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# Temporal and Spatial Trends of Chloride and Sodium in Groundwater in New Hampshire, 1960–2011

By Laura Medalie

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## Conversion Factors and Datum

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square foot (ft <sup>2</sup> )	0.09290	square meter (m <sup>2</sup> )
square mile (mi <sup>2</sup> )	2.590	square kilometer (km <sup>2</sup> )

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

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

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

## Abbreviations

Cl	chloride
DWGB	Drinking Water and Groundwater Bureau
IOC	inorganic contaminant
Na	sodium
NHDES	New Hampshire Department of Environmental Services
NHDHHS	New Hampshire Department of Health and Human Services
NHDOT	New Hampshire Department of Transportation
PWS	public water system
RL	reporting limit
SMCL	secondary maximum contaminant level
SL	New Hampshire Department of Health and Human Services State Laboratory
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

# Temporal and Spatial Trends of Chloride and Sodium in Groundwater in New Hampshire, 1960–2011

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## Abstract

Data on concentrations of chloride and sodium in groundwater in New Hampshire were assembled from various State and Federal agencies and organized into a database. This report provides documentation of many assumptions and limitations of disparate data that were collected to meet wide-ranging objectives and investigates temporal and spatial trends of the data. Data summaries presented in this report and analyses performed for this study needed to take into account the 27 percent of chloride and 5 percent of sodium data that were censored (less than a reporting limit) at multiple reporting limits that systematically decreased over time. Throughout New Hampshire, median concentrations of chloride were significantly greater during 2000-2011 than in every decade since the 1970s, and median concentrations of sodium were significantly greater during 2000-2011 than during the 1990s. Results of summary statistics showed that the 50th, 75th, and 90th percentiles of the median concentrations of chloride and sodium by source (well) from Rockingham and Strafford counties were the highest in the State; and the 75th and 90th percentiles from Carroll, Coos, and Grafton counties were the lowest. Large increases in median concentrations of chloride and sodium for individual wells after 1995 compared with concentrations for years before were found in parts of Belknap and Rockingham counties and in small clusters within Carroll, Hillsborough, and Merrimack counties.

## Introduction

Several studies suggest that concentrations of chloride and sodium in ambient groundwater in New Hampshire have increased from the advent of the 20th century, ostensibly from road salt and other anthropogenic sources. Increases in concentrations of chloride in natural waters from approximately 1945 through 1970 were documented in Hall (1975) where it was noted that increasing concentrations coincided with increased road deicing salt applications. Other studies in New Hampshire have shown that imported road salt may have long-term effects on water quality by raising baseflow concentrations of chloride and sodium due to storage in shallow (Harte and Trowbridge, 2010) and deep (Emery & Garrett Groundwater, Inc., 2007) aquifers. In a regional study of the northern United States, upward trends associated with use of deicing salt for roads and parking areas, number of septic systems, volume of wastewater discharge, and saline groundwater plumes from landfills and salt storage areas were seen in chloride loads (Mullaney and others, 2009). In a study of 56 well networks representing 22 principal aquifers nationwide, the New England coastal basins, which encompasses more than half of New Hampshire's area, had the second largest median decadal increases in concentrations of chloride between 1988 and 2010 (Lindsey and Rupert, 2012).

The U.S. Environmental Protection Agency (USEPA) has established a nonenforceable secondary maximum contaminant level (SMCL) of 250 milligrams per liter (mg/L) for chloride (for potential cosmetic or aesthetic effects) and a nonregulatory drinking water advisory concentration of

20 mg/L for sodium for individuals on a 500-milligram-per-day sodium-restricted diet (U.S. Environmental Protection Agency, 2011). The concentration of chloride, when associated with sodium, for the protection of freshwater aquatic organisms is 230 mg/L averaged over 4 days no more than once every 3 years on average (U.S. Environmental Protection Agency, 1988). In addition, sodium is included on the drinking water contaminant candidate list because of its possible association with hypertension in some individuals (U.S. Environmental Protection Agency, undated). The New Hampshire Department of Environmental Services (NHDES) receives water quality sample results submitted on behalf of public water systems (PWSs) to determine compliance with State (New Hampshire Department of Environmental Services, 2008) and Federal drinking water requirements.

According to compliance water quality monitoring data reported to the NHDES between 1988 and 2010, about 100 PWSs had at least one groundwater sample with concentrations of chloride equal to or exceeding 250 mg/L (Laurie Cullerot, New Hampshire Department of Environmental Services Drinking Water and Groundwater Bureau, written commun., July 22, 2011). Increasing concentrations of chloride and sodium in drinking water sources may require substantial changes to infrastructure for finding alternative water supply sources, diverting stormwater drainage, blending waters from wells or inducing artificial recharge (dilution), or abandoning public supply wells. Each of these options could involve significant cost and in some cases may not be viable. The need to find alternative water sources because of elevated concentrations of chloride and sodium due to road salt application along State highways has been seen occasionally in private wells. For example, the New Hampshire Department of Transportation (NHDT) database on private wells that have been replaced because of concentrations of chloride exceeding 250 mg/L documents more than 500 such cases from 1973 through 2010 (Philip Huntley, New Hampshire Department of Transportation, written commun., March 11, 2011).

The sources of groundwater for the dataset assembled for this study are primarily the fractured bedrock and stratified drift (overburden) aquifers of New Hampshire. Out of 5,544 untreated and unblended wells in the database created for this project, 61 percent are classified as bedrock, 16 percent are overburden, 22 percent are unclassified, and the remaining 1 percent is springs, infiltration, or artesian wells. From 1984 through 2007, static water levels at bedrock wells in the State decreased by about 13 feet, a change that is possibly related to synchronous changes in water use, well yield, well depth and construction, well position on the landscape, land use, or climate change (Ayotte and others, 2010). Any of these factors could be related to changes in concentrations of chloride and sodium.

A comprehensive assessment of chloride and sodium in groundwater in New Hampshire is needed for prioritizing and allocating resources to maintain high-quality groundwater from public and private water supply wells and for other purposes, such as supporting aquatic life in surface waters. The primary objective of this study is to describe spatial and temporal trends in chloride and sodium in groundwater used or potentially used for drinking water supplies in New Hampshire. A secondary objective is to assemble an integrated and thoroughly documented dataset of concentrations of chloride and sodium in groundwater in New Hampshire as a foundation for a comprehensive assessment.

The purpose of this report is to integrate all data on concentrations of chloride and sodium from groundwater in New Hampshire available from the NHDES, the New Hampshire Department of Health and Human Services (NHDHHS), the NHDT, the USEPA, and the U.S. Geological Survey (USGS) that meet quality assurance conditions for this study. Depending on different types of analyses and depictions, median concentrations are shown for individual wells, towns, decades, or regions in the State (fig. 1). For the purposes of this study, the State was divided into five regions, as follows: region 1, northern New Hampshire, included Carroll, Coos, and Grafton Counties; region 2, central New Hampshire, was Belknap County; region 3, south-central New Hampshire, included Hillsborough and Merrimack Counties; region 4, southwestern New Hampshire, included Cheshire and Sullivan Counties;

and region 5, southeastern New Hampshire, included Rockingham and Strafford Counties. Quality assurance conditions include having adequate documentation or assurances from data providers to be judged comparable and suitable for inclusion. Only data from single-source wells before water treatment were included in most of the summaries and analyses for this report. Data from contaminated sites were not used. Most of the available data were from samples collected between the late 1980s and 2011, although there also are some data from the 1960s and 1970s and a few samples from the 1950s.

## **Data and Methods**

The goal of data compilation was to collect all data on concentrations of chloride and sodium in untreated single sources of ambient groundwater in the State of New Hampshire into a single database usable for statistical summaries and analyses. The term ambient is used to describe background groundwater, as opposed to groundwater contaminated by a known contaminant source, such as a landfill or toxic spill. Because of the many differences among data provided from the various sources, this section and appendix 1 (which describes the database created for this project) provide a detailed documentation and description of data sources, assumptions, and limitations that are essential to understand the data and the analytical tools that were used to summarize the data. Table 1 lists the sources of data that were compiled for the database for salt data in New Hampshire (NH salt database).

Because several terms—detection limit, quantitation limit, reporting limit—each with a specific definition, were used for the lower limit of data that delineate the censoring threshold in the various sources of data, for uniformity in this report, the censoring threshold is referred to as a general reporting limit (RL). The effect for data summaries or statistics is the same regardless of how censoring is determined. Use of the term reporting limit also recognizes that low-concentration data provided from the various agencies in all cases were qualified with the <(less than) censoring symbol without a more specific definition.

### **Data Limitations and Assumptions**

Data on concentrations of chloride and sodium that were provided to the USGS by the NHDES originally had been collected to serve compliance or storage purposes. This section of the report thoroughly documents the data and describes limitations and assumptions that were needed in order to transform data from the disparate sources into a standardized and consistent dataset suitable for analysis.

#### **Identification of Data Less Than the Reporting Limit**

The NHDES Drinking Water and Groundwater Bureau (DWGB) and NHDHHS State Laboratory (SL) databases were each developed to serve a different function—regulatory compliance (DWGB) or repository of results for samples analyzed at the SL. The two databases provided most of the data on concentrations of chloride and sodium for public water systems in the NH salt database. Input of data for sodium and chloride into the two original databases depended on the sample collection date, concentration in relation to the RL, and whether the public water system sample was analyzed at the SL or at a private laboratory (table 2). Beginning in 2008, chemical results for public water systems analyzed at the SL and initially in the SL database were transferred to the DWGB database. Also in 2008, the NHDES developed the Data Warehouse database to receive sample results through online reporting. By 2011, all private laboratories were reporting sample results online directly to the Data Warehouse. After review by the DWGB program, results from the Data Warehouse are transferred into the DWGB database.



The NHDES historically entered into the DWGB database all results from inorganic contaminant (IOC) samples, including chloride and sodium, that were greater than the RL and that were processed at private laboratories. Results with values less than the RL were not available in an electronic database and therefore were estimated by an extrapolation method explained in the next section. Results of public water system samples analyzed at the SL were obtained from either the SL or DWGB databases. Before 2000, the NHDES protocol (developed to enable close oversight by DWGB staff) for entering IOC results of samples processed at the SL was to enter results equal to or greater than 50 percent of the SMCL (125 mg/L) into the DWGB database. Because the SL was a more complete repository, including all results less than and greater than the RL, results before 2000 were obtained from the SL database. Beginning in 2001, the NHDES entered all results from SMCL samples, including chloride and sodium, equal to or greater than the RL into the DWGB database. Because data for the sources of the samples (wells) in the DWGB database are identified by a numerical field rather than a descriptive field as is the case in the SL database, making it easier to match to data already in the NH salt database, results for samples analyzed at the SL from 2001 through 2008 were obtained from the DWGB database rather than the SL database. As with results for public water systems that were analyzed at private laboratories, results for samples analyzed at the SL that were less than the RL had to be estimated and added in a separate step.

#### Extrapolation of Dataset for Values Less Than the Reporting Limit

Because of the interest in documenting changes over time in ambient conditions where the entire range of concentrations of chloride and sodium is important, results had to be deduced when samples with resulting concentrations less than the RL were collected and analyzed but were not entered into a database. A result of “less than the RL” is valuable information for the purpose of statistical summaries and trends. There is a need to supplement the datasets for sample results that were less than the RL (non-detects) and analyzed at private laboratories before 2010 or at the SL between 2001 and 2008.

Non-detects were deduced by examining records of all chemical tests on samples from PWSs for IOCs available from the DWGB database. All groundwater sources of PWSs are required to have IOC tests every 3 years to comply with State regulations (New Hampshire Department of Environmental Services, 2011). If the values of all individual constituent results for the IOC test were less than the RL, then there would still be an IOC record for that water sample showing “N” in the “Detect” field. If an IOC record existed for a given groundwater sample with no corresponding result for chloride or sodium, then it was inferred that the sample was tested for chloride and sodium and had a resulting concentration less than the RL. In these cases, records for chloride and sodium were added to the NH salt database with the value of the RL in the “Concentration” field of the ChemResults (chemical results) table and “N” in the “Remark” field to flag the data as being at a nondetectable level. These added records were given the entry of “DW–IOC” in the “Data source” field.

The value of the RL varied depending on the analytical method used and on protocols defined in laboratory-specific quality assurance plans. Different laboratories may use different methods for the same constituent and their methods may change over time. In order to add records to the NH salt database for results for chloride or sodium that are inferred to be less than the RL, a value of the RL needed to be assigned. In some cases, the RL for a given constituent for a given laboratory at a particular period of time could be presumed by examining reported data that included that laboratory’s value for the RL. For other cases of missing values for RLs or where added records were from the data source designated “DW–IOC,” the default value of 3 was assigned as the RL for chloride and for sodium samples analyzed before January 1990; the default value of 1 was used for sodium samples analyzed beginning in January 1990. These are conservative values for the RL (many values for RL

were lower and none were higher) that were reported with results of samples analyzed at the SL for the time that covered the scope of this report (Patricia Bickford, New Hampshire Department of Health and Human Services, written commun., November, 2011).

### Exclusion of Results From Treated Wells

Because one goal of this project was to provide statistics of concentrations of chloride and sodium in ambient groundwater in New Hampshire, it was important to exclude sample results for treated water. Some PWSs treat groundwater before distribution. The DWGB and SL databases use two fields (“source ID” and “source/entity type”) to indicate whether a PWS sample is from a treated source. However, when a given PWS has records for both treated and groundwater sources, there may be cases where records that appear as groundwater sources show results for treated water that is not raw water. Without looking at paper files or being familiar with the PWS, there is no way to tell from the DWGB or SL databases at what point in the distribution system the water sample was collected relative to the addition of treatment.

A conservative approach was used to infer which samples may have been treated. The date field “Treatment added” was added to the ChemResults table in the NH salt database and populated with dates provided by NHDES (Diana Morgan, New Hampshire Department of Environmental Services, written commun., October 2011). Samples collected after the date that treatment was added were disregarded for graphical depictions and statistical analyses in this report because they may have been treated. It is possible that valid samples were omitted because of this assumption. For many PWSs, treatment has been added only in recent years; thus, most systems with long-term records were not affected greatly by loss of data.

### Sample Representativeness

The data that populate the NH salt database consist primarily of samples that were collected to satisfy regulatory programs. They are not a random representation of water quality of groundwater in New Hampshire. For example, much of the data are from public supply wells, but many households and commercial or industrial facilities across the State that are self-supplied do not use water from public supply wells. Only about one-third of statewide water withdrawals for public supply were from groundwater in 2000 (with the other two-thirds coming from surface water sources) according to the USGS National Water-Use Information Program (U.S. Geological Survey, undated). Furthermore, the percentage of withdrawals for public supply from groundwater ranged widely for individual counties from about 18 percent in Hillsborough County to as much as 80 percent in Carroll County. These percentages have not changed substantially over time.

Conversely, the data for samples collected from private wells in the SL database reflect growth and development patterns for nonurban parts of the State or for areas not served by PWSs; thus they do not represent a uniform statewide coverage of information. Because of confidentiality issues, locations of wells were not provided more specifically than by town name. As a result, it was not possible to determine whether each record was from a unique well. Also, it was not possible to determine whether chemical results from data in the SL database were affected by normal ion exchange or backwash generated from household water softeners.

Two additional cautions come with the nature of the data from diverse sources. The first is that the composition of individual wells in the decadal time bins is not constant over time. In other words, the set of individual wells with data values in the 1990s differed from the set with data values in the 2000s. If the set of wells with data was constant over time, the statistical conclusions for the temporal comparison would be stronger. The second is that, while the method of extrapolating data for values less

than the RL was based on solid assumptions, it created a time bias in the dataset for the low values that it generated because the source of data that the method was based upon (chemical tests for the IOC group) simply was not available before 1990. As a result of extrapolating the dataset, many values were added during the 1990s, few values during the 2000s, and no values before 1990.

## Data Analysis

Data for chloride and sodium from all data sources listed in table 1, except the private well data from the SL, USEPA, and NHDOT databases, were summarized and analyzed statistically. About 27 percent of the results for chloride and 5 percent of the results for sodium were censored (less than a threshold detection or RL). Further complications stemmed from data censored at multiple RLs. Common practice in dealing with censored values in environmental data (including water-quality data) is to assign the value of one-half of the RL before applying statistical tests. However, Helsel (2005) demonstrated that this method leads to potentially erroneous conclusions and should be avoided. Because censored concentrations of chloride and sodium showed systematic reductions in the RL from 10 mg/L to 2 or 3 mg/L over time, a robust adjustment was needed (Helsel and Hirsch, 2002). The adjustment consisted of changing all censored and observed values less than the highest RL to that limit (10 mg/L) before running any of the statistical procedures including summary statistics and boxplot construction. Percentiles reported as “<10” incorporate some unknown combination of censored and observed concentrations. Although the adjustment has resulted in some loss of information for lower concentrations, all the information about higher concentrations is preserved.

Preliminary exploration of data grouped by region and by decade (table 3) showed significant differences among the groups. Since both factors (decades and regions) defined unique populations, statistical comparisons of all data by decade or by region were not suitable. Data were examined in two ways—as summary statistics with percentiles for decades and regions compared qualitatively and by comparing data across decades for individual regions. The decade “2000s” included data through 2011.

Summary statistics presented by decade and region and statistical comparisons across decades for regions were calculated using one value of concentration per individual source (well) for each category (either decade or region). If there were multiple values for a source within a decade or region, then the median value was used so that no single source would have excessive weight. Summary statistics were derived as a modification (Helsel, 2005) of the nonparametric Kaplan-Meier method (Kaplan and Meier, 1958), which is a standard method used to analyze right-censored data (values “greater than” or “more than” a number) in the survival analysis branch of statistics. Nonparametric tests that evaluated differences between all pairs of data across four decades (1970s through 2000s) for chloride and two decades (1990s and 2000s) for sodium were conducted using the Peto and Peto modification to the Gehan-Wilcoxon test for left-censored data (Harrington and Fleming, 1982; Helsel, 2005). Data for chloride from the 1960s and for sodium from the 1960s through the 1980s were too sparse to include in the statistical comparison though they are included in the summary statistics and boxplots for a qualitative comparison. Methods that adapted statistical procedures to censored datasets were implemented using the version of the USGS library of data for TIBCO Spotfire S+ (Lorenz and others, 2011) or the R Project for Statistical Computing NADA package (Lee, 2012), which deals with values that are less than the RL in environmental data.

## Spatial and Temporal Trends in Concentrations

Data are presented in several different formats. Summary statistics are presented by decade and region (table 3) to address the primary objective of this study. Counties were grouped into five regions (fig. 1) based on general similarities in concentrations of chloride and county demographics. To use data from the largest dataset (private well data from the SL), which were only geographically located to the town level, median townwide concentrations of chloride or sodium for 3 different years were compared. In another analysis, concentrations for individual wells were examined for changes before and after 1995. This was done in a map-based graphic for the 900 or 800 wells for which there is at least one value for chloride or sodium before and after the 1995 date. Possible effects on the results of some of the data limitations and differences among data sources also are examined.

### Chloride

A comparison of median concentrations of chloride for 1985, 1995, and 2005 by town (fig. 2) shows a shift towards higher concentrations in 2005. The pie charts in figure 2 show that the number of towns with median concentrations of chloride greater than 10 mg/L was 82 in 1985, 74 in 1995, and 96 in 2005. Because towns indicated in the maps with white polygons have no data (rather than low concentrations), only towns with colored polygons should be compared across the decades. In 1985, a large majority of the towns had no data; consequently, interpretations based on 1985 data should be made cautiously. This is the only figure in the report (and the equivalent sodium figure) that includes data from private wells in the SL database.

Between 1985 and 1995, the number of towns with a median concentrations of chloride greater than 40 mg/L decreased by more than one-half, and the number of towns with a median concentration of chloride between 10 and 40 mg/L stayed approximately the same. The most distinctive differences are related to the lack of data availability in 1985 rather than actual observations, thus furthering the case for cautious use of 1985 data; most of the data in 1985 were based on three or fewer values (black dot in center of polygon in figure 2) and the number of towns with data increased more than fourfold in 1995. Between 1995 and 2005, the number of towns with median concentrations of chloride greater than 20 mg/L almost doubled from 35 to 65 towns. The pattern of higher concentrations of chloride (darker polygons) in the southeastern part of the State that can be seen in the 1995 graph became more pronounced in 2005. Compared with 1995, about one-third more towns had no data in 2005. This probably reflects the exclusion of more of the 2005 data because of potential treatment effects (see “Exclusion of Results From Treated Wells” section).

A similar spatial pattern of clusters of increasing concentrations of chloride over time can be seen when examining median concentrations of chloride from individual wells for periods before and after January 1, 1995 (fig. 3; table 4). This date falls approximately midpoint in time for the entire dataset. Many of the data points coded as “no difference or small increase ( $\leq 5$  mg/L)” reflect an assumed “0” value that was assigned to signify no change when the medians of both the before and after values were censored. Viewed statewide, 24 percent of the wells showed decreases in median concentrations of chloride, 34 percent showed no difference or small increase (less than or equal to 5 mg/L), and 42 percent showed large increases (greater than 5 mg/L). Whereas wells that showed a decrease or no difference or a small increase in concentrations of chloride appear scattered uniformly throughout the State, clusters of wells with large increases are most evident in parts of Belknap and Rockingham Counties and in smaller clusters in Hillsborough and eastern Merrimack Counties. Region 5 (southeastern) had the largest percentage (56 percent) of wells with increases in median concentrations of chloride greater than 5 mg/L; regions 3 (south-central, 44 percent) and 4 (southwestern, 43 percent)

were next largest; and region 1 (northern) had the smallest percentage (29 percent). Regions 1 and 2 (central) had the largest percentages (27 percent each) of wells with decreases in median concentrations of chloride, and region 5 had the smallest percentage (21 percent) of wells with decreases.

Summary statistics for median concentrations of chloride in groundwater by source (well) by decade and region are shown in table 3. The 10th and 25th percentile median concentrations listed in table 3 cannot be compared (all censored and observed median concentration values that were less than 10 were adjusted to “<10”). Although most median concentration values at the 50th percentile were equal to or less than 10, median concentrations of chloride from the 2000s and from region 5 were higher than the RL of 10. The 75th and 90th percentiles for median concentrations of chloride in the 2000s were higher than for all decades since the 1960s and at least double the previous two decades. The median concentration of chloride in the 2000s was approximately 1.5 times higher than the median for the 1960s through the 1980s. Data from the 1960s and 1970s should be viewed cautiously because there were few wells with data on concentrations of chloride. Given that qualification, the 75th and 90th percentiles for median concentrations of chloride from the 1960s and 1970s were higher than percentiles in the 1980s and 1990s, which were similar to one another. A possible explanation is that most of the early data were retrieved from the USGS National Water Information System database (table 1) and included data from a variety of projects, not all of which necessarily targeted ambient conditions (John Cotton, U.S. Geological Survey (retired), oral commun., February 10, 2012).

Statewide, the percentage of raw observations (including data from private wells in the SL database, which were not included in the summary statistics of table 3) whose values were greater than the SMCL of 250 mg/L for concentrations of chloride ranged from one to seven, with the highest percentage for data from the 1960s. The 50th, 75th, and 90th percentiles for median concentrations of chloride were approximately 1.3 to 3 times higher in region 5 than in other regions. Region 1 had the lowest 75th and 90th percentiles compared with other regions, and regions 2, 3, and 4 were similar to one another. By region, the percentage of raw observations (including data from private wells in the SL database) whose values were greater than the SMCL of 250 mg/L for concentrations of chloride ranged from 2 to 5 percent, with the highest percentage for data in region 5. High concentrations of chloride in groundwater in region 5, which is near the seacoast, could be due to naturally higher concentrations of these elements in coastal precipitation from marine aerosols (Pearson and Fisher, 1971), which would remain constant over time, or to saltwater intrusion into aquifers, which might increase over time if withdrawals from groundwater increase (Masterson and Barlow, 1997). However, figure 3 shows that individual wells that are closest to the seacoast (easternmost part of Rockingham County) show a mixture of increases and decreases in concentrations of chloride, while the dense cluster of large increases is seen further southwest along the eastern border with Massachusetts. An alternative explanation for the higher concentrations and larger increases in region 5 in recent decades could be related to greater road density in that area (fig. 1) and greater use of road salt. Further exploration of this hypothesis, though beyond the scope of this study, would be a worthwhile focus of future work.

Although it was not valid to statistically compare concentration data by decade or region for the entire State, statistical comparisons among decades could be made for individual regions. Figure 4 provides this detailed look at temporal changes in median concentrations of chloride for individual wells by region. Data from the 1960s and the 1970s, if available, are included only for a qualitative comparison. The minimum boundary of the plots is 10 mg/L, the highest of the multiple RLs. For each region except region 4, median concentrations of chloride were significantly higher in the 2000s than in any other decade. In region 4, median concentrations in the 1970s were not significantly different than those in the 2000s. For regions 1 through 4, median concentrations were not significantly different during the 1970s, 1980s, and 1990s. Percentiles in the rightmost boxplot in figure 4, showing all regions

together (statewide data), match values in the “All” column of table 3 (section A. By decade). The percentiles for median concentrations of chloride were higher in almost all measures for all decades in region 5 than all other regions. However, even the 90th percentile for region 5 in the 2000s, which was 155 mg/L, was 38 percent less than the SMCL of 250 mg/L.

## Sodium

In many towns, median concentrations of sodium in groundwater samples from wells increased between 1995 and 2005 (fig. 5). The number of towns with median concentrations greater than 10 mg/L changed from 89 to 114, with increases distributed fairly evenly throughout the State. The northern part of the State had the lowest median concentrations in 1995 and 2005 and the southeast the highest. As with chloride, the number of towns without data for concentrations of sodium was greater in 2005 than in 1995, probably because of the effect of weeding out results due to possible treatment. The median concentrations of sodium from groundwater samples from the few towns that could be analyzed for 1985 were generally larger than those in 1995. However, the distribution of data from 1985 was too sparse to make a statewide assessment.

A comparison of median concentrations of sodium for individual wells before and after 1995 (fig. 6; table 5) shows clusters of large increases in regions 5 and 2 and parts of region 1, similar to the map for chloride concentrations (fig. 3). The distribution of the number of wells in each group (decrease, no difference or small change, and large increase) among regions is similar to that for the data on concentrations of chloride except that, for sodium, region 5 did not differ as much from the other regions and was very similar to region 2.

Summary statistics for median concentrations of sodium in groundwater by source (well) (table 3) show that all percentiles in the 1970s and 1980s and the 10th, 25th, and 50th percentiles in the 1990s were less than 10 mg/L. All the percentiles were greater than 10 in the 2000s. Between the 1990s and 2000s, all the percentiles for median concentrations of sodium increased—the 50th and the 75th percentiles by more than threefold, and the 90th percentile by a factor of six. The number of censored values for sodium in table 3 changed from 654 in the 1990s to 0 in the 2000s (the same pattern was seen, though less dramatically, for chloride). During the 1990s, almost all the censored values came from a single source of data, the DWGB database (either as reported values or as values deduced from IOC records (table 2)). For comparisons among decades, the percentage of raw observations (including data from private wells in the SL database) whose values were greater than the drinking water advisory of 20 mg/L for concentrations of sodium increased from 13 percent of data during the 1970s to 30 percent of data during the 2000s. Analysis of the original data from the NHDES, which were used to deduce censored values from IOC records, showed that 95 percent occurrences of those censored sodium values were during the 1990s, and the remaining 5 percent, during the 2000s.

Distinctions among regions are very similar to those for chloride. The only median concentration with a value greater than 10 mg/L was in region 5. Region 1 had the lowest 75th and 90th percentiles, region 5 had the highest, and regions 2, 3, and 4 were all similar with values in between the other two. The percentage of raw observations (including data from private wells in the SL database) with values for concentration of sodium higher than the drinking water advisory of 20 mg/L ranged from 19 and 20 percent in regions 4 and 1, respectively, to 40 percent in region 5.

Boxplots that summarize median concentrations of sodium for individual wells for each decade within each region are shown in figure 7. Because even the 90th percentiles for all regions were less than 10 mg/L during the 1970s and 1980s, data from these decades were omitted from the figure. Increases in all percentiles between the 1990s and 2000s seen in the summary statistics are confirmed by statistical tests that show significantly different medians. The pattern of significant increases for all

percentiles for median concentrations of sodium between the 1990s and the 2000s is distributed uniformly throughout the five regions of the State. A small difference among regions is seen with slightly higher 50th, 75th, and 90th percentiles for regions 3 and 5 during the 2000s compared with the other regions. For all regions, during the 1990s, even the 90th percentile of median concentrations of sodium was less than the 20 mg/L drinking water advisory; but during the 2000s, median concentrations of sodium increased so that the 25th percentiles were higher than 20 mg/L.

## Summary

Several studies of groundwater in New Hampshire on a statewide and regional level have suggested that concentrations of chloride and sodium have been increasing throughout much of the 20th century and into the 21st century primarily from anthropogenic sources, such as road salt. To examine the spatial and temporal trends of chloride and sodium on a statewide basis, the U.S. Geological Survey, in cooperation with the New Hampshire Department of Environmental Services, assembled all available data from State and Federal agencies that met specified criteria (untreated, single source, and unbiased sources) into a single database, performed quality assurance procedures on the compiled dataset, explained features of the data that may affect results, and summarized the data graphically and statistically.

One feature of the data was the presence of many censored values (concentrations with values less than a reporting limit), especially for chloride. Multiple reporting limits that changed systematically over time further complicated the analysis. A robust adjustment was made whereby all censored and observed chloride and sodium concentrations less than the highest reporting limit of 10 milligrams per liter (mg/L) were adjusted to 10 mg/L before compiling summary statistics or performing other statistical analyses. Counties in New Hampshire were grouped into five regions for summarizing data geographically. Summary statistics presented by decade and by region and statistical comparisons across decades for regions were calculated using the median concentration per individual well for each decade or region.

Median concentrations of chloride and sodium by town for 1985, 1995, and 2005 showed shifts in many towns towards higher concentrations in 2005 for both constituents, especially in the southeastern part of the State. Data from 1985 were too sparse statewide to make meaningful comparisons with more recent data. Viewed qualitatively, region 1 in northern New Hampshire had the lowest median concentrations of chloride and sodium, and region 5 had the highest. For each region, median concentrations of chloride and sodium increased significantly between earlier decades and the 2000s. Increases in median concentrations of sodium were dramatic and relatively uniform for all regions—during the 1990s, all 90th percentiles were less than the 20 mg/L U.S. Environmental Protection Agency drinking water advisory, and during the 2000s, all 25th percentiles were higher than 20 mg/L.

For data grouped by decades, the percentage the values of raw observations (including data from private wells in the New Hampshire Department of Health and Human Services State Laboratory database) higher than the secondary maximum contaminant level of 250 mg/L for concentrations of chloride ranged from 1 to 7 percent, with the highest percentage for data from the 1960s; and for regions, the percentage of values higher than the secondary maximum contaminant level ranged from 2 to 5 percent, with the highest percent for data in region 5. For comparisons among decades, the percentage of the values of raw observations higher than the drinking water advisory of 20 mg/L for concentrations of sodium increased from 13 percent for data from the 1970s to 30 percent for data during the 2000s; and by regions, the percentage of values higher than 20 mg/L ranged from 19 and 20 percent in regions 4 and 1, respectively, to 40 percent in region 5.

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## Appendix 1. Description of the Database for Salt in New Hampshire Groundwater

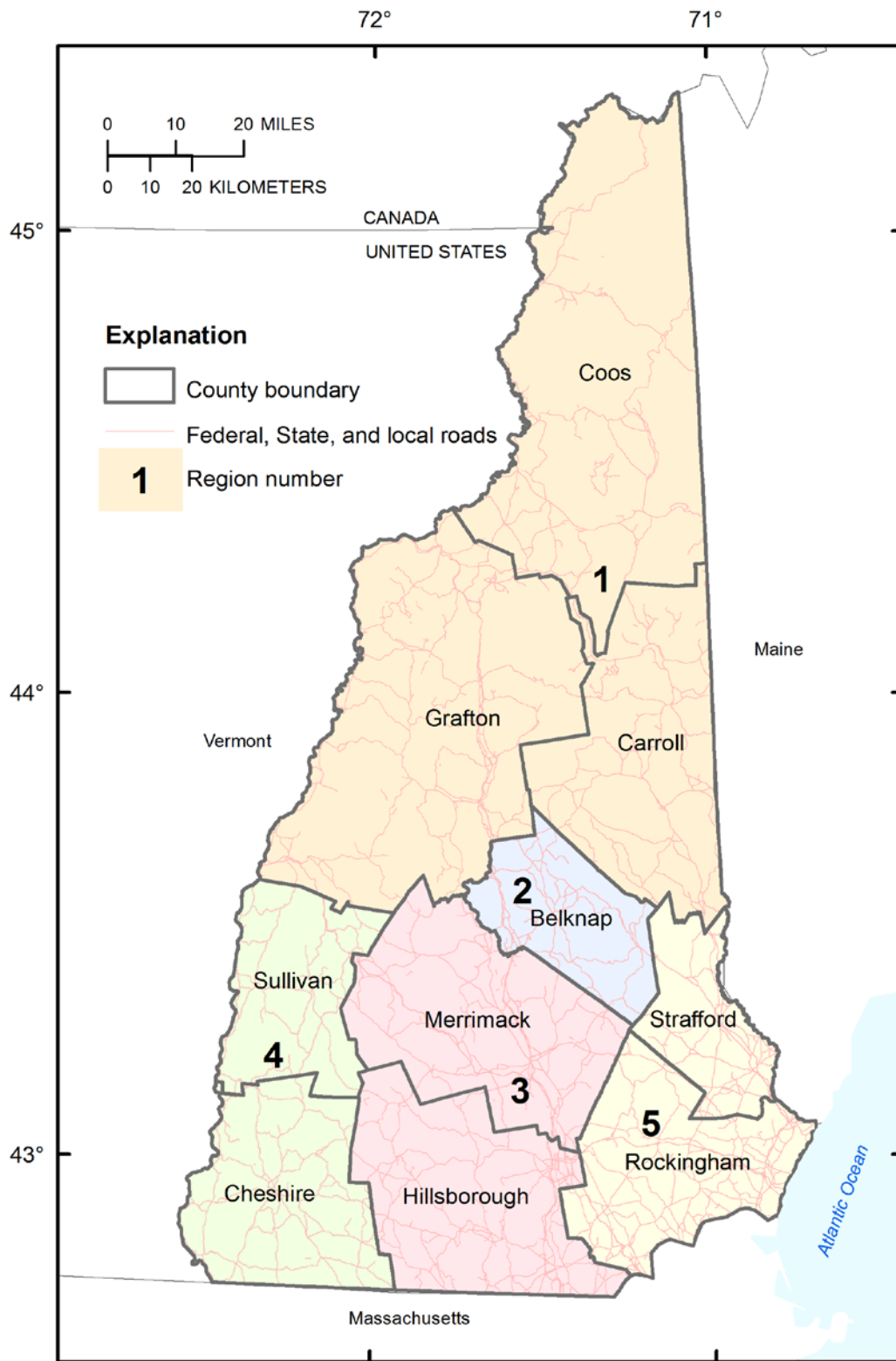
The database for salt in New Hampshire groundwater (NH salt database) is the data product that was compiled from several sources (table 1) and used to generate data summaries and statistics shown in this report. The main part of the database, which is a Microsoft Access® relational database, consists of three tables—Systems, Wells, and ChemResults. The PWS ID FED field of the Systems table contains the primary identifier of the public water system (PWS) (for New Hampshire Department of Environmental Services [NHDES] wells) or well identifier (for National Water Information System data). Other fields in the Systems table provides basic locational and descriptive information about the system (Name, Town, County, CPN [type of PWS system], and Population Served). The Wells table contains fields for the well identifier (Source) and the link to the PWS system table (PWS ID FED). Fields with other information (Site Description, Source Description, Lat, Long, WELL\_DEPTH, SAFE\_YIELD, and Strata) about the well are included if available. The ChemResults table contains links to the Systems and Wells tables (the PWS ID FED and Source fields); other fields include Date Sampled, DataSource, Cl, and Na (the latter two fields are chloride and sodium results expressed in units of milligrams per liter). Other information (laboratory identifier, sample identifier (assigned by the laboratory), chloride or sodium detect flag, chloride or sodium qualifier for censored values (values less than the detection limit), chloride or sodium laboratory method, and date that treatment was added) about the results also are included in the ChemResults table if available.

Because data potentially available for the NH salt database came from many different sources, quality assurance of the data before entry into the database involved a thorough check of duplicate entries based on system identifier in combination with well identifier (together making a unique combination), sample collection date, and concentration value. Other quality assurance measures were implemented to bring data from several disparate sources into a uniform organization. For example, the strata and well depth fields in the well table were often blank but sometimes could be populated by eliciting information from the source description field. In some cases, town and county names were added by using a geographic information system (GIS) to overlay latitude and longitude points with administrative boundary maps. In other cases, a source identifier was not available, but because this field was necessary to link wells with their chemical results, a manufactured entry would be generated (using a unique prefix to distinguish it from numbers meaningful to the State databases) for use in the NH salt database. Ultimately, there also were cases where data could not be incorporated into the NH salt database because it was not possible to determine a key piece of information, such as whether the sample result was from a groundwater or surface-water source, whether the sample was from an untreated and unblended source, or how to match multiple wells from different source databases if the two databases did not use the same naming conventions for identifying specific wells.

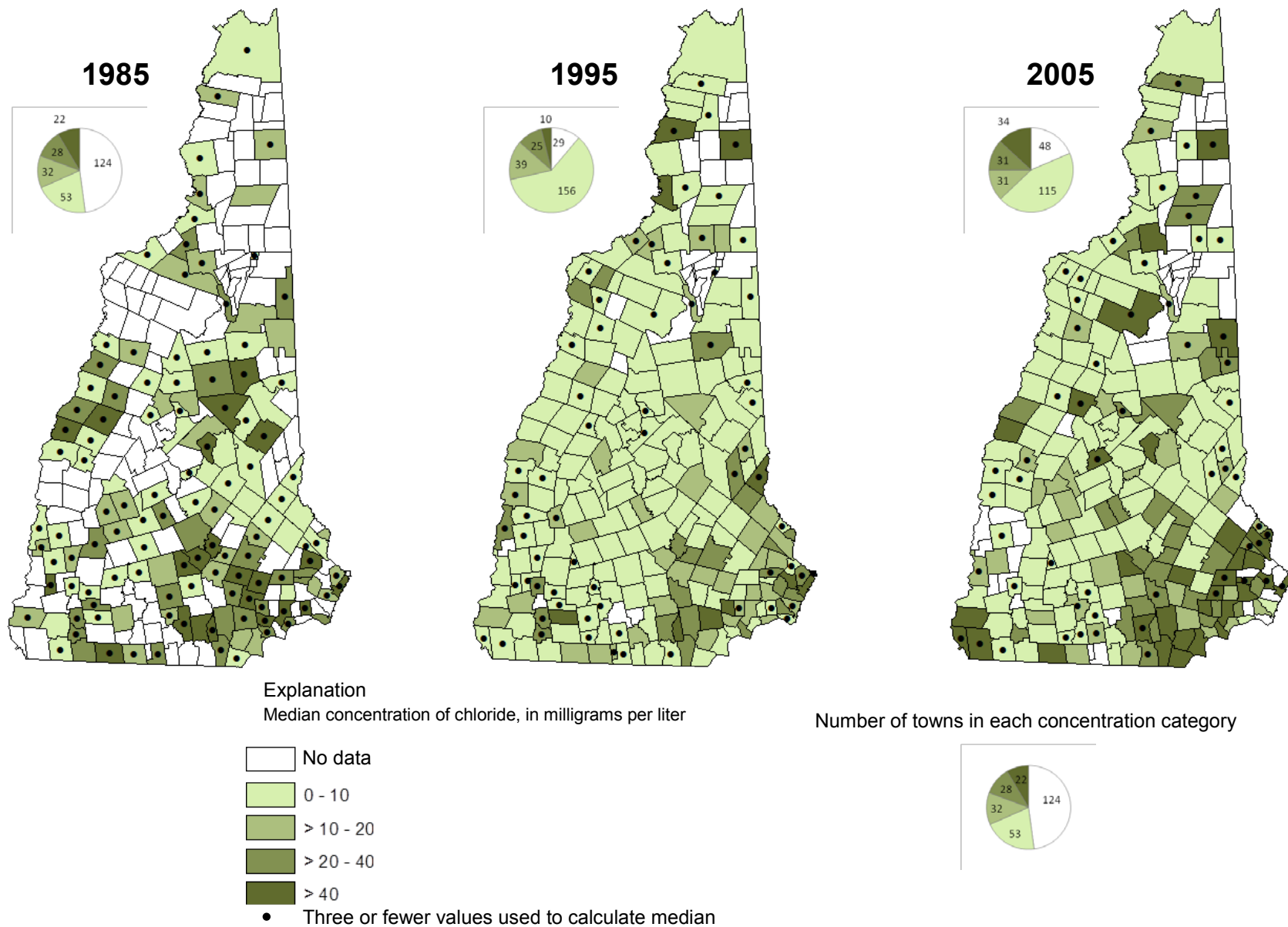
Two additional tables in the NH salt database contain chloride and sodium records from private (domestic) well data stored in the New Hampshire Department of Health and Human Services State Laboratory (SL) database. These standalone tables, named Homeowners\_Cl and Homeowners\_Na, could not be integrated within the structure of the linked systems, wells, and ChemResults tables because individual wells were not identified, and, consequently, each record was assumed to be from a unique source. This assumption is not completely realistic; some percentage of the records were probably from nonunique wells (that is, from the same well), but this percentage is probably small. Because of this feature, private well data from the SL database were not used for statistical analyses.

Database queries were developed to filter and retrieve the data for various purposes. An initial query excluded information that was provided with the original data from the NHDES or NHDHHS databases that met the following criteria for this project: data from surface-water sources, data from treated or potentially treated and blended sources, and data from wells that were known to be contaminated. Subsequent queries created subsets of data to explore trends over time and geographic areas.

For more information concerning the database, contact: Director, New England Water Science Center, *dc\_nh@usgs.gov* or visit <http://nh.water.usgs.gov/>.



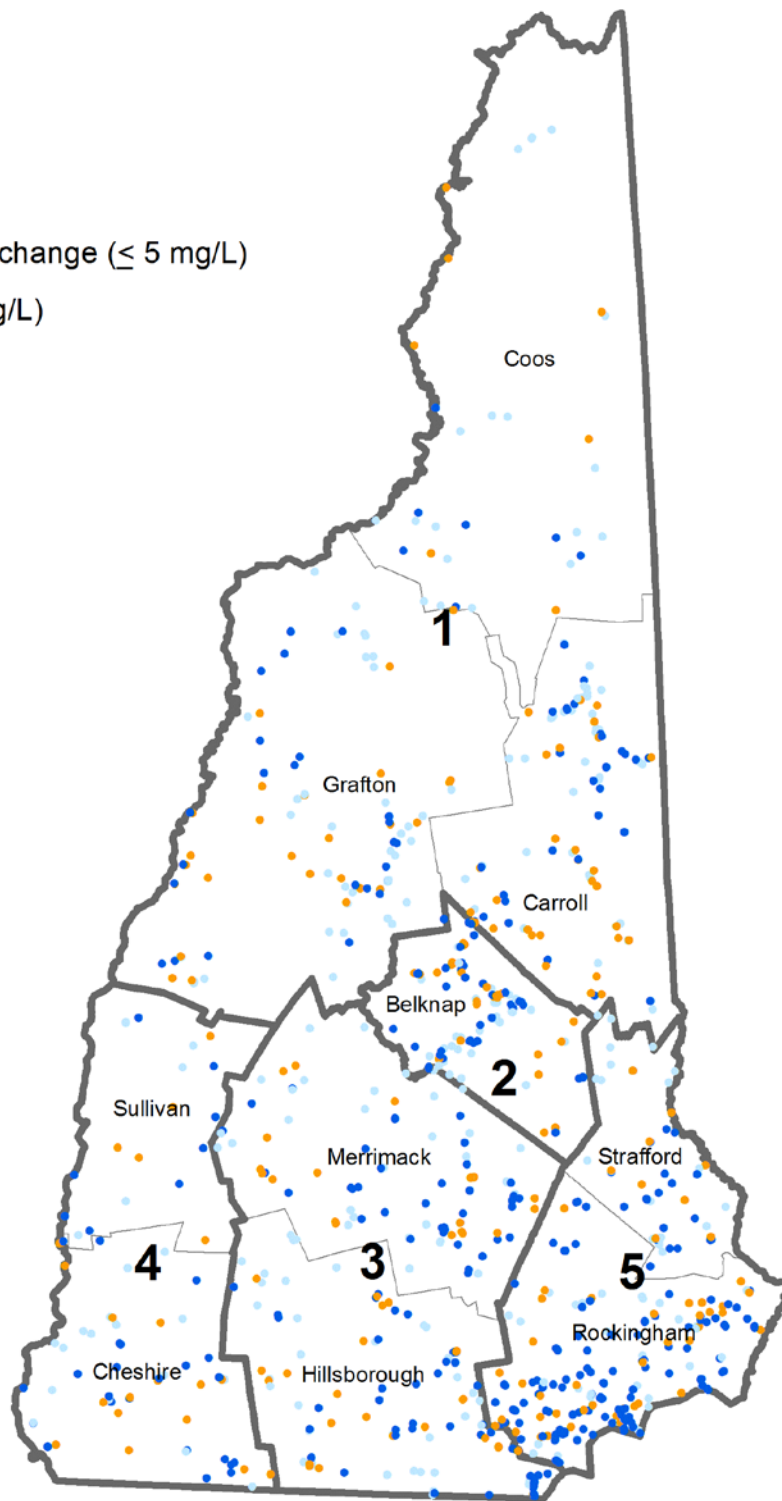
**Figure 1.** Index map of New Hampshire, showing county boundaries, major roads, and regions as used in this report.



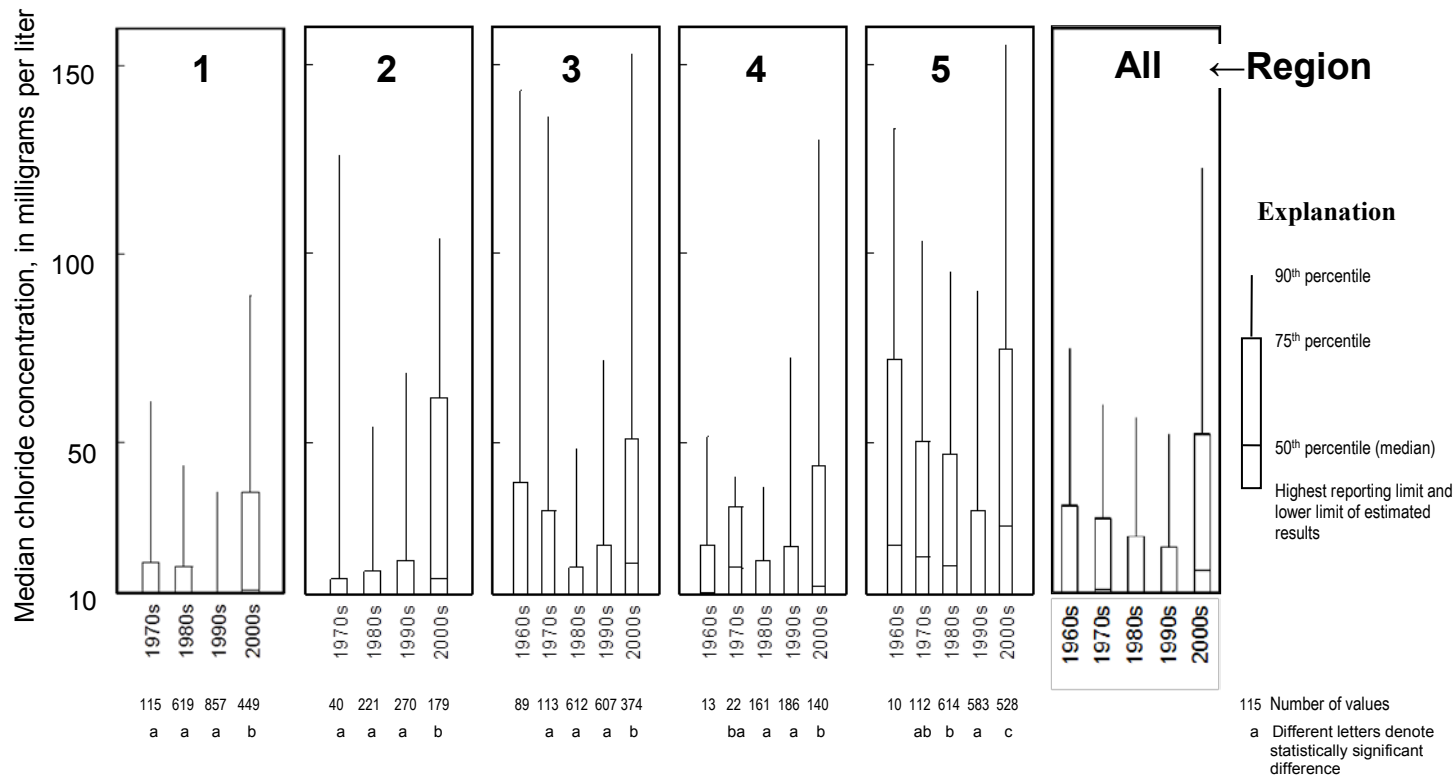
**Figure 2.** Median concentrations of chloride in water samples from wells by town in New Hampshire in 1985, 1995, and 2005.

## Explanation

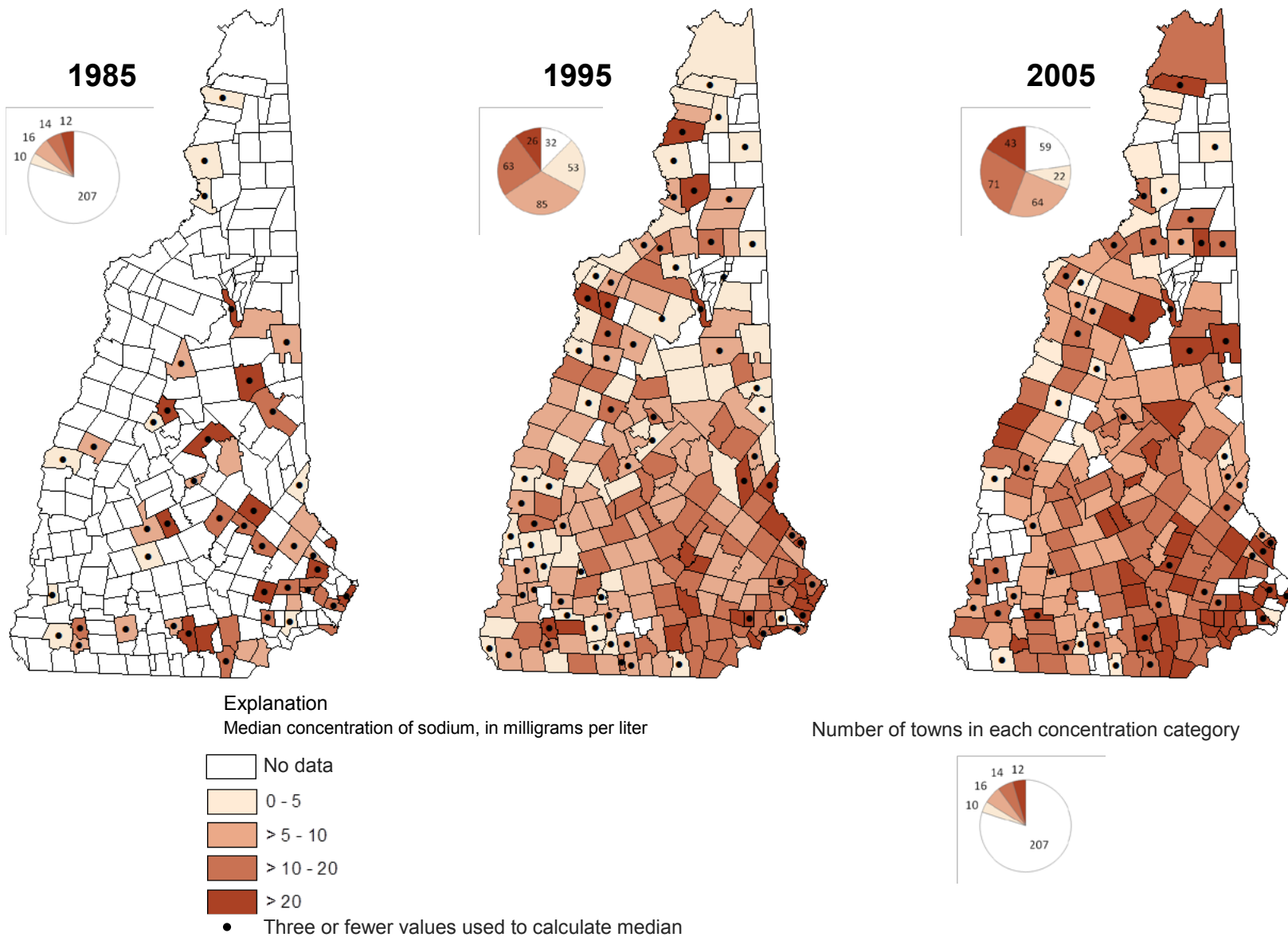
- 1** Region number
- Decrease
- No difference or small change ( $\leq 5$  mg/L)
- Large increase ( $> 5$  mg/L)
- Region boundary
- County boundary



**Figure 3.** Differences in median concentrations of chloride at individual wells in New Hampshire for data before and after January 1, 1995. mg/L, milligrams per liter;  $\leq$ , less than or equal to;  $>$  greater than.



**Figure 4.** Boxplots of median concentrations of chloride in groundwater by source (well) in New Hampshire, grouped by decade (beginning with the 1960s and ending with the [extended] decade 2000-11) and region. The extents of the regions are shown in figure 1. Boxplots for early decades may be missing for some regions where data are sparse.

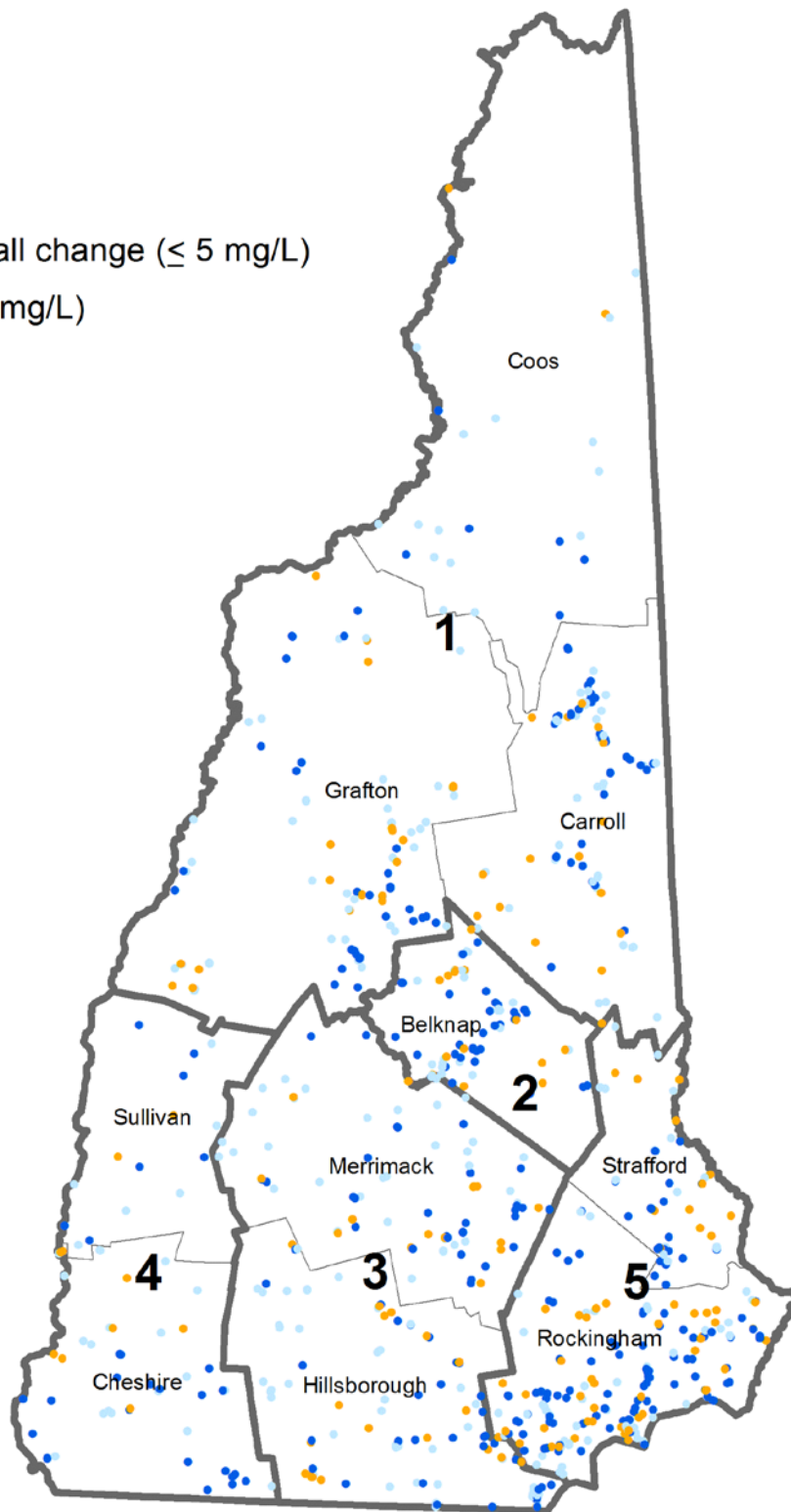


**Figure 5.** Median concentrations of sodium in water samples from wells by town in New Hampshire in 1985, 1995, and 2005.

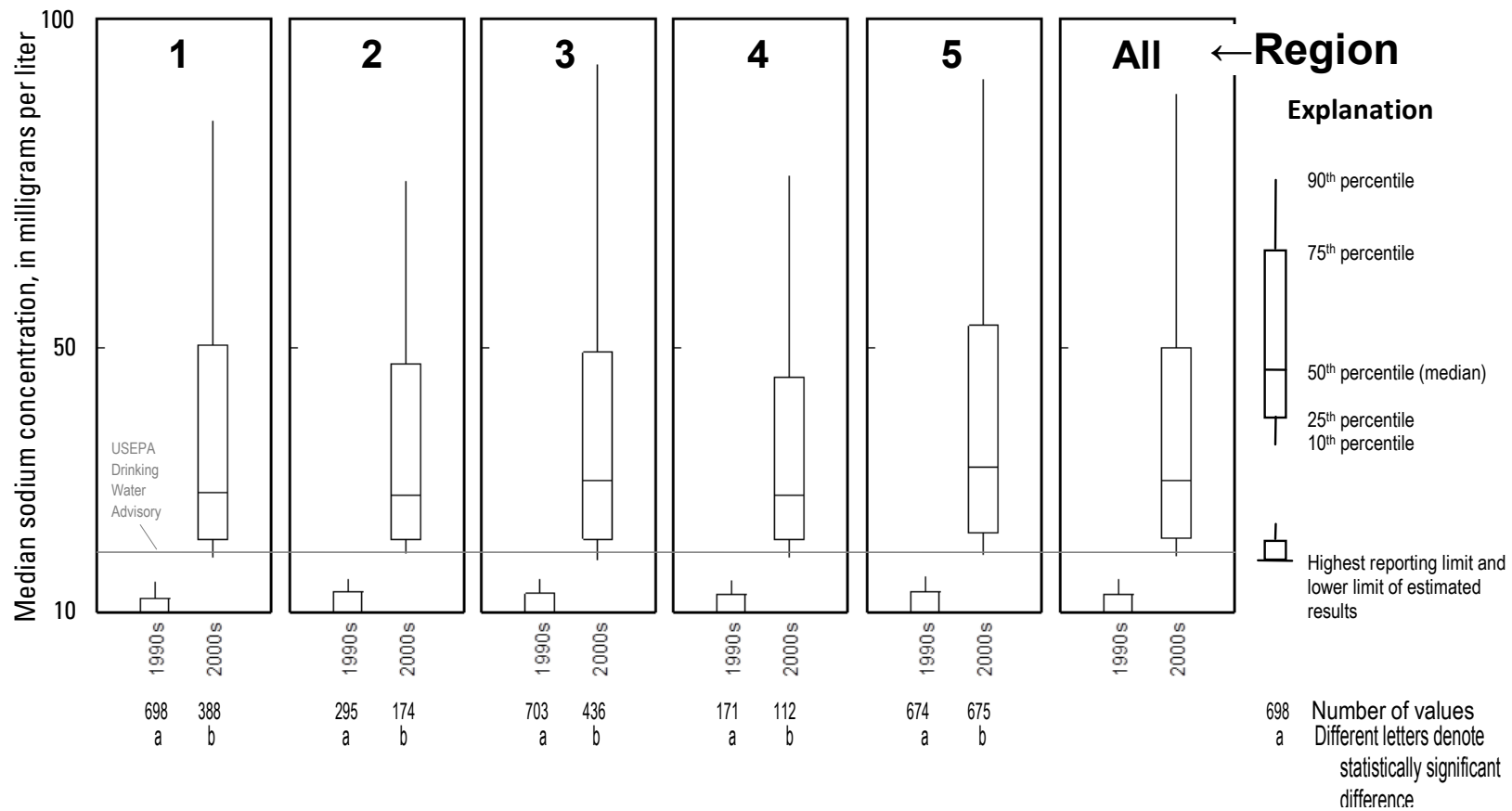


## Explanation

- 1** Region number
- Decrease
- No difference or small change ( $\leq 5$  mg/L)
- Large increase ( $> 5$  mg/L)
- Region boundary
- County boundary



**Figure 6.** Differences in median concentrations of sodium at individual wells in New Hampshire for data before and after January 1, 1995. mg/L, milligrams per liter;  $\leq$ , less than or equal to;  $>$  greater than.



**Figure 7.** Boxplots of median concentrations of sodium in groundwater by source (well) in New Hampshire for two decades by region. Regions are defined in figure 1. Percentiles for the 1970s and 1980s are all below 10 milligrams per liter. USEPA, U.S. Environmental Protection Agency..

**Table 1.** Sources of data for concentrations of chloride and sodium in groundwater in New Hampshire.

[mg/L, milligrams per liter; na, not available; NHDES, New Hampshire Department of Environmental Services; NHDHHS, New Hampshire Department of Health and Human Services; NHDOT, New Hampshire Department of Transportation; STORET, U.S. Environmental Protection Agency’s STORAge and RETrieval database for water quality monitoring data; USEPA, U.S. Environmental Protection Agency; USGS, U. S. Geological Survey]

Dataset Name	Agency	Years of data	Reporting limit, in mg/L		Number of records		Number of wells	Description
			Chloride	Sodium	Chloride	Sodium		
Drinking Water and Groundwater Bureau (DWGB) <sup>1</sup>	NHDES	1988–2011	2 or 3	1 or 5	3,582	2,994	1,405	Compliance database for public water system wells, sampled once every 3 years.
State Laboratory (SL): Public-water systems <sup>1</sup>	NHDHHS	1984–2000	2 or 3	1 or 3	2,497	2,090	959	Database of chemical results for water samples from public water systems analyzed at the NHDES SL
Private wells	NHDHHS	1994–2011	2 or 3	1 or 2	31,949	22,486	32,082	Database of chemical results for water samples from private wells that have been analyzed at the NHDES SL. Town names were the only locational information provided.
Data Warehouse (DW)	NHDES	2008–2011	1 or 3	1	64	874	19	Database developed to receive water sample results from the State and private laboratories through online reporting. After review, results are transferred to the DWGB database.
Environmental Monitoring (EMD)	NHDES	1972–2011	2, 3, or 10	5 or 10	1,382	551	934	Consists of NHDES data that have been stored in paper files. One part of this dataset consists of “old” records (before routine electronic filing) from small community-water systems. Another part are water-quality data from pump tests, including those required for new community-water systems and are frequently the last raw water samples available before the addition of treatment. Data from these two sources are currently (2011) being entered into the electronic EMD to make them available for various purposes.
National Water Information System (NWIS)	USGS	1952–2010	2, 3, or 10	1, 3, 5, or 10	2,052	1,824	1,801	Database of water-related data, including chemical results, from various U.S. Geological Survey projects.
Legacy STORET	USEPA	1971–1983	na	na	50	63	17	Database of chemical results from water samples from U.S. Forest Service wells in Carroll, Coos, and Grafton Counties.
Salt replacement wells <sup>2</sup>	NHDOT	1973–2011	na	na	426	0	426	Database of chemical results for water samples for wells possibly contaminated with road salt.

<sup>1</sup>Distinctions between and apparent overlap of data between these two data sources are explained in table 2.

<sup>2</sup>Because data are biased towards high concentrations and do not reflect ambient conditions, they are not used in summary or statistical analyses for this study but were put into the New Hampshire salt database for other potential mapping applications.

**Table 2.** Sources of data for public water system wells in the U.S. Geological Survey New Hampshire salt database.

[RL, reporting limit<sup>1</sup>; DWGB, New Hampshire Department of Environmental Services Drinking Water and Groundwater Bureau; IOC, inorganic contaminants; SL, New Hampshire Department of Health and Human Services State Laboratory; DW, New Hampshire Department of Environmental Services Data Warehouse]

Sample collection date	Source of data
Samples analyzed at private laboratories	
1990 through 2010:	
Samples with concentrations above RL <sup>2</sup>	DWGB database
Samples with concentrations below RL <sup>3</sup>	Deduced from IOC records of DWGB database
After 2010, all samples	DW database
Samples analyzed at the State Laboratory	
Before 2001, all samples <sup>4</sup>	
2001 through 2008:	
Samples with concentrations above RL	DWGB database
Samples with concentrations below RL	Deduced from IOC records of DWGB database
After 2008, all samples	DW database

<sup>1</sup>The lower limit of data that delineates the censoring threshold is called the reporting limit in this report.

<sup>2</sup>Less than 0.1 percent of the data provided were for samples collected before 1990.

<sup>3</sup>A few dozen results that had values below the RL were provided with the DWGB database.

<sup>4</sup>Several hundred results that had values below the RL were provided with the DWGB database.

**Table 3.** Summary statistics for median concentrations of chloride and sodium in groundwater by source (well) in New Hampshire grouped by A, decade and B, region.

[Data for concentrations of chloride and sodium reflect the median for each source (well) for each A, decade and B, region. Before running statistical tests, all censored (less than a detection or reporting limit) and uncensored values less than 10 milligrams per liter were adjusted to 10 milligrams per liter. Summary statistics were calculated using the modified (Helsel, 2005) Kaplan-Meier (1958) test. mg/L, milligrams per liter; NA, not available; SMCL, secondary maximum contaminant level; USEPA, U.S. Environmental Protection Agency; <, less than]

A. By decade						
	1960s	1970s	1980s	1990s	2000s	All
Chloride concentrations, in mg/L						
10th percentile	<10	<10	<10	<10	<10	<10
25th percentile	<10	<10	<10	<10	<10	<10
50th percentile	10	11	10	<10	17	<10
75th percentile	33	30	25	22	52	30
90th percentile	88	77	60	61	122	79
Number of median observations	114	402	2,227	2,503	1,671	6,917
Number censored	0	159	640	831	102	1,732
Percentage of observations higher than the SMCL of 250 mg/L <sup>1</sup>	7	3	1	3	3	3
Sodium concentrations, in mg/L						
10th percentile	NA	<10	<10	<10	19	<10
25th percentile	NA	<10	<10	<10	21	<10
50th percentile	NA	<10	<10	<10	30	<10
75th percentile	NA	<10	<10	13	50	19
90th percentile	NA	<10	<10	15	89	40
Number of median observations	NA	183	1,616	2,542	1,785	6,126
Number censored	NA	0	157	654	0	811
Percentage of observations higher than the USEPA drinking water advisory level of 20 mg/L <sup>1</sup>	NA	13	23	23	30	27
B. By region						
	Region 1	Region 2	Region 3	Region 4	Region 5	All
Chloride concentrations, in mg/L						
10th percentile	<10	<10	<10	<10	<10	<10
25th percentile	<10	<10	<10	<10	<10	<10
50th percentile	<10	<10	<10	<10	17	<10
75th percentile	17	27	28	27	46	30
90th percentile	53	82	80	75	105	79
Number of median observations	2,043	710	1,795	522	1,847	6,917
Number censored	650	215	477	120	270	1,732
Percentage of observations higher than the SMCL of 250 mg/L <sup>1</sup>	2	2	3	2	5	3
Sodium concentrations, in mg/L						
10th percentile	<10	<10	<10	<10	<10	<10
25th percentile	<10	<10	<10	<10	<10	<10
50th percentile	<10	<10	<10	<10	14	<10
75th percentile	14	19	18	17	27	19
90th percentile	29	35	39	34	55	40
Number of median observations	1,867	621	1,548	431	1,659	6,126
Number censored	263	101	189	58	200	811
Percentage of observations higher than the USEPA drinking water advisory level of 20 mg/L <sup>1</sup>	20	27	27	19	40	27

<sup>1</sup>Percentages include data for private wells in the New Hampshire Department of Health and Human Services State Laboratory database, which are not included with results of summary statistics shown in the rest of this table.

**Table 4.** Change in median concentrations of chloride before and after January 1, 1995.

Region	Total number of wells	Percentage of wells		
		Decrease	Small increase <sup>1</sup>	Large increase <sup>2</sup>
1	245	27	44	29
2	107	27	36	37
3	206	21	35	44
4	81	26	31	43
5	261	21	23	56
Total	900	24	34	42

<sup>1</sup>Change in median concentration less than or equal to 5 milligrams per liter (mg/L).

<sup>2</sup>Change in concentration greater than 5 mg/L.

**Table 5.** Change in median concentrations of sodium before and after January 1, 1995.

Region	Total number of wells	Percentage of wells		
		Decrease	Small increase <sup>1</sup>	Large increase <sup>2</sup>
1	224	28	38	35
2	78	32	23	45
3	185	26	37	37
4	65	23	32	45
5	248	29	25	45
Total	800	28	32	40

<sup>1</sup>Change in median concentration less than or equal to 5 milligrams per liter (mg/L).

<sup>2</sup>Change in concentration greater than 5 mg/L.