of Lexington, Lincoln, and Weston; and in part of the city of Waltham (fig. 1). The Cambridge drinking-water source area encompasses the Hobbs Brook Basin that includes the Cambridge Reservoir Basin, and the Stony Brook Reservoir Basin. Only about 9 percent of the land in the drinking-water source area (including the reservoir areas) is owned by the City of Cambridge. Major transportation corridors (U.S. Interstate 95, State Routes 2, 2A, 20, and 117), as well as large areas of light industrial, commercial, and residential land uses, are within the drinking-water source area.

Effective management of the Cambridge drinking-water source area requires an understanding of how stream-water quality is affected by natural and cultural watershed factors. Drought and severe weather are examples of natural factors, whereas the amount of impervious area and application of deicing compounds are cultural factors. Because of the diverse land use within the Cambridge drinking-water source area, there are various transport mechanisms that mobilize constituents to the drinking-water supply.

In 1997, the U.S. Geological Survey (USGS), in cooperation with the CWD, began operation of continuous water-quality monitoring stations (streamflow, water temperature, and specific conductance; hereafter referred to as stations) at various locations in the drinking-water source area (Socolow and others, 1999, 2000, 2001, 2002, 2003, 2004; Smith, 2005, 2007, 2008, 2011, 2013; U.S. Geological Survey, 2009). In 2004, the USGS, in cooperation with the CWD, established a program to characterize concentrations of total phosphorus (TP) in tributaries to the Cambridge and Stony Brook Reservoirs (fig. 1). These stations were identified by Waldron and Bent (2001), Smith (2013), and the CWD as draining areas that are potentially important sources of deicing compounds and TP. Monitoring data can be used to characterize current surface-water-quality conditions; to establish a baseline for future comparisons of surface-water quality; and if sufficient data are available, to describe trends in surface-water quality. These data also can be used to assess the effects of various watershed characteristics on surface-water quality and to provide information to guide future watershed management. Water samples collected from 2009 to 2015 were used in this current study, which was conducted by the USGS in cooperation with the City of Cambridge Water Department, to characterize water quality in the Cambridge drinking-water source area.

Purpose and Scope

The purpose of this report is to describe water-quality conditions in the drinking-water source area for the city of Cambridge during water years¹ 2009–15. Loads and yields of selected major ions associated with deicing compounds, and TP, were computed by combining continuous records of streamflow with constituent concentration data from water samples collected at 10 USGS stations within the drinking-water source area or by combining continuous records of streamflow with estimated concentration data. Mathematical relations between measurements of specific conductance and constituent concentrations that were used to estimate concentrations are presented. Temporal trends in annual mean concentrations of chloride (Cl) and sodium (Na) in samples collected at USGS stations 01104430 (Hobbs Brook at the outlet of Cambridge Reservoir) and 01104460 (main stem of Stony Brook) during water years 1998–2015 are discussed. Finally, concentrations of TP in samples collected during water years 2005–7 and 2013–15 are compared for USGS stations 01104415, 01104455, and 01104475.

Previous Investigations

Since 1997, hydrologic and water-quality data were obtained for various periods from tributaries in the Cambridge Reservoir and Stony Brook Reservoir Basins (table 1). Waldron and Bent (2001) assessed limnological conditions in the three serial storage reservoirs and described the water-quality conditions in the drinking-water source area during 1997–98. They also identified sources of various constituents, including calcium (Ca), Cl, Na, sulfate (SO₄), total nitrogen, and TP, in the drinking-water source area and outlined a source-water protection program for the CWD. Smith (2013) further examined loads and yields of constituents in deicing compounds, total nutrients, selected pesticides, and caffeine for water years 2005–7. The USGS, in cooperation with the CWD, continues to operate and maintain a monitoring network in the drinking-water source area (table 1). Streamflow, water-quality, and meteorological data from this network are available to the public through the USGS National Water Information System (NWIS; <https://waterdata.usgs.gov/nwis/ma/rt>) and in various reports (Socolow and others, 1999, 2000, 2001, 2002, 2003, 2004; Smith, 2005, 2007, 2008, 2011, 2013; U.S. Geological Survey, 2009).

Study Area

The drinking-water supply area includes three serial storage reservoirs—Cambridge Reservoir (also known as the Hobbs Brook Reservoir), Stony Brook Reservoir, and Fresh

¹A water year is the 12-month period beginning October 1 and ending September 30 of the following year. The water year is designated by the year in which it ends.



Figure 1. Location of U.S. Geological Survey continuous water-quality monitoring and periodic sampling stations in the Cambridge drinking-water supply area, Massachusetts.

4 Deicing Compounds and Total Phosphorus in the Cambridge Drinking-Water Source Area, Mass., Water Years 2009–15

Table 1. Description of, and period of record for, U.S. Geological Survey continuous water-quality monitoring stations in the Cambridge drinking-water source area, Massachusetts, 1998–2015.

[Location of stations is shown on figure 1. Latitude and longitude are in degrees, minutes, and seconds. USGS, U.S. Geological Survey; km², square kilometer; C, continuous monitoring station (streamflow, temperature, and specific conductance); P, periodic sampling station; S, stormwater sampling station; T, continuous measurements of turbidity; --, data not available]

USGS station name	USGS station number	Station type	Latitude	Longitude	Subbasin drainage area (km ²)	Period of continuous streamflow record (water years)
Cambridge Reservoir Basin						
Hobbs Brook at Mill Street, near Lincoln	01104405	C S	42 26 11	71 16 12	5.56	1998–99; 2012–15
Cambridge Reservoir, unnamed tributary 1, near Lexington	01104410	C	42 26 11	71 15 53	0.88	1998; 2012–15
Cambridge Reservoir, unnamed tributary 2, near Lexington	01104415	C S	42 26 09	71 15 38	1.06	1998–99; 2004–present
Cambridge Reservoir, unnamed tributary 3, near Lexington	01104420	C S	42 25 11	71 15 29	1.99	1998; 2012–present
Hobbs Brook below Cambridge Reservoir, near Kendall Green	01104430	C	42 23 53	71 16 26	17.8	1998–present
Stony Brook Reservoir Basin						
Stony Brook at Viles Street, near Weston	01104370	C	42 23 08	71 17 22	26.4	2010–present
Stony Brook, unnamed tributary 3, near Winter St., Lincoln	01104305	P	42 24 33	71 16 34	0.23	--
Stony Brook, unnamed tributary 2, near Weston Station	01104453	C	42 22 17	71 16 31	5.78	2006; 2010–15
Stony Brook, unnamed tributary 1, near Waltham	01104455	C S T	42 22 21	71 16 15	1.27	1998–99; 2001–present
Stony Brook at Route 20 at Waltham	01104460	C	42 21 08	71 16 16	57.0	1998–99; 2002–present
Stony Brook Reservoir, unnamed tributary 1, near Weston	01104475	C S	42 21 16	71 16 07	2.20	2004–present

Pond Reservoir (fig. 1). The Cambridge Reservoir Basin includes Hobbs Brook and three unnamed tributaries that flow directly into the reservoir. These three unnamed tributaries have drainage areas less than 2 square kilometers (km²; table 1) and have natural channels, but receive runoff from parts of State Routes 2 and 2A, Interstate 95, and other local roads. Water is released from the southern end of the Cambridge Reservoir into Hobbs Brook, which receives additional inflow from an unnamed tributary about 0.8 kilometer (km) downstream from the reservoir. The confluence of Hobbs Brook and Stony Brook is about 2.6 km downstream from the Cambridge Reservoir. Two unnamed tributaries flow into Stony Brook about 0.4 km north of the Stony Brook Reservoir. The small unnamed tributary west of Stony Brook drains from a shallow pond that receives runoff from portions of State Route 20 and other local roads. The small unnamed tributary east of Stony Brook runs parallel to Interstate 95 and is largely channeled through subsurface pipes. In water years 2011–12, a structural source control consisting of a series of wet ponds separated by elevated gravel wetlands was constructed about 300 feet upstream from USGS station 01104455 to reduce concentrations of suspended sediment and associated constituents, and provide a method to contain hazardous spills in the tributary (fig. 1). The wet ponds provide a permanent pool, and subsequent tributary flow, including base flow, is continuously diverted through the structure. In addition to Stony Brook, an

unnamed tributary flows directly into the Stony Brook Reservoir on the southwestern side of the reservoir. Additional water enters both reservoirs from other minor tributaries and storm drains. Water from Stony Brook Reservoir is piped through an aqueduct directly to Fresh Pond Reservoir, which is within the city of Cambridge about 16 km east of the drinking-water source area, where it is stored prior to treatment. Overflow and controlled releases from the Stony Brook Reservoir flow into the Charles River.

Land Use

Land-use data were obtained, in part, from the Massachusetts Office of Geographic Information (MassGIS) and the geographic information system (GIS) developed by the CWD with data from MassGIS, the USGS National Mapping Division, Harvard Design and Mapping, and Boston Edison, and from orthophotographs (Massachusetts Office of Geographic Information, 2002, 2005). Areas occupied by specific land-use classes were subtracted from the more generalized land-use categories so that the aggregate of all areal coverages for each subbasin was 100 percent. For example, roadways and parking lots that were within residential areas were not included in the residential category. Land-use data for each subbasin are listed in table 2.

Table 2. Land-use area percentages for subbasins upstream from U.S. Geological Survey continuous water-quality monitoring stations in the Cambridge Reservoir and Stony Brook Basins, Massachusetts.

[Locations of stations are shown in figure 1. Land-use data were obtained, in part, from the Office of Geographic Information (MassGIS, 2002) and the geographic information system (GIS) developed by the Cambridge Water Department with data from MassGIS, U.S. Geological Survey National Mapping Division, Harvard Design and Mapping, and Boston Edison.]

Land-use category	Percentage of subbasin area by U.S. Geological Survey station number										
	01104305	01104370	01104405	01104410	01104415	01104420	01104430 (cumulative)	01104453	01104455 (cumulative)	01104460 (cumulative)	01104475
Agriculture	0.0	7.5	5.8	7.7	6.1	0.4	2.8	4.0	0.0	5.1	7.0
Commercial or industrial	0.0	0.8	0.2	15.4	4.5	12.4	7.8	2.5	19.5	5.1	0.7
Forest	54.9	30.9	46.5	45.9	26.1	22.0	34.9	28.2	44.1	31.7	18.8
Railroad and quarry	0.0	1.2	0.0	0.0	0.0	0.0	0.0	1.4	2.0	1.0	0.0
Residential	43.5	37.6	21.3	2.5	42.4	37.5	21.9	46.9	13.3	31.4	65.5
Parking lot	0.0	0.5	0.6	5.9	4.4	3.7	3.1	0.9	8.5	2.3	0.6
Interstate-State highway	0.0	0.2	0.9	0.9	9.4	3.0	2.6	0.7	8.1	1.3	0.0
Town road	0.2	2.1	1.5	3.3	4.9	7.1	3.3	2.7	4.1	2.7	2.5
Water body	0.0	4.6	1.6	2.1	0.0	0.7	14.0	3.1	0.3	7.1	1.2
Wetland	1.0	14.6	21.6	16.3	2.2	13.2	10.0	9.7	0.2	11.9	3.6
Total area	100	100	100	100	100	100	100	100	100	100	100
Total roadway/parking	0.2	2.8	3.0	10.1	18.7	13.8	9.0	4.3	20.7	6.3	3.1

Land uses in the Cambridge Reservoir (area upstream from USGS station 01104430) and the Stony Brook Reservoir Basins (area upstream from USGS station 01104460) are similar. In general, these suburban basins are largely residential with relatively low percentages of commercial and light-industrial development. State and Interstate highways traverse each basin, and the percentages of forest and wetland areas are similar (31.7–34.9 and 10–11.9 percent, respectively). However, the amount of constructed impervious area (roadways and parking lots) differs between the two basins. Cambridge Reservoir Basin contains about twice as much impervious area and about 35 percent more open water than Stony Brook Reservoir Basin (fig. 1). About 28 percent of the total roadway area in the Cambridge Reservoir Basin is maintained by the Massachusetts Department of Transportation (MassDOT), compared to about 15 percent of total roadway area in the Stony Brook Basin. The upper Stony Brook Reservoir Basin (area upstream from USGS station 01104370), which accounts for nearly one-half of the drinking-water source area (table 1), is largely residential with low percentages of constructed impervious area.

Data Collection Methods and Results of Quality-Assurance Sampling

The continuous water-quality monitoring network for the Cambridge drinking-water source area includes five USGS stations in the Cambridge Reservoir Basin (USGS stations 01104405, 01104410, 01104415, 01104420, and 01104430; fig. 1) and five USGS stations in the lower Stony Brook Reservoir Basin (USGS stations 01104370, 01104453, 01104455, 01104460, and 01104475; fig. 1). Continuous measurements of water level (stream stage), water temperature, and specific

conductance were recorded at each station. During the present study, the USGS collected water samples at all stations to be analyzed for concentrations of TP and concentrations of selected dissolved major ions found in common deicing compounds (table 3). At five USGS stations in the Cambridge Reservoir and Stony Brook Reservoir Basins, water samples were collected manually during base-flow conditions and automatically during rain and mixed-precipitation stormflow conditions. Stations equipped with automatic samplers are on Hobbs Brook north of the Cambridge Reservoir (USGS station 01104405; fig. 1) and on four smaller tributaries (USGS stations 01104415, 01104420, 01104455, and 01104475; fig. 1). The samples were collected primarily during water years 2013–15.

Continuous Monitoring of Streamflow, Water Quality, and Precipitation

Streamflow data were necessary to estimate constituent loads and yields in each subbasin. At each station, stream stage was recorded at a minimum interval of 15 minutes and more frequently at many stations. Streamflow at each station was computed with a stage-discharge relation (or rating), which was developed and maintained on the basis of periodic manual measurements of streamflow (Rantz and others, 1982). Continuous water-temperature and specific conductance data were recorded concurrently with stage by water-quality monitors at each station. Continuous measurements of turbidity also were recorded at USGS station 01104455 in the Stony Brook Basin. Although most of the sensors provided high-quality measurements, particularly water temperature and specific conductance sensors, all sensors were subject to fouling from aquatic growth, sedimentation, and debris. In such cases, corrections were applied to the data to improve accuracy as described by

Table 3. Physical properties and constituents measured in water samples, reporting levels, and analytical methods used in the Cambridge Reservoir and Stony Brook Basins, Massachusetts study.

[$\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; NTRU, nephelometric turbidity ratio units; mg/L, milligrams per liter; EPA, U.S. Environmental Protection Agency; IC, ion chromatography; ICP–AES, inductively coupled plasma-atomic emission spectrometry]

Physical property or constituent	Reporting level	Analytical technique	Reference
Specific conductance, in $\mu\text{S}/\text{cm}$	5	Wheatstone Bridge	Radtke and others, 2005
Turbidity, NTRU	0.05	EPA 180.1	Anderson, 2005
Calcium, filtered, mg/L	0.022	ICP–AES	Fishman, 1993
Chloride, filtered, mg/L	0.02	IC	Fishman and Friedman, 1989
Magnesium, filtered, mg/L	0.011	ICP–AES	Fishman, 1993
Potassium, filtered, mg/L	0.03	ICP–AES	Clesceri and others, 1998
Sodium, filtered, mg/L	0.06	ICP–AES	Fishman, 1993
Sulfate, filtered, mg/L	0.02	IC	Fishman and Friedman, 1989
Phosphorus, low level, unfiltered, mg/L	0.004	Colorimetry	U.S. Environmental Protection Agency, 1993
Phosphorus, unfiltered, mg/L	0.01	Alkaline persulfate digestion	Patton and Kryskalla, 2003

Wagner and others (2006). Precipitation was measured near the Cambridge Reservoir at USGS station 01104430. Precipitation data were collected with a heated tipping-bucket precipitation gage that measures the volume of rain or melted snow in increments of 0.01 inch (in.). The gage was fitted with a wind screen that reduces bias generated by precipitation missing the instrument.

Collection of Water-Quality Samples

Water samples were collected from tributaries in all of the subbasins in the drinking-water source area during water years 2009–15 (table 4), and collection continued during water year 2016. At five stations (USGS stations 01104405, 01104415, 01104420, 01104455, and 01104475; fig. 1) water samples were collected manually during base-flow conditions, and composite samples were collected with automatic samplers during stormflow conditions during water years 2013–15. Four composite samples also were collected at USGS station 01104455 during water year 2012. Water samples were collected manually at USGS stations 01104370, 01104410, 01104430, 01104453, and 01104460 about five times each year during routine site visits in water years 2013–15 during varying flow conditions. Water samples were collected less frequently prior to water year 2013. Annual water samples were collected manually at USGS station 01104305 (periodic sampling station in fig. 1) during base-flow conditions. The subbasin upstream from this station contains a very low percentage of roads (0.2 percent) and represents background or

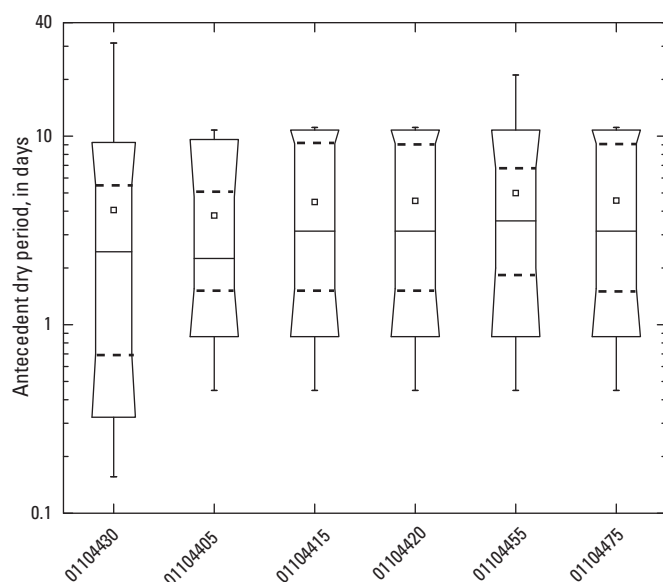
minimally affected water-quality conditions in contrast to the land-use characteristics of the other subbasins.

Samples of base flow were collected throughout the year to reflect seasonal variations. Base-flow conditions were preceded by a dry period of at least 2 days. Typically, the stream channels at most of the stations were only a few feet (ft) wide and less than 1 ft deep during base-flow conditions. Therefore, grab samples of base flow were collected manually by immersing a clean polyethylene bottle in the centroid of each stream. Stormflow sampling periods were selected to reflect seasonal variation and variation in the length of antecedent dry conditions existing throughout the study period (fig. 2).

Table 4. Number of samples of tributary water collected during each water year at U.S. Geological Survey continuous water-quality monitoring stations in the Cambridge Reservoir and Stony Brook Basins, Massachusetts, water years 2009–15.

[Locations of stations are shown in figure 1. USGS, U.S. Geological Survey; (X), number of composite samples]

USGS station number	Water year						
	2009	2010	2011	2012	2013	2014	2015
01104305	0	0	0	1	1	1	1
01104370	0	0	1	1	5	6	7
01104405	0	0	0	1	5 (6)	7 (6)	7 (4)
01104410	0	0	0	1	5	7	6
01104415	3	1	2	1	5 (6)	7 (6)	7 (5)
01104420	0	0	0	3	4 (6)	7 (5)	7 (5)
01104430	0	0	1	1	5	6	6
01104453	0	0	1	1	5	6	7
01104455	3	1	8	1 (4)	5 (6)	10 (5)	12 (9)
01104460	0	0	1	1	5	6	4
01104475	3	1	1	1	7 (6)	7 (5)	7 (5)



U.S. Geological Survey continuous water-quality monitoring station number

EXPLANATION

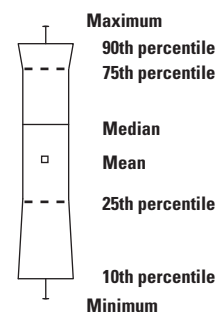


Figure 2. Distribution of antecedent dry periods for storms at U.S. Geological Survey (USGS) continuous water-quality monitoring station 01104430 in the Cambridge Reservoir Basin, Massachusetts, and the antecedent dry periods for storms during which runoff samples were collected at USGS stations 01104405, 01104415, 01104420, 01104455, and 01104475 in the Cambridge drinking-water source area, Massachusetts, during water years 2013–15. Dry antecedent periods are based on precipitation data from USGS station 01104430 for all periods. Locations of stations are shown in figure 1.

In this study, the median antecedent dry period for storms during which runoff samples were collected was about 3 days, which is slightly greater than the median antecedent dry period for all storm events during water years 2013–15 when most composite samples of stormflow were collected. Storms are defined, in terms of wet precipitation, as the sum of precipitation that occurred from 6 hours prior to an increase in tributary streamflow (beginning of runoff) to the end of the event when streamflow returned to base-flow conditions. Most of the precipitation totals for storms sampled at five USGS stations during water years 2013–15 were greater than the median of precipitation totals for storms greater than 0.10 in. recorded at Cambridge Reservoir (USGS station 01104430) for all storms during the same period (fig. 3). The distribution of precipitation totals for storm events recorded at station 01104430 during water years 2013–15 is similar to the distribution of precipitation totals for the period of record (water years 2001–15).

Stormflow samples were collected with automatic samplers controlled by a datalogger. Samples were generally collected using flow proportional methods; however, during some winter runoff events, the sampling algorithm was modified, and grab samples also were collected in response to incremental changes in the measurement of specific conductance. For composite samples, the first subsample was collected when flow exceeded a flow threshold that was marginally greater than prestorm base flow, and subsequent subsamples were collected at flow-proportional intervals (fig. 4). A flow-proportional interval is a unit of equal flow estimated on the basis of the prestorm base-flow condition and the amount of runoff anticipated from the storm. Collection of subsamples continued throughout the flow recession following the peak flow. The length of the recession period was calculated on the basis of the size of each drainage area at the location of the USGS station using the following equation:

$$T = (A)^{0.2} \quad (1)$$

where

- T is the time value, in days, for the length of the recession period; and
- A is the area of the drainage basin, in square miles, upstream from the sampling station; 0.2 is a constant (Bedient and Huber, 2002).

To collect composite samples, each automatic sampler was configured to hold one 14-liter (L) polyethylene churn and fitted with a precleaned ½-in. inner-diameter polyethylene intake and a short piece of silicon pump-head tube. To collect discrete samples, each automatic sampler was configured to hold twenty-four 1-L bottles.

Physical properties, including water temperature, specific conductance, and turbidity, were measured during the collection of base-flow water samples. These properties also were measured in the composite samples of stormflow. Water

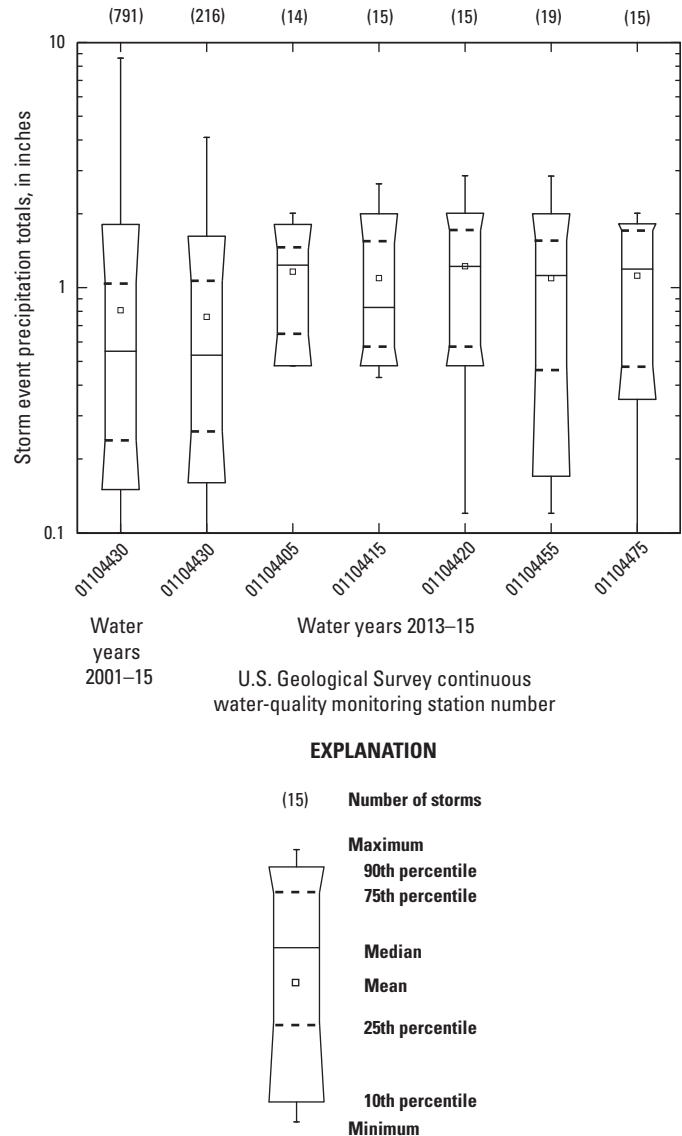


Figure 3. Distribution of all storm precipitation totals greater than 0.10 inch recorded at U.S. Geological Survey (USGS) continuous water-quality monitoring station 01104430 during water years 2001–15 and during water years 2013–15, and precipitation totals for storms during which samples were collected at USGS stations 01104405, 01104415, 01104420, 01104455, and 01104475 in the Cambridge drinking-water source area, Massachusetts, water years 2013–15. Precipitation data are from USGS station 01104430 for all periods. Locations of stations are shown in figure 1.

samples were processed in the USGS New England Water Science Center laboratory in Northborough, Mass., at the conclusion of each storm or scheduled sampling. For water samples collected during base-flow conditions when the flow and depth of water in the streams were small, the water generally was collected in the centroid of the stream in separate bottles designated for whole water and dissolved constituents;

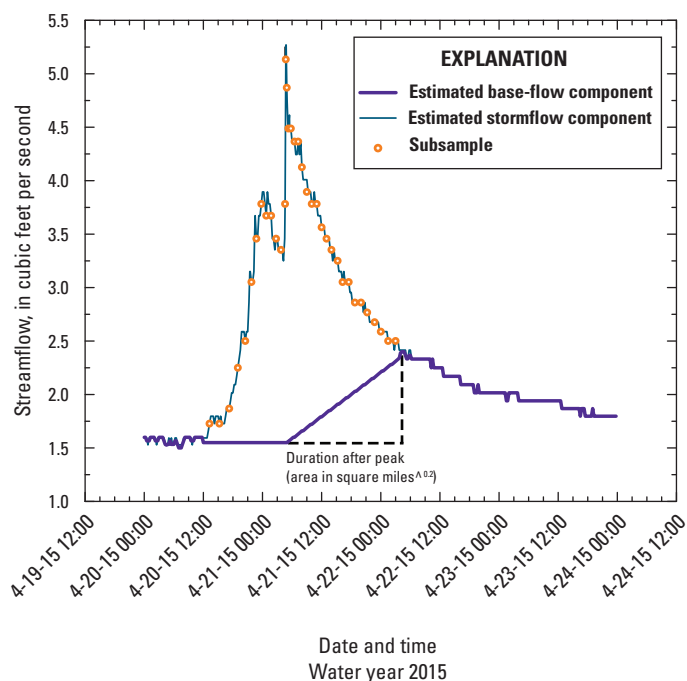


Figure 4. Example of automated flow-proportional collection of stormflow subsamples at U.S. Geological Survey continuous water-quality monitoring station 01104415, Cambridge drinking-water source area, Massachusetts, 2015. Location of station is shown in figure 1.

therefore, only limited splitting was necessary at the laboratory. For water samples collected during storms, subsamples were split directly from the 14-L polyethylene churn. Water to be analyzed for dissolved inorganic constituents was filtered through a 600-square centimeter (cm^2) capsule filter with a 0.45-micrometer pore size. After the processing, the samples were packed in ice and shipped overnight to the USGS National Water Quality Laboratory in Lakewood, Colorado, where they were analyzed for concentrations of dissolved major ions and TP (table 3; Fishman and Friedman, 1989; Fishman, 1993; U.S. Environmental Protection Agency, 1993; Clesceri and others, 1998; Patton and Kryskalla, 2003).

Quality-Assurance and Quality-Control Samples

Quality-assurance samples were collected to determine bias and precision associated with the sample data. These quality-control samples include 7 field blanks and 27 concurrent-replicate samples. Analytical results for these samples provided the basis for the interpretation of chemical data collected in the drinking-water source area. In general, the quality-assurance data indicate that the sample data were free from contamination and analytical results were generally precise, except for concentrations of TP collected during storms which had greater variability in replicate samples.

A field blank is used to test for positive bias that can result from contamination at any stage of sample collection, processing, or analysis. Field blanks were collected and processed with manual discrete sampling techniques and with stormflow sampling equipment. Constituent concentrations in all field blanks were all less than the reporting limits (table 3).

Concurrent-replicate samples are samples that are thought to be identical in composition to the environmental samples. Comparisons of replicate samples provide a measure of bias and variability for the method of sample collection, sample processing (splitting, filtering, and preservation), and laboratory analysis. Replicate grab samples were manually collected simultaneously during base-flow conditions. During storms, one sample was collected manually using isokinetic techniques at equal width increments (U.S. Geological Survey, 2006) across the stream channel while simultaneously collecting a replicate sample with an automatic sampler. The relative percent differences (RPDs) calculated for analytes detected in each pair of replicate samples indicate good agreement between replicates (fig. 5). The mean RPDs for dissolved Ca, Cl, Mg, Na, and SO_4 were 1 percent, and the mean RPD for dissolved potassium (K) was 3 percent. The mean RPD for TP was 10 percent for samples collected during base-flow conditions and 13 percent for samples collected during stormflow. The maximum RPD for all major ions was not greater than 5 percent; however, the maximum RPD for TP concentrations was as high as 69 percent for samples collected during base-flow conditions and 41 percent for samples collected during stormflow. Concentrations of TP were typically about 0.02 mg/L during base-flow conditions; therefore, even minor variations in concentrations may cause large RPDs. Concentrations of TP in quality-control samples were higher in samples collected during storms (0.02–0.56 mg/L) than in base-flow samples. The large RPD for some of these samples may be related to the collection of stormflow from a fixed point by the autosampler compared to the collection of sample water using isokinetic methods across the stream channel, which is more representative of mean stream concentrations.

Data Analysis Methods

Water-quality data were used to calculate constituent loads and yields, and to assess temporal trends in selected constituents. Concentration data, along with continuous records of streamflow and specific conductance, were used to estimate loads and yields of selected constituents during the study period. Trend analysis was performed for annual mean concentrations of Cl and Na for selected USGS stations during water years 1998–2015, the period of record for USGS data. Data were statistically analyzed to determine whether concentrations of TP in samples collected during water years 2005–7 (Smith, 2013) differed significantly from concentrations in samples collected during this study (2009–15).

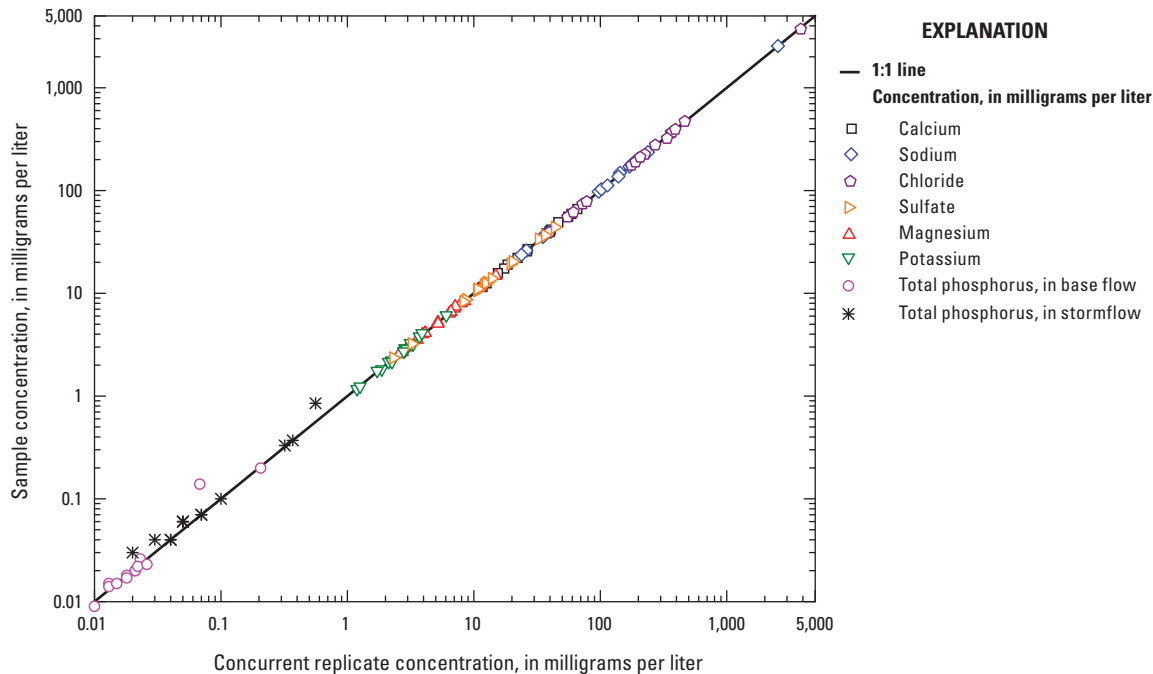


Figure 5. The relation of concentrations of selected constituents detected in concurrent replicate samples, Cambridge drinking-water source area, Massachusetts, water years 2013–15.

Estimated Loads and Yields

Loads are the quantity of a constituent transported by a stream during a specific time interval and are determined by multiplying the concentration or mass of a constituent by the streamflow. Yields are loads normalized by the drainage area of each subbasin. Loads and yields of Ca, Cl, Mg, Na, and SO_4 were estimated from continuous records of streamflow and specific conductance and from relations between dissolved major ions and specific conductance for all stations with these records. Loads and yields for TP were estimated from analyte concentrations in samples of base flow and stormflow and from streamflow data for water years 2013–15, the period when samples were routinely collected and analyzed for TP. Yields were estimated using the subbasin area for each of the stations (table 1).

Concentrations of Major Ions Estimated from Specific-Conductance Monitoring Data

Specific conductance is the measure of the capacity of water to conduct an electrical current and is related to the sum of the concentration and mobility of free ions in the solution (Miller and others, 1988). Specific conductance measurements, which typically are used to approximate concentrations of dissolved major ions (Hem, 1982, 1992; Miller and others, 1988; Church and others, 1996; Granato and Smith, 1999; Smith and Granato, 2010; Smith and Breault, 2011; Smith, 2013),

are used in this study to estimate concentrations of dissolved Ca, Cl, Mg, Na, and SO_4 in tributary water and to estimate concentrations and loads of these constituents in the drinking-water source area. Continuous records of specific conductance are available for all USGS streamgages in the drinking-water source area and are available for nearly every day of the study, representing a variety of hydrologic conditions (base flow, rain, mixed precipitation, and snowmelt runoff events).

Instantaneous concentrations of Ca, Cl, Mg, Na, and SO_4 were estimated from continuous measurements of specific conductance by using equations developed to relate specific conductance to concentrations of the respective ions (eq. 2) for each USGS station. In general, measurements of specific conductance in discrete and composite water-quality samples used in the regression analysis were similar in range to the daily flow-weighted specific conductance values at each USGS station during water years 2009–15 (fig. 6). The regression equations were developed using the MOVE.1 technique (Maintenance of Variance-Extension, type 1), also known as the line of organic correlation (Helsel and Hirsch, 2002), on the basis of concurrent measurements of log-transformed values of specific conductance and concentrations of Ca, Cl, Mg, Na, and SO_4 in samples collected from tributaries in the drinking-water source area (U.S. Geological Survey, 2016). The MOVE.1 technique was chosen for regression analysis because it minimizes errors in both the x and y directions, producing a unique equation that can be used to predict either variable from the other (Helsel and Hirsch, 2002). The bias correction factor or

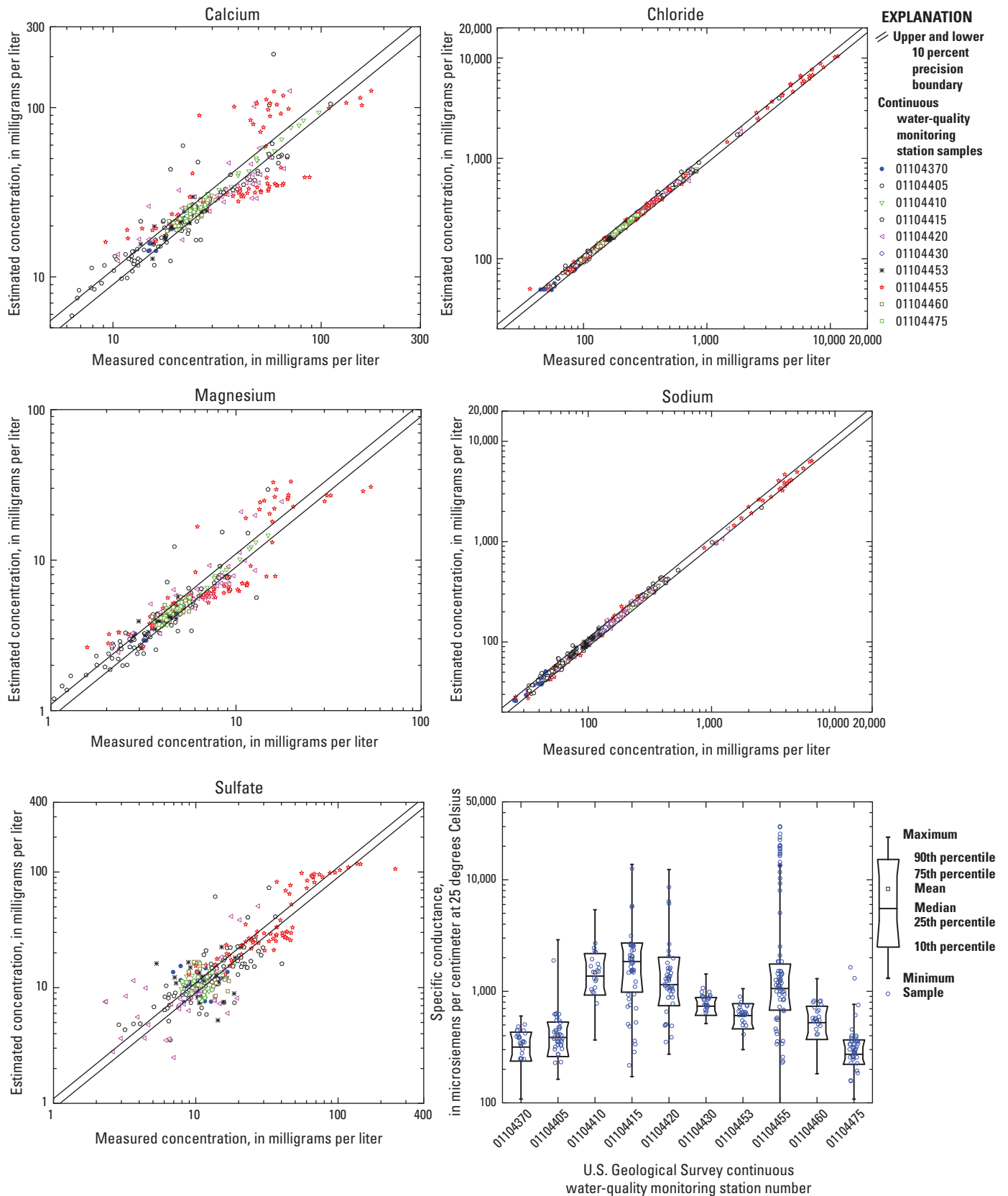


Figure 6. Relations between measured and estimated concentrations of calcium, chloride, magnesium, sodium, and sulfate and distribution of specific conductance values in water-quality samples compared to the distribution of daily flow-weighted values of specific conductance for the Cambridge drinking-water supply area, Massachusetts, water years 2009–15.

smearing estimator is calculated from the mean of the residual values (eq. 2; Duan, 1983). Similar regression equations also were developed to estimate concentrations of K, but the results were poor. Because K is not a major constituent in commonly used deicing compounds (Massachusetts Department of Transportation, 2012), estimated concentrations for K were not pursued. The equation used to relate specific conductance to concentrations of ions is

$$C = Spc^m \times b \times BCF \quad (2)$$

where

C	is the concentration of the ion of interest, in milligrams per liter (mg/L);
Spc	is the specific conductance, in microsiemens per centimeter at 25 degrees Celsius ($\mu S/cm$ at 25 °C);
m	is the slope from the MOVE.1 analysis (table 5);
b	is the intercept from the MOVE.1 analysis (table 5); and
BCF	is the bias correction factor.

The equations provide reasonable estimates for concentrations of dissolved Ca, Cl, Mg, Na, and SO_4 on the basis of specific conductance measurements (fig. 5). The standard error of regression results for Cl and Na, the ions with the highest concentrations in the sample matrix, were particularly precise (table 5). Results of regressions between measurements for specific conductance and concentrations of Ca, Mg, and SO_4 were less precise, and the concentrations of these ions typically were small in comparison to the concentration of Cl and Na in water samples. Typically the milliequivalent relation between Cl and Ca, Mg, and SO_4 in samples decreased with specific conductance, but the relation remained relatively constant between Cl and Na, the principal constituents of road salt and primary constituents affecting specific conductance. For example, the relation between Cl and Na in water samples remains relatively constant over a specific conductance range of nearly 40,000 $\mu S/cm$ at 25 °C (fig. 7). Therefore, changes in specific conductance measurement do not precisely reflect changes in the concentration of Ca, Mg, and SO_4 because the contribution of these ions to the overall sum of the concentration of free ions in each sample was small.

Loads of Major Ions

Annual loads of Ca, Cl, Mg, Na, and SO_4 were estimated for water years 2009–15 for all USGS stations. Annual loads for each ion were calculated by multiplying estimated daily flow-weighted concentrations of Ca, Cl, Mg, Na, and SO_4 , in milligrams per liter, by daily flow, in liters per day, and added. The percentages of load associated with base flows and stormflows also were estimated at USGS stations, except for stations 01104430 and 01104460 where flow was affected by regulation, and station 01104453 where flow often was

affected by beaver activity. Annual base-flow and stormflow volumes were estimated using the area-base hydrograph separation method described earlier (fig. 4). Similar to the fixed-base method for hydrograph separation, the assigned base-flow specific conductance (specific conductance value just prior to the event) is extended to the time of the peak flow as long as a mass balance between the base-flow specific conductance and stormflow specific conductance is achieved. Beginning with the point of peak flow, the specific conductance assigned to the base-flow component is adjusted over time for the remainder of the event on the basis of the slope derived from the starting specific conductance value and the specific conductance on the recession limb of the hydrograph at the end of the event (fig. 8). During this projection, the specific conductance initially assigned to the base-flow component converges to the specific conductance at the end point. Annual base-flow and stormflow loads of Ca, Cl, Mg, Na, and SO_4 for each station were estimated by multiplying flow-weighted concentrations associated with each flow component by the respective flow. These loads were summed for the period of available record for each station beginning in water year 2009, and the ratio of the storm load to the total load for the entire period was calculated for each station.

Loads of Total Phosphorus Estimated from Streamflow

Annual loads of TP were estimated for water years 2013–15 for all USGS stations where streamflow data were available. Loads for TP were estimated on the basis of streamflow and a measure of the central tendency of concentration. Mean concentrations, as opposed to medians, are particularly appropriate for characterizing loads because the inclusion of outlier values (either high or low), which typically represent large flows, is important when characterizing transport of constituent masses. Although concentrations of TP generally increased with flow, satisfactory relations between TP and flow could not be achieved because of the lack of sufficient sample data to characterize such relations and factors that affect flow at some stations (regulation and beaver activity).

For USGS stations 01104405, 01104415, 01104420, 01104455, and 01104475, where both base-flow and stormflow samples were collected, annual base-flow and stormflow loads were estimated using the area-base hydrograph separation method described earlier. Data used to estimate these loads were stratified into two classes (base flow and stormflow). The stratification was performed on the basis of the two sampling strategies and the separation of streamflow into strictly a base-flow period and a stormflow period; the stormflow period represents the sum of base flow, bank storage, and overland stormflow runoff. This method for identifying the period of the storm runoff is consistent with the fixed-base method used for hydrograph separation and is described by Chow and others (1988), although in this study, the method was used only to

Table 5. Regression equation coefficients used to estimate concentrations of calcium, chloride, magnesium, sodium, and sulfate from values of specific conductance for each U.S. Geological Survey continuous water-quality monitoring station in the Cambridge drinking-water source area, Massachusetts, 2009–15.

[Locations of stations are shown in figure 1. Parameter codes are as follows: specific conductance, 90095; calcium, 00915; chloride, 00940; magnesium, 00925; sodium, 00930; and sulfate, 00945. USGS, U.S. Geological Survey]

USGS station number	Sample count	Sample data range (month/day/year)	Calcium				Chloride				Sodium			
			Slope	Intercept	Standard error of regression (percent)	Bias correction factor	Slope	Intercept	Standard error of regression (percent)	Bias correction factor	Slope	Intercept	Standard error of regression (percent)	Bias correction factor
01104370	22	6/20/11 to 2/2/16	0.918	0.090	8.4	1.001	1.271	0.044	8.2	1.001	1.136	0.049	9.4	1.002
01104405	36	2/06/12 to 2/8/16	0.932	0.053	39.2	1.031	1.108	0.128	10.0	1.002	1.101	0.077	14.8	1.005
01104410	19	2/06/12 to 2/2/16	1.103	0.015	6.8	1.001	1.052	0.193	5.7	1.001	1.037	0.112	6.8	1.001
01104415	44	5/13/09 to 3/14/16	0.876	0.053	38.2	1.039	1.061	0.177	7.7	1.001	1.035	0.125	10.0	1.002
01104420	41	2/6/12 to 2/3/16	0.745	0.161	46.7	1.043	1.089	0.148	8.5	1.001	1.085	0.083	11.0	1.002
01104430	22	6/20/11 to 2/3/16	0.948	0.041	10.1	1.002	1.001	0.272	3.9	1.000	1.144	0.057	6.8	1.001
01104453	22	6/21/11 to 2/8/16	1.080	0.019	15.6	1.005	1.136	0.105	5.7	1.001	1.092	0.080	7.1	1.001
01104455	71	5/13/09 to 1/10/16	0.422	1.621	79.6	1.099	1.101	0.122	11.2	1.003	1.117	0.063	12.8	1.003
01104460	20	6/21/11 to 2/1/16	0.621	0.446	14.1	1.004	1.203	0.069	5.7	1.001	1.217	0.034	8.1	1.001
01104475	43	5/13/09 to 1/10/16	0.587	0.615	22.4	1.012	1.352	0.023	16.0	1.005	1.261	0.024	13.2	1.003

USGS station number	Sample count	Sample data range (month/day/year)	Magnesium				Sulfate						
			Slope	Intercept	Standard error of regression (percent)	Bias correction factor	Slope	Intercept	Standard error of regression (percent)	Bias correction factor			
01104370	22	6/20/11 to 2/2/16	0.935	0.017	10.1	1.002	1.005	0.030	50.4	1.046			
01104405	36	2/06/12 to 2/8/16	0.938	0.010	39.6	1.031	1.208	0.007	85.5	1.096			
01104410	19	2/06/12 to 2/2/16	1.104	0.002	9.7	1.002	0.691	0.080	31.6	1.018			
01104415	44	5/13/09 to 3/14/16	0.846	0.010	42.7	1.029	0.747	0.063	62.4	1.055			
01104420	41	2/6/12 to 2/3/16	0.743	0.032	35.1	1.025	0.971	0.009	117	1.150			
01104430	22	6/20/11 to 2/3/16	0.910	0.010	7.9	1.001	1.105	0.006	36.8	1.024			
01104453	22	6/21/11 to 2/8/16	1.016	0.006	15.4	1.005	1.871	0.000	111	1.123			
01104455	71	5/13/09 to 1/10/16	0.520	0.156	64.4	1.069	0.453	1.100	56.4	1.051			
01104460	20	6/21/11 to 2/1/16	0.620	0.088	17.6	1.006	0.989	0.022	68.1	1.070			
01104475	43	5/13/09 to 1/10/16	0.519	0.172	28.2	1.019	0.591	0.556	37.2	1.027			

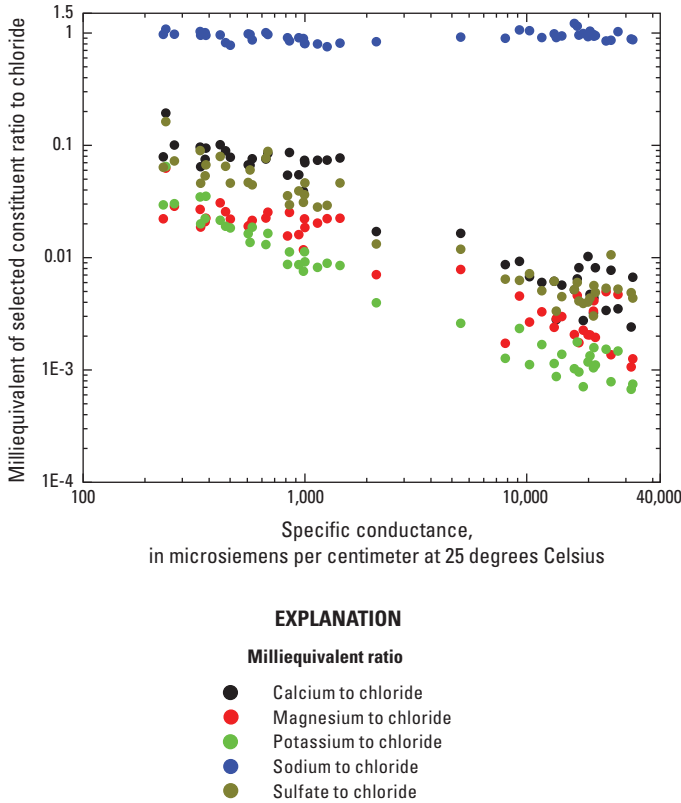


Figure 7. Milliequivalent ratio for calcium, magnesium, potassium, sodium, and sulfate to chloride in samples collected at U.S. Geological Survey continuous water-quality monitoring station 01104455 in the Cambridge drinking-water source area, Massachusetts, water years 2009–15. Location of station is shown in figure 1.

identify the beginning and end of each storm and the associated volume of flow between these two points.

