

STUDY DESIGN AND METHODS

The study approach involved three general components: (1) collection of existing public and some private drinking-water chemistry data for ground water in stratified drift and bedrock aquifers from State agencies responsible for monitoring Safe Drinking-Water Act regulations; (2) compilation and reclassification of State geologic-map data into 'lithogeochemical' units for the four states in the study unit; and (3) statistical analyses of variance of arsenic, iron, and manganese data by various groupings and combinations of lithogeochemical and land-use data.

Several considerations are worth noting with respect to relating water-quality data to regional data layers such as generalized lithogeochemical and land-use maps. First, land use and geology are heterogeneous even at the local scale (Alley, 1993). For example, in the study unit, water quality in private bedrock-supply wells can vary markedly from house-to-house over short distances (horizontal heterogeneity due to factors including differences in ground-water flow paths or lithologic changes). Additionally, for the bedrock aquifers, lithology can vary with depth for any well (vertical heterogeneity). This variation, however, is not expected to have a significant effect for this regional-scale evaluation because well depths, for wells used in this study, are less than the thickness of the geologic units in which they are completed and are less than the spatial uncertainty of most unit boundaries. Small-scale horizontal and vertical heterogeneity are not represented in the lithogeochemical data set; regional variation could outweigh these small-scale heterogeneous effects, especially when a large number of wells are available across the study unit. Another factor to consider, when evaluating land use, is the relevance of the time period of the land-use data (Alley, 1993). For example, in bedrock-aquifer systems where flow paths of ground water are complex and travel times of ground water can be long, it is difficult to determine which time period of land-use data could be responsible for the observed water quality in a well.

Lithogeochemical Reclassification of Bedrock Units and Regional-Scale Approach

The geologic data were compiled from statewide geologic maps of Maine (Osberg and others,

1985, 1:500,000 scale), New Hampshire (Lyons and others, 1997, 1:250,000 scale), Massachusetts (Zen and others, 1983, 1:250,000 scale), and Rhode Island (Hermes and others, 1994, 1:100,000 scale). Digital versions of the state geologic maps were obtained for Maine, New Hampshire, and Rhode Island. For Massachusetts, a digitized data layer based on Zen and others (1983), and created under the direction of Dr. Rudolph Hon, Department of Geology, Boston College, was obtained and verified. Lithogeochemical codes were added in ARC/INFO to each statewide geologic map. For Maine, metamorphic grade and protolith (pre-metamorphism source rock) rock type were used to classify polygons into lithogeochemical categories using a digital data layer of generalized regional metamorphic zones obtained from the Maine Geological Survey (Osberg and others, 1985). For example, rocks with protoliths of "limestone and (or) dolostone" were classified as "limestone, dolomite, and carbonate-rich clastic sediments" in areas with or without weak regional metamorphism and as "marble, which include some calc-silicate rock," in areas of greenschist-facies- or higher-grade metamorphism. Coded statewide data were joined to create one data layer for the New England Coastal Basins study unit.

Because the state geologic maps were produced at somewhat different scales, the level of detail of adjacent maps is variable; there are also discrepancies between bedrock units at state borders. The more than 700 bedrock geologic units on the four state maps were combined into a study-unit-wide digital map and were reclassified into 29 general 'lithogeochemical' units. These 29 units were then combined into 7 groups of similar geochemical nature, which were used in the analysis of arsenic, iron, and manganese concentration trends (fig. 3). These seven groups are described in figure 3; however, group I_u, which consists of primarily ultramafic igneous rocks, occupied less than 1 percent of the study unit and was omitted from the analysis. The thick unconsolidated sediments of Cape Cod (2 percent of the study unit) also were omitted from this study.

The lithogeochemical classification scheme was originally developed as part of an adjacent NAWQA study that included the Connecticut, Housatonic, and Thames River Basins (Robinson and others, 1999); a detailed description of the classification scheme and associated expected water-quality and ecosystem characteristics is presented in Robinson (1997).

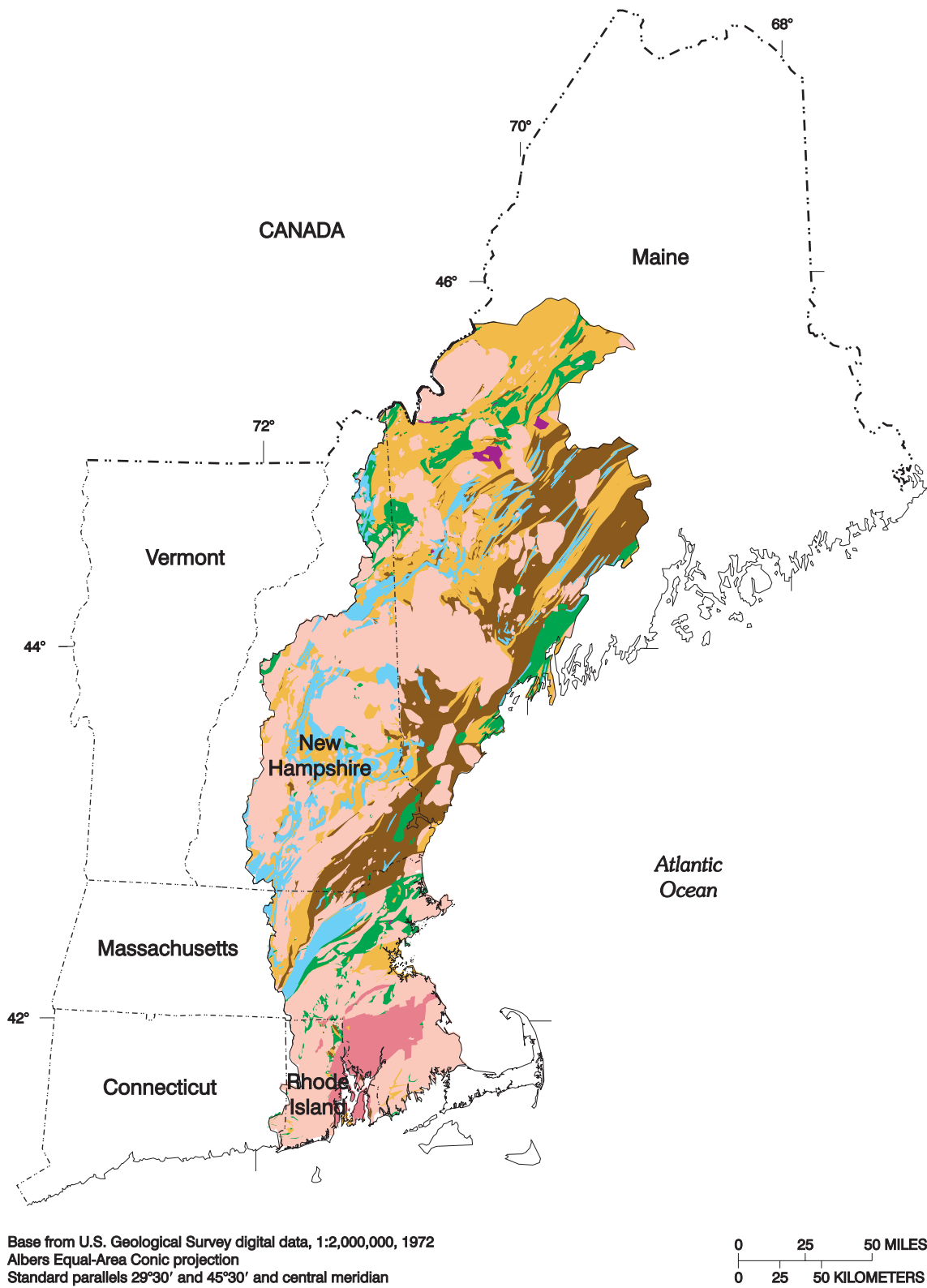










Figure 3. Areal distribution and description of major lithochemical groups of bedrock geologic units.

EXPLANATION

MAJOR LITHOGEOCHEMICAL GROUPS

-  **M_C** Clastic metasedimentary rocks derived predominantly from moderately calcareous sedimentary protoliths. Generally deformed and at or above greenschist facies of regional metamorphism; at lower metamorphic grades, bulk units typically contain 5-45 percent of carbonate minerals distributed either throughout the rock unit or in discrete carbonate-rich layers or laminae. At higher metamorphic grades, the percentage of carbonate minerals typically decreases and the percentage of calc-silicate minerals increases. May include locally noncalcareous rocks, sulfidic rocks, and metavolcanic rocks
-  **M_S** Clastic metasedimentary rocks derived predominantly from variably sulfidic sedimentary protoliths. Generally deformed and at or above greenschist facies of regional metamorphism. Bulk units are characterized by rusty-weathering intervals that typically contain a small percentage of pyrite and (or) pyrrhotite distributed either throughout the rock unit or in discrete sulfide-rich layers or laminae. May include locally nonsulfidic rocks, calcareous and calc-silicate rocks, and metavolcanic rocks
-  **M_U** Undifferentiated clastic metasedimentary rocks derived predominantly from noncalcareous and nonsulfidic sedimentary protoliths. Generally deformed and at or above greenschist facies of regional metamorphism. May include locally sulfidic rocks, calcareous and calc-silicate rocks, and metavolcanic rocks
-  **M_{md}** Undifferentiated clastic metasedimentary rocks derived predominantly from noncalcareous and nonsulfidic sedimentary protoliths occurring in fault-bounded depositional basins at or below greenschist facies of regional metamorphism. May contain volcanic rocks
-  **I_m** Mafic igneous rocks and their metamorphic equivalents. May contain local areas of felsic and intermediate volcanic and intrusive rocks and metasedimentary rocks
-  **I_f** Felsic igneous rocks and their metamorphic equivalents. May contain areas of mafic and intermediate volcanic and intrusive rocks and metasedimentary rocks
-  **I_u** Ultramafic igneous rocks and their metamorphic equivalents
-  STUDY AREA BOUNDARY

The geologic-unit descriptions and structural and metamorphic data from the four state geologic maps were reviewed for information on the chemical character of the bedrock (Robinson and others, 1999; Robinson, 1997). The geologic units were assigned to 'lithogeochemical' units on the basis of these data (fig. 3). The lithogeochemical classification scheme is based on the relative stability or "weatherability" of the constituent minerals and on the presence of carbonate and sulfide minerals in the bedrock or in the bedrock protolith. Carbonate and sulfide minerals are distinguished because these highly reactive minerals can have a disproportionately large effect on water chemistry compared to other minerals commonly found in the rocks of this region. For metamorphosed bedrock units in Maine, information about metamorphic grade also was used.

The lithogeochemical map, which was produced with the aid of a Geographic Information System (GIS), was designed to be flexible enough to regroup units based on relevance to the particular constituent being studied. For example, the number of groups and the composition of those groups relative to the occurrence of arsenic could differ from those chosen to assess the occurrence of radon.

Sources of Ground-Water Data and Well Selection

The most readily available source of ground-water chemical data in all states across the study area is data collected by states and public-water suppliers for monitoring compliance with the Federal Safe Drinking Water Act. These data are collected to ensure the safe delivery of public drinking-water supplies to communities, schools, and businesses. Each state operates its safe drinking-water program in accordance with Federal standards, and each uses the same sample-collection and laboratory-analysis methods. This standardization means that the data from each state are comparable, and thus usable for a regional analysis.

One disadvantage of using data collected for compliance with the Safe Drinking Water Act is that the testing is done on water being delivered to customers, not necessarily on the source water. Thus, any of the drinking-water suppliers can blend water from many wells or from wells and reservoirs before testing, and can also treat the water before testing. In

order to eliminate wells that treat the water or that blend samples, data were selected from public water suppliers who (a) had only one supply source (a single well), and (b) were not required to do any treatment, because the raw water met current Federal drinking-water standards, and (c) had sampled for arsenic, iron, or manganese (table 2, appendixes 1 and 2). By meeting these criteria, the data represent conditions as close to natural conditions as possible, from this source of data, in the aquifers used for supplying drinking water to the public.

Data that met these criteria were collected from the Maine Department of Health; the New Hampshire Department of Environmental Services, Water Division, Water Supply Engineering Bureau; the Massachusetts Department of Environmental Protection, Bureau of Resource Protection, Drinking Water Program; and the Rhode Island Department of Health. The resulting data base of 804 bedrock wells and 145 surficial wells represents mostly small, non-community suppliers (such as restaurants) (table 2). Because of our requirement that the selected wells have no treatment, the data base is skewed away from systems that obtain water from sources that have naturally high concentrations of arsenic. The total number of systems requiring treatment, however, is not large. In Maine, for example, only 26 of 800 single-source ground-water systems in the study area (not all of which had arsenic analyses) required any sort of treatment, and only 4 of those required treatment for removing arsenic.

In addition, because the lowest common detection limit for the analytical results in this data set is 0.005 mg/L, there are a high number of non-detections for the accompanying arsenic analyses. The data set also is limited because the supplier is required to meet the USEPA MCL of 0.05 mg/L; a few samples from this data set, however, exceeded 0.05 mg/L. Thus, this data set represents a limited range of concentrations and represents a range of concentrations that are associated with public-supply drinking-water wells.

Data on well depth were analyzed only for public-supply wells in Rhode Island, New Hampshire, and Maine. From these, well depths ranged from 25 to 1,180 ft. Ninety-five percent of the wells are less than 620 ft deep. A survey of bedrock wells drilled in New Hampshire from 1984 to 1990 indicated that the median well depth in these New Hampshire bedrock

Table 2. Summary of public water supplies compiled by State and aquifer type in the New England Coastal Basins study unit [mg/L, milligrams per liter]

State	Number of wells with chemistry data								
	Arsenic			Iron			Manganese		
	Surficial	Bed-rock	Detection limit (mg/L)	Surficial	Bed-rock	Detection limit (mg/L)	Surficial	Bed-rock	Detection limit (mg/L)
Maine	20	168	0.001	20	167	0.01	20	167	0.01
New Hampshire	40	296	.005	0	296	.05	0	296	.01
Massachusetts	0	197	.005	0	18	.05	0	18	.03
Rhode Island	85	143	.005	81	99	.02	81	99	.02
Entire New England Coastal Basins study unit	145	804	.005	101	580	.05	101	580	.03

wells was 295 ft. (F.H. Chormann, written commun., 1990); it is likely that the median depth of bedrock wells in Massachusetts is similar.

The geographic distribution of the final set of wells used in this study is shown in figures 4a and 4b. Bedrock wells in Massachusetts are more clustered because there is an absence of wells in the large service areas of the Massachusetts Water Resources Authority, which serves the Boston Metropolitan area and other area communities with surface water. Cape Cod is served primarily by water withdrawn from a large stratified-drift aquifer and was not included in this study.

The greatest limitation of the data set used is its reliance on data from public-supply wells, which, by the nature of their use, are skewed towards supplies of cleaner, less contaminated water. Another limitation is that different states used different reporting limits for arsenic; these range from 0.001 to 0.005 mg/L. All sample results were converted to the single, highest reporting limit for each constituent. