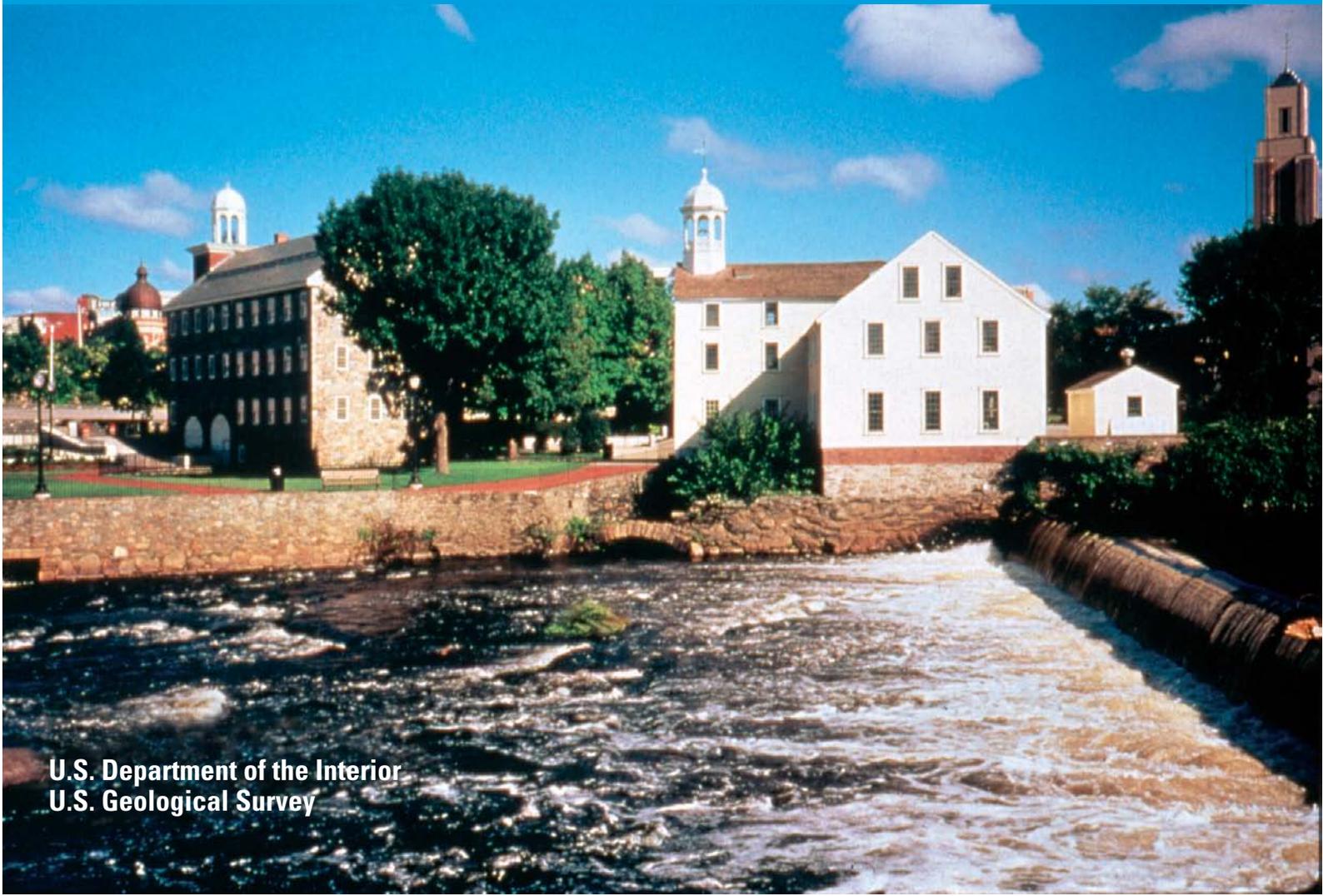




NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Water-Quality Trends in New England Rivers During the 20th Century

Water-Resources Investigations Report 03-4012



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

Cover photograph shows the Blackstone River and Slater Mill in Pawtucket, R.I. (Photograph reprinted from John H. Chafee Blackstone River National Heritage Corridor, National Park Service, and published with permission)

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By Keith W. Robinson, Jean P. Campbell, *and* Norbert A. Jaworski

U.S. GEOLOGICAL SURVEY

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U.S. DEPARTMENT OF THE INTERIOR

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FOREWORD

The U.S. Geological Survey (USGS) is committed to serve the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life, and facilitates effective management of water, biological, energy, and mineral resources. (<http://www.usgs.gov/>). Information on the quality of the Nation's water resources is of critical interest to the USGS because it is so integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and that is suitable for industry, irrigation, and habitat for fish and wildlife. Escalating population growth and increasing demands for the multiple water uses make water availability, now measured in terms of quantity *and* quality, even more critical to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. (<http://water.usgs.gov/nawqa/>). Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. NAWQA results can contribute to informed decisions that result in practical and effective water-resource management and strategies that protect and restore water quality.

Since 1991, the NAWQA Program has implemented interdisciplinary assessments in more than 50 of the Nation's most important river basins and aquifers, referred to as Study Units. (<http://water.usgs.gov/nawqa/nawqamap.html>). Collectively, these Study Units account for more than 60 percent of the overall water use and population served by public water supply, and are representative of the Nation's major hydrologic

landscapes, priority ecological resources, and agricultural, urban, and natural sources of contamination.

Each assessment is guided by a nationally consistent study design and methods of sampling and analysis. The assessments thereby build local knowledge about water-quality issues and trends in a particular stream or aquifer while providing an understanding of how and why water quality varies regionally and nationally. The consistent, multi-scale approach helps to determine if certain types of water-quality issues are isolated or pervasive, and allows direct comparisons of how human activities and natural processes affect water quality and ecological health in the Nation's diverse geographic and environmental settings. Comprehensive assessments on pesticides, nutrients, volatile organic compounds, trace metals, and aquatic ecology are developed at the national scale through comparative analysis of the Study-Unit findings.

(<http://water.usgs.gov/nawqa/natsyn.html>).

The USGS places high value on the communication and dissemination of credible, timely, and relevant science so that the most recent and available knowledge about water resources can be applied in management and policy decisions. We hope this NAWQA publication will provide you the needed insights and information to meet your needs, and thereby foster increased awareness and involvement in the protection and restoration of our Nation's waters.

The NAWQA Program recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The Program, therefore, depends extensively on the advice, cooperation, and information from other Federal, State, interstate, Tribal, and local agencies, non-government organizations, industry, academia, and other stakeholder groups. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch

Associate Director for Water

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CONVERSION FACTORS

Multiply	By	To obtain
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
square miles (mi ²)	12.590	square kilometers (km ²)
gallons (gal)	3.785	liter (L)
ton	0.9072	megagram (Mg)
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)

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

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ABSTRACT

Water-quality data from the Merrimack, Blackstone, and Connecticut Rivers in New England during parts of the 20th century were examined for trends in concentrations of sulfate, chloride, residue upon evaporation, nitrate, and total phosphorus. The concentrations of all five of these constituents show statistically significant trends during the century. Annual concentrations of sulfate and total phosphorus decreased during the second half of the century, whereas annual concentrations of nitrate, chloride, and residues increased throughout the century. In the Merrimack River, annual chloride concentrations increased by an order of magnitude. Annual nitrate concentrations also increased by an order of magnitude in the Merrimack and Connecticut Rivers. These changes in the water quality probably are related to changing human activities. Most notable is the relation between increasing use of road de-icing salts and chloride concentrations in rivers. In addition, changes in concentrations of nitrate and phosphorus probably are related to agricultural use of nitrogen and phosphorus fertilizers. For all the water-quality constituents assessed, concentrations were greatest in the Blackstone River. The Blackstone River Basin is smaller and more highly urbanized than the other basins studied. Data-collection programs that span multiple decades can provide valuable insight on the effects of changing human population and societal activities on the water quality of rivers. This study was done as part of the U.S. Geological Survey's National Water-Quality Assessment Program.

INTRODUCTION

The 20th century has been marked by major landscape and lifestyle changes in New England. The transition from an agricultural to an urban-based society began in the mid-19th century and continued through the 20th century. During this transition, automobile use increasingly dominated the way of life and settlement patterns. Older industries, such as paper and textile mills and agriculture, were replaced by service-oriented and high-technology industries. Human and industrial wastes that were routinely discharged untreated into waterways at the beginning of the century were eventually handled by wastewater-treatment facilities. These landscape and societal changes are likely to have affected the quality of New England rivers.

Forest clearing and agricultural expansion in New England began with European settlement and slowed in the mid-1800s (Foster, 1992). Reforestation then occurred in the region and has continued in many areas to the present (2003). The decline of agriculture was replaced by increases in mills and manufacturing industries in the major cities and along rivers. Rivers such as the Merrimack and Blackstone provided hydropower for the mills and other manufacturing industries ([figs. 1 and 2](#)). The construction of dams to provide mill power became so extensive that the Blackstone River, for example, had a dam present for almost every mile along its entire length (Shanahan, 1994). The change to an industrial society resulted in large population increases in urban areas. For example, the population of New Bedford, Mass., increased from about 27,000 in 1880, when there were 2 textile mills, to about 121,000 in 1920 when there were 31 mills (U.S. Environmental Protection Agency, 2001). During the 40 years from 1880 to 1920, New England's population almost doubled from 4.01 to 7.40 million people (U.S. Census Bureau, 2001).



Figure 1. The “Mile of Mills” along the Merrimack River in Lowell, Mass., in 1893 (Photograph reprinted from the Lowell National Historic Park and published with permission).



Figure 2. The confluence of the Concord and Merrimack Rivers in Lowell, Mass., in 2001 (Photograph by Britt Stock, U.S. Geological Survey).

Throughout the 20th century, New England’s population continued to increase. As of year 2000, 13.92 million residents lived in the six New England states; an increase of 149 percent from the 1900 population of 5.59 million people (U.S. Census Bureau, 2001). As in other areas of the United States, the introduction of the automobile and the subsequent building of roads and interstate highways in the 20th century led to the expansion of urban areas throughout New England. The expanding suburbs centered on the cities of Hartford, Conn., Providence R.I., and Boston, Mass. The growth of suburban areas also has been fueled by the building of new commercial and industrial facilities along major roadways. The number of vehicle miles traveled in the region almost doubled during the 25 years from 1970 to 1995, from 60 million miles (mi) to 110 million mi yearly (U.S. Environmental Protection Agency, 1996).

During the early to mid 20th century, rivers in New England were among the most polluted rivers in the United States because large amounts of untreated municipal and industrial sewage were released directly into surface waters. At the turn of the 20th century, outbreaks of typhoid fever and other infectious diseases were common in urban areas that used polluted rivers as a source of drinking water. As late as the mid-1960s, more than 120 million gallons per day (Mgal/d) of untreated or minimally treated wastewater were discharged into the Merrimack River (U.S. Department of the Interior, 1968). In the early 1970s, the

Connecticut River was so polluted it was referred to as a “landscaped sewer” (U.S. Environmental Protection Agency, 2000a). The passage of the Federal Water Pollution Control Act in 1972 resulted in significant improvements in wastewater treatment throughout New England. At the beginning of the 21st century, most routinely discharged wastewaters in New England were being treated by facilities that removed 80-95 percent of the organic loads (Peter Kudarauskas, U.S. Environmental Protection Agency, oral commun., 2002).

The resulting effects of societal changes during the 20th century on the quality of New England’s major rivers has been minimally explored. Roman and others (2000) described total nitrogen and total phosphorus loadings from riverine sources to coastal estuaries from 1900 to 1994 in the Northeastern United States. They reported that total nitrogen loadings increased steadily as a result of increasing use of nitrogen-based fertilizers and increased atmospheric deposition of nitrogen. Total phosphorus loadings to surface waters increased until the 1960s because of the use of phosphate-containing detergents, then decreased because of bans in the use of these detergents. Jaworski and Hetling (1996) presented water-quality trends for chloride, nitrate, and total residue concentrations in 12 rivers in the eastern United States during the 20th century. They found that concentrations of chloride, nitrate, and total residue increased during the century by a factor of 5.3, 4.7 and 1.6, respectively. Jaworski

and Hetling (1996) attributed the increasing total residue concentrations in the Blackstone River to municipal and industrial wastewater discharges. The small increases in total residue concentrations in the Connecticut River were probably related to reforestation of much of the basin (Jaworski and Hetling, 1996).

A number of studies have assessed water-quality changes in New England rivers over the last three decades of the 20th century. These studies were possible because of an increase in water-quality monitoring that began in the late 1960s and early 1970s. Several studies reported upward trends in specific conductance and dissolved chloride concentrations in rivers in Connecticut, Massachusetts, Rhode Island, and New Hampshire (Trench, 1996; Strause, 1993; Kulp and Bohr, 1993; Bell, 1993; and Toppin, 1993). Zimmerman (1997) and Trench (1996) found increasing nitrate and decreasing total phosphorus concentrations in many Connecticut rivers. No trends in nitrate were reported in Massachusetts, New Hampshire, Rhode Island, and Maine streams between 1980-89 (Strause, 1993; Bell, 1993; Olsen and Cowing, 1993; and Toppin, 1993). Total-dissolved-solids concentrations in these States during 1980-89 also showed little change. Trench (1996) reported increasing total-dissolved solids in many Connecticut Rivers from 1969-88. Smith and others (1987 and 1993) described water-quality trends Nationally for 1974-81 and 1980-89, respectively. They reported generally increasing dissolved-solid concentrations in streams throughout the country primarily as a result of increased use of de-icing salts on roads, increasing and decreasing nitrate concentrations as a result of changing agricultural fertilizer use patterns, and decreasing total phosphorus concentrations in streams from reductions in phosphorus fertilizer use and phosphate-detergent bans.

There have been no studies that describe water-quality changes in New England rivers from the beginning to the end of the 20th century. The U.S. Geological Survey (USGS) National Water-Quality Assessment Program has used a combination of historical and current data to characterize changing water-quality conditions in New England rivers during the 20th century. This information will be useful in assessing how modifications in society and our lifestyles are affecting the quality of the region's rivers.

Purpose and Scope

This report examines trends in water quality in three large New England rivers—the Merrimack, Blackstone, and Connecticut Rivers—during the 20th century ([fig. 3](#)). Analyses of changes in the concentrations of sulfate, chloride, residues, nitrate, and total phosphorus in the three rivers for parts of the 20th century are on the basis of the availability of historical and current water-quality data. Possible causes of the trends in concentrations of the five constituents ([table 1](#)) also are presented by examining information on changing human activities and environmental pollution-control measures during the century.

Acknowledgments

The authors acknowledge reviews of this report by Sarah Flanagan, Alisa Mast, Kenneth Toppin, and Debra Foster of the U.S. Geological Survey. Ann Marie Squillacci and Anita Cotton of the U.S. Geological Survey prepared the manuscript for publication.

DATA SOURCES AND METHODS OF ANALYSIS

The water-quality data used in this report for the Merrimack, Blackstone, and Connecticut Rivers are from 1900 to 1920 and from 1955 to 2000, and were collected in monitoring programs conducted by the State Department of Health of Massachusetts (DOH), the Massachusetts Department of Environmental Protection, formerly called the Massachusetts Department of Environmental Quality Engineering (DEQE), and the USGS ([table 2](#)). Few data are available for the period 1920 to 1955. Streamflow data for most of the 20th century from the USGS also were available for the analyses. Because the water-quality data are from nearly 100 years of monitoring efforts by several agencies, the data reflect changes in methods of sample collection and analysis and sampling location. Despite these changes, these data are comparable for the purpose of determining the relative change in concentration over time for the five constituents described in this report.

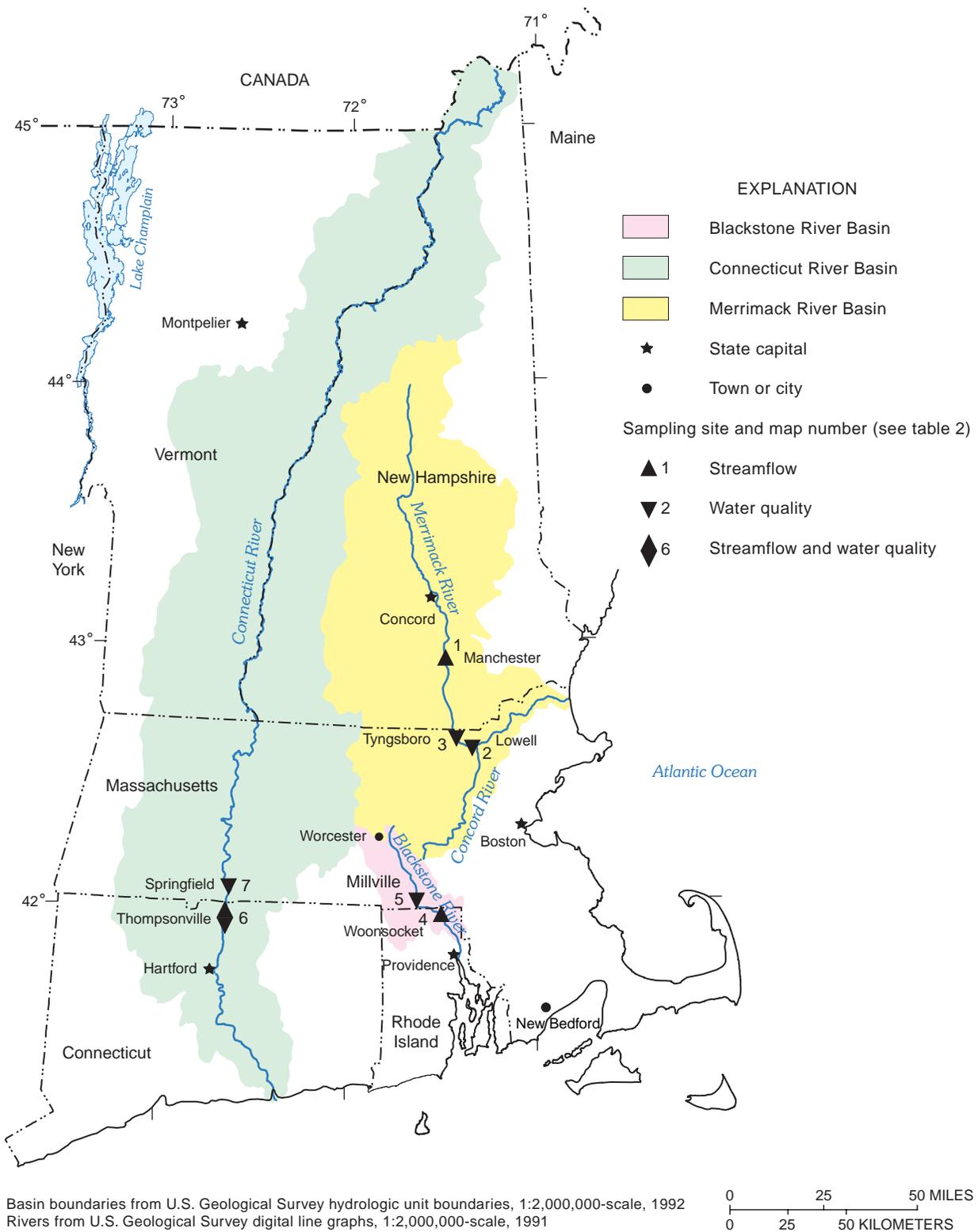


Figure 3. Location of the Merrimack, Blackstone, and Connecticut Rivers in New England, and streamflow and water-quality data sites used to assess changes in the 20th century.

Table 1. Anthropogenic sources of sulfate, chloride, residues, nitrate and phosphorus in rivers

[Data from Hem (1989)]

Sulfate	Chloride	Residues	Nitrate	Phosphorus
Combustion of fossil fuels, coal, and oil	Municipal and industrial wastewater	Municipal and industrial wastewater	Combustion of fossil fuels, coal, and oil	Detergents
Industrial processes (smelting)	Road salt	Soil erosion (construction, forestry, agricultural)	Failing septic systems	Failing septic systems
Municipal and industrial wastewater	Rock weathering	Urban runoff	Fertilizer (lawns and cropland)	Fertilizer (lawns and cropland)
Rock weathering		Rock weathering	Livestock waste	Livestock waste
			Municipal and industrial wastewater	Municipal and industrial wastewater
				Synthetic organic chemicals (insecticides)
				Rock weathering

Water-quality data were collected at more than one location on the three rivers during the 20th century (table 2). For the Merrimack River, the data represent samples collected from locations in and near Lowell, Mass., and at the confluence of the Concord River. Samples from the Blackstone River were collected in the area of Millville, Mass. Most data for the Connecticut River were from samples collected at Thompsonville, Conn. (fig. 4), although data from 1900-17 were from samples collected about 7 mi upstream from Thompsonville at a site downstream from Springfield, Mass. Collectively, the data for each river represent the most similar sampling locations over time and reduce location as a source of variability in these data.

The mean of all available concentration data for each year was determined for sulfate, chloride, residues, nitrate, and total phosphorus and are referred to as annual concentrations in this report. Typically, sampling frequencies were from 4 to 6 samples per year for DOH and DEQE data, and from 4 to 12 samples per year for USGS data. Samples generally were collected throughout the year and represent a variety of streamflow conditions that range from low to high flows. Water-quality data from 1900-17 were based on annual mean concentrations reported in the Third Annual Report of the DOH (State Department of Health of Massachusetts, 1918).

Concentration values less than the reporting limit, or censored data, were set equal to the reporting limit for purposes of computing a mean concentration. The resulting annual concentrations of the constituents determined by this method will be slightly greater than

if the mean concentration were determined using censored data set equal to half the reporting limit. Data were screened to eliminate concentration values that were either three times lower or higher than other concentrations from a similar time period.

The water-quality data analyzed for this report reflect a variety of sample-collection procedures and laboratory-analytical methods that were used throughout the 20th century. The accuracy and precision of the different methods were not compared, but the constituents being reported were verified to be consistent throughout the length of record. For example, the DOH reported chlorine data from 1900-17, whereas other agencies reported chloride. Chlorine and chloride are different terms for the same constituent. A comparison of analytical methods used by the USGS are discussed in Trench and Vecchia (2002), who summarized the effect of changing USGS analytical methods during 1968-98 on values of sulfate, chloride, and total phosphorus. Sulfate concentrations could be biased high before 1990, and total phosphorus could be biased low before 1991.

For some constituents, different analytes were used to generate a common constituent measure. Either total- or dissolved-nitrate values were used to calculate annual concentrations, depending on which of the two analyses had the largest number of samples in a given year. A comparison of USGS total and dissolved nitrate data from the same sample was performed using the Wilcoxon signed rank statistical method with the statistical software StatView (SAS Institute, Inc., 1999). This test indicated no difference between total and dissolved nitrate concentrations ($p = 0.59$);

Table 2. Sources of water-quality and streamflow data for the Merrimack, Blackstone, and Connecticut Rivers[USGS, U.S. Geological Survey; NWIS, National Water Inventory Systems, No., number. Site locations and map numbers are shown in [figure 1.](#)]

Constituent	Date	Collecting agency	Data source	Data collection		Map No.
				Site location	Station No.	
Merrimack River at Lowell, Massachusetts						
Streamflow	1937-99	USGS	NWIS	Manchester, N.H.	01092000	1
Sulfate	1967-69	USGS	NWIS	Lowell, Mass.	01096570	2
	1970-95	USGS	NWIS	above Lowell, Mass.	01096550	3
Chloride	1900-17	State Department of Health of Massachusetts	Third Annual Report ¹	above Lowell, Mass.	None	2
	1937	Massachusetts Department of Public Health	Report on Sources of Pollution Merrimack River Valley, Massachusetts ²	Tyngsboro, Mass.	Station #2	3
	1967-69	USGS	NWIS	Lowell, Mass.	01096570	2
	1970-95	USGS	NWIS	above Lowell, Mass.	01096550	3
Nitrate	1900-14	State Department of Health of Massachusetts	Third Annual Report ¹	above Lowell, Mass.	None	2
	1967-69	USGS	NWIS	Lowell, Mass.	01096570	2
	1970-80, 1985-95	USGS	NWIS	above Lowell, Mass.	01096550	3
	1981	Massachusetts Department of Environmental Quality Engineering	The Merrimack River 1981 ³	Rte. 113 bridge, Tyngsboro, Mass.	MR01	3
Phosphorus, total	1969-95	USGS	NWIS	above Lowell, Mass.	01096550	3
Blackstone River at Millville, Massachusetts						
Streamflow	1930-99	USGS	NWIS	Woonsocket, R.I.	01112500	4
Sulfate	1973, 1978-2000	USGS	NWIS	Millville, Mass.	01111230	5
Chloride	1900-17	State Department of Health of Massachusetts	Third Annual Report ¹	Millville, Mass.	None	5
	1971, 1973, 1978-2000	USGS	NWIS	Millville, Mass.	01111230	5
	1977	Massachusetts Department of Environmental Quality Engineering	Blackstone River 1977 ⁴	Millville, Mass.	BS18	5
Residues, total	1900-17	State Department of Health of Massachusetts	Third Annual Report ¹	Millville, Mass.	None	5
	1970	Massachusetts Department of Environmental Quality Engineering	Blackstone River Study 1970 ⁵	Railroad Bridge, Millville, Mass.	BS20	5
	1977	Massachusetts Department of Environmental Quality Engineering	Blackstone River 1977 ⁴	Millville, Mass.	BS18	5
	1978-2000	USGS	NWIS	Millville, Mass.	01111230	5
Nitrate	1900-14	State Department of Health of Massachusetts	Third Annual Report ¹	Millville, Mass.	None	5
	1971, 1973, 1978-2000	USGS	NWIS	Millville, Mass.	01111230	5

Table 2. Sources of water-quality and streamflow data for the Merrimack, Blackstone, and Connecticut Rivers--Continued

[USGS, U.S. Geological Survey; NWIS, National Water Inventory Systems, No., number. Site locations and map numbers are shown in [figure 1](#).]

Constituent	Date	Collecting agency	Data source	Data collection		Map No.
				Site location	Station No.	
Blackstone River at Millville, Massachusetts--Continued						
Phosphorus, total	1973, 1978-2000	USGS	NWIS	Millville, Mass.	01111230	5
	1977	Massachusetts Department of Environmental Quality Engineering	Blackstone River 1977 ⁴	Millville, Mass.	BS18	5
Connecticut River at Thompsonville, Connecticut						
Streamflow	1929-99	USGS	NWIS	Thompsonville, Conn.	01184000	6
Sulfate	1952-56, 1966-2000	USGS	NWIS	Thompsonville, Conn.	01184000	6
Chloride	1900-17	State Department of Health of Massachusetts	Third Annual Report ¹	below Springfield, Mass.	None	7
	1952-56, 1966-2000	USGS	NWIS	Thompsonville, Conn.	01184000	6
Residues, total	1900-04, 1906-17	State Department of Health of Massachusetts	Third Annual Report ¹	below Springfield, Mass.	None	7
	1969, 1974-2000	USGS	NWIS	Thompsonville, Conn.	01184000	6
Nitrate	1900-04, 1906-14	State Department of Health of Massachusetts	Third Annual Report ¹	below Springfield, Mass.	None	7
	1952-56, 1966-74, 1980-2000	USGS	NWIS	Thompsonville, Conn.	01184000	6
Phosphorus, total	1966-2000	USGS	NWIS	Thompsonville, Conn.	01184000	6

¹State Department of Health of Massachusetts, 1918.

²Massachusetts Department of Public Health, 1938.

³Massachusetts Department of Environmental Quality Engineering, 1982.

⁴Massachusetts Department of Environmental Quality Engineering, 1978.

⁵Massachusetts Department of Environmental Quality Engineering, 1971.



Figure 4. The Connecticut River at Thompsonville, Conn., 2002 (Photograph by Karen Beaulieu, U.S. Geological Survey).

therefore, total and dissolved nitrate concentrations were used together to evaluate trends. For several samples, the USGS reported dissolved-nitrate concentrations “as nitrate.” These concentrations were converted to dissolved nitrate as “nitrogen,” by multiplying the “as nitrate” values by a correction factor (0.226) based on the atomic weight of nitrogen and oxygen. Total-phosphate concentrations analyzed by the USGS were converted to total phosphorus by multiplying the total-phosphate values by a correction factor (0.326) based on the atomic weight of phosphorus and oxygen.

The DOH reported total residues on evaporation, and the DEQE reported either total residues or total solids; all of these analyses measure the weight of material left in a vessel after evaporation. For the Blackstone and Connecticut Rivers, the total residues concentrations from 1900-17 were used with total-solids concentrations collected by the USGS from 1970 to 2000. For the Merrimack River, the early total-residues concentrations were available along with dissolved-solids, and to a lesser amount, total-solids concentrations from the USGS in the later years of the 20th century. Because the dissolved concentrations are statistically less than total concentrations based on the results of the Wilcoxon signed rank test ($p < 0.001$), the two data sets could not be combined to create a complete data set for 1970-2000. As a result, residues or solids data were not analyzed for trends at the Merrimack River. Both total residues and total solids are referred to as residues.

Annual-mean streamflow data were examined for temporal trends to assess the potential effects of discharge on chemical constituent concentrations. Annual-mean streamflow is presented in cubic foot per second (ft³/s) in this report. The USGS stream-gaging stations used to determine annual streamflow for each water-quality site are listed in [table 2](#). Estimates of streamflow were made for the Merrimack River at Lowell, Mass., and the Blackstone River at Millville, Mass., because continuous streamflow data were not available directly at the water-quality-sampling sites. For the Merrimack River water-quality site, the nearest continuous-record stream-gaging station with long-term streamflow data is the Merrimack River near Goffs Falls, below Manchester, N.H. ([fig. 3](#)). A correction factor based on the difference in drainage areas between the water-quality sampling site and stream-gaging station was applied to the annual-mean streamflow from the Goffs

Falls station. Estimated streamflow at the Lowell sampling site, about 17 mi downstream from the Goffs Falls station, is about 128 percent greater than the streamflow at Goffs Falls. For the Blackstone River at Millville, Mass., the nearest stream-gaging station with long-term streamflow data is the Blackstone River at Woonsocket, R.I. ([fig. 3](#)). A correction factor based on the difference in drainage areas between the water-sampling site and the stream-gaging station was applied to the annual-mean streamflow from the Woonsocket station. Estimated streamflow at the Millville site, about 6.0 mi upstream from the Woonsocket station, is about 67 percent less than the streamflow at Woonsocket.

Changes in annual concentration over time at the Merrimack, Blackstone, and Connecticut Rivers were plotted on scatter plots. The relation of annual concentration to time was demonstrated with a locally weighted scatter plot (LOWESS) smoothed line that shows a general trend. The LOWESS smoothed line was generated using the statistical computer software S-PLUS (MathSoft, 1999). The relation of streamflow to time was determined by use of linear regression. Trends in discharge and water-quality constituents were assessed with Kendall’s tau using S-PLUS software (MathSoft, 1999). Kendall’s tau computes the significance level of the trend based on ranks of the data and not the values themselves. A significance level (p -value) greater than 0.05 indicates that the trend observed is not statistically significant. Tau ranges from -1 to +1 and shows the strength of an upward trend (positive value) or a downward trend (negative value).

The magnitude of change in annual concentrations of the constituents was determined by calculating the difference (as a percentage) in the mean-annual concentration for one time period to the mean-annual concentration for a second time period. Data for each constituent was divided into two time periods. For chloride, residues, and nitrate, the two time periods were the first two decades of the 20th century and last four to five decades of the century. For sulfate and total phosphorus, the period of water-quality records was split into roughly two equal time periods.

Finally, annual concentrations of chloride, nitrate, and total phosphorus were compared to ambient water-quality criteria for the protection of aquatic life or human health. No such criteria have been established for sulfate and residues.

DESCRIPTION OF THE MERRIMACK, BLACKSTONE, AND CONNECTICUT RIVERS

The Merrimack, Blackstone, and Connecticut Rivers have drainage areas at their mouths of 5,010, 480, and 11,260 mi², respectively. The Connecticut River is the largest river in New England. The Merrimack and Connecticut Rivers originate in forested and mountainous lands in north-central New England and flow southward through heavily populated urban centers before discharging into coastal waters. The Blackstone River originates in central Massachusetts and flows south through a primarily urban watershed to the Narragansett Bay in Rhode Island.

The drainage areas for the Merrimack River at Lowell, Mass., Blackstone River at Millville, Mass., and the Connecticut River at Thompsonville, Conn., where water-quality data were collected, have drainage areas of 3,950, 277, and 9,660 mi², respectively. The percentage of the drainage area classified as urban land in the Blackstone River Basin upstream of the water-quality-monitoring site is three to five times greater than that found in the Merrimack and Connecticut River Basins (table 3).

The Merrimack, Blackstone, and Connecticut Rivers were a focal point for human settlement and industrial development and played an important role in the development and expansion of the industrial revolution in the early and mid-1800s by serving as a source of waterpower for many mills and factories present along their waterways. The Blackstone River valley has been described as the birthplace of the American Industrial Revolution and was home to the

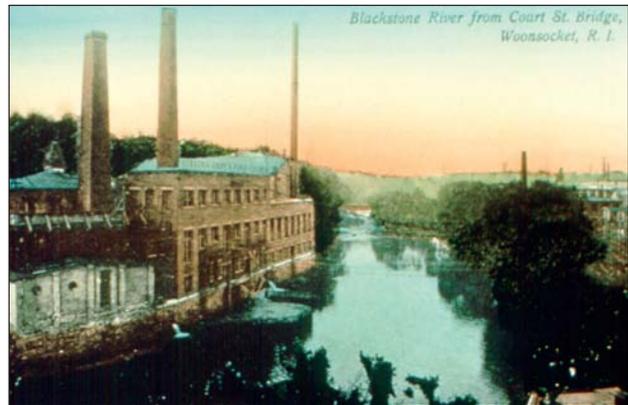


Figure 5. Historic mills in the early years of the 20th century along the Blackstone River, Woonsocket, R.I. (Photograph reprinted from the John H. Chafee Blackstone River National Heritage Corridor, National Park Service and published with permission).

first textile mill built in the United States. The mills, factories, and cities released large amounts of untreated wastewater to the rivers (fig. 5). Shanahan (1994) describes the history of industrial development and population growth in the Blackstone River Basin and its resultant effects on water quality in the river. Untreated wastes from pulp and paper and textile mills had detrimental effects on the quality of the Merrimack River from the 19th century to the late-1960s (U.S. Department of Interior, 1968). Because of disease outbreaks and water-quality problems in the Connecticut River and other waterbodies, the Connecticut State Supreme Court in 1900 ruled that the release of noxious substances to the State’s rivers were not permitted if the substances were harmful to downstream users (Symons, 2001).

Table 3. Land-use characteristics, population estimates, and municipal wastewater discharge yields in the Merrimack, Blackstone, and Connecticut Rivers Basins (Sources: Land-use data from Vogelmann and others, 2001; Population data from U.S. Census decennial files; Municipal wastewater discharge data from Medalie, 1996)

[Mgal/d, million gallons per day; mi², square mile]

River basin	Data for					
	Urban (percent of basin)	Forests (percent of basin)	Agriculture (percent of basin)	1990 population	1990 population density (people/mi ²)	Municipal wastewater discharge yields (Mgal/d/mi ²)
Merrimack at Lowell, Mass. (above Concord River)	7	76	7	813,000	197	0.08
Blackstone at Millville, Mass.	21	58	6	268,000	1,020	.35
Connecticut at Thompsonville, Conn.	4	80	8	1,093,000	113	.18

Flows in all three rivers are regulated by numerous dams that were built for power generation, flood control, and recreational purposes. Streamflow data during the length of record for the three rivers ([fig. 6](#)) show much year-to-year variation in the mean-annual flows, but only the Blackstone River had a significant increase in annual-mean flows during 1930-99. The cause(s) of this trend is not known, but may be a result of reduced water consumption by industries, changes in flow regulation, and increased impervious surface area in the basin. The increased flows could also be contributing greater amounts of dissolved and suspended materials to the river or resulting in the dilution of some constituents, and may be contributing to changes in water quality during the 20th century. In the Merrimack and Connecticut Rivers, the lack of changes in annual-mean river flows indicates that water-quality changes are more likely a result of factors other than changing river flow.

CHANGES IN THE WATER QUALITY OF THE MERRIMACK, BLACKSTONE, AND CONNECTICUT RIVERS DURING THE 20TH CENTURY

Statistical analysis of annual concentrations of chloride, residues, and nitrate indicated upward trends in all three rivers ($\alpha \leq 0.05$) ([table 4](#)). Total phosphorus decreased in the three rivers, whereas sulfate decreased in the Connecticut and Merrimack Rivers. Residues increased in the Blackstone and Connecticut Rivers. For all the constituents analyzed in this report, annual concentrations in the Blackstone River are typically twice the annual concentrations in the Merrimack and Connecticut Rivers. This is likely the result of greater densities of population, wastewater discharges, and urban land use in the Blackstone River Basin compared to the Merrimack and Connecticut Rivers Basins ([table 3](#)).

The following sections describe the magnitude of change in annual concentrations of sulfate, chloride, residues, nitrate, and total phosphorus in the Merrimack, Blackstone, and Connecticut Rivers in the 20th century. Ancillary data and literature information that characterize changes in the potential sources of these constituents in water are used to help identify potential causes for the observed water-quality changes.

Sulfate

Sulfate data were available for only the second half of the 20th century for the three rivers studied. The Connecticut River has the longest length of record, from 1952 to 1956, and from 1966 to 2000 ([table 2](#)). Although all three rivers show a decrease in annual sulfate concentrations between 1950 and 2000 ([fig. 7](#)), the decrease in the Blackstone River is not statistically significant ($p = 0.26$) ([table 4](#)). The largest decreases occurred in the Connecticut River. The mean-annual sulfate concentrations (1) in the Connecticut River decreased by 31 percent from 14 mg/L (1952-56) to 9.6 mg/L (1984-2000), (2) in the Merrimack River decreased by 11 percent from 10.4 mg/L (1967-83) to 9.3 mg/L (1984-2000), and in the Blackstone River decreased by 10 percent from 21.1 mg/L (1973-83) to 18.1 mg/L (1984-2000).

The positive bias on sulfate concentrations reported by the USGS before 1990, could be contributing to the magnitude of change in sulfate concentrations in the three rivers. Annual sulfate concentrations, however, continued to decrease in the 1990s, indicating that the changes during the decade were not solely the result of analytical methods.

Atmospheric deposition and weathering of sulfur-containing minerals are important sources of sulfate in water (Hem, 1989; and Mast and Turk, 1999). Mast and Turk (1999) concluded that wet and dry atmospheric deposition accounted for most of the sulfate in the Wild River in Maine, a generally undisturbed watershed. They also concluded that the decreases in annual sulfate concentrations in the Wild River from 1964 to 1995 may be the result of decreasing sulfur-dioxide emissions in the Northeastern United States. Clow and Mast (1999) also found decreasing sulfate concentrations in stream water and precipitation at a number of sites in the Northeastern United States during 1984-96; concluding that a reduction in sulfur-dioxide emissions was the likely cause. Sulfur-dioxide emissions increased in the United States from 1955 to 1970, but decreased from 1970 to 1998 (U.S. Environmental Protection Agency, 2000b) ([fig. 7](#)). These emission reductions are the result of the conversion of the use of coal to natural gas, oil, and nuclear energy for electric power production, economic recessions, use of low-sulfur coals, and emission controls mandated by the Clean Air Act of 1970 (U.S. Environmental Protection Agency, 2000b; Nizich and others, 1995). Although minimal sulfate data for streams (only for the Connecticut and

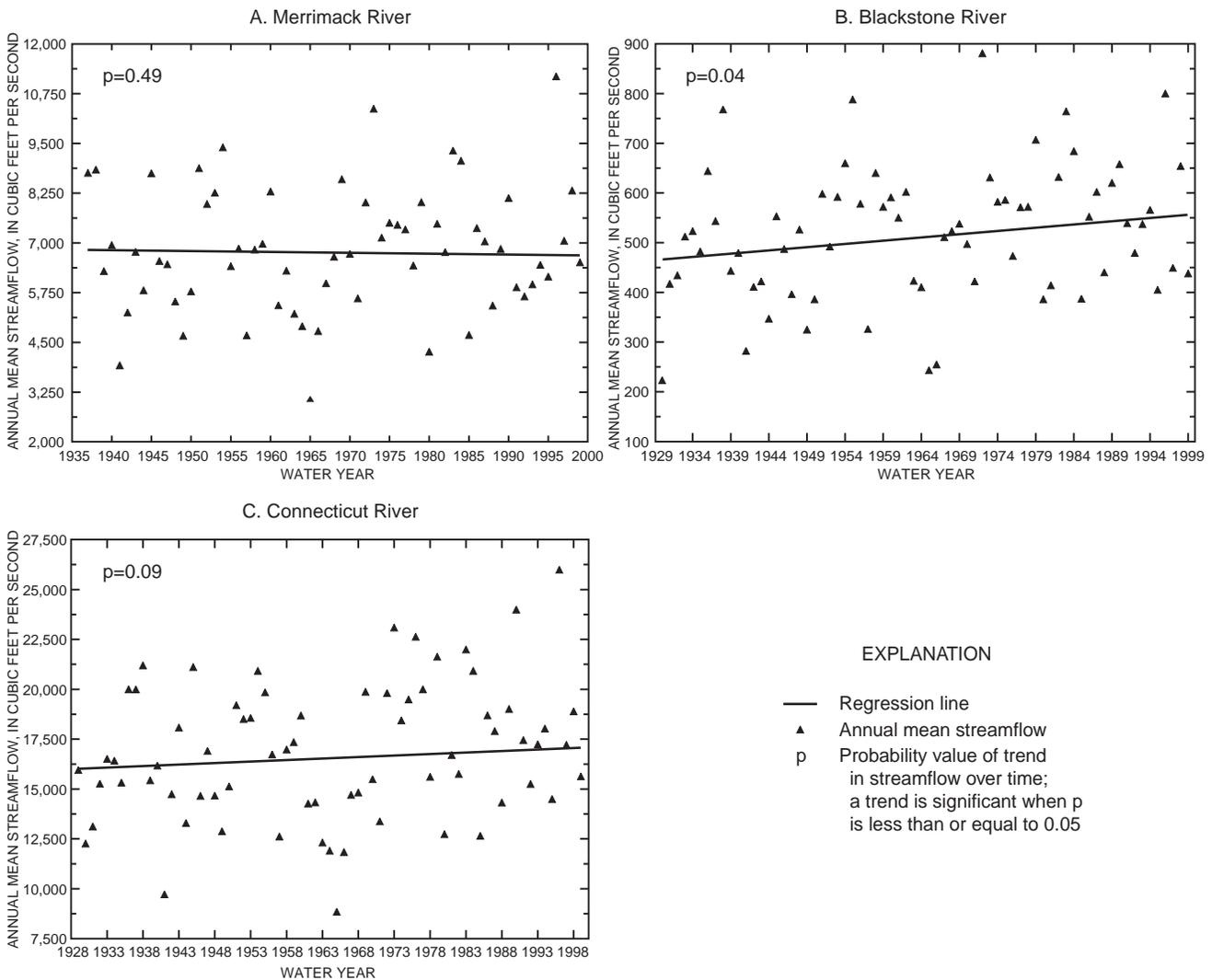


Figure 6. Annual mean streamflow and streamflow trends in the (A) Merrimack River at Lowell, Mass., during 1935-2000; (B) Blackstone River at Millville, Mass., during 1929-2000; and (C) Connecticut River at Thompsonville, Conn., during 1928-2000.

Merrimack Rivers) for 1955-70 is available that corresponds to the period of increasing sulfur-dioxide emissions (fig. 7), annual sulfate concentrations in the three New England Rivers do appear to decrease corresponding to sulfur-dioxide-emission reductions post 1970. This pattern indicates that sulfur-dioxide emissions likely affected the concentrations of sulfate in the Merrimack, Blackstone, and Connecticut Rivers. The significance of other factors affecting sulfate concentrations in the Blackstone River, such as wastewater discharges and industrial operations, is not known.

Chloride

Annual chloride concentrations in the Merrimack, Blackstone, and Connecticut Rivers increased during the 20th century (fig. 8 and table 4). The magnitude of these increases is greatest in the Merrimack River where the mean-annual concentration increased 760 percent from 2.9 mg/L (1900-17) to 24.9 mg/L (1976-95). Mean-annual concentrations of chloride in the Blackstone and Connecticut Rivers increased 186 percent and 344 percent, respectively, from 1900-17 to 1966-2000. In the 1990s, annual chloride concentrations approached 75 mg/L in the Blackstone River, whereas those in the Merrimack and

Table 4. Summary of Kendall's tau analysis for trends in streamflow and annual concentrations of sulfate, chloride, residues, nitrate, and total phosphorus in the Merrimack, Blackstone, and Connecticut Rivers from 1900-2000

[p-values less than 0.05, shown in **bold** type, indicate that a significant trend was found; --, no data]

Constituent	Merrimack River			Blackstone River			Connecticut River		
	Kendall's Tau		Number of samples in comparison	Kendall's Tau		Number of samples in comparison	Kendall's Tau		Number of samples in comparison
	p-value	tau		p-value	tau		p-value	tau	
Streamflow	0.4877	0.0599	63	0.0441	0.1644	70	0.0868	0.1388	71
Sulfate	.0146	-.3202	29	.2582	-.160	24	.0000	-.6885	40
Chloride	.0000	.7270	48	.0000	.7252	44	.0000	.7005	57
Residues	--	--	--	.0000	.5903	43	.0010	.3394	45
Nitrate	.0157	.2622	41	.0000	.5436	40	.0003	.3597	49
Phosphorus, total	.0002	-.5100	27	.0054	-.3967	25	.0001	-.4756	35

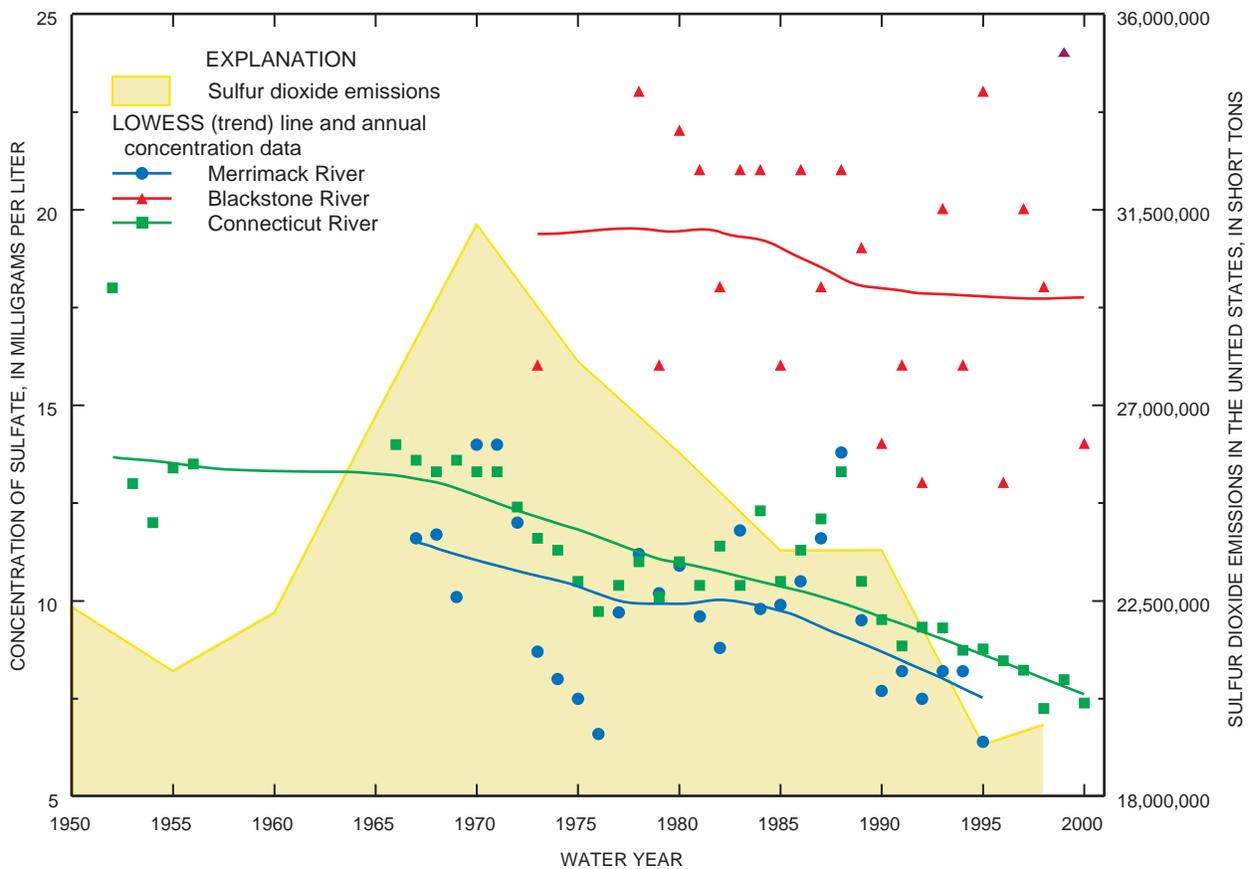


Figure 7. Trends in annual sulfate concentrations in the Merrimack, Blackstone, and Connecticut Rivers from 1952-2000, and annual sulfur-dioxide emissions in the United States from 1950-98 (Annual sulfur dioxide emissions data from the U.S. Environmental Protection Agency, 2000b).

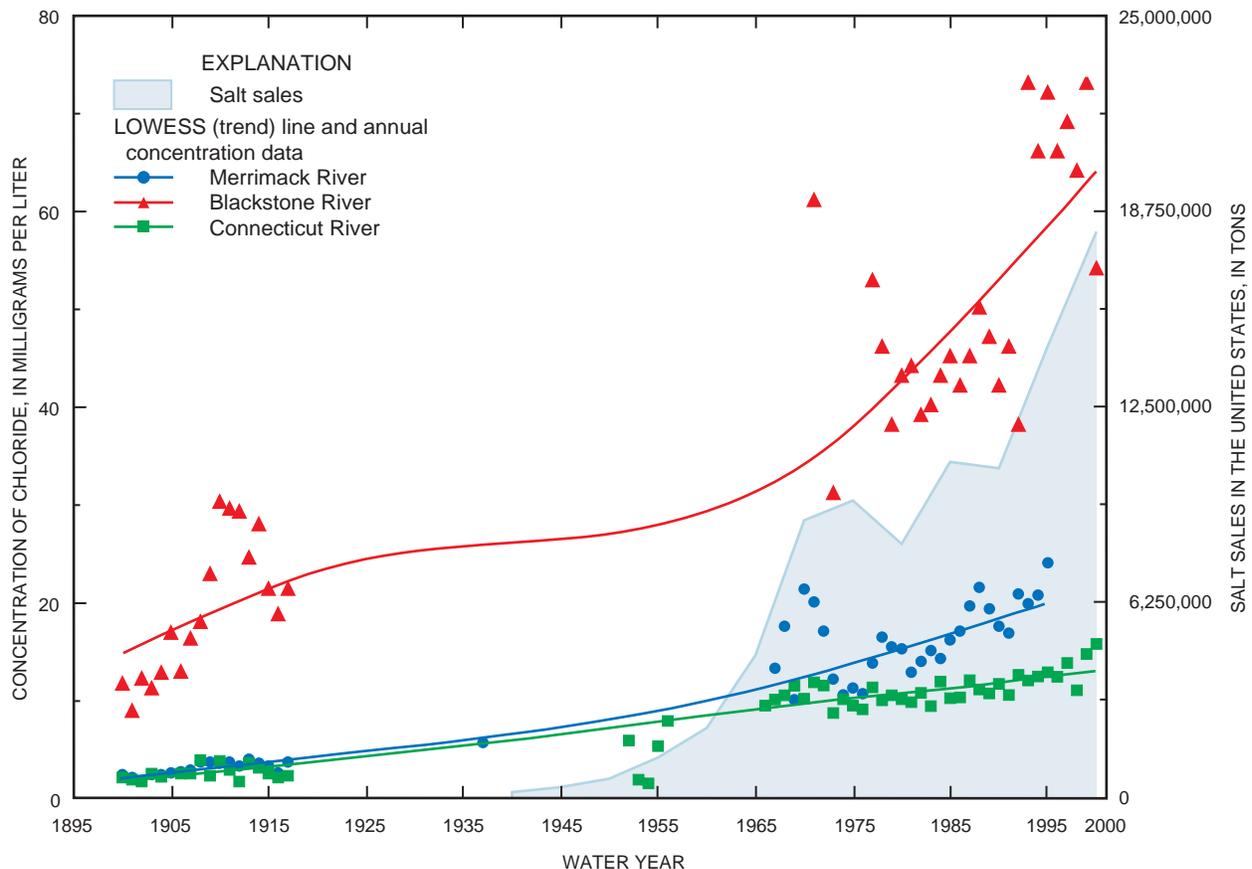


Figure 8. Trends in annual chloride concentrations in the Merrimack, Blackstone, and Connecticut Rivers from 1900-2000, and annual amount of salt sold for highway de-icing in the United States from 1940-2000 (Annual salt sales data from the Salt Institute, 2001).

Connecticut Rivers approached 25 and 15 mg/L, respectively. These concentrations are well below the recommended ambient chloride water-quality criteria of 230 mg/L (U.S. Environmental Protection Agency, 1988).

Increasing chloride concentrations of streams have been reported by other studies in New England, the Northeast, and throughout the United States (Trench, 1996; Strause, 1993; Toppin, 1993; Robinson and others, 1996; and Smith and others, 1987). The upward chloride trends reported in some of these studies are likely the result of road-salt application for de-icing purposes (Robinson and others, 1996; and Smith and others, 1987). From 1940 to 2000, the annual amount of salt sold for highway de-icing in the United States increased from 164,000 to 18,101,000 tons; an increase of over 1,000 percent (fig. 8) (Salt Institute, 2001). The increases in chloride concentrations in the three New England rivers does

generally correspond to road-salt sales for the United States in the second half of the 20th century. Measures of other water-quality indicators, such as specific-conductance values and sodium concentrations also are thought to mirror the increasing concentrations of chloride; this pattern was seen in other areas (Robinson and others 1996, and Trench, 1996).

Residues

Residues data from 1900 to 1917 are compared to total solids data from 1969 to 2000 for the Blackstone and Connecticut Rivers (fig. 9). Residues increased in both rivers during the 20th century (table 4). Mean-annual concentrations of residues increased in the Blackstone River by 47 percent from 116 mg/L (1900-17) to 170 mg/L (1970-2000), and in the Connecticut River by 17 percent from 71.5 mg/L

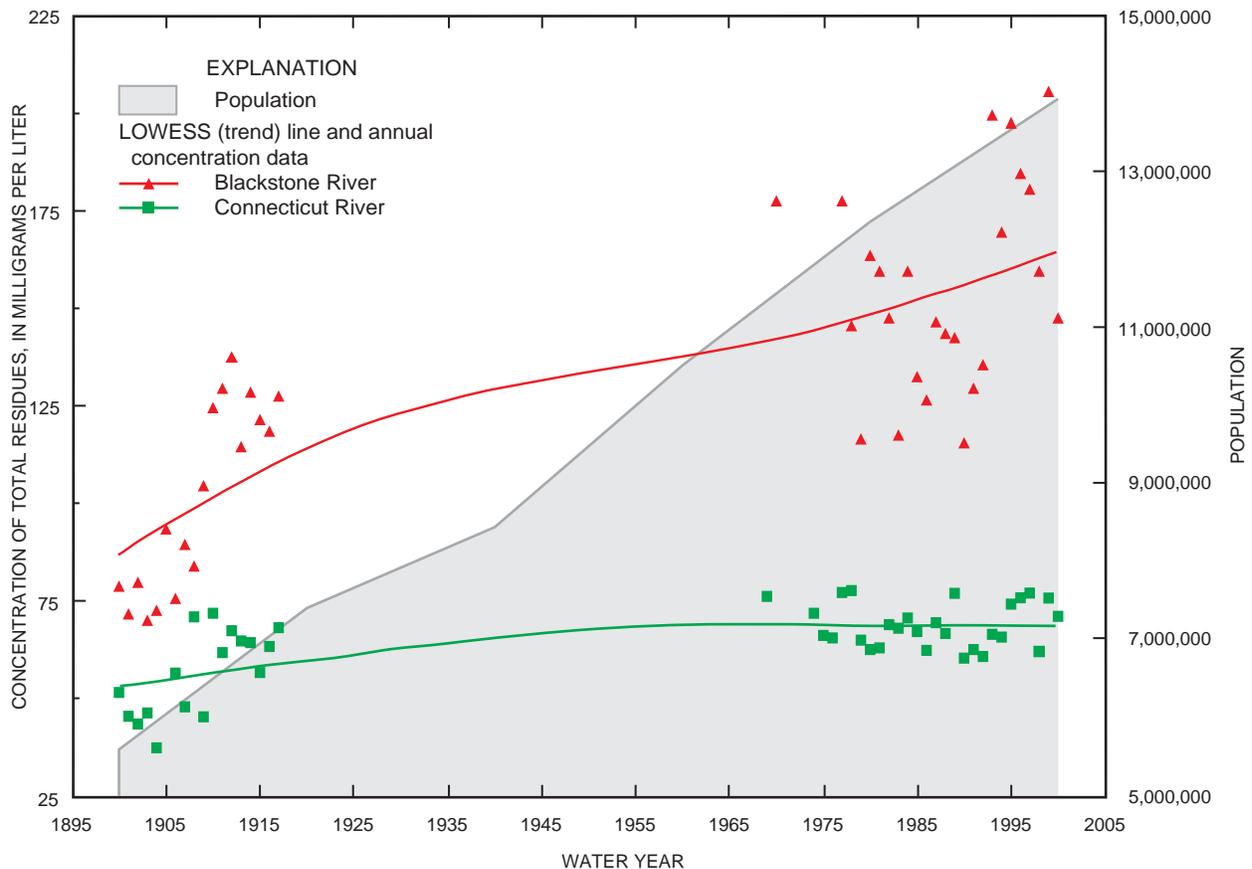


Figure 9. Trends in annual residue concentrations in the Blackstone and Connecticut Rivers from 1900-2000, and population of New England from 1900-98 (Population data from the U.S. Census Bureau, 2001).

(1900-17) to 83.7 mg/L (1969-2000). In the last decade of the 20th century, annual residue concentrations continue to increase in the Blackstone River, but changed little in the Connecticut River (fig. 9).

Residues data can be used to reflect a variety of anthropogenic activities in a watershed—including wastewater discharges, soil erosion, and road salting. Annual residues concentration increased during 1900-17, which generally corresponds to the growth of New England’s population during the same period (fig. 9). The relation of residues to population is less obvious from 1969 to 2000. This may be the result of improved wastewater treatment, and reforestation of the New England landscape that has resulted in reductions in soil erosion during the later part of the 20th century.

There were notable increases in residues during 1910-17 in all three rivers. Changes in laboratory methods during 1910-17 may have contributed to the increasing concentrations. A review of standard

laboratory methods from 1905 to 1917 identified changes in the suggested method of evaporating liquids and volatile substances (heating at 103°C for one-half hour changed to heating at 180°C for 1 hour) to determine total residues (American Public Health Association, 1905 and 1917).

Nitrate

Annual nitrate concentrations in all three New England rivers increased during the 20th century (table 4 and fig. 10). In the Merrimack and Connecticut Rivers, mean-annual concentrations increased by an order of magnitude. During 1900 to 1914, the mean-annual concentration in both rivers was 0.04 mg/L. This compares to a mean-annual concentration of 0.33 mg/L in the Merrimack River from 1967 to 1996, and 0.35 mg/L in the Connecticut River from 1966 to 2000. In the Blackstone River, mean-annual nitrate

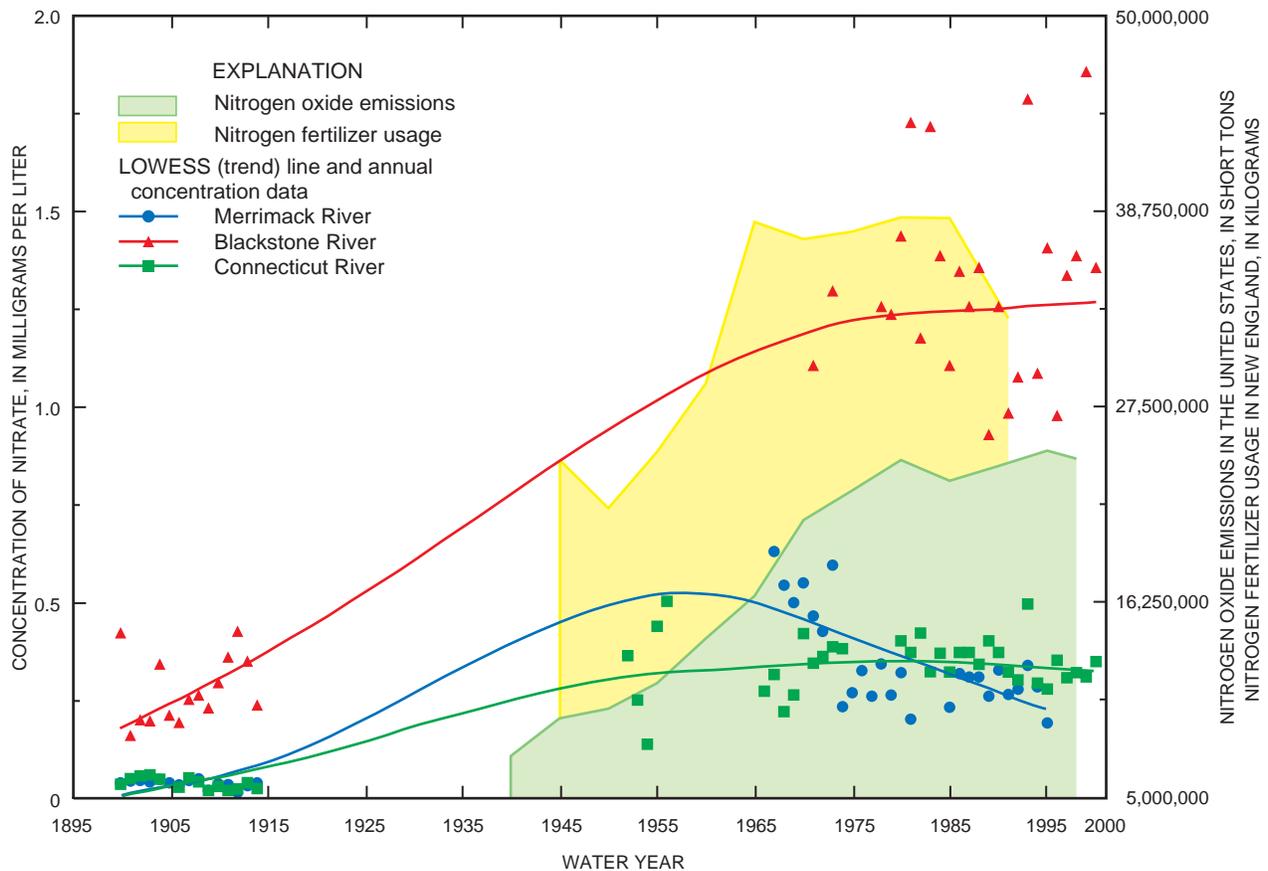


Figure 10. Trends in annual nitrate concentrations in the Merrimack, Blackstone, and Connecticut Rivers from 1900-2000, annual nitrogen oxide emissions in the United States from 1940-98, and annual agricultural usage of nitrogen fertilizer in New England from 1945-91 (Annual nitrogen oxide emissions data from the U.S. Environmental Agency, 2000b; annual nitrogen fertilizer usage data from Alexander and Smith, 1990, and Alexander, R.B., U.S. Geological Survey, written commun., 2001).

concentrations increased nearly 400 percent in the 20th century from 0.27 mg/L (1900-14) to 1.31 mg/L (1971-2000). During the last 10-20 years of the century, the increases in annual nitrate concentrations appear to have slowed in the Blackstone and Connecticut Rivers or been reversed in the Merrimack River. All annual nitrate concentrations are well below the U.S. Environmental Protection Agency (USEPA) criteria of 10 mg/L for the protection of human health (U.S. Environmental Protection Agency, 1986).

Large increases in nitrogen concentrations in rivers have been previously noted by a number of investigators (National Research Council, 2001). In addition, because nitrogen is often a limiting nutrient in estuarine and ocean waters, a number of studies have quantified and analyzed nitrogen loadings to coastal waters of the northeastern United States. Jaworski and

Hetling (1996), using some of the data presented in this report, found nitrate concentrations in 12 rivers in the eastern United States increased by an average of 470 percent in the 20th century. Roman and others (2000) and Jaworski and Hetling (1996) report total nitrogen concentrations in rivers in the northeastern United States increased by 300 percent during the 20th century. These same studies show that the upward trends of nitrogen leveled off from 1970 to 1980. Howarth and others (1996) estimated the amount of total nitrogen from rivers to estuaries in northeastern United States increased 5-20 times in the 20th century.

Sources of the increasing nitrate concentrations in the Merrimack, Blackstone, and Connecticut Rivers during the 20th century likely include atmospheric deposition, fertilizer applications and other agricultural practices, and the presence of an increasing population.

Jaworski and others (1997) show a relation between increasing total nitrogen loads in rivers in the northeastern United States with increasing nitrogen-oxide emissions from fossil-fuel combustion and nitrogen-fertilizer application rates on agricultural lands. They also report a slight decrease in total nitrogen in rivers as decreases in both atmospheric deposition of nitrogen and agricultural fertilizer use occurred in the 1980s. Data on nitrogen-oxide emissions in the United States from the U.S. Environmental Protection Agency (2000b) show about a three-fold increase in emissions from 1940 to 1998 ([fig. 10](#)).

Agricultural use of nitrogen fertilizers in New England increased from the 1950s to early 1960s, changed little from the mid-1960s to mid 1980s, and then decreased from 1985 to 1990 (Alexander and Smith, 1990; and Richard Alexander, U.S. Geological Survey, written commun., 2001) ([fig. 10](#)). The lack of change or downward change in agricultural nitrogen fertilizer use from 1965 to 1991 matches the overall lack of nitrate concentration trends in the Blackstone and Connecticut Rivers for the later years of the 20th century. Increased human population density was related to increased nitrate fluxes in major rivers worldwide (Peierls and others, 1991). The increasing New England population ([fig. 9](#)) may be a contributing factor in the overall nitrate concentration increases in the three rivers. The cause(s) of decreasing annual nitrate concentrations in the Merrimack River during 1967-95 are not known.

Total Phosphorus

Total phosphorus data from the three rivers studied were limited during 1965-2000 ([table 2](#)). Total phosphorus generally was not measured in stream water until the 1960s, when eutrophication of waters from phosphate-containing detergents became a concern. Annual concentrations of total phosphorus decreased in all three rivers during the last third of the 20th century ([table 4](#) and [fig. 11](#)). Comparisons of the annual concentration from each river from 1967 to 1984, and from 1985 to 2000 were used to assess the amount of change. Mean-annual concentrations of total phosphorus in the Merrimack River decreased by 38 percent, from 0.13 (1967-84) to 0.08 mg/L (1985-

2000). The mean-annual concentrations decreased in the Blackstone River by 19 percent, from 0.31 mg/L (1967-84) to 0.25 mg/L (1985-2000), and in the Connecticut River by 40 percent, from 0.10 mg/L (1967-84) to 0.06 mg/L (1985-2000). Annual concentrations of total phosphorus at the end of the 20th century continue to decline in the Merrimack and Blackstone Rivers, but appear to have stabilized in the Connecticut River ([fig. 11](#)). Nearly all annual concentrations of total phosphorus in these rivers are greater than the USEPA draft total phosphorus criteria of 0.031 mg/L for coastal areas of New England (U.S. Environmental Protection Agency, 2000c).

The changes in total phosphorus concentrations detected in the three rivers are similar to the declines reported by Roman and others (2000) and Litke (1999). Both of these studies report that concentrations of total phosphorus in streams in the United States likely peaked in the 1960s and early 1970s as a result of phosphorus fertilizer use and discharged wastewater containing high phosphate levels from detergents and soaps. Litke (1999) also noted that loadings of total phosphorus in wastewater decreased by as much as 50 percent during the last quarter of the 20th century as phosphate detergent bans took effect. At the same time, phosphorus fertilizer use on agricultural lands nationally peaked in the early 1980s, and has since remained generally the same (Litke, 1999). In New England, agricultural use of phosphorus fertilizers decreased by 45 percent between 1965-91 ([fig. 11](#)), indicating that national phosphorus-fertilizer-use patterns are different than those found in New England (Alexander and Smith, 1990; and Richard Alexander, written commun., 2001).

The trend in agricultural phosphorus fertilizer use in New England has a similar pattern to the decrease in total phosphorus concentrations seen in the Merrimack, Blackstone, and Connecticut Rivers. Although changes in total phosphorus releases by wastewater-treatment facilities during 1965-2000 have not been documented in New England, the changes seen in the total phosphorus concentrations in the three rivers are likely a result of reductions in phosphorus loads from wastewater-treatment facilities and in agricultural phosphorus fertilizer use.

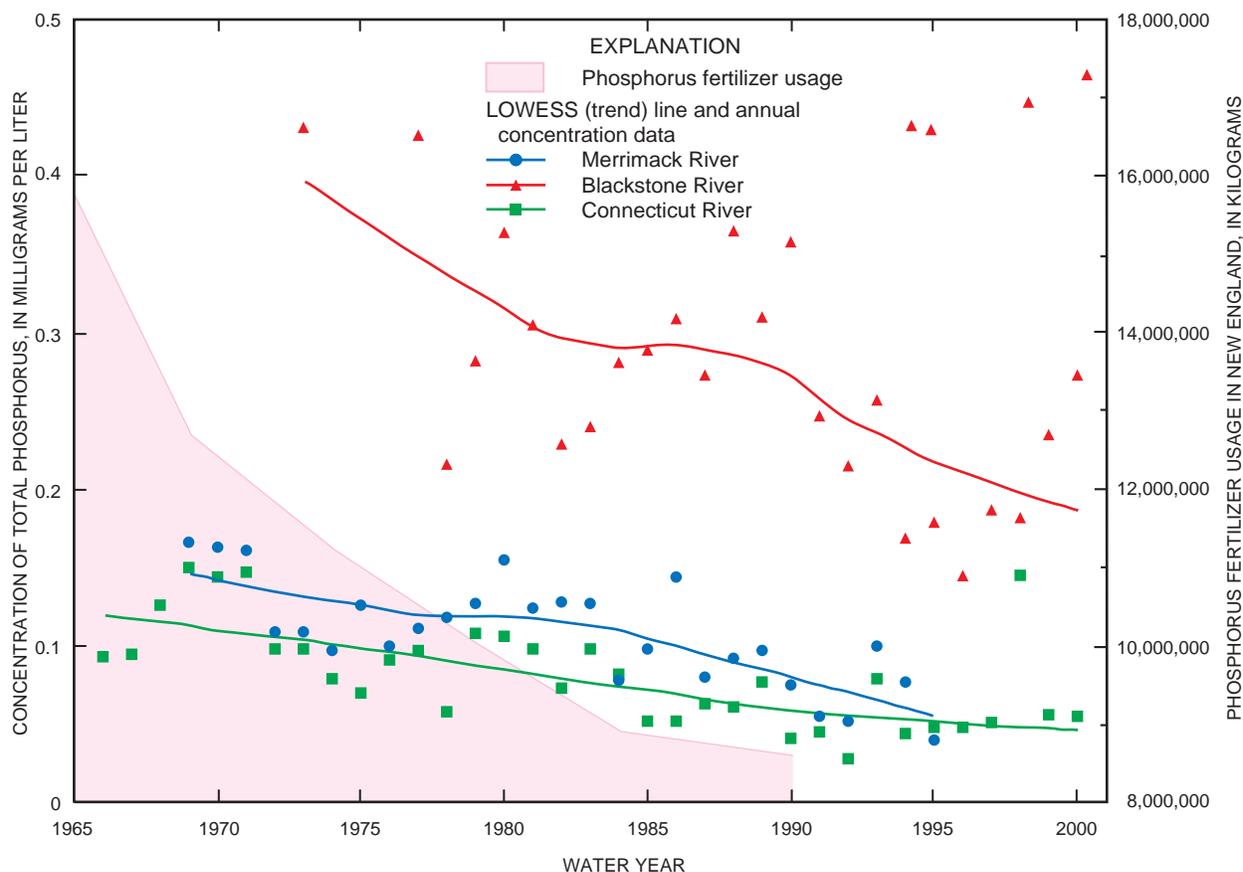


Figure 11. Trends in annual total phosphorus concentrations in the Merrimack, Blackstone, and Connecticut Rivers from 1966-2000, and annual agricultural usage of phosphorus fertilizer in New England from 1965-91 (Annual phosphorus fertilizer usage data from Alexander and Smith, 1990, and Alexander, R.B., U.S. Geological Survey, written commun., 2001).

SUMMARY

A combination of historical and recent data for sulfate, chloride, residues, nitrate, and total phosphorus are used to determine how water-quality conditions have changed in the Merrimack, Blackstone, and Connecticut Rivers during the 20th century in New England. These data were collected by the U.S. Geological Survey and by the State of Massachusetts for different purposes and using different analytical methods. These data, however, are considered sufficiently comparable for identifying changes in water quality.

All of the water-quality constituents analyzed for this report show statistically significant trends in one or more of the three rivers during the 20th century. Annual concentrations of chloride and nitrate increased in all

three rivers, whereas annual concentrations of residues increased only in the Blackstone and Connecticut Rivers. Annual chloride concentrations increased by an order of magnitude for the Merrimack, Blackstone, and Connecticut Rivers. Annual nitrate concentrations increased by an order of magnitude in the Merrimack and Connecticut Rivers. Annual sulfate concentrations in the three rivers decreased during the second half of the 20th century, although the decrease in the Blackstone River was not statistically significant. Annual total phosphorus concentrations also decreased in all three rivers during the last third of the century. The lack of statistical trends in annual-mean flow in the Merrimack and Connecticut Rivers during the period-of-flow record indicates that water-quality trends in these rivers are likely the result of factors other than

streamflow. The Blackstone River had an increase in annual-mean flows that could be resulting in changing water-quality conditions in this river.

The changes in river-water quality detected in the Merrimack, Blackstone, and Connecticut Rivers are similar to those reported in the literature. Decreases in sulfate concentrations follow a similar pattern of decreasing sulfur-dioxide emissions in the United States. The increased use of road de-icing salts and increasing chloride concentrations appear related. Increasing nitrate concentrations in rivers follow the general patterns of upward and stabilizing trends in the agricultural use of nitrogen fertilizers in New England, and, to a lesser degree, nitrogen-oxide emissions in the United States. Finally, decreases in annual total phosphorus concentrations are similar to decreases in the agricultural use of phosphorus fertilizer. In addition, bans on the use of phosphate-containing detergents by the New England States has likely contributed to the decrease in concentrations of phosphorus.

The Blackstone River consistently had greater concentrations than the Merrimack and Connecticut Rivers of all five constituents analyzed. Greater densities of population, wastewater discharges, and urban land uses are likely the primary reasons for these large concentrations.

The ability to synthesize water-quality data that represent a century of major societal changes in New England provides insight on how those changes affect the quality of rivers. As the human population and its associated development activities continue to increase in the 21st century, further changes in water quality are expected. The ability to predict and document these effects cannot be made by assuming that the rate of change observed in the 20th century will continue. These predictions will be dependent on additional water-quality data-collection programs that provide new information in the future.

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