The Mann-Whitney test, also referred to as the rank-sum test, was used to determine whether TP concentrations in base-flow and stormflow samples differed statistically (*p*-value less than 0.05). The Mann-Whitney test is a nonparametric method that makes no assumptions about the distribution of data and is used to determine whether groups of data come from the same population or alternatively whether the median values are different (Helsel and Hirsch, 2002). With a few exceptions, concentrations of TP in base-flow samples and stormflow composite samples were significantly different at the five stations where stormflow samples were collected (table 6), and an independent mean concentration was determined for each dataset.

Loads for USGS stations 01104430 and 01104460 (stations where flow is regulated by the CWD) were calculated by multiplying the mean concentration of TP at each station, in milligrams per liter, by daily flow, in liters per day, and added. Likewise, loads were calculated at USGS station 01104453 in the same manner because streamflow was often affected

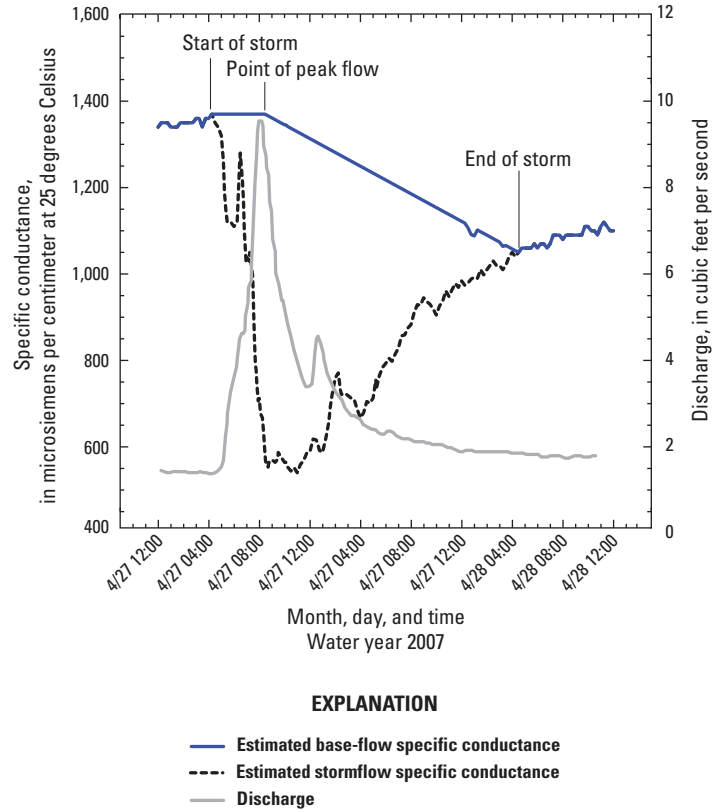


Figure 8. Example of separation of base-flow and stormflow specific conductance at U.S. Geological Survey continuous water-quality monitoring station 01104415, Cambridge drinking-water source area, Massachusetts. Location of station is shown in figure 1.

by beaver activity. The USGS station 01104453 is adjacent to an office park, and maintenance workers regularly (weekly in some cases) removed a beaver dam upstream from the station, causing increases in streamflow during what would normally be base-flow conditions. In some cases, storm effects were unnoticed when the dams were rebuilt by beavers and water was impounded behind the new dams.

Relation Between Chloride and Streamflow

The Pearson product moment correlation and Spearman rank-order correlation (Spearman’s rho) tests were used to evaluate the relation between Cl and streamflow. The Pearson Product Moment Correlation method measures the degree of linear relations between two variables. The correlation coefficient ranges from –1 to +1 (Helsel and Hirsch, 2002). A negative coefficient indicates that one variable tends to increase as the other decreases, and a positive coefficient indicates that the two variables tend to increase together. The absolute value of the correlation coefficient indicates the strength of the relation between variables. The Spearman rank-order correlation

Table 6. Attained significance levels (p -values) from Mann-Whitney tests for paired sample sets of total phosphorus in samples collected at selected U.S. Geological Survey continuous water-quality monitoring stations during base-flow and stormflow conditions in the Cambridge drinking-water source area, Massachusetts, water years 2013–15.

[Locations of stations are shown in figure 1. Shaded areas indicate values that are significant at a 95-percent confidence interval. A significant result (p value less than or equal to 0.05) indicates that the median value for concentrations of total phosphorus is higher in samples collected during stormflow than in samples collected during base-flow conditions. USGS, U.S. Geological Survey; <, less than]

USGS station number	Number of samples (base flow)	Base-flow sample median	Number of samples (storm-flow)	Storm-flow sample median	p value
01104405	17	0.03	14	0.06	0.002
01104415	20	0.01	15	0.10	<0.001
01104420	16	0.02	15	0.07	0.003
01104455	21	0.01	23	0.12	<0.001
01104475	22	0.02	15	0.07	<0.001

evaluates the monotonic relation between two continuous variables. In contrast to a simple linear relation, variables tend to change together but at dissimilar rates in a monotonic relation (Helsel and Hirsch, 2002).

Determination of Trends

Trends in concentrations or loads over time for water-quality constituents can indicate long-term changes in stream-water quality. Statistical tests to identify trends were performed for annual loads of Cl and Na estimated from records of flow and specific conductance at USGS stations 01104430 and 01104460 for water years 1998–2015. Trend tests were not performed on Cl and Na data, nor were tests performed on other major ion or TP concentrations at other stations within the drinking-water source area because the length of record either was not continuous or was insufficient in length to produce reliable test results. Trends for Cl and Na at the two stations were analyzed using a computer program for various Kendall tests (Helsel and others, 2006). Because concentration data were affected by regulation at each station, Cl and Na data were adjusted for the effects of flow, thus the Mann-Kendall test was performed on the residuals or flow adjusted concentrations. A trend was considered significant if the p -value was less than or equal to 0.05. In addition to the trend test, the Mann-Whitney test was used to determine whether TP concentrations in samples collected during water years 2005–7 and 2013–15 differed statistically.

Water-Quality Conditions

Summary statistics for the water-quality constituents in, and properties of, water samples collected in the Cambridge drinking-water source area are presented, and factors, such as streamflow and land use, that potentially affect water quality are discussed in this section. Measurements of turbidity and concentrations of Cl, Na, SO_4 , and TP are compared to water-quality criteria and used to describe water-quality conditions.

Specific Conductance

Specific conductance was measured in samples of base flow and composite samples of stormflow; specific conductance also was continuously recorded using in situ monitors at all USGS stations in the Cambridge drinking-water source area (table 1). Specific conductance measured in water samples collected throughout the study period at all USGS stations ranged from 115 to 30,100 $\mu\text{S}/\text{cm}$ at 25 °C (fig. 9). In contrast, recorded values of specific conductance, which included many more measurements obtained over a wide range of flow conditions, ranged from 19 to 32,600 $\mu\text{S}/\text{cm}$ at 25 °C for the same period (U.S. Geological Survey, 2016). Measurements of specific conductance in discrete and composite samples collected during runoff events, both storms and snowmelts, represent a broad range of conditions compared to the relatively narrow range of specific conductance values in samples collected during base-flow conditions.

In-situ measurements of specific conductance in water released from the Cambridge Reservoir (USGS station 01104430) ranged from about 450 to 1,450 $\mu\text{S}/\text{cm}$ at 25 °C (U.S. Geological Survey, 2016). In-situ measurements of specific conductance in Stony Brook above the confluence with Hobbs Brook (USGS station 01104370; fig. 1; U.S. Geological Survey, 2016) ranged from 206 to 971 $\mu\text{S}/\text{cm}$ at 25 °C, although these values were generally near 325 $\mu\text{S}/\text{cm}$ at 25 °C. Because the quantity and quality of water in some tributaries respond rapidly to stormflow runoff, discrete in-situ measurements of specific conductance for USGS stations 01104415, 01104420, and 01104455 on three tributaries often differed by several orders of magnitude from the annual mean values at each station (U.S. Geological Survey, 2016). The specific conductance during base flow at these tributaries was typically greater than 1,000 $\mu\text{S}/\text{cm}$ at 25 °C; however, specific conductance during runoff events ranged by as much as two orders of magnitude in either direction. USGS stations 01104415, 01104420, and 01104455 on the three tributaries, which parallel Interstate 95 and that have large percentages of constructed impervious areas, had the greatest range in measured specific conductance values (30–21,470 $\mu\text{S}/\text{cm}$ at 25 °C, 36–30,700 $\mu\text{S}/\text{cm}$ at 25 °C, and 19–32,600 $\mu\text{S}/\text{cm}$ at 25 °C, respectively). The range of in-situ measurements of specific conductance in tributaries that have drainage areas with low percentages of constructed impervious area had the smallest range in measured values. These stations include USGS station 01104405 in the Cambridge Reservoir Basin

A

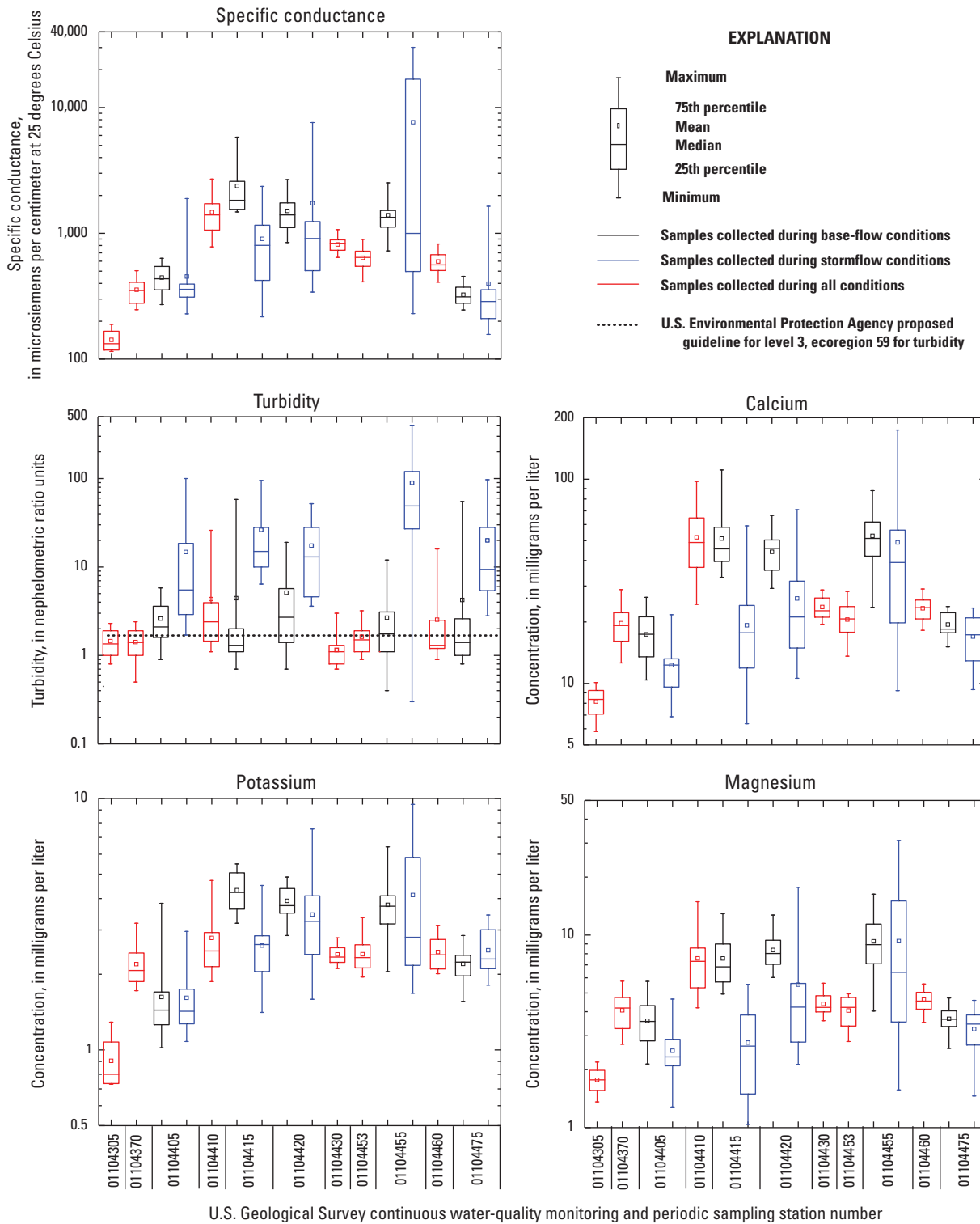


Figure 9. Distribution of selected water-quality property values and constituent concentrations in samples from 11 U.S. Geological Survey continuous water-quality and periodic sampling monitoring stations in the Cambridge drinking-water source area, Massachusetts, water years 2009–15. From U.S. Environmental Protection Agency (2000). Locations of stations are shown in figure 1.

B

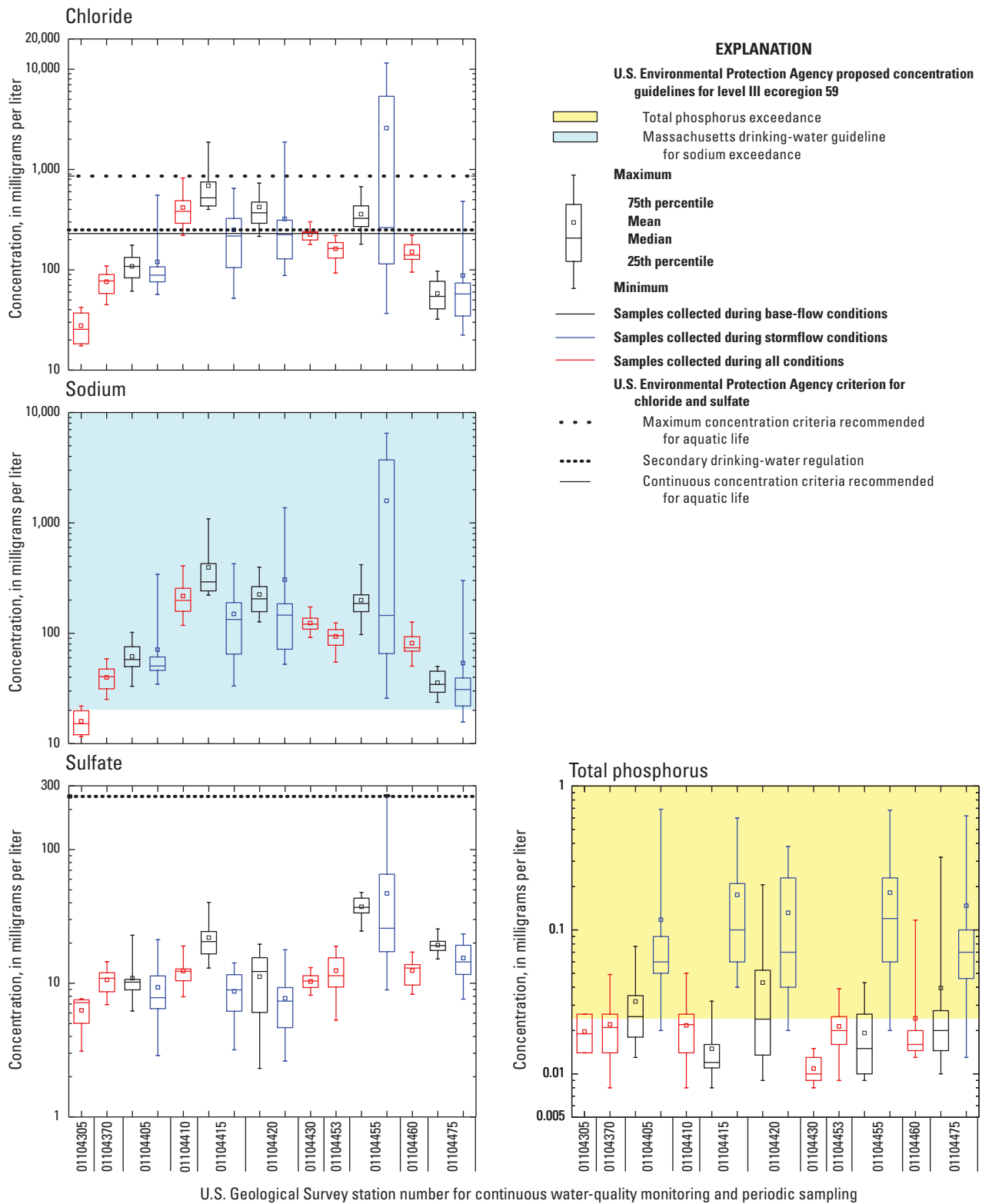


Figure 9. Distribution of selected water-quality property values and constituent concentrations in samples from 11 U.S. Geological Survey continuous water-quality and periodic sampling monitoring stations in the Cambridge drinking-water source area, Massachusetts, water years 2009–15. From U.S. Environmental Protection Agency (2000). Locations of stations are shown in figure 1.—Continued

(39–2,010 $\mu\text{S}/\text{cm}$ at 25°C; U.S. Geological Survey, 2016) and USGS stations 01104453 and 01104475 in the Stony Brook Reservoir Basin (284–1,090 and 39–2,010 $\mu\text{S}/\text{cm}$ at 25°C, respectively; U.S. Geological Survey, 2016). The drainage areas upstream from these three stations, as well as the drainage area upstream from USGS station 01104370 on Stony Brook, contain constructed impervious areas that range from 3 to 5 percent of the drainage areas (table 2).

Specific conductance of samples collected annually (water years 2012–15) at USGS station 01104305 on a tributary that drains a small subbasin that is minimally affected by development (table 2; U.S. Geological Survey, 2016) was less than 190 $\mu\text{S}/\text{cm}$ at 25 °C. Median values of specific conductance in water samples collected at all of the USGS stations ranged from 256 to 838 $\mu\text{S}/\text{cm}$ at 25 °C (fig. 9; U.S. Geological Survey, 2016). The range in specific conductance measurements for samples of stormflow, including samples collected during snowmelt events, was greater than the range in measurements for samples at the same stations collected during base-flow conditions. In general, specific conductance values for composite samples tended to be lower than values for samples collected during base-flow conditions, but discrete samples collected during snowmelts and mixed precipitation runoff events during the winter often had high specific conductance. Subbasin areas upstream from USGS stations 01104415, 01104420, and 01104455 that have large percentages of constructed impervious areas typically had the highest values of specific conductance during base flows and stormflows (fig. 9). Specific conductance for samples collected at USGS station 01104410 (U.S. Geological Survey, 2016), which is on a tributary that receives groundwater previously contaminated with road salt from a formerly uncovered Massachusetts Department of Transportation (MassDOT) storage facility within the subbasin (Waldron and Bent, 2001), also was higher than the specific conductance for samples collected at most other USGS stations (table 7).

Turbidity

Turbidity is a measure of the scattering and absorption of light caused by suspended materials (such as silt, clay, and fine organic particles) and dissolved materials that produce color. Turbidity was measured in base-flow and stormflow samples. Turbidity values for all samples collected within the drinking-water source area ranged from 0.3 to 400 nephelometric turbidity ratio units (NTRUs) with a median of 4.5 NTRUs. Typically, composite samples of stormflow collected at streamgages in the smaller subbasins (USGS stations 01104405, 01104415, 01104420, 01104455, and 01104475) had the highest turbidity (fig. 9; U.S. Geological Survey, 2016). Median turbidity values in samples collected during base-flow conditions at these stations, as well as at the other stations where routine samples were collected, were less than 3 NTRUs (table 7).

In-situ measurements of turbidity at USGS station 01104455, the only station equipped with a turbidity monitor,

ranged from 0.1 to 2,800 formazin nephelometric units (FNUs) for water years 2009–15. Turbidity measurements in FNUs differ from measurements in NTRUs in that the turbidity sensor light source for FNU measurements has a wavelength of 860 nanometers (nm) with a bandwidth of 60 nm, whereas the sensor light source for NTRUs has a wavelength range from 400 to 680 nm. The angle of the sensor detector in both measurements is 90 degrees from incident light (Anderson, 2005). Measurements of turbidity during base flow at USGS station 01104455 generally were near 1 FNU, reflecting the effects of a tributary that was often channeled through a subsurface pipe resulting in base flow (groundwater) with relatively low water temperature and limited exposure to sunlight. In water years 2011–12, a structural source control was constructed about 300 ft upstream from this station by MassDOT to reduce concentrations of suspended sediment and associated constituents, and provide a method to contain hazardous spills (fig. 10). During the construction period, various construction and dewatering activities often resulted in elevated turbidity, and once the structural source control was completed, the rerouting of base flow through the wet ponds resulted in elevated water temperatures and a chronic increase in base-flow turbidity (fig. 11). In-situ turbidity increased rapidly during storms and other runoff events, often increasing from a few FNUs during base-flow conditions to several hundred FNUs near peak runoff (U.S. Geological Survey, 2016), even after the implementation of the upstream structural source control. In some cases, elevated turbidity values in tributary water after the completion of the structural source control could have been caused by fine-grained sediment from bank erosion entering the wet ponds during storms.

Major Ions

The major ions Ca, Cl, Mg, Na, K, and SO_4 are commonly found in natural waters at concentrations greater than 1.0 mg/L (Hem, 1992). Elevated concentrations of Cl and Na are of special concern in the Cambridge drinking-water source area (Smith, 2007) because they are not readily removed by conventional treatment processes. High concentrations of Cl can affect the taste of finished drinking water, and high concentrations of Na contribute to hypertension in susceptible individuals (U.S. Environmental Protection Agency, 2009). Although Ca, Cl, Mg, Na, and SO_4 are common in precipitation (National Atmospheric Deposition Program, 2016), minerals and soils in the environment (Hem, 1992; Smith, 2005), septic effluent, light industrial wastes, and wastewater (Mullaney and others, 2009), most of these elements also are constituents of road salt and other deicing compounds used within the drinking-water source area. Deicing compounds readily dissolve, and associated ions are transported to nearby streams by surface runoff and groundwater discharge. Considering the numerous roadways in the drinking-water source area (fig. 1 and table 2), deicing compounds are a potentially important source of these ions.

Table 7. Summary statistics for selected water-quality properties and concentrations of major ions and total phosphorus in periodic samples or samples specifically collected during base flow and stormflow conditions collected at 10 U.S. Geological Survey continuous water-quality monitoring stations and one periodic sampling station in the Cambridge drinking-water source area, Massachusetts, water years 2009–15.

[Locations of stations are shown in figure 1. Periodic samples include discrete samples collected during base-flow and storm conditions; base-flow samples include discrete samples collected only under base-flow conditions; stormflow composite samples were collected throughout the hydrograph of storm events. Shaded areas indicate values that exceed U.S. Environmental Protection Agency secondary drinking-water standards (U.S. Environmental Protection Agency, 2007) or Massachusetts Department of Environmental Protection (MassDEP, 2016) water-quality standards for surface water on the basis of the intended use for waters designated as Class A. All constituents were not necessarily analyzed for each sample set. n, number of samples; NTRU, nephelometric turbidity ratio unit; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L , milligram per liter]

Property or constituent	U.S. Geological Survey periodic sampling station 01104305							U.S. Geological Survey continuous-monitoring station 01104370							
	Periodic samples (n=4)							Periodic samples (n=19)							
	Minimum	Mean	Median	Maximum	Standard deviation	Minimum	Mean	Median	Maximum	Standard deviation	Minimum	Mean	Median	Maximum	Standard deviation
Turbidity, NTRU	0.80	1.5	1.4	2.3	0.64	0.50	1.4	1.4	2.4	0.58					
Specific conductance, $\mu\text{S}/\text{cm}$	115	142	133	189	33.6	247	356	351	504	79.9					
Calcium, mg/L	5.82	8.16	8.36	10.1	1.76	12.6	19.7	19.2	28.8	4.13					
Chloride, mg/L	17.5	27.7	25.5	42.3	11.7	44.9	78.3	80.7	118	21.7					
Magnesium, mg/L	1.36	1.77	1.77	2.19	0.34	2.71	4.07	4.18	5.76	0.86					
Potassium, mg/L	0.73	0.91	0.80	1.29	0.26	1.72	2.19	2.07	3.19	0.41					
Sodium, mg/L	11.6	16	15.2	21.9	4.82	25.2	39.9	40.4	58.7	10.3					
Sulfate, mg/L	3.10	6.27	7.17	7.65	2.13	6.93	10.6	10.9	14.5	2.12					
Total phosphorus, mg/L	0.014	0.023	0.023	0.032	0.008	0.008	0.022	0.021	0.049	0.010					
Property or constituent	U.S. Geological Survey continuous-monitoring station 01104405							Stormflow composite samples (n=15)							
	Base-flow samples (n=17)							Stormflow composite samples (n=15)							
	Minimum	Mean	Median	Maximum	Standard deviation	Minimum	Mean	Median	Maximum	Standard deviation	Minimum	Mean	Median	Maximum	Standard deviation
Turbidity, NTRU	0.9	2.5	2.1	5.8	1.4	1.7	15	6	100	25					
Specific conductance, $\mu\text{S}/\text{cm}$	271	436	426	633	112	229	357	355	623	93					
Calcium, mg/L	10.4	17.4	17.4	26.4	4.85	6.87	11.7	12.3	18.8	3.18					
Chloride, mg/L	61.3	108	108	176	34.1	56.8	90.9	88.0	165	26.6					
Magnesium, mg/L	2.14	3.59	3.56	5.75	0.98	1.28	2.37	2.31	3.77	0.66					
Potassium, mg/L	1.02	1.62	1.44	3.83	0.66	1.08	1.55	1.42	2.96	0.52					
Sodium, mg/L	33.1	61.6	57.8	102	19.8	34.6	53.0	48.5	95.0	14.7					
Sulfate, mg/L	6.20	10.9	10.2	22.9	3.72	2.88	9.05	7.57	21.2	5.03					
Total phosphorus, mg/L	0.013	0.032	0.025	0.077	0.019	0.020	0.120	0.060	0.690	0.170					

Table 7. Summary statistics for selected water-quality properties and concentrations of major ions and total phosphorus in periodic samples or samples specifically collected during base flow and stormflow conditions collected at 10 U.S. Geological Survey continuous water-quality monitoring stations and one periodic sampling station in the Cambridge drinking-water source area, Massachusetts, water years 2009–15.—Continued

[Locations of stations are shown in figure 1. Periodic samples include discrete samples collected during base-flow and storm conditions; base-flow samples include discrete samples collected only under base-flow conditions; stormflow composite samples were collected throughout the hydrograph of storm events. Shaded areas indicate values that exceed U.S. Environmental Protection Agency secondary drinking-water standards (U.S. Environmental Protection Agency, 2007) or Massachusetts Department of Environmental Protection (MassDEP, 2016) water-quality standards for surface water on the basis of the intended use for waters designated as Class A. All constituents were not necessarily analyzed for each sample set. n, number of samples; NTRU, nephelometric turbidity ratio unit; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L , milligram per liter]

Analyte	U.S. Geological Survey continuous-monitoring station 01104410						U.S. Geological Survey continuous-monitoring station 01104430					
	Periodic samples (n=17)						Periodic samples (n=18)					
	Minimum	Mean	Median	Maximum	Standard deviation		Minimum	Mean	Median	Maximum	Standard deviation	
Turbidity, NTRU	1.1	4.3	2.4	26	6.14		0.7	1.2	1.1	3.0	0.54	
Specific conductance, $\mu\text{S}/\text{cm}$	780	1,480	1,400	2,700	514		664	825	840	1,070	106	
Calcium, mg/L	24.4	48.6	46.9	97.5	19.3		19.5	23.8	23.1	28.7	2.83	
Chloride, mg/L	221	418	383	822	157		182	227	236	301	29.5	
Magnesium, mg/L	4.19	7.57	7.31	14.9	2.96		3.59	4.42	4.26	5.62	0.52	
Potassium, mg/L	1.87	2.79	2.48	4.72	0.89		2.11	2.41	2.37	2.79	0.2	
Sodium, mg/L	118	218	199	408	80.8		98.3	125	124	173	19.4	
Sulfate, mg/L	7.93	12.4	12.3	19	2.91		8.14	10.3	10.4	13.1	1.54	
Total phosphorus, mg/L	0.008	0.022	0.022	0.05	0.011		0.008	0.011	0.01	0.015	0.002	

Analyte	U.S. Geological Survey continuous-monitoring station 01104415						Stormflow composite samples (n=16)					
	Base-flow samples (n=20)						Stormflow composite samples (n=16)					
	Minimum	Mean	Median	Maximum	Standard deviation		Minimum	Mean	Median	Maximum	Standard deviation	
Turbidity, NTRU	0.7	1.4	1.2	2.3	0.47		6.4	26.1	14.5	95	26.5	
Specific conductance, $\mu\text{S}/\text{cm}$	1,480	1,970	1,830	2,630	433		217	903	803	2,360	633	
Calcium, mg/L	33.1	49.6	46.8	68.8	11.8		6.35	16.8	15.7	34	8.16	
Chloride, mg/L	399	573	525	860	153		52.1	251	217	649	187	
Magnesium, mg/L	4.94	7.29	6.67	12.9	1.99		1.04	2.76	2.65	5.55	1.42	
Potassium, mg/L	3.19	4.31	4.32	5.49	0.79		1.41	2.6	2.63	4.51	0.75	
Sodium, mg/L	222	322	301	535	86.5		33.3	150	134	426	111	
Sulfate, mg/L	13	22.2	20.7	40.3	6.34		3.18	8.71	8.92	14.2	3.47	
Total phosphorus, mg/L	0.008	0.014	0.012	0.032	0.006		0.040	0.180	0.100	0.600	0.180	

Table 7. Summary statistics for selected water-quality properties and concentrations of major ions and total phosphorus in periodic samples or samples specifically collected during base flow and stormflow conditions collected at 10 U.S. Geological Survey continuous water-quality monitoring stations and one periodic sampling station in the Cambridge drinking-water source area, Massachusetts, water years 2009–15.—Continued

[Locations of stations are shown in figure 1. Periodic samples include discrete samples collected during base-flow and storm conditions; base-flow samples include discrete samples collected only under base-flow conditions; stormflow composite samples were collected throughout the hydrograph of storm events. Shaded areas indicate values that exceed U.S. Environmental Protection Agency secondary drinking-water standards (U.S. Environmental Protection Agency, 2007) or Massachusetts Department of Environmental Protection (MassDEP, 2016) water-quality standards for surface water on the basis of the intended use for waters designated as Class A. All constituents were not necessarily analyzed for each sample set. n, number of samples; NTRU, nephelometric turbidity ratio unit; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L , milligram per liter]

Analyte	U.S. Geological Survey continuous-monitoring station 01104420					
	Base-flow samples (n=17)			Stormflow composite samples (n=15)		
	Minimum	Mean	Median	Maximum	Standard deviation	
Turbidity, NTRU	0.7	4.9	2.1	19	5.8	15.1
Specific conductance, $\mu\text{S}/\text{cm}$	643	1,460	1,380	2,670	527	319
Calcium, mg/L	20.9	42.7	45.1	66.5	11.3	7.25
Chloride, mg/L	179	416	370	731	169	99.2
Magnesium, mg/L	3.82	8.1	7.94	12.7	2.12	1.21
Potassium, mg/L	2.23	3.82	3.71	4.87	0.72	0.8
Sodium, mg/L	91.7	217	199	397	85.4	52.1
Sulfate, mg/L	2.31	11.2	11.9	19.6	5.35	3.02
Total phosphorus, mg/L	0.009	0.041	0.023	0.21	0.05	0.12
U.S. Geological Survey continuous-monitoring station 01104453						
Property or constituent	Periodic samples (n=19)					
	Minimum	Mean	Median	Maximum	Standard deviation	
Turbidity, NTRU	0.9	1.6	1.5	3.2	0.57	3.6
Specific conductance, $\mu\text{S}/\text{cm}$	411	639	643	896	117	135
Calcium, mg/L	13.6	20.5	20.7	28.2	3.87	3.13
Chloride, mg/L	93	162	163	219	32.2	41.4
Magnesium, mg/L	2.8	4.06	4.21	4.95	0.7	0.63
Potassium, mg/L	1.95	2.4	2.33	3.36	0.36	0.35
Sodium, mg/L	54.8	93.6	95.1	124	17.8	22.7
Sulfate, mg/L	5.3	12.5	11.4	18.9	3.8	2.78
Total phosphorus, mg/L	0.009	0.021	0.020	0.039	0.007	0.026
U.S. Geological Survey continuous-monitoring station 01104460						
Property or constituent	Periodic samples (n=17)					
	Minimum	Mean	Median	Maximum	Standard deviation	
Turbidity, NTRU	0.9	1.6	1.5	3.2	0.57	3.6
Specific conductance, $\mu\text{S}/\text{cm}$	411	639	643	896	117	135
Calcium, mg/L	13.6	20.5	20.7	28.2	3.87	3.13
Chloride, mg/L	93	162	163	219	32.2	41.4
Magnesium, mg/L	2.8	4.06	4.21	4.95	0.7	0.63
Potassium, mg/L	1.95	2.4	2.33	3.36	0.36	0.35
Sodium, mg/L	54.8	93.6	95.1	124	17.8	22.7
Sulfate, mg/L	5.3	12.5	11.4	18.9	3.8	2.78
Total phosphorus, mg/L	0.009	0.021	0.020	0.039	0.007	0.026

Table 7. Summary statistics for selected water-quality properties and concentrations of major ions and total phosphorus in periodic samples or samples specifically collected during base flow and stormflow conditions collected at 10 U.S. Geological Survey continuous water-quality monitoring stations and one periodic sampling station in the Cambridge drinking-water source area, Massachusetts, water years 2009–15.—Continued

[Locations of stations are shown in figure 1. Periodic samples include discrete samples collected during base-flow and storm conditions; base-flow samples include discrete samples collected only under base-flow conditions; stormflow composite samples were collected throughout the hydrograph of storm events. Shaded areas indicate values that exceed U.S. Environmental Protection Agency secondary drinking-water standards (U.S. Environmental Protection Agency, 2007) or Massachusetts Department of Environmental Protection (MassDEP, 2016) water-quality standards for surface water on the basis of the intended use for waters designated as Class A. All constituents were not necessarily analyzed for each sample set. n, number of samples; NTRU, nephelometric turbidity ratio unit; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L , milligram per liter]

Property or constituent	U.S. Geological Survey continuous-monitoring station 01104455									
	Base-flow samples (n=22)				Stormflow composite samples (n=22)					
	Minimum	Mean	Median	Maximum	Standard deviation	Minimum	Mean	Median	Maximum	Standard deviation
Turbidity, NTRU	0.30	2.3	1.2	12	2.6	12	65	46	300	67
Specific conductance, $\mu\text{S}/\text{cm}$	725	1,340	1,290	2,520	407	230	690	573	2,100	442
Calcium, mg/L	23.6	50.2	48.7	87.9	16.3	9.22	25.3	22	55.9	13
Chloride, mg/L	180	344	324	674	119	37	173	137	625	134
Magnesium, mg/L	4.03	8.80	8.14	16.30	3.10	1.57	4.51	3.79	10.2	2.32
Potassium, mg/L	2.05	3.58	3.66	6.42	1.05	1.68	2.41	2.5	3.29	0.47
Sodium, mg/L	97.2	191	180	418	68.6	25.8	98.0	83.5	339	70
Sulfate, mg/L	21.2	35.5	36.8	47.9	7.88	8.93	19.8	17.9	35.4	7.21
Total phosphorus, mg/L	0.009	0.018	0.012	0.043	0.010	0.020	0.180	0.120	0.680	0.170

Analyte	U.S. Geological Survey continuous-monitoring station 01104475									
	Base-flow samples (n=21)				Stormflow composite samples (n=15)					
	Minimum	Mean	Median	Maximum	Standard deviation	Minimum	Mean	Median	Maximum	Standard deviation
Turbidity, NTRU	0.58	1.8	1.4	4.6	1.1	2.8	20	9.4	97	25.4
Specific conductance, $\mu\text{S}/\text{cm}$	246	322	312	455	56.8	157	357	256	1,640	376
Calcium, mg/L	15.1	19.2	18.4	23.8	2.65	9.33	16.1	16.8	23.2	4.32
Chloride, mg/L	2.94	50.2	51.8	97.0	26.5	22.4	78.4	41.6	481	118
Magnesium, mg/L	2.1	3.48	3.51	4.71	0.7	1.46	3.08	3.44	3.92	0.76
Potassium, mg/L	1.56	6.24	2.24	33.5	10.2	1.81	2.52	2.3	3.44	0.55
Sodium, mg/L	23.7	37.6	34.8	57.9	9.83	15.7	47.2	25.8	300	73.3
Sulfate, mg/L	15.2	19	18.7	25.5	2.36	7.62	14.6	14.2	23.4	4.53
Total phosphorus, mg/L	0.010	0.019	0.019	0.038	0.007	0.005	0.150	0.070	0.620	0.200

A*B**C*

Figure 10. *A*, Construction of a structural source control—wet ponds separated by elevated gravel wetlands—in November 2011, *B*, bank erosion around the nearly completed structural source control in June 2012, and *C*, completed project, November 2012, upstream from U.S. Geological Survey continuous water-quality monitoring station 01104455 in the Cambridge drinking-water source area, Massachusetts. Photographs courtesy of David Kaplan, Cambridge Water Department, Massachusetts. Location of station is shown in figure 1.

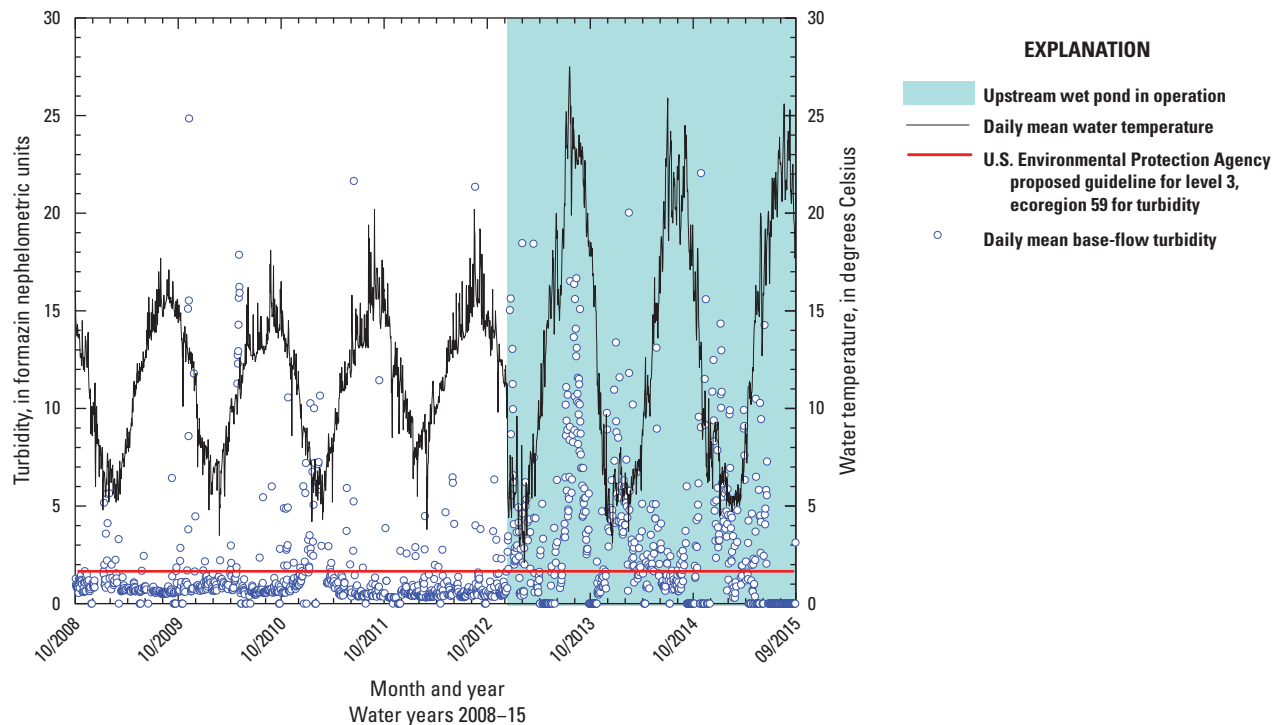


Figure 11. Daily mean turbidity in base flow and daily mean water temperature measured at U.S. Geological Survey continuous water-quality monitoring station 01104455 in the Cambridge drinking-water source area, Massachusetts, water years 2008–15, prior to and after the upstream installation of a structural source control. Location of station is shown in figure 1.

Concentrations of Ca, Cl, Mg, Na, K, and SO_4 in samples varied widely among the tributaries in the drinking-water source area (fig. 9). Concentrations of major ions in samples collected annually (water years 2012–15) at USGS station 01104305, the least developed subbasin (table 2), were the lowest in the drinking-water source area (table 7). Concentrations of major ions were greatest at USGS stations 01104410, 01104415, 01104420, and 01104455 (fig. 9). Similar to measurements of specific conductance, the distribution of concentrations of major ions in composite samples collected during stormflow was greater than the distribution of concentrations for samples collected during base-flow conditions (fig. 9). The median concentrations of Ca, Cl, Mg, Na, and K for samples collected in tributaries to the Cambridge Reservoir Basin were 27.2, 273, 4.7, 154.5, and 2.8 mg/L, respectively, whereas median concentrations for samples from the tributaries in the Stony Brook Reservoir Basin, excluding samples from USGS stations 01104430 and 01104460 that drain from the Cambridge Reservoir Basin, were lower at 22.2, 128, 4.3, 77.1, and 2.5 mg/L, respectively. The median concentration of SO_4 for samples collected from tributaries to the Cambridge Reservoir Basin (10.7 mg/L) was lower than the median concentration for samples collected in the Stony Brook Reservoir Basin (18.0 mg/L). Concentrations of SO_4 in samples collected at

USGS station 01104455 were substantially higher than those in samples from all other stations.

Major ion concentrations in samples from a subbasin in upper Stony Brook Reservoir Basin (USGS station 01104370), as well as other subbasins with less constructed impervious area (USGS stations 01104405 and 01104475), were lower than those from subbasins that are more developed (table 7). Median concentrations of Cl and Na in samples collected at USGS station 01104370 in upper Stony Brook Reservoir Basin were 80.7 and 40.4, respectively. Median concentrations of Cl and Na in samples collected at USGS station 01104460, below the confluence with Hobbs Brook (fig. 1), were 140 and 73.9 mg/L, respectively, indicating that high concentrations of Cl and Na in waters from the Cambridge Reservoir (USGS station 01104430; median concentrations of Cl and Na of 236 and 124 mg/L, respectively) were diluted by streamflow from the upper Stony Brook Reservoir Basin (USGS station 01104370) that drains a larger and overall less urbanized area of the drinking-water source area.

Chloride was the most abundant major ion, followed by Na, in samples from all tributaries in the drinking-water source area. These ions dominated the major-ion matrix in samples from each tributary. Median milliequivalent mass ratios of Cl:Na ranged from 0.77 to 0.93 (fig. 12), approaching the ratio of pure sodium chloride (1:1). Expressing concentrations in

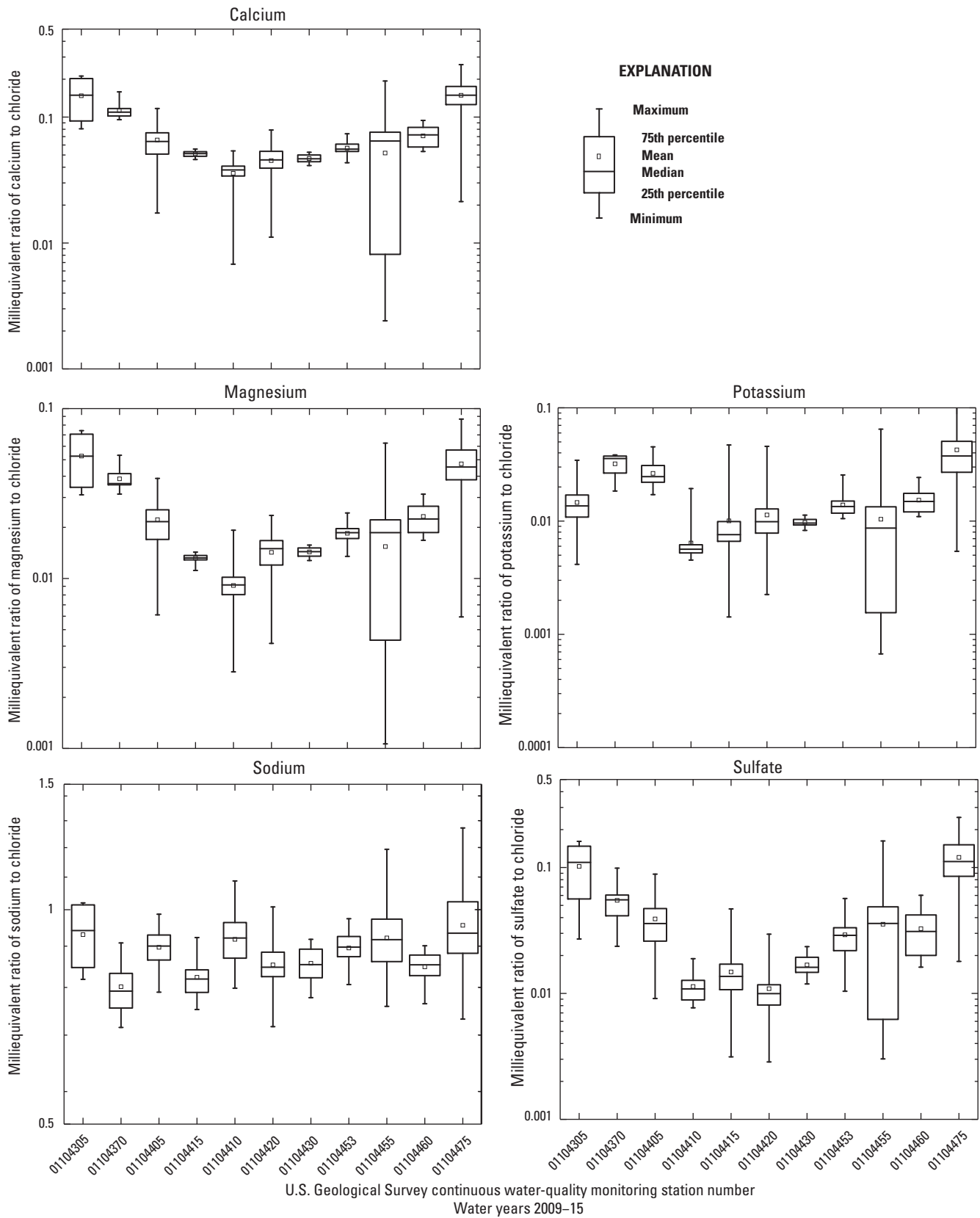


Figure 12. Distribution of milliequivalent ratios for calcium, magnesium, potassium, sodium, and sulfate to chloride in samples from 11 U.S. Geological Survey continuous water-quality and periodic sampling monitoring stations in the drinking-water source area for Cambridge, Massachusetts, water years 2009–15. Locations of stations are shown in figure 1.

terms of milliequivalent mass normalizes the charge of each ion. Median milliequivalent mass ratios for Ca, Mg, K, and SO_4 to Cl ranged from 0.04 to 0.15, 0.01 to 0.05, 0.01 to 0.04, and 0.01 to 0.11, respectively. The highest median milliequivalent mass ratios for Ca, Mg, K, and SO_4 to Cl were for samples collected at USGS stations 01104305 and 01104475 in subbasins with low percentages of development and impervious area (table 2). The highest median milliequivalent mass ratio for K to Cl also was found in samples collected at USGS station 01104475. Tributaries with high percentages of constructed impervious area, likely affected by runoff or groundwater discharges containing deicing compounds, generally had low milliequivalent mass ratios of Ca, Mg, and SO_4 to Cl because deicing compounds typically contain only trace amounts of these ions (Smith and Granato, 2010), and the resulting water matrix is then dominated by Na.

Mean annual flow-weighted concentrations of Ca, Cl, Mg, Na, and SO_4 estimated from records of specific conductance and flow at USGS station 01104430, at the outlet of the Cambridge Reservoir, for water years 2009–15 were 22, 204, 4.0, 110, and 9.2 mg/L, respectively (table 8). Mean annual flow-weighted concentrations of Ca, Cl, and Na for the main stem of Stony Brook upstream from the Stony Brook Reservoir (USGS station 01104460), estimated in the same manner and for the same period, were lower at 21, 122, and 65 mg/L, respectively. However, mean annual flow-weighted concentrations of Mg and SO_4 were higher at 4.1 and 11 mg/L. Concentrations of estimated major ions in the upper Stony Brook Basin at USGS station 01104370 were among the lowest in the drinking-water supply area and were responsible in part for dilution of downstream concentrations at USGS station 01104460. Mean annual flow-weighted concentrations for Ca, Cl, Mg, Na, and SO_4 at USGS station 01104475 on the only other tributary that flows directly into the Stony Brook Reservoir (fig. 1) were 16, 45, 3.1, 28, and 15 mg/L, respectively.

Total Phosphorus

Phosphorus is a nutrient that is essential to the health and diversity of aquatic organisms. Phosphorus can be mobilized through biological and chemical processes to or from the soil, reservoir sediments, water column, atmosphere, and organisms. Algae and aquatic plants consume various species of each nutrient until limited by availability. In the reservoirs in the drinking-water source area, phosphorus was determined to be the limiting nutrient (Waldron and Bent, 2001). Thus, high concentrations of phosphorus in the reservoirs can result in overgrowth of plant life, algal blooms, reduction in oxygen levels, and decline or shift in the biological community. Common sources of phosphorus include weathering of natural rocks and soils, fertilizers, and leaking or failing septic tanks. In general, phosphorus is somewhat insoluble and tends to be associated with sediment and plant matter (Smith and Granato, 2010; Smith, 2005; Breault and others, 2005). As a result, erosion of local soils and even application of sand to

roads and parking lots during winter maintenance activities (Smith and Granato, 2010) can increase TP concentrations in receiving waters.

The concentration of TP in water samples for all subbasins ranged from 0.008 to 0.69 mg/L (table 7). The median concentration of TP in all samples collected in the Cambridge Reservoir Basin was about 0.03 mg/L, whereas the median concentration for the tributaries in the less developed Stony Brook Reservoir Basin (table 2), excluding samples collected from tributaries draining to the Cambridge Reservoir, was 0.02 mg/L. Concentrations of TP in samples of base flow collected at the five USGS stations equipped to collect stormflow samples (stations 01104405, 01104415, 01104420, 01104455, and 01104475) ranged from 0.009 to 0.21 mg/L, although concentrations of TP tended to be less than 0.07 mg/L during base flow at most stations (fig. 9). Prior to water year 2013, concentrations of TP generally were about 0.01 mg/L during base flow at USGS station 01104455; however, concentrations of TP noticeably increased after water year 2012, when the upstream structural source control was installed (fig. 13). Thereafter, concentrations of TP followed a cyclical mode, where TP concentrations were lower in the winter than in the summer. The higher measured TP concentrations, as well as higher turbidity (fig. 11), during the summer may be the result of algae and colloidal phosphorus complexes from the upstream structural source control. Concentrations of TP in composite samples of stormflow ranged from 0.01 to 0.69 mg/L at the five USGS stations where the samples were automatically collected during storms (fig. 9). Results for Mann-Whitney tests indicate that concentrations of TP in base-flow and stormflow samples were significantly different (table 6). Concentrations for TP were typically low (<0.02 mg/L) in samples collected at the outlet of the Cambridge Reservoir (01104430). The Cambridge Reservoir was previously found to be a sink for TP because of settling characteristics resulting from the long retention time of the reservoir (Waldron and Bent, 2001).

Factors Affecting Water-Quality Properties and Constituent Concentrations

The quality of water in the tributaries of the Cambridge drinking-water source area is affected by streamflow and the amount of upstream development, particularly the amount of constructed impervious area. Streamflow is a mixture of various volumes of base flow (derived from groundwater discharge) and surface-water runoff (stormflow and snowmelt). Each of these aspects potentially affects the quality of water in the tributaries. Surface water that infiltrates into the ground may later discharge into tributaries far from the point of infiltration. Through this process, the water is exposed to various soils and parent materials that can affect the original major-ion matrix. Some elements in groundwater, such as Cl, are nonreactive or conservative. However, other cations (Ca, Na, and Mg for example) are affected through cation exchange on

Table 8. Annual mean streamflow and annual mean concentrations of calcium, chloride, sodium, sulfate, and magnesium estimated for subbasins that contribute water to Cambridge and Stony Brook Reservoirs, Massachusetts, 2009–15.

[Locations of stations are shown in figure 1. USGS, U.S. Geological Survey; ft³/s, cubic foot per second; mg/L, milligram per liter; E, estimated from incomplete data]

USGS station number	Water year	Annual mean streamflow (ft ³ /s)	Annual mean concentration				
			Calcium (mg/L)	Chloride (mg/L)	Sodium (mg/L)	Magnesium (mg/L)	Sulfate (mg/L)
01104370	2010	E26	E12	E43	E23	E2.6	E6.9
	2011	17	15	53	28	3.1	8.1
	2012	17	14	49	26	2.9	8.0
	2013	17	15	53	28	3.1	8.1
	2014	14	19	72	37	3.8	11
	2015	15	20	79	40	4.2	11
Mean annual average	2012–15	16	17	63	33	3.5	10
Mean annual average	2009–15	17	16	58	30	3.3	8.8
01104405	2012	E3.1	9.4	61	36	2.0	6.1
	2013	E3.1	12	79	47	2.5	8.3
	2014	E2.1	18	128	75	3.6	14
	2015	E2.5	15	103	58	3.0	11
	Mean annual average	2012–15	E2.7	13	93	54	2.8
Mean annual average	2009–15	E3.0	14	82	46	3.0	10
01104410	2012	0.73	32	292	149	5.1	9.8
	2013	0.71	36	317	174	5.7	10
	2014	0.39	46	376	202	6.9	12
	2015	0.46	41	362	184	6.3	11
	Mean annual average	2012–15	0.57	39	337	177	6.0
Mean annual average	2009–15	0.57	31	254	135	5.0	10
01104415	2009	0.90	35	472	273	5.3	16
	2010	1.1	22	271	160	3.4	11
	2011	0.70	35	494	287	5.4	16
	2012	0.55	27	327	190	3.9	12
	2013	0.65	29	396	224	4.6	14
	2014	0.47	29	404	231	4.5	14
	2015	0.58	33	424	251	5.0	15
	Mean annual average	2012–15	0.56	29	388	224	4.5
Mean annual average	2009–15	0.71	30	398	231	4.6	14
01104420	2012	E1.8	26	249	137	5.1	7.5
	2013	1.9	29	300	165	5.7	8.8
	2014	1.4	35	381	203	6.7	11
	2015	1.5	32	346	184	6.3	10
	Mean annual average	2012–15	1.6	31	319	172	5.9
Mean annual average	2009–15	1.6	30	344	191	5.5	11
01104430	2009	17	21	200	107	4	9.3
	2010	22	18	167	87	3.4	7.3
	2011	10	22	201	108	4	9.1
	2012	10	20	188	100	3.7	8.5
	2013	6.9	21	195	104	3.9	8.8
	2014	9.3	25	236	130	4.6	11
	2015	11	26	245	135	4.7	11
Mean annual average	2012–15	9.4	23	216	117	4.2	9.7
Mean annual average	2009–15	12.3	22	204	110	4.0	9.2

28 Deicing Compounds and Total Phosphorus in the Cambridge Drinking-Water Source Area, Mass., Water Years 2009–15

Table 8. Annual mean streamflow and annual mean concentrations of calcium, chloride, sodium, sulfate, and magnesium estimated for subbasins that contribute water to Cambridge and Stony Brook Reservoirs, Massachusetts, 2009–15.—Continued

[Locations of stations are shown in figure 1. USGS, U.S. Geological Survey; ft³/s, cubic foot per second; mg/L, milligram per liter; E, estimated from incomplete data]

USGS station number	Water year	Annual mean streamflow (ft ³ /s)	Annual mean concentration				
			Calcium (mg/L)	Chloride (mg/L)	Sodium (mg/L)	Magnesium (mg/L)	Sulfate (mg/L)
01104453	2011	3.4	19	150	87	3.7	12
	2012	3.3	15	120	68	3.1	8.2
	2013	5.2	17	132	75	3.5	9.7
	2014	2.9	21	168	97	4.3	14
	2015	3.5	23	180	101	4.4	16
Mean annual average	2012–15	3.7	19	150	86	3.8	12
Mean annual average	2009–15	3.7	19	150	86	3.8	12
01104455	2009	1.1	30	263	147	5.8	25
	2010	1.4	27	195	109	5	22
	2011	0.93	30	278	157	5.7	25
	2012	0.91	27	196	112	4.9	22
	2013	0.88	32	268	153	6	26
	2014	0.72	36	326	186	6.7	28
	2015	0.81	36	344	207	6.7	29
	Mean annual average	2012–15	0.83	33	284	164	6.1
Mean annual average	2009–15	0.96	31	267	153	5.8	25
01104460	2009	51	20	115	62	4	10
	2010	66	18	88	47	3.6	8.3
	2011	39	21	120	65	4	11
	2012	37	20	110	59	4	10
	2013	37	20	115	62	4	10
	2014	30	23	145	78	4.4	13
	2015	34	24	158	85	4.6	13
	Mean annual average	2012–15	35	22	132	71	4.2
Mean annual average	2009–15	42	21	122	65	4.1	11
01104475	2009	1.4	17	47	29	3.2	16
	2010	1.8	14	30	19	2.7	13
	2011	1.2	16	41	26	3.1	14
	2012	1.1	15	39	25	3	14
	2013	1.2	15	37	23	2.9	14
	2014	0.95	19	60	37	3.5	18
	2015	1.1	19	64	38	3.5	18
	Mean annual average	2012–15	1.1	17	50	31	3.3
Mean annual average	2009–15	1.3	16	45	28	3.1	15

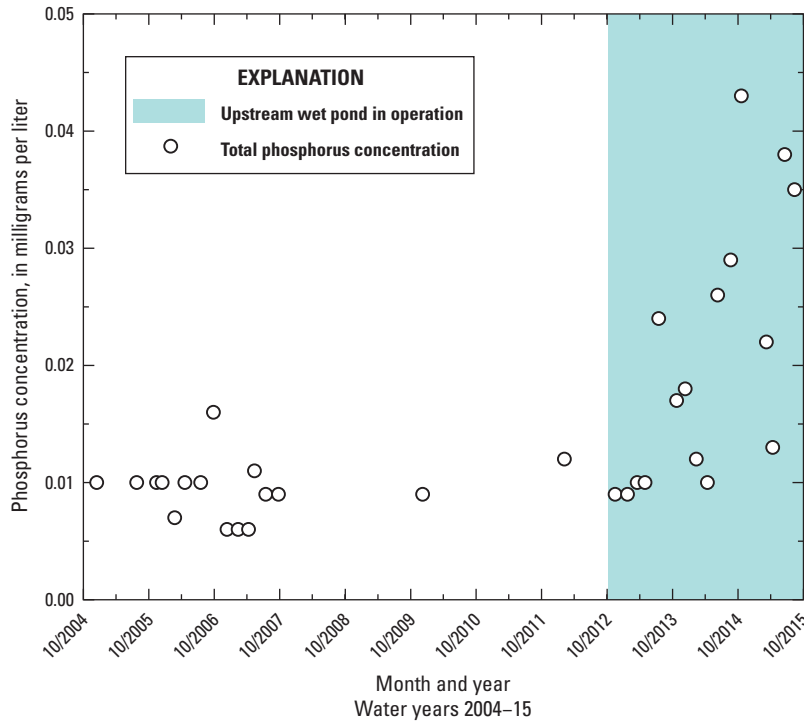


Figure 13. Concentrations of total phosphorus in base-flow samples collected at U.S. Geological Survey continuous water-quality monitoring station 01104455 in the Cambridge drinking-water source area, Massachusetts, water years 2004–15, prior to and after the upstream installation of a structural source control. Location of station is shown in figure 1.

mineral surfaces (Millar and Turk, 1949); as a result, Ca and Mg in groundwater are exchanged for Na that was adsorbed to aquifer solids such as clay minerals, resulting in higher Na concentrations. The extent of the flow paths not only increases the potential for cation exchange to occur, but also affects the timing of the discharge (and transport of constituents) to the tributaries.

Daily mean streamflow was negatively correlated with daily flow-weighted concentrations of Cl at all USGS stations (table 9) unaffected by regulation. Similar correlations between streamflow and concentrations of other major ions that strongly correlate with Cl also were found. Results of all tests between streamflow and daily flow-weighted concentrations of Cl were significant. Correlation coefficients for the Spearman rank-order correlation tests were generally higher than those for the Pearson Product Moment Correlation method. These results indicate that Cl concentrations at the stations tend to increase during the summer when streamflow is low and decrease during high base-flow conditions and periods of stormflow runoff, indicating that groundwater is an important source and pathway for Cl. In many cases, a portion of the base-flow load for major ions results from salt-laden runoff that infiltrates to the groundwater near roadways or in various structural source controls and eventually discharges to the streams. This was particularly true for USGS station 01104410 that received groundwater affected by a previously uncovered salt depot.

The subbasin in the upper Stony Brook Reservoir Basin (USGS station 01104370) also had a strong negative correlation between streamflow and daily flow-weighted

Table 9. Results and attained significance levels (*p*-values) for Pearson product moment correlation and Spearman Rho tests for daily mean values of streamflow and daily flow-weighted concentrations of chloride for selected U.S. Geological Survey continuous water-quality monitoring stations in the Cambridge drinking-water source area, Massachusetts, water years 2009–15.

[Locations of stations are shown in figure 1. USGS, U.S. Geological Survey; <, less than]

USGS station number	Pearson Product Moment Correlation	<i>p</i> -value	Spearman Rho	<i>p</i> -value
01104370	-0.48	<0.001	-0.64	<0.001
01104405	-0.17	<0.001	-0.44	<0.001
01104410	-0.50	<0.001	-0.68	<0.001
01104415	-0.19	<0.001	-0.49	<0.001
01104420	-0.17	<0.001	-0.23	<0.001
01104453	-0.21	<0.001	-0.15	<0.001
01104455	-0.12	<0.001	-0.30	<0.001
01104475	-0.28	<0.001	-0.32	<0.001

concentrations of Cl (table 9). The land use upstream from this station is largely residential with a low percentage of constructed impervious area. This subbasin resides in parts of the towns of Lincoln and Weston that do not contain sewers. Thus, wastewater in this subbasin treated by septic systems was a constant source of Cl and Na and may explain, in part, the strong correlation between streamflow and daily flow-weighted concentrations for this subbasin. Nevertheless, the seasonal application of deicing compounds on roadways has a great effect on the year-to-year load variability. Although the relation between streamflow and Cl is affected by the volume of streamflow, the amount of deicing compounds applied each year, which generally varies with the amount of annual snowfall, had a direct effect on the relation between streamflow and daily flow-weighted concentrations of Cl (fig. 14). Both the slope and offset for the relation between streamflow and Cl shifted upward for water years with higher annual snowfall totals compared to water years with lower amounts of snowfall.

Surface runoff is the other major component of streamflow. Surface runoff, particularly from impervious surfaces, readily mobilizes salts, sediment, and associated constituents that are in some cases transported directly to the tributaries as overland flow or through conveyance structures. As a result, the quality of water in tributaries that receive large amounts of stormflow changed rapidly compared to tributaries receiving

moderate stormflow. Some of the lowest, as well as the highest, concentrations of major ions were in samples collected during runoff events. Concentrations of major ions associated with deicing compounds often caused an order of magnitude increase over concentrations in base flow during runoff events in the winter (fig. 15A). In contrast, concentrations of major ions in stormflow substantially decreased from pre-storm concentrations (fig. 15B) during runoff events in other seasons.

The turbidity of the tributary water often increases following rainfall and snowmelt events as suspended sediment is mobilized from the streambed or is entrained in surface runoff. Phosphorus is commonly associated with, or sorbed to, suspended sediment (Smith and Granato, 2010; Smith, 2005) and increases with turbidity (fig. 16). As previously discussed, concentrations of TP in composite samples collected during storms were significantly different from concentrations in base-flow samples. Similarly, concentrations of all major ions in base flow and stormflow composite samples were significantly different at USGS stations 01104415, 01104420, and 01104455 (table 7; fig. 9). Results from Mann-Whitney tests (table 10) were significant for concentrations of Ca and Mg in base-flow and stormflow composite samples collected at USGS station 01104405 and for concentrations of SO₄ at USGS station 01104475. The latter two stations have less constructed impervious area in the subbasins compared to USGS stations 01104415, 01104420, and 01104455 (table 2).

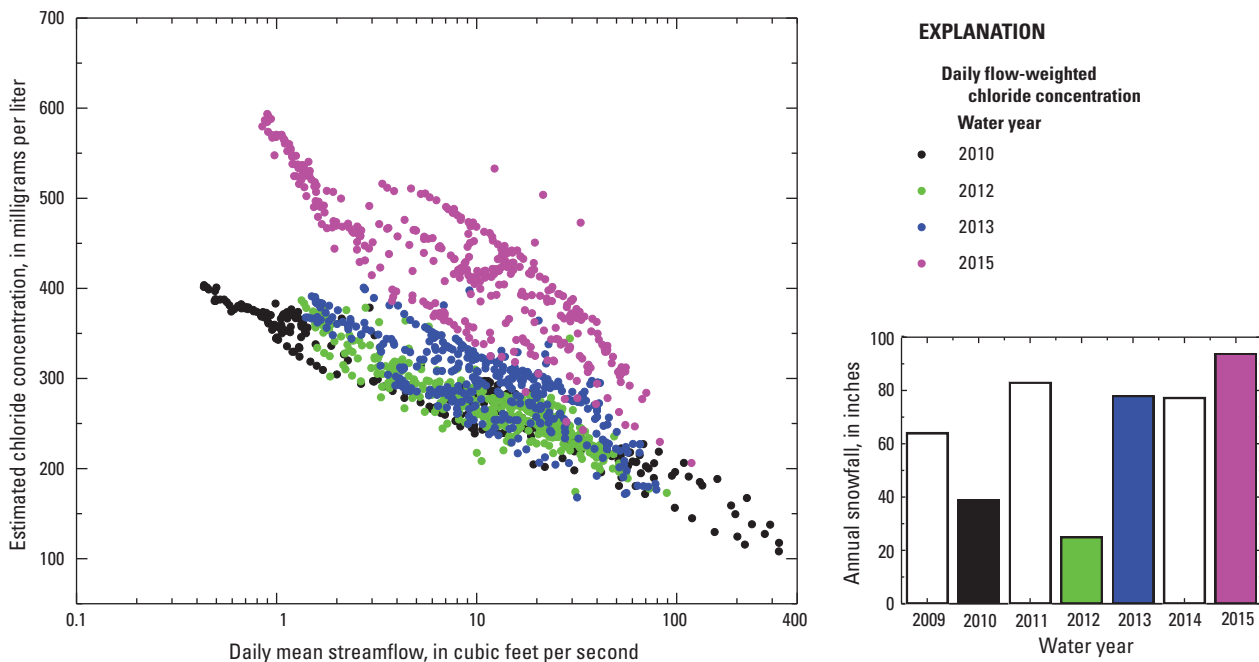


Figure 14. Relation of daily mean streamflow to estimated daily flow-weighted concentrations of chloride for Stony Brook at U.S. Geological Survey continuous water-quality monitoring station 01104370 for selected water years and annual snowfall, Cambridge drinking-water source area, Massachusetts, water years 2009–15. Location of station is shown in figure 1.

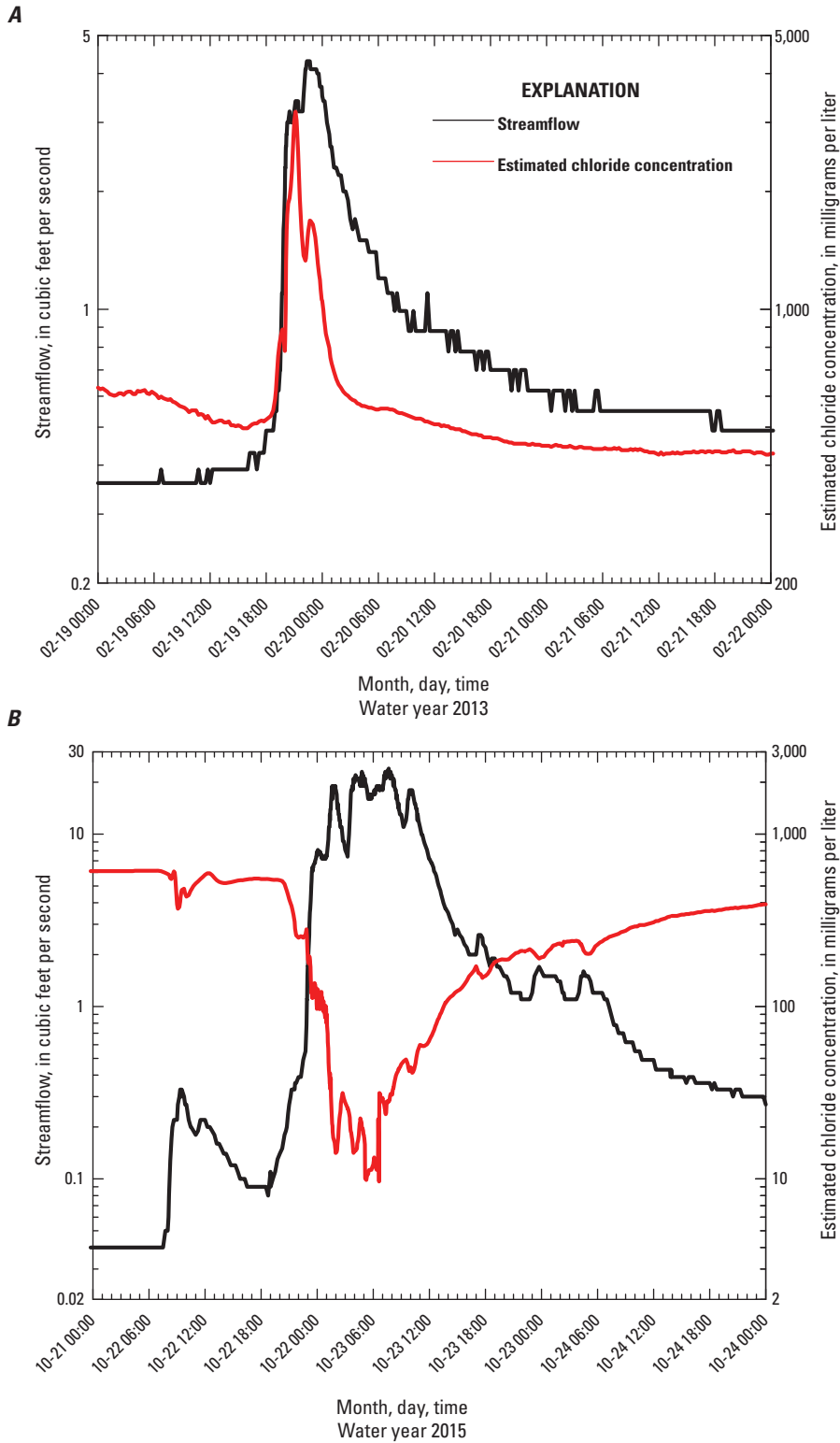


Figure 15. Records of streamflow and estimated concentrations of chloride during *A*, winter storm runoff and *B*, fall storm runoff at U.S. Geological Survey continuous water-quality monitoring station 01104415, Cambridge Reservoir Basin, Massachusetts, water years 2013 and 2015. Location of station is shown in figure 1.

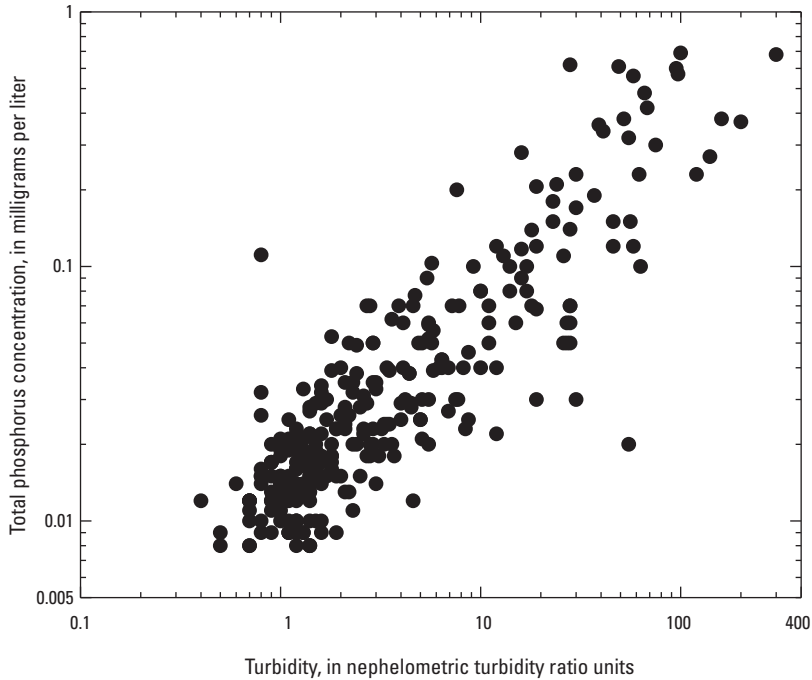


Figure 16. Relation of turbidity to total phosphorus in samples collected from 11 U.S. Geological Survey continuous water-quality monitoring stations in the Cambridge drinking-water source area, Massachusetts, water years 2009–15.

Table 10. Attained significance levels (*p*-values) from Mann-Whitney tests for paired sample sets of selected major ions in samples collected during base-flow and stormflow conditions at five U.S. Geological Survey continuous water-quality monitoring stations in the Cambridge drinking-water source area, Massachusetts, water years 2012–15.

[Locations of stations are shown in figure 1. Shaded areas indicate values are significant at the 95-percent confidence interval. A significant result (*p* value less than or equal to 0.05) indicates that the median constituent concentration for samples collected during stormflow is different from the median constituent concentration for samples collected during base-flow conditions is different. USGS, U.S. Geological Survey; <, less than]

USGS station number	Calcium	Magnesium	Potassium	Sodium	Chloride	Sulfate
01104405	0.003	0.002	0.885	0.313	0.207	0.105
01104415	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
01104420	<0.001	<0.001	0.002	<0.001	<0.001	0.034
01104455	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
01104475	0.074	0.119	0.109	0.308	0.492	0.003

Comparison of Water-Quality Properties and Constituent Concentrations with Water-Quality Criteria and Guidelines

Values of water-quality properties and concentrations of constituents in samples from the drinking-water source area are compared to various criteria and guidelines. The Commonwealth of Massachusetts, Executive Office of Energy and Environmental Affairs, Department of Environmental Protection, Water, Wastewater & Wetlands: Regulations & Standards (Massachusetts Department of Environmental Protection, 2016) sets water-quality standards for surface water on the basis of the intended use. Waters designated as Class A specifically include sources of public water supplies and their tributaries. Standards for Class A waters applicable to the data presented in this report pertain to Na in drinking water (Massachusetts Department of Environmental Protection, 2016). The U.S. Environmental Protection Agency (EPA) has established various water-quality guidelines, including the criterion continuous concentration (CCC) also referred to as a chronic concentration, the criterion maximum concentration (CMC) for freshwater aquatic life, and secondary drinking-water regulations. The EPA CCC is an estimate of the highest concentration of a constituent to which an aquatic community can be exposed indefinitely without adverse effects. In contrast, the EPA CMC is an estimate of the highest concentration of a constituent to which an aquatic community can be exposed briefly without adverse effects. Secondary drinking-water regulations (SDWRs) are non-mandatory water-quality guidelines established by the EPA and are designed to assist public water suppliers in managing aesthetic aspects of water, such as taste, odor, color, foaming, corrosivity, staining, scaling, and sedimentation; the regulations are not related to risk to human health (U.S. Environmental Protection Agency, 2007). Although these guidelines typically are applied to finished water, the presence of these constituents at concentrations exceeding SDWRs can result in damage to equipment and reduce the effectiveness of treatment for other constituents (Smith, 2007). The EPA SDWRs and guidelines for drinking water are useful benchmarks used for comparison with constituent concentrations in the drinking-water source area. In this study, turbidity and TP data were compared to the EPA reference values, which are considered representative of pristine or minimally affected waters (U.S. Environmental Protection Agency, 2000).

Measurements of turbidity in about 56 percent of water samples exceeded the EPA proposed reference value of 1.68 nephelometric turbidity units (NTUs, which are similar to NTRUs for data reported in this study) for level 3, ecoregion 59 (U.S. Environmental Protection Agency, 2000, table 4A), which covers eastern Massachusetts, except for Cape Cod. Turbidity of most composite stormflow samples exceeded this reference value (fig. 9). About 50 percent of the turbidity measurements in base-flow samples collected at USGS station 01104455 exceeded the reference value; however, nearly all

of the turbidity measurements of base-flow samples collected during water years 2014–15 exceeded the reference value. During water years 2005–7, the turbidity of base-flow samples from this station was consistently low and below the reference value (Smith, 2013), likely the result of the containment of much of the upstream tributary in a subsurface pipe where the water was not exposed to sunlight and algal growth was limited. As previously discussed, the tributary was later diverted through a structural source control constructed upstream from this station to treat stormflow runoff in water years 2011–12 (fig. 10). Exposure of the tributary water as it passes through the shallow wet ponds resulted in a water temperature increase of about 6 °C during the summer, as well as an increase for in situ measurements of turbidity that often exceeded the reference value (fig. 11).

Concentrations of dissolved Cl and Na in water samples frequently exceeded the EPA SDWR for Cl (250 mg/L) and the Massachusetts Department of Environmental Protection (MassDEP; Massachusetts Department of Environmental Protection, 2016) drinking-water guideline for Na (20 mg/L). About 42 and 38 percent of concentrations of Cl in water samples collected in the drinking-water source area during 2009–15 exceeded the EPA CCC and SDWR, respectively. During this study, Cl guidelines were not exceeded in water samples from USGS stations 01104305, 01104370, and 01104453, which are on tributaries to the Stony Brook Reservoir that drain less developed parts of the drinking-water source area (fig. 9). These same guidelines also were not exceeded in samples from the main stem of Stony Brook (USGS station 01104460), which receives flow from the Cambridge Reservoir. The EPA SDWR standards for Cl were exceeded in a single sample collected from Hobbs Brook upstream from the Cambridge Reservoir (USGS station 01104405) during a winter runoff event. The EPA CCC guideline was exceeded in 10 consecutive samples collected at the outlet to the Cambridge Reservoir from February 2014 through August 2015; the EPA SDWR standard was exceeded in March and April 2015 as well. Concentrations of Cl exceeded both standards in only two samples collected at USGS station 01104475 on a small tributary to the Stony Brook Reservoir (fig. 1). Guidelines for Cl were exceeded in samples of base flow and in stormflow composite samples collected at USGS stations 01104415, 01104420, 01104455, and 01104475, although exceedances for Cl in stormflow composite samples typically occurred only in samples collected during the winter. Concentrations of Cl exceeded the EPA CMC in 21 discrete samples of winter runoff collected from USGS stations 01104415, 01104420, and 01104455 on tributaries along Interstate 95 north of the Cambridge Reservoir. Concentrations of Cl in these samples ranged from 860 to 11,500 mg/L.

As discussed previously, concentrations of many major ions tend to decrease with increasing flows. This also tends to be the case during some winter storms despite high concentrations of deicing compounds in runoff flushed from paved surfaces at the onset of storms. Data on Cl concentrations, as well as concentrations of other constituents discussed in this report,

are limited by the number of samples collected in the tributaries of the drinking-water source area. However, estimates for major ions calculated from relations with specific conductance are available for nearly the entire study period. These estimated daily values indicate that the EPA CCC and SDWR for Cl were exceeded at all stations but were most frequently exceeded (exceeding the EPA CCC more than 300 days each water year) at USGS stations 01104410, 01104415, 01104420, and 01104455 (fig. 17); the constructed impervious areas for the subbasins represented by these stations ranged from 11 to 28 percent (table 2). Estimated daily concentrations of Cl at these four stations also exceeded the EPA CMC standard for as many as 50 days per water year (fig. 17). These data indicate that concentrations of Cl in many of the tributaries in the drinking-water supply area likely are chronically affected by the application of deicing compounds. Estimated daily concentrations for Cl rarely exceeded the SDWR and CCC thresholds for Cl at USGS stations 01104370, 01104405, 01104453, and 01104475 in largely forested and residential areas (fig. 1). About 7 percent of the estimated daily concentrations for Cl in water released from the Cambridge Reservoir exceeded the concentration for the SDWR threshold during water years 2009–15. Estimated daily concentrations for Cl in Stony Brook (USGS station 01104460), which receives a mixture of water from the Cambridge Reservoir and from the less developed areas of the upper Stony Brook Reservoir Basin, were rarely (less than 0.9 percent of the time) greater than the SDWR and CCC thresholds for Cl.

Concentrations of dissolved Na in water samples collected throughout the drinking-water supply area routinely exceeded the MassDEP drinking-water guideline (20 mg/L). With the exception of most samples collected at USGS station 01104305 and some composite samples of stormflow collected at USGS station 01104475, concentrations of Na in samples of tributary water typically were greater than the MassDEP drinking-water guideline (table 7; fig. 9B). Concentrations of Na estimated from records of specific conductance also tended to be greater than the guideline. The EPA SDWR for SO₄ (250 mg/L) was exceeded in a single discrete stormflow sample (253 mg/L) collected at USGS station 01104455 during a snowmelt runoff event. Estimated daily flow-weighted concentrations of SO₄ did not exceed the EPA SDWR at any station.

About one-half of the concentrations of TP collected in samples from the drinking-water source area exceeded the proposed reference concentration of 0.024 mg/L, respectively, for level 3, ecoregion 59 (U.S. Environmental Protection Agency, 2000). The reference value represents the 25th percentile of all nutrient data for the ecoregion 59 and is intended to protect streams and rivers from the adverse effects of nutrient enrichment (U.S. Environmental Protection Agency, 2000). With few exceptions, concentrations of TP in all composite stormflow samples exceeded the proposed reference value of 0.024 mg/L (table 7; fig. 9B). Generally, concentrations of TP in samples collected during base-flow conditions were near or below the proposed reference concentration. Concentrations of TP at

USGS station 01104455 were less than the proposed reference value through June 2014; afterwards, concentrations generally were greater than the proposed reference value ranging from 0.013 to 0.043 mg/L (fig. 13). The increase in TP concentrations at this station occurred about 1.5 years after the upstream structural source control was completed (fig. 10).

Constituent Loads and Yields

Load and yield estimates for the stations provide information about the rates at which masses of constituents are transported to the reservoirs. Tributaries with higher flows tend to have higher loads because the greater volume of water can carry more of the constituent (assuming similar constituent concentrations in each tributary) to the reservoir per unit time. Yields represent the constituent load per unit of drainage area and are calculated by dividing the estimated load for a station by the drainage area for the station. Yields are useful for comparison of different drainage-area sizes because the effects of basin size and, therefore, total streamflow volume are normalized with respect to basin area. Yields are useful for examining potential differences among basin properties that may affect water quality.

Loads and yields of Ca, Cl, Mg, Na, and SO₄ were estimated for all USGS stations in the drinking-water supply area for water years 2009–15 on the basis of streamflow and continuous specific conductance data, where available (table 11). Loads for major ions were estimated on the basis of the correlations between concentration data for Ca, Cl, Mg, Na, and SO₄ and values of specific conductance. Loads for TP were estimated on the basis of the measure of the central tendency of concentration and annual volumes of base flow and total flow during storms for water years 2013–15. Concentrations of TP at most stations followed a log-normal distribution, and the population means were estimated with the assumption that the logarithms of the data were symmetric. This approach provides a reasonable estimate of the population mean (Helsel and Hirsch, 2002).

Loads and Yields of Calcium, Chloride, Magnesium, Sodium, and Sulfate, Water Years 2009 to 2015

Loads and yields estimated on the basis of continuous records of specific conductance are expected to represent a broad range of hydrologic conditions, accounting for all runoff events, including snowmelts, which would not be possible using a typical sampling program. Mean annual yields of Ca, Cl, Na, Mg, and SO₄ for the drinking-water source area (data from USGS stations 01104460 and 01104475; table 11) for water years 2009–15, estimated on the basis of continuous records of specific conductance, were 13, 75, 40, 2.6, and 6.9 metric tons per square kilometer, respectively. The tributary adjacent to Interstate 95 in the Cambridge Reservoir Basin

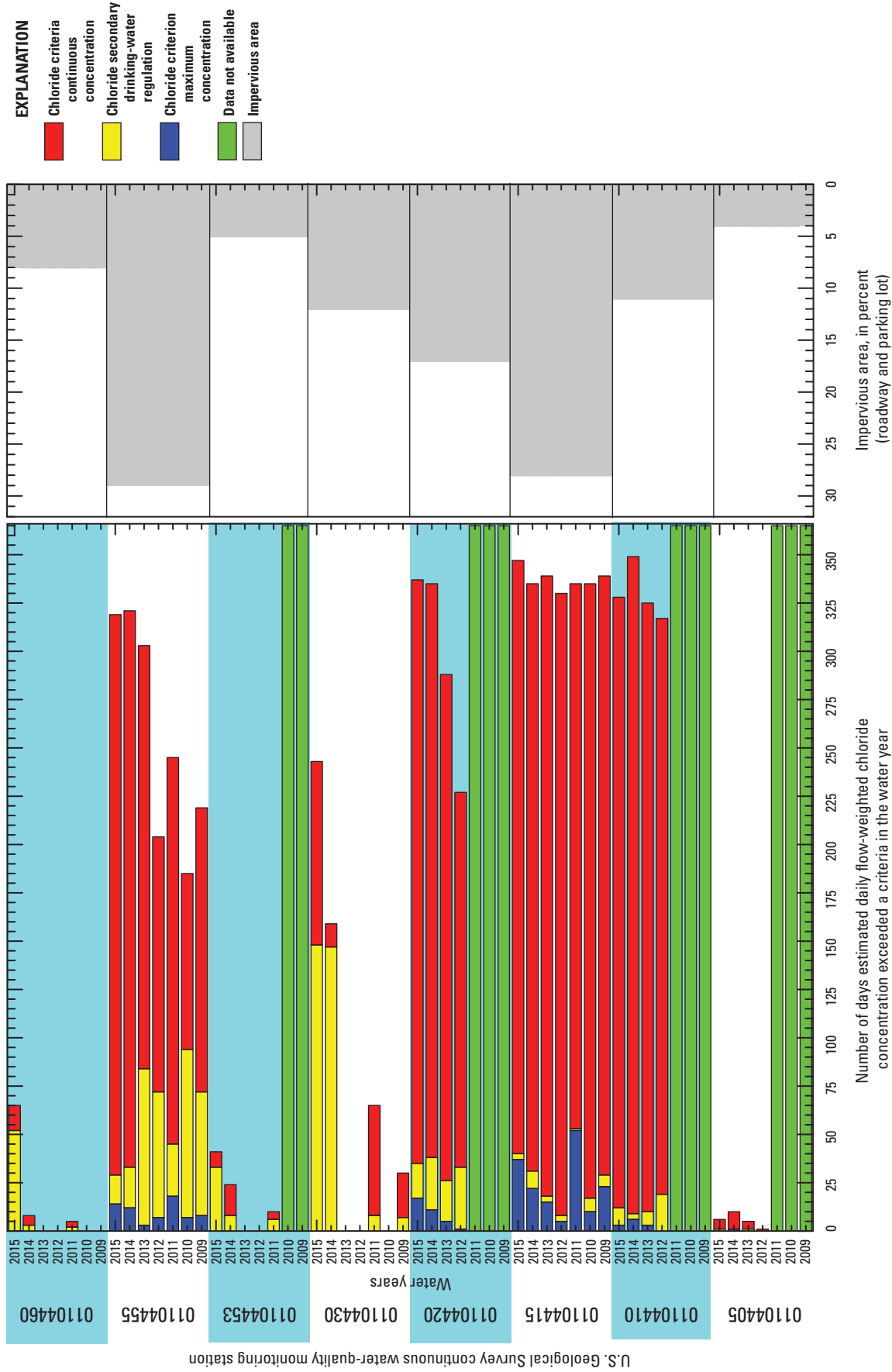


Figure 17. Frequency for estimated daily flow-weighted concentrations of chloride that exceed U.S. Environmental Protection Agency water-quality criteria for chloride and amount of impervious area in eight selected continuous water-quality monitoring stations in the Cambridge drinking-water source area, Massachusetts, 2009–15. Locations of stations are shown in figure 1.

Table 11. Annual mean streamflow and calcium, chloride, sodium, sulfate, magnesium, and total phosphorus annual loads estimated for subbasins that contribute water to Cambridge and Stony Brook Reservoirs, Massachusetts, 2009–15.

[Locations of stations are shown in figure 1. Loads and yields for total phosphorus for the drinking-water supply area are estimated for water years 2013–15; . USGS, U.S. Geological Survey; ft³/s, cubic foot per second; t, metric ton; E, estimated from incomplete or estimated data; —, unable to calculate as a result of regulation of discharge; CI, confidence interval; t/km², metric ton per square kilometer]

USGS station number	Water year	Annual mean streamflow, ft ³ /s	Runoff percentage	Calcium (t)	Chloride (t)	Sodium (t)	Magnesium (t)	Sulfate (t)	Total phosphorus (t)
01104370	2010	E26	E28	E290	E990	E530	E60	E160	—
	2011	17	21	220	780	410	45	120	—
	2012	17	21	210	730	390	43	120	—
	2013	17	23	220	790	410	46	120	0.31
	2014	14	22	230	890	450	47	130	0.26
	2015	15	17	260	1050	530	55	150	0.28
95-percent CI (percent)				+15	+15	+15	+16	+52	+28
Storm load percentage				17	16	16	17	17	—
Mean annual yield (t/km ²)				8.7	33	17	1.9	5.0	0.011
01104405	2012	E3.1	E26	E26	E170	E99	E5.5	E17	—
	2013	E3.1	E36	E33	E220	E130	E6.8	E23	E0.12
	2014	E2.1	E33	E33	E240	E140	E6.7	E26	E0.077
	2015	E2.5	E26	E33	E230	E130	E6.7	E24	E0.093
95-percent CI (percent)				+43	+20	+23	+44	+87	-21 to +70
Storm load percentage				29	31	31	29	32	61
Mean annual yield (t/km ²)				4.7	39	22	1.2	4.1	0.017
01104410	2012	E0.73	E48	E21	E190	E97	E3.3	E6.4	—
	2013	0.71	38	23	200	110	3.6	6.6	0.014
	2014	0.39	43	16	130	70	2.4	4.1	0.008
	2015	E0.46	E24	E17	E150	E76	E2.6	E4.6	E0.005
95-percent CI (percent)				+19	+18	+18	+20	+36	+31
Storm load percentage				37	37	37	37	37	—
Mean annual yield (t/km ²)				21.9	188	102	3.4	6.1	0.01
01104415	2009	0.90	40	28	380	220	4.3	13	—
	2010	1.1	50	22	270	160	3.4	11	—
	2011	0.70	45	22	310	180	3.4	10.0	—
	2012	0.55	47	13	160	93	1.9	6.0	—
	2013	0.65	45	17	230	130	2.7	8.1	0.050
	2014	0.47	47	12	170	97	1.9	5.8	0.038
	2015	0.58	46	17	220	130	2.6	7.7	0.050
95-percent CI (percent)				+47	+23	+23	+52	+70	-25 to +84
Storm load percentage				31	31	31	31	32	92
Mean annual yield (t/km ²)				18.0	235	136	2.7	8.3	0.043
01104420	2012	E1.8	E35	E42	E400	E220	E8.2	E12	—
	2013	1.9	31	50	510	280	9.6	15.0	0.12
	2014	1.4	38	43	470	250	8.3	13.0	0.096
	2015	1.5	30	42	450	240	8.2	13.0	0.091
95-percent CI (percent)				+57	+27	+28	+46	+124	-28 to +97
Storm load percentage				31	31	31	31	32	61
Mean annual yield (t/km ²)				22.0	230	124	4.3	6.7	0.051

Table 11. Annual mean streamflow and calcium, chloride, sodium, sulfate, magnesium, and total phosphorus annual loads estimated for subbasins that contribute water to Cambridge and Stony Brook Reservoirs, Massachusetts, 2009–15.—Continued

[Locations of stations are shown in figure 1. Loads and yields for total phosphorus for the drinking-water supply area are estimated for water years 2013–15; . USGS, U.S. Geological Survey; ft³/s, cubic foot per second; t, metric ton; E, estimated from incomplete or estimated data; —, unable to calculate as a result of regulation of discharge; CI, confidence interval; t/km², metric ton per square kilometer]

USGS station number	Water year	Annual mean streamflow, ft ³ /s	Runoff percentage	Calcium (t)	Chloride (t)	Sodium (t)	Magnesium (t)	Sulfate (t)	Total phosphorus (t)
01104430	2009	17	—	320	3,030	1,620	60	140	—
	2010	22	—	350	3,210	1,680	65	140	—
	2011	10	—	190	1,770	950	35	80	—
	2012	10	—	180	1,710	910	34	77	—
	2013	6.9	—	130	1,200	640	24	54	0.068
	2014	9.3	—	210	1,950	1,070	38	90	0.091
	2015	11	—	260	2,480	1,370	48	110	0.11
95-percent CI (percent)				+16	+13	+14	+15	+39	+19
Storm load percentage				—	—	—	—	—	—
Mean annual yield (t/km ²)				13.1	123	66	2.4	5.6	0.005
01104453	2011	3.4	15	58	450	260	11	36	—
	2012	3.3	12	45	350	200	9.1	24	—
	2013	5.2	11	78	610	350	16	45	0.18
	2014	2.9	12	55	430	250	11	37	0.10
	2015	3.5	10	72	570	320	14	51	0.12
95-percent CI (percent)				+26	+20	+21	+25	+114	+25
Storm load percentage				—	—	—	—	—	—
Mean annual yield (t/km ²)				10.8	83	48	2.1	6.7	0.023
01104455	2009	1.1	25	29	250	140	5.5	24	—
	2010	1.4	39	35	250	140	6.4	28	—
	2011	0.93	39	25	230	130	4.7	21	—
	2012	0.91	38	22	160	91	4	18	—
	2013	0.88	29	25	210	120	4.7	20	0.059
	2014	0.72	30	23	210	120	4.3	18	0.045
	2015	0.81	32	26	250	150	4.9	21	0.058
95-percent CI (percent)				+85	+24	+24	+69	+61	-37 to +57
Storm load percentage				23	22	23	22	23	76
Mean annual yield (t/km ²)				21.0	175	100	3.9	17.0	0.043
01104460	2009	51	—	930	5,230	2,810	180	470	—
	2010	66	—	1,050	5,190	2,780	210	490	—
	2011	39	—	730	4,180	2,250	140	380	—
	2012	37	—	660	3,620	1,950	130	330	—
	2013	37	—	670	3,780	2,030	130	340	0.75
	2014	30	—	620	3,920	2,110	120	340	0.62
	2015	34	—	730	4,800	2,590	140	410	0.70
95-percent CI (percent)				+21	+16	+17	+24	+70	-15 to +39
Storm load percentage				—	—	—	—	—	—
Mean annual yield (t/km ²)				14.0	77	41	2.6	6.9	0.012

Table 11. Annual mean streamflow and calcium, chloride, sodium, sulfate, magnesium, and total phosphorus annual loads estimated for subbasins that contribute water to Cambridge and Stony Brook Reservoirs, Massachusetts, 2009–15.—Continued

[Locations of stations are shown in figure 1. Loads and yields for total phosphorus for the drinking-water supply area are estimated for water years 2013–15; USGS, U.S. Geological Survey; ft³/s, cubic foot per second; t, metric ton; E, estimated from incomplete or estimated data; —, unable to calculate as a result of regulation of discharge; CI, confidence interval; t/km², metric ton per square kilometer]

USGS station number	Water year	Annual mean streamflow, ft ³ /s	Runoff percentage	Calcium (t)	Chloride (t)	Sodium (t)	Magnesium (t)	Sulfate (t)	Total phosphorus (t)
01104475	2009	1.4	14	21	59	37	4.1	20	--
	2010	1.8	30	22	48	31	4.3	20	--
	2011	1.2	20	18	46	29	3.4	16	--
	2012	1.1	19	15	38	24	2.9	14	--
	2013	1.2	20	16	40	25	3.2	15	0.049
	2014	0.95	20	16	51	31	3	15	0.038
	2015	1.1	17	19	63	38	3.5	18	0.041
95 percent CI (percent)				+28	+24	+22	+33	+41	-29 to +88
Storm load percentage				17	14	14	17	17	57
Mean annual yield (t/km ²)				8.3	22	14	1.6	7.7	0.019
Drinking-water source area									
Mean annual load (t)	2009–15			788	4,440	1,070	2,390	2,880	0.73
Mean annual yield (t/km ²)	2009–15			13	75	2.6	40	6.9	0.012

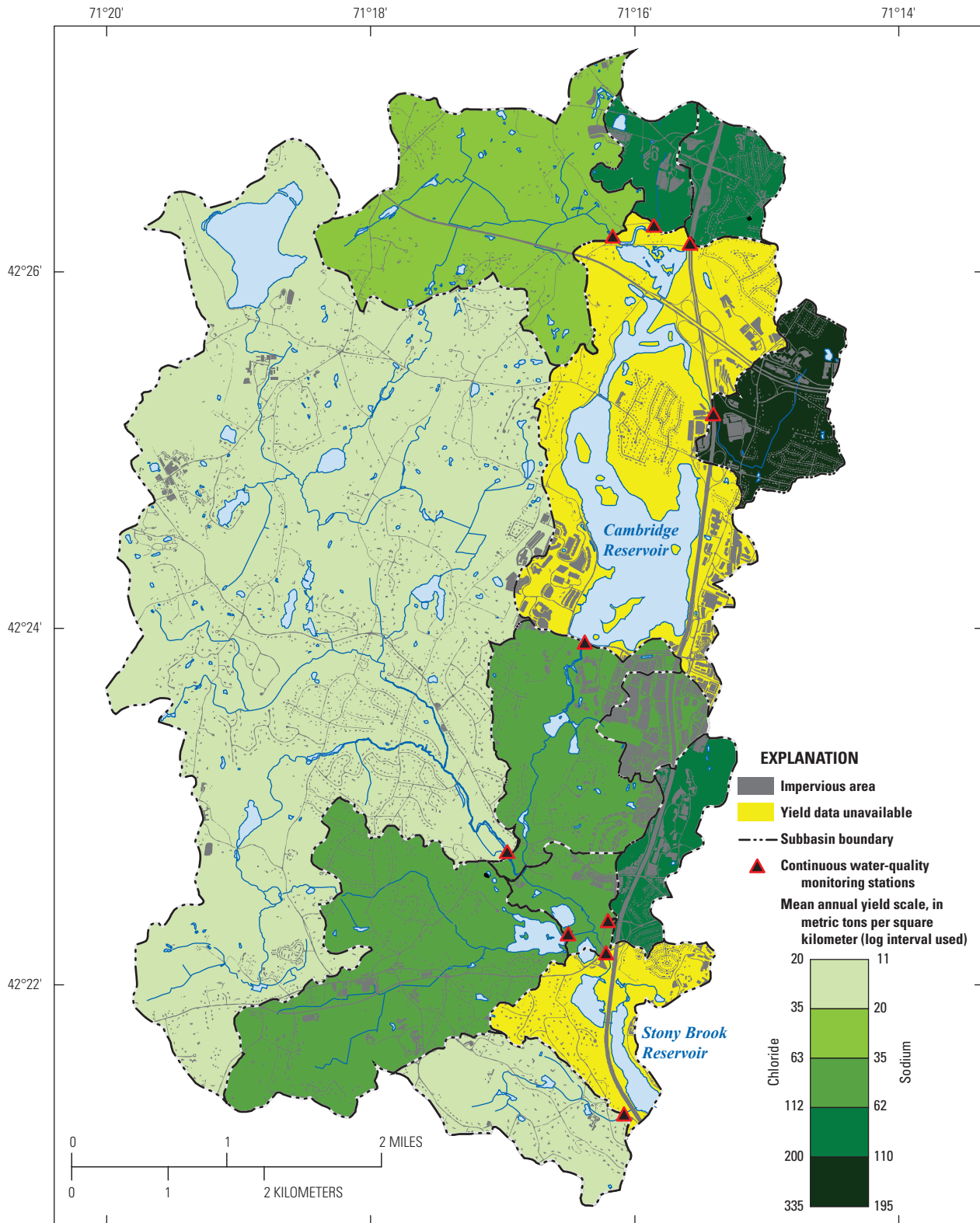
(USGS station 01104415) had the highest annual mean yields for all major ions; however, when only water years 2012–15 are considered (the period when all stations in the drinking-water supply area were operational), USGS station 01104420, also adjacent to Interstate 95, had the highest annual mean yields for Cl and Na (fig. 18). Mean annual yields of Ca, Cl, Na, and Mg at this station for water years 2009–15 were 1.6 to 3.1 times higher than the respective mean annual yields for the drinking-water source area for the same period. The mean annual yield for SO₄ at USGS station 01104455 for water years 2009–15 was about 2 times greater than the mean annual yield for the drinking-water source area (table 11).

Mean annual yields of major ions at USGS stations 01104410, 01104415, and 01104420 in the Cambridge Reservoir Basin and at USGS station 01104455 in the Stony Brook Reservoir Basin, areas that contain large amounts of roadways and parking lots (table 2), were 60 to 240 percent higher than mean annual yields for the drinking-water source area (table 11). Mean annual yields of major ions for USGS stations 01104370, 01104405, 01104453, and 01104475, which drain subbasins with the highest percentage of residential land use and among the lowest percentages of roadways, were the lowest in the drinking-water source area.

The combined subbasin area for USGS stations 01104405, 01104410, 01104415, and 01104420 accounts for 53 percent of the Cambridge Reservoir Basin. The sum of estimated loads for Cl at these stations ranged from 920 to 1,160 metric tons (t) during water years 2012–15 (table 11; fig. 19). The remaining 47 percent of the Cambridge Reservoir

Basin is unengaged. Aside from the reservoir areas, the unengaged subbasin has land-use characteristics similar to those in the subbasin areas upstream from the stations; therefore, loads of Cl and other major ions discharged from these unengaged areas are likely proportional to those loads estimated for the stations in the Cambridge Reservoir Basin. The mean annual Cl load for the unengaged area during water years 2012–15 was 800 t; in contrast, the mean annual Cl load for the USGS stations was 1,035 t. Loads of Cl were estimated for this unengaged area by subtracting the sum of the tributary loads (USGS stations 01104405, 01104410, 01104415, and 01104420) from the loads estimated at the outlet of the Cambridge Reservoir (USGS station 01104430).

The accuracy of individual annual loads estimated for the unengaged area was poor because tributary loads to the reservoir during any given year are not necessarily reflected in the loads discharged from the reservoir during the same year. Between water years 2012 and 2015, the mean reservoir storage volume and outlet streamflow for the Cambridge Reservoir ranged from 1,849 to 2,208 million gallons and from 6.9 to 11.3 cubic feet per second, respectively (fig. 19). These data indicate that the residence time of water in the reservoir, assuming plug flow, ranged from about 9 to 15 months during water years 2012–15. Consequently, some portion of the load discharged from the reservoir may in fact be from prior water years. A reduction in annual mean discharge also can affect the quality of the estimate for the unengaged area by reducing the difference between the summed tributary loads and the outlet load, as is apparent for the estimated load for water year 2013 (fig. 19)



Base from U.S. Geological Survey, Massachusetts Office of Geographic Information, Cambridge Water Department, Harvard Design and Mapping, and Boston Edison digital data, April 1998

Figure 18. Mean annual yields of chloride and sodium in samples collected from U.S. Geological Survey continuous water-quality monitoring stations in the Cambridge drinking-water source area, Massachusetts, water years 2012–15.

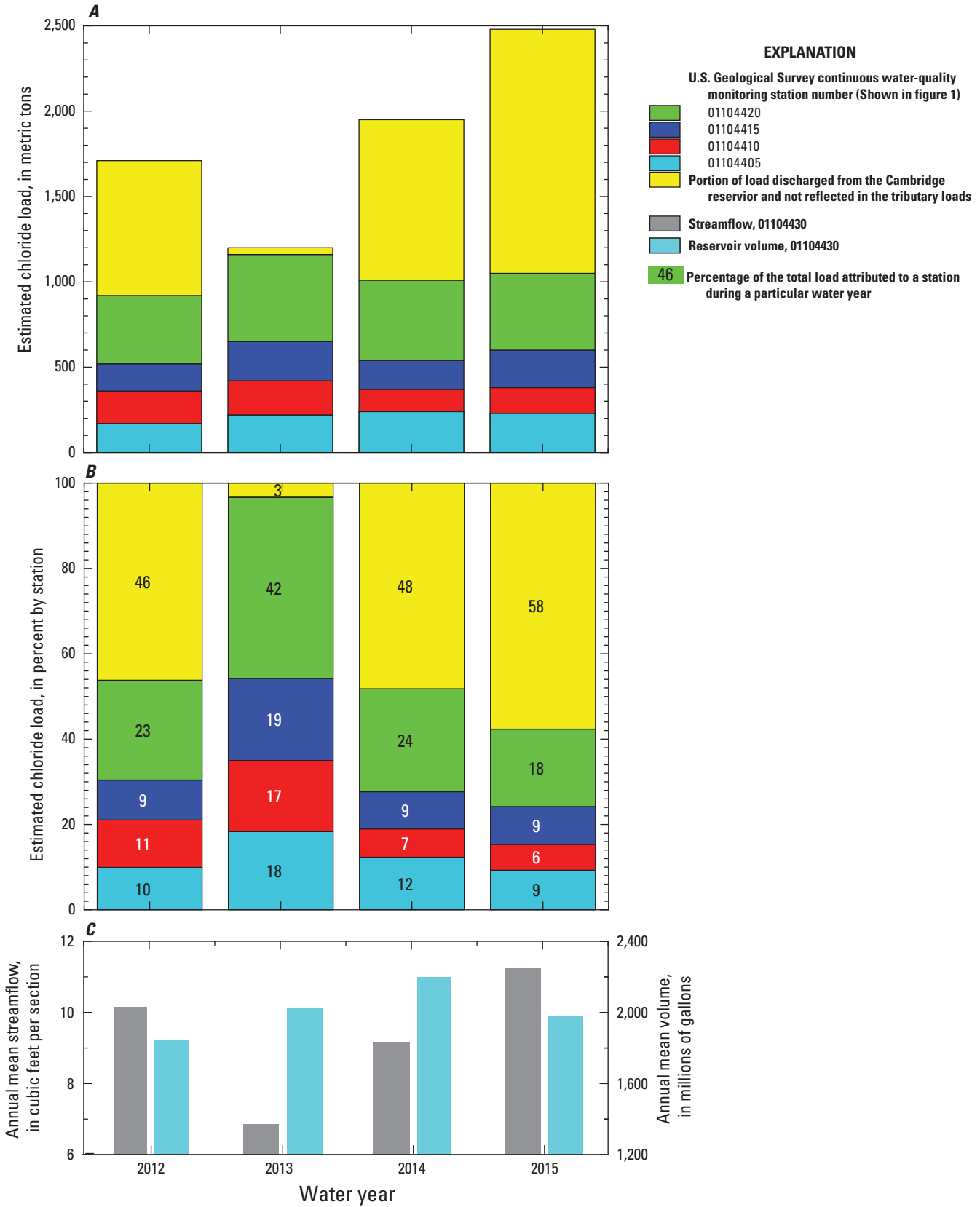


Figure 19. Distribution of *A*, estimated chloride loads at selected U.S. Geological Survey continuous water-quality monitoring stations in the Cambridge Reservoir Basin and portion of chloride loads discharged from the Cambridge Reservoir that are not reflected in tributary loads, *B*, percentage of chloride loads by station, and *C*, annual mean streamflows and reservoir volume for the Cambridge Reservoir, Massachusetts, water years 2012–15.

when water was stored in the reservoir and the outlet annual mean discharge (6.9 cubic feet per second) was substantially less than in other years.

The largest estimated loads of Ca, Cl, Na, Mg, and SO₄ in the Cambridge Reservoir Basin were for USGS station 01104420 during water years 2012–15 (table 11; fig. 19). Loads of Cl at this station accounted for between 18 and 42 percent of the annual estimated Cl load released from the Cambridge Reservoir (USGS station 01104430). The mean annual estimated loads for major ions at USGS station 01104415 were about 60 percent greater during water years 2009–11 than during water years 2012–15 (table 11). Data were not available to estimate loads of major ions at the other three stations in the Cambridge Reservoir Basin during water years 2009–11. Loads of major ions associated with stormflows accounted for about 30 percent of the total load at each of the stations in the Cambridge Reservoir Basin (table 11).

The sum of constituent loads at USGS station 01104460 on Stony Brook upstream from the Stony Brook Reservoir and at USGS station 01104475 on a tributary to Stony Brook Reservoir represents about 96 percent of the loads in the drinking-water source area for the Stony Brook Reservoir Basin. During water years 2009–15, the estimated mean annual loads for Ca, Cl, Mg, Na, and SO₄ to the drinking-water source area were 788, 4,440, 2,390, 1,070, and 2,880 t. About one-half of the estimated loads for Cl and Na that flow into the Stony Brook Reservoir were from the Cambridge Reservoir Basin. Estimated loads of Ca, Mg, and SO₄ from the Cambridge Reservoir Basin ranged from 24 to 30 percent of the estimated loads for the drinking-water source area and are proportional to the basin area. Although the magnitude of loads varied for each water year, the proportion of the load for each subbasin was relatively consistent for each water year (fig. 20). Loads for USGS station 01104430 (Cambridge Reservoir) were lowest in water year 2013 when flows were reduced to store water in the reservoir.

Loads and Yields of Total Phosphorus, Water Years 2013 to 2015

Annual loads of TP ranged from 0.005 to 0.75 t at the 10 stations in the drinking-water supply area during water years 2013–15 (table 11). Estimated loads of TP for tributaries to the Cambridge Reservoir during this same period totaled 0.76 t; however, only about a one-third of the inflow load was reflected in the load estimated at the outlet of the reservoir (USGS station 01104430). The difference between the inlet and outlet loads indicates that the reservoir continues to trap about two-thirds of the TP (Waldron and Bent, 2001). The mean annual combined load of TP at stations 01104460 on the main stem of Stony Brook and at 01104475 on a small tributary was 0.73 t, representing about 96 percent of the load for the Stony Brook Reservoir Basin (the drinking-water supply area). Most of the TP loads were transported during storms at the tributaries. At five stations, between 57 and 92 percent of

the TP load in the tributaries was associated with stormflow (table 11).

Loads of TP estimated for water years 2013–15 at USGS stations 01104415, 01104455, and 01104475 were about 50 percent lower than loads estimated for water years 2005–7 (Smith, 2013). Streamflow often is associated with TP, and higher streamflow values tend to result in greater TP loads. The mean annual streamflow for water years 2005–7 was about 30 percent higher than the mean annual streamflow for 2013–15, which may explain much of the difference between the loads. The percentages of streamflow representing the base flow and stormflow component are similar for each period. The load of TP associated with each flow component decreased at USGS stations 01104415 and 01104475 with the lower volume of streamflow for water years 2013–15. The load of TP also decreased with the low volume of stormflow at USGS station 01104455 for water years 2013–15; however, the load of TP associated with the base flow was about 70 percent higher for water years 2013–15 than for water years 2005–7 despite lower streamflow in the more recent period.

Mean annual yields for TP in the drinking-water supply area ranged from 0.005 to 0.051 t/km² during water years 2013–15 (table 11). Yields of TP estimated for Hobbs Brook at the outlet of the Cambridge Reservoir (USGS station 01104430) were the lowest for any station. Mean annual yields for TP tended to be lower at the stations with larger subbasin areas or subbasins with large percentages of wetland (table 2; fig. 21). Tributary subbasins with higher percentages of constructed impervious areas (USGS stations 01104415, 01104420, and 01104455) had the highest yields of TP. The mean annual yield of TP for the subbasin area upstream from the Stony Brook Reservoir, but excluding yields at three stations (USGS stations 01104370, 01104453, and 01104455) and the Cambridge Reservoir (USGS station 01104430), was 0.023 t/km². This area includes a small subbasin southeast of the Cambridge Reservoir that is highly developed and contains substantial amounts of constructed impervious areas (fig. 20). Yields of TP from this small subbasin were offset by the yields of the remaining less-developed areas that were likely lower. The mean annual yield of TP for the drinking-water source area for water years 2013–15 was 0.012 t/km².

Accuracy of Estimated Loads

The accuracy of annual load and yield estimates in this study was affected by errors associated with sample collection and processing techniques, analytical techniques, and estimation of the central tendency for TP concentrations; the accuracy is related to the size of each dataset and the range of measured flows and constituent concentrations. In addition, the accuracy of annual loads estimated from continuous records of streamflow and specific conductance was affected by the accuracy and range of measured flow and specific conductance, and the accuracy of the relations between specific conductance and the constituent concentrations.

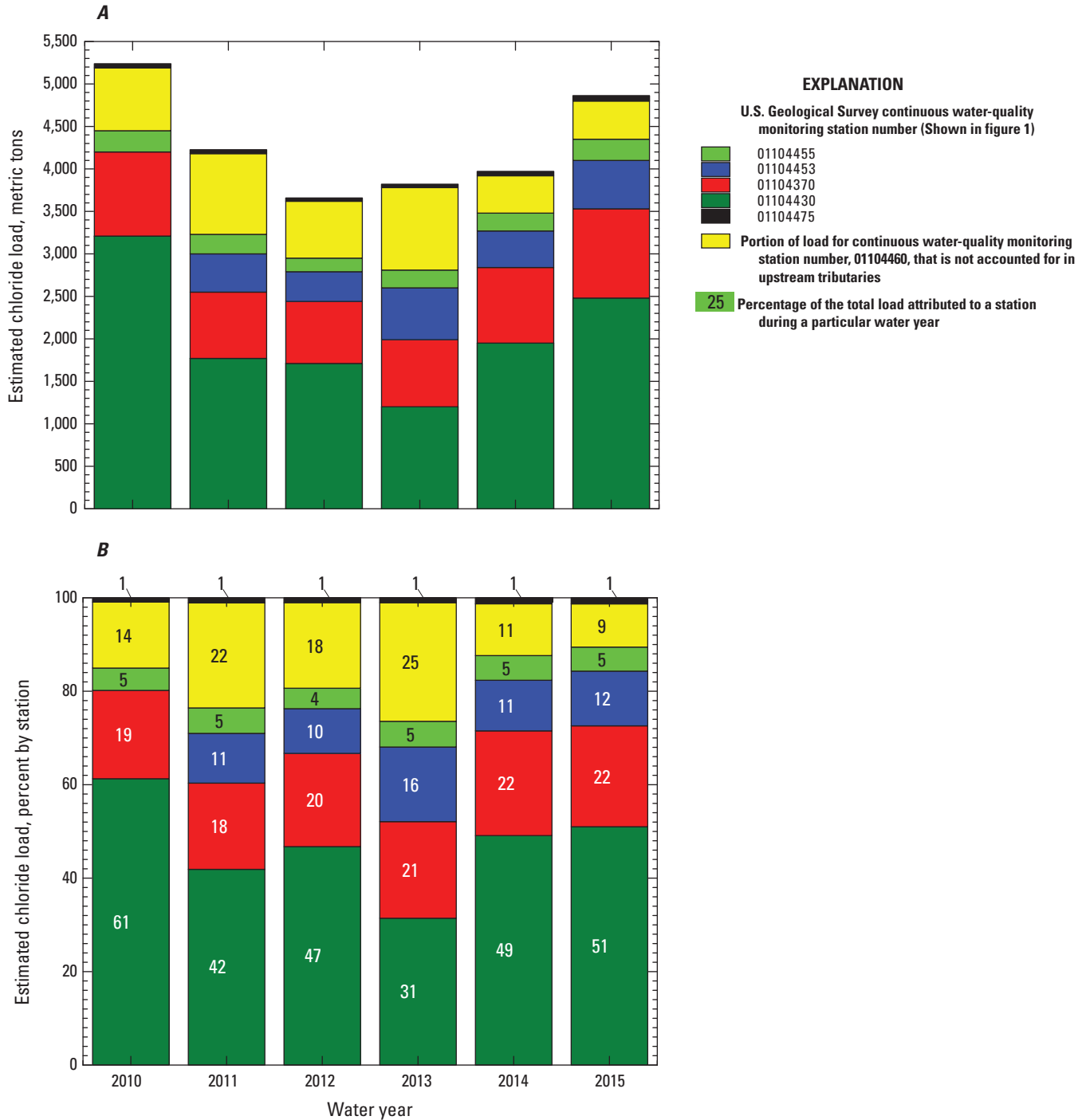
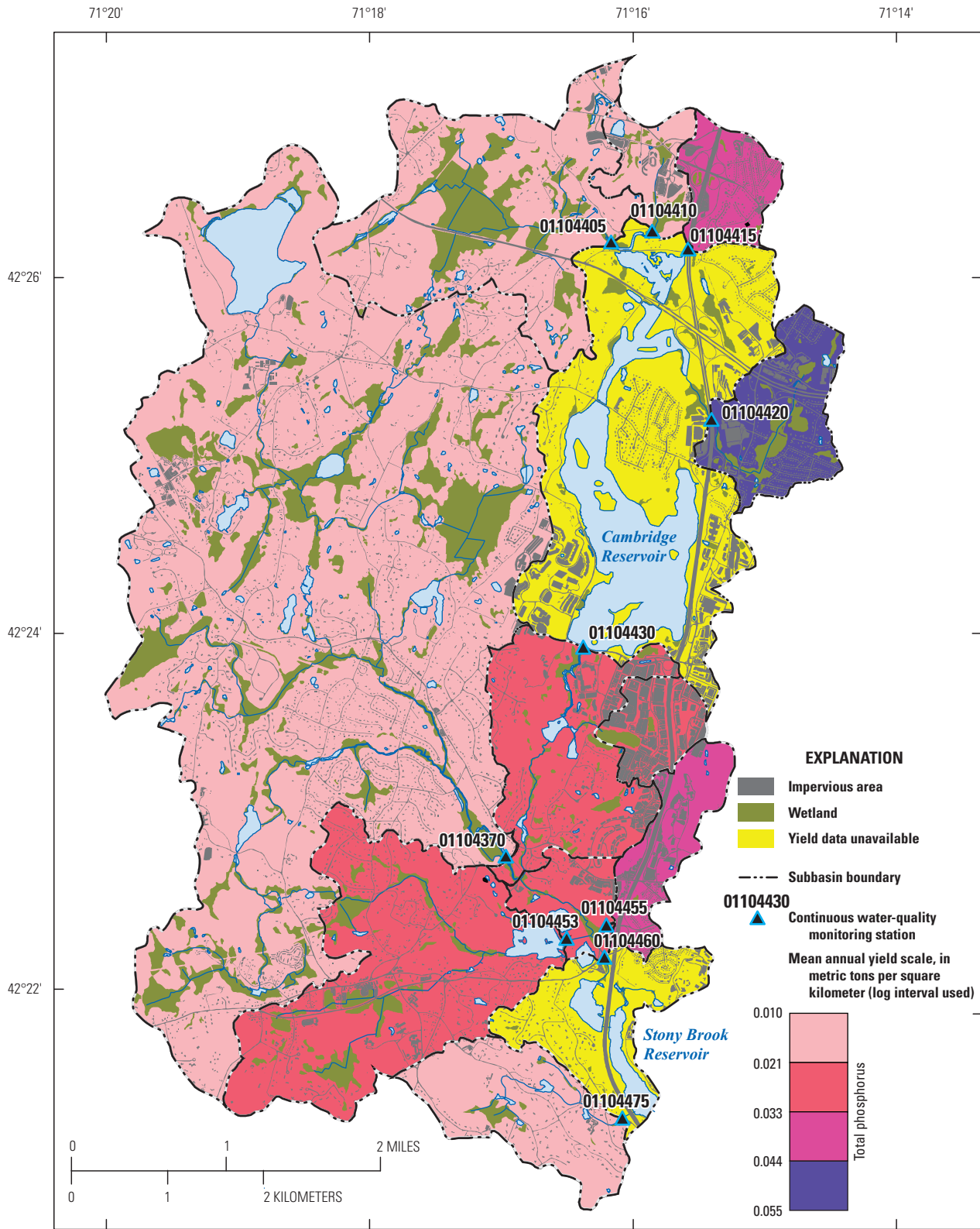


Figure 20. Distribution of estimated chloride loads at selected U.S. Geological Survey continuous water-quality monitoring stations in the Stony Brook Reservoir Basin, Massachusetts, water years 2010–15: *A*, in metric tons and *B*, in percent by station. Chloride loads for station 01104453 were unavailable for water year 2010 and are represented as a portion of load for station 01104460 that is not accounted for in upstream tributaries.



Base from U.S. Geological Survey, Massachusetts Office of Geographic Information, Cambridge Water Department, Harvard Design and Mapping, and Boston Edison digital data, April 1998

Figure 21. Mean annual yields of total phosphorus from tributary subbasins in the Cambridge drinking-water source area, Massachusetts, water years 2013–15.

Concentration errors or bias can vary from sample to sample on the basis of the uniformity of the constituent concentrations throughout the stream and the method of sample collection. Typically, less error is associated with dissolved constituents that tend to be evenly distributed throughout the water column than with constituents, such as TP that tend to be associated with suspended sediment. Concentration error also can result during sample processing from contamination, non-uniform sample splitting, and sample degradation. Analytical method errors often vary with the concentration of the constituent: smaller concentrations near the detection level of the method are often less accurate than concentrations greater than the laboratory reporting level. Concentrations of major ions and TP measured in this study generally were greater than the laboratory reporting limits. As discussed previously, the accuracy and precision of constituent concentration data are measured on the basis of the accuracy of the collection of field blank and concurrent replicate samples.

Loads are calculated from streamflow and concentration data. Therefore, the accuracy of streamflow records affects the accuracy of load estimates. The USGS rates the accuracy of streamflow records on the basis of the performance of the water-level recorder, the accuracy and range of discharge measurements, and the stability of the stage-discharge relation at a given station. Accuracy ratings assigned to streamflow records may vary over time or range of flow and indicate the difference between the computed and true values of discharge (Kennedy, 1983). For example, a USGS rating of “good” indicates that 95 percent of the daily streamflow values are within 5 to 10 percent of the true values. In general, most continuous records of streamflow collected in the drinking-water source area have mean errors at the 95-percent confidence limit of ± 5 to 10 percent (U.S. Geological Survey, 2009).

The relative accuracy of load data, as reported in table 11, is inclusive of available quality-control data. The mean-square-error propagation method (Harmel and others, 2006) was used to estimate the 95-percent confidence interval of the load estimates. This method treats potential errors as bidirectional as opposed to additive. It combines all available estimates of error for streamflow, sample precision, and estimates of constituent population means or regression estimates to produce realistic estimates of overall error. In some cases, the error for TP was not normally distributed around the load estimate but was asymmetrical and skewed to the positive side as a result of the statistics of the available concentration data. Loads of major ions estimated from continuous records of flow and specific conductance were more accurate than loads of TP estimated using the stratified approach because the accuracy of the relation of the concentrations of major ions to measured specific conductance was better than the variance about the mean concentration data for each station.

Chloride and Sodium Trends

Intermittent measurements of Cl and Na concentrations over the last few decades indicate that the respective concentrations in water from the Cambridge Reservoir have increased. Daily mean values for specific conductance and concentrations of Cl in samples collected from water released from the Cambridge Reservoir increased from about 500 $\mu\text{S}/\text{cm}$ and 129 mg/L (median sample concentration), respectively, in water year 1998 to more than 800 $\mu\text{S}/\text{cm}$ and 210 mg/L (estimated concentration), respectively, in water year 2002 (Smith, 2013; Waldron and Bent, 2001). During water year 2008, the specific conductance and concentration of Cl increased briefly to nearly 1,800 $\mu\text{S}/\text{cm}$ and 504 mg/L, respectively. Daily mean values for specific conductance and concentrations of Cl in samples varied widely since water year 2008 but remain elevated compared to the respective values from water year 1998 (fig. 22). Daily mean values for specific conductance and median concentrations of Cl in samples were nearly 900 $\mu\text{S}/\text{cm}$ and 245 mg/L, respectively, in water year 2015 (fig. 22). The mean concentration of Na in water released from the Cambridge Reservoir during 1967–83 was about 43 mg/L (Geotechnical Engineers, Inc., 1985). The mean concentration of Na in water released from the Cambridge Reservoir in 1985 was 51 mg/L (Geotechnical Engineers, Inc., 1985). The median Na concentration in samples collected at the outlet of the reservoir during 1997–98 was 64 mg/L (Waldron and Bent, 2001). The median Na concentration in samples collected at the outlet of the reservoir during 2005–7 was 90 mg/L (Smith, 2013), and the median Na concentration in samples collected at the outlet of the reservoir during 2015 was 140 mg/L. From water year 1999 to water year 2008, annual mean concentrations of Na in water released from the Cambridge Reservoir were estimated from records of streamflow and specific conductance and ranged from 62 to 135 mg/L (Smith, 2013). In this study, annual mean concentrations for Cl and Na for Hobbs Brook (USGS station 01104430) ranged from 167 and 87 mg/L, respectively, in water year 2010 to 245 and 135 mg/L, respectively, in water year 2015 (table 8). Annual mean concentrations for Cl and Na varied by as much as 20 percent from water year to water year during this study.

During dry years, annual mean concentrations of Cl and Na are likely to increase, assuming that natural and anthropogenic inputs of the constituents are similar from year to year. In contrast, concentrations tend to decrease during wet years under the same circumstances. Therefore, flow-weighted time trends for annual mean concentrations of Cl and Na, which are more resistant to shifts in streamflow related to differences in annual precipitation than are concentrations alone, were investigated for the 17-year period of water years 1998–2015 at USGS stations 01104430 at the outlet of the Cambridge Reservoir and 01104460 on Stony Brook upstream from Stony

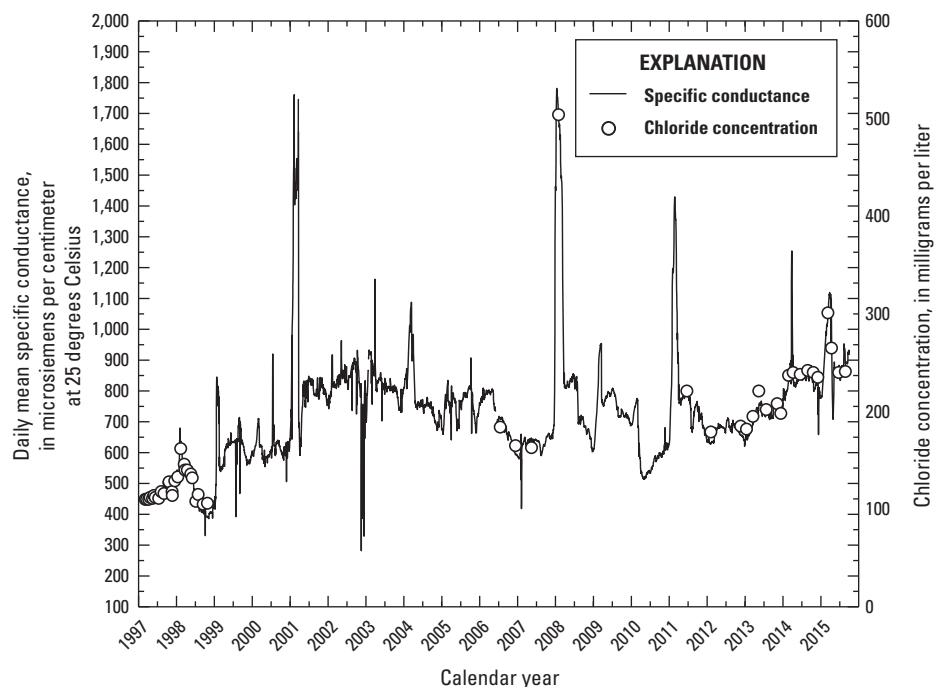


Figure 22. Daily mean specific conductance values and chloride concentrations in water samples collected at U.S. Geological Survey continuous water-quality monitoring station 01104430 below the Cambridge Reservoir, in the Cambridge drinking-water source area, Massachusetts, water years 1998–2015.

Brook Reservoir. The Mann-Kendall test between annual mean concentration data and annual mean streamflow data was used to test for trends in Cl and Na. Although upward trends in Cl and Na seem apparent from historical sample data collected from the outlet of the Cambridge Reservoir, results of Mann-Kendall tests on annual mean concentrations and annual mean streamflow for water years 1998–2015 indicate that a trend for either constituent was not significant with 95-percent confidence (p -value 0.096 for each constituent). Results for similar Mann-Kendall tests on annual mean concentrations of Cl and Na for the same period at USGS station 01104460, the other long-term station, also were not significant (p -value 0.743 and 1.00, respectively). The results of the tests indicate that trends for mean annual Cl and Na concentrations at each station were neither upward nor downward during the test period.

Comparison of Total Phosphorus Concentrations

A trend analysis was not performed for TP because concentrations for discrete and composite samples were available only for specific water years within the period of record (water years 1998–2015). However, sample data were statistically analyzed to determine whether concentrations of TP in samples collected during water years 2005–7 differ significantly from concentrations in samples collected for this study during base-flow and stormflow conditions at three

USGS stations. The distribution of TP concentrations in base flow was greater at each of three stations for water years 2013–15 than for water years 2005–7 (fig. 23). In contrast, the distribution of concentrations of TP in stormflow composite samples was similar for each period (fig. 23). Concentrations of TP in base flows during water years 2013–15 were significantly higher than during water years 2005–7, based on Mann-Whitney test results (table 12). Results of the Mann-Whitney tests between TP concentrations in stormflow composite samples collected during water years 2005–7 and 2013–15, however, were not significant for any station. The significant increase in base-flow concentrations of TP for USGS station 01104455 is likely related to the subsequent effects from the installation of the structural source control upstream from the station, as previously discussed. The small increase in the median base-flow concentrations of TP at USGS stations 01104415 and 01104475 during water years 2013–15 and significant test results between water years 2005–7 and 2013–15 cannot be explained with available information. Test results indicate that TP concentrations in stormflow composite samples collected during either period were not significantly different. This is particularly important because it indicates that the structural source control upstream from USGS station 01104455 did not reduce concentrations of TP in runoff. In part, the preliminary effectiveness of the structure may have been affected by additional suspended sediment entering stormflows from shoreline bank erosion around the wet ponds prior to establishment of permanent vegetation (fig. 10C).

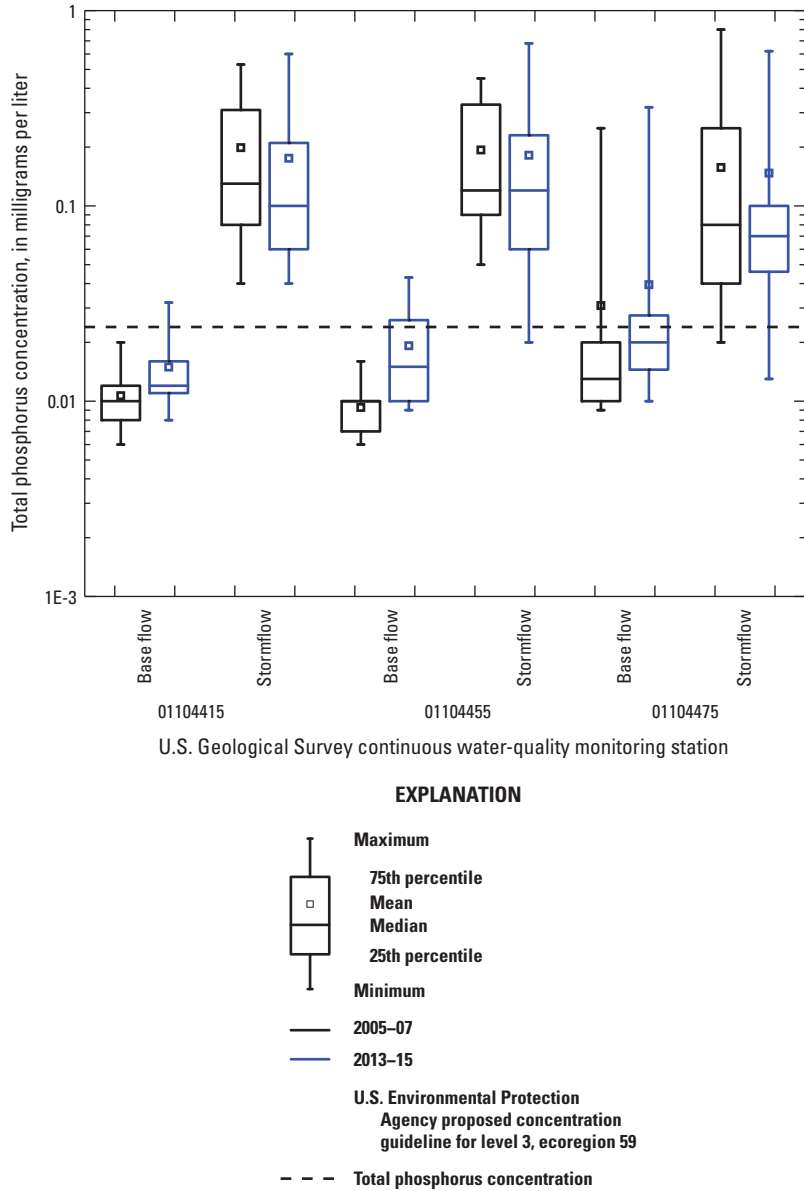


Figure 23. Distributions of concentrations of total phosphorus in base-flow and stormflow samples from three U.S. Geological Survey continuous water-quality monitoring stations in the Cambridge drinking-water source area, Massachusetts, water years 2005–7 and 2013–15. From U.S. Environmental Protection Agency, 2000.

Table 12. Attained significance levels (*p*-values) from Mann-Whitney tests for paired sample sets of total phosphorus concentrations collected during base-flow and stormflow conditions at three U.S. Geological Survey continuous water-quality monitoring stations in the Cambridge drinking-water source area, Massachusetts, water years 2005–7 and 2013–15.

[Locations of stations are shown in figure 1. Shaded areas indicate values that are significant at a 95-percent confidence interval. USGS, U.S. Geological Survey; mg/L, milligram per liter; <, less than]

USGS station number	Flow component	Number of samples (2005–07)	Number of samples (2013–15)	Median concentration, 2005–07 (mg/L)	Median concentration, 2013–15 (mg/L)	<i>p</i> value
01104415	Base flow	15	20	0.010	0.012	0.023
01104415	Stormflow	15	15	0.130	0.100	0.395
01104455	Base flow	15	21	0.010	0.012	<0.001
01104455	Stormflow	15	23	0.120	0.120	0.411
01104475	Base flow	14	22	0.013	0.020	0.023
01104475	Stormflow	15	15	0.080	0.070	0.662

Summary

The City of Cambridge, Massachusetts, Water Department (CWD) obtains its raw water primarily from reservoirs outside the city in parts of the towns of Lexington, Lincoln, and Weston and the city of Waltham. The Cambridge drinking-water source area encompasses major transportation corridors, as well as large areas of light industrial, commercial, and residential land use; as a result, the drinking-water source area is potentially at risk from a variety of contaminants. Continuous-monitoring data—specific conductance, water temperature, and streamflow—collected by the U.S. Geological Survey (USGS) since water year 1998 and data from water samples collected during base flow and stormflow during water years 2009–15 were used to identify current water-quality conditions, estimate loads and yields, and where sufficient data are available, describe trends in stream-water quality. These data strengthen an existing baseline for future comparisons and provide information that can be used to guide future watershed management.

In this study by the USGS, in cooperation with the CWD, concentrations of dissolved calcium (Ca), chloride (Cl), magnesium (Mg), sodium (Na), potassium (K), and sulfate (SO₄) in samples collected from 2009 to 2015 from the tributaries throughout the drinking-water source area varied widely, particularly in the small subbasins where the effects of stormflow and the percentages of constructed impervious area are greater than in the less developed subbasins. Median concentrations of Ca, Cl, Mg, Na, K, and SO₄ for samples collected in the Cambridge Reservoir Basin were 27.2, 273, 4.7, 154.5, 2.8, and 10.7 mg/L milligrams per liter (mg/L), respectively; in contrast, median concentrations for samples from

the tributaries in the Stony Brook Reservoir Basin were lower (except for SO₄) at 22.2, 128, 4.3, 77.1, 2.5, and 18.0 mg/L, respectively. Concentrations of SO₄ in samples collected at the USGS continuous water-quality monitoring station (hereafter referred to as station) 01104455 in the Stony Brook Reservoir Basin were substantially higher than those in samples from any of the other tributary subbasins.

For samples collected from 2009–2015, median concentrations of Cl and Na were 236 and 124 mg/L, respectively, for samples collected from the outlet of the Cambridge Reservoir in Hobbs Brook at USGS station 01104430 but were lower at 80.7 and 40.4 mg/L, respectively, in samples collected in the upper Stony Brook Reservoir Basin above the confluence with Hobbs Brook at USGS station 01104370 in an area that is less developed. Median concentrations of Cl and Na in samples collected in the lower Stony Brook Reservoir Basin and below the confluence of Stony Brook and Hobbs Brook at USGS station 01104460 were 140 and 73.9 mg/L, respectively. Flow-weighted daily mean concentrations of Ca, Cl, Mg, Na, and SO₄ were negatively correlated with daily mean streamflow. As a result, the concentrations of major ions, as well as specific conductance, in tributaries tend to increase during the summer when streamflow is low and decrease during high base-flow conditions and stormflows. This pattern indicates that groundwater is an important pathway for many major ions that may have originated from the application of deicing compounds that infiltrated to groundwater along roadways, parking lots, or in various structural source controls.

Concentrations of Cl and Na in samples collected from tributary base flows often were greater than the U.S. Environmental Protection Agency (EPA) secondary drinking-water regulation (SDWR) for Cl and the Massachusetts Department

of Environmental Protection, drinking-water guideline for Na. About 42 and 38 percent of concentrations of Cl in water samples collected in the drinking-water source area during 2009–15 exceeded the EPA criterion continuous concentration (CCC) and SDWR standards, respectively. The EPA criterion maximum concentration (CMC) also was exceeded in 21 samples collected from USGS stations 01104415, 01104420, and 01104455 where the maximum concentrations of Cl ranged from 860 to 11,500 mg/L. In addition to concentrations of Cl in periodic samples, flow-weighted daily mean concentrations of Cl estimated from continuous records of specific conductance exceeded the EPA CCC and SDWR for Cl at all stations, but the EPA CCC and SDWR were most frequently exceeded at USGS stations 01104410, 01104415, 01104420, and 01104455. The subbasin upstream from USGS station 01104410 likely continued to be affected by prior groundwater contamination from a previously uncovered salt storage depot, whereas salt in runoff from highways (Interstate 95 and other State routes) and other constructed impervious areas adjacent to USGS stations 01104415, 01104420, and 01104455 likely affected the water quality of the tributaries. The EPA CCC for Cl was exceeded at these stations for as many as 300 days each water year, and the EPA CMC standard was exceeded for as many as 50 days each water year. Flow-weighted daily mean concentrations for Cl rarely exceeded the SDWR and CCC thresholds for Cl at USGS stations 01104370, 01104405, 01104453, and 01104475. The subbasins upstream from these stations had relatively higher percentages of forested and residential areas and lower percentages of constructed impervious areas than the subbasins of tributaries adjacent to Interstate 95. Samples from Stony Brook (USGS station 01104460), which receives a mixture of water from the Cambridge Reservoir and the less developed areas of the upper Stony Brook Reservoir Basin, rarely exceeded the SDWR and CCC thresholds for Cl.

The median concentration of total phosphorus (TP) in samples collected from the tributaries in the Cambridge Reservoir Basin (0.03 mg/L) was similar to the median concentration in samples collected from tributaries in the less developed Stony Brook Reservoir Basin (0.02 mg/L). Concentrations for TP were typically low (less than 0.02 mg/L) in most samples of base flow and in samples collected at the outlet of the Cambridge Reservoir. Concentrations of TP in base flow at USGS station 01104455 increased from about 0.01 mg/L prior to water year 2012 to 0.02–0.04 mg/L (during the warm months) after a structural source control was installed upstream to reduce concentrations of suspended sediment and sediment associated constituents, and to contain hazardous spills. The distribution of concentrations of TP in composite samples of stormflow varied widely (0.01–0.69 mg/L) in comparison to concentrations in discrete base-flow samples. Test results for the comparison of concentrations of TP in composite samples of stormflow to concentrations in samples of base flow indicated significant differences at each station. Most concentrations of TP in samples collected during base-flow conditions were near or below the EPA proposed reference concentration of 0.024 mg/L for level 3, ecoregion 59. In

contrast, nearly all composite samples of stormflow exceeded the reference concentration.

Annual loads and yields for Ca, Cl, Mg, Na, and SO₄ were estimated for 10 USGS stations using continuous records of streamflow and specific conductance and the relation between ion concentration and specific conductance. These estimates represent a dataset that encompasses all base-flow conditions and runoff events, including snowmelts. Mean annual loads of Ca, Cl, Mg, Na, and SO₄ to the Stony Brook Reservoir, which represents 96 percent of the drinking-water source area, for water years 2009–15, were estimated to be 788, 4,440, 2,390, 1,070, and 2,880 metric tons (t), respectively, on the basis of continuous records of specific conductance. Mean annual yields for Ca, Cl, Mg, Na, and SO₄ to the Stony Brook Reservoir were 13, 75, 40, 2.6, and 6.9 metric tons per square kilometer (t/km²), respectively, for water years 2009 to 2015. Mean annual yields of major ions at USGS stations 01104410, 01104415, and 01104420 in the smaller Cambridge Reservoir Basin and at USGS station 01104455 in the Stony Brook Reservoir Basin were 60 to 240 percent higher than the mean annual yields of Ca, Cl, Mg, Na, and SO₄ for the drinking-water source area or the combined area upstream from the Stony Brook Reservoir.

Annual loads and yields of TP were estimated using a stratified flow approach and a measure of the central tendency of the sample set for each station. Mean annual loads of TP ranged from 0.005 to 0.70 t at the 10 stations in the drinking-water supply area during water years 2013–15. The mean annual load for TP to the Stony Brook Reservoir was 0.73 t. The difference between loads of TP to the larger Cambridge Reservoir and estimated loads of TP downstream from the reservoir at USGS station 01104430 indicates that the reservoir continues to trap about two-thirds of the phosphorus entering the reservoir. The transport of TP was mainly associated with stormflow that accounted for between 57 and 92 percent of the annual load at each station on the small tributaries. The estimated mean annual yield of TP for the Cambridge drinking-water supply area during water years 2013–15 was 0.012 t/km², and mean annual yields for individual stations ranged from 0.005 to 0.051 t/km². Mean annual yields for TP tended to be lower at the stations with larger subbasin areas or subbasins with large percentages of wetland than at stations with subbasin areas that have a large percentage of constructed impervious area. At three USGS stations, loads of TP estimated for water years 2013–15 were about 50 percent lower than loads previously estimated for water years 2005–7. The reduction in loads is attributed to lower annual mean streamflow during the recent period where the load of TP associated with base flow and stormflow decreased at each station. At USGS station 01104455, the mass of TP associated with base flow was about 70 percent higher for water years 2013–15 than for water years 2005–7 despite lower streamflows.

Median concentrations of Cl and Na in samples from Hobbs Brook (USGS station 01104430; the outlet of the Cambridge Reservoir) increased from 129 and 64 mg/L, respectively, in 1998, to 245 and 140 mg/L, respectively,

in water year 2015. In the current study period of 2009–15, estimated annual mean concentrations for Cl and Na for Hobbs Brook were lowest in water year 2010 (167 and 87 mg/L, respectively) and highest in water year 2015 (245 and 135 mg/L, respectively) but varied by as much as 20 percent each year. Trends in annual concentrations for Cl and Na at Hobbs Brook (USGS station 01104430; the outlet of the Cambridge Reservoir) and Stony Brook (USGS station 01104460) from 1998 to 2015 were not significant, based on Mann-Kendall tests.

Median concentrations of TP in base-flow samples collected at three stations (USGS stations 01104415, 01104455, and 01104475) were slightly greater (less than 0.01 mg/L) during water years 2013–15 than during the prior sampling period in water years 2005–7. Mann-Whitney test results for concentrations of TP for each period were significant for each station. The significant increase in concentrations of TP in base flow for USGS station 01104455 is likely related to algae or colloidal material containing phosphorus from the structural source control installed upstream from the station during this study. The small but significant increase in the median concentrations of TP in base flow during water years 2013–15 compared to 2005–7 at stations 01104415 and 01104475 cannot be explained with available information. Results were not significant for any station for similar tests between concentrations of TP in flow-weighted composite samples collected during storms for the same periods. This includes results for USGS station 01104455 that is downstream from the structural source control, which was in place during 2013–15, indicating that the structural source control did not reduce concentrations of TP in runoff. Concentrations of TP in composite samples collected at this station after the installation of the structural source control may have been affected by the addition of suspended sediment, often associated with phosphorus, entering stormflows from shoreline bank erosion around the wet ponds prior to establishment of permanent vegetation.

Data-collection activities in the drinking-water source area are important for effective management and protection of the drinking-water supply. These water-quality data enhance the understanding of the physical, chemical, and biological state of the water supply. Without accurate information on the past and current condition of the water supply, effective preservation and remediation programs cannot be implemented or evaluated. The data presented in this report represent the quality of water throughout the drinking-water source area with a focus on the base-flow and stormflow conditions of four tributaries and the primary stream to the Stony Brook Reservoir for water years 2013–15. The water-quality data indicate the importance of an integrated sampling strategy for accurate assessments of many constituents. Load and yield data estimated as part of this study may serve as benchmarks for future comparisons.

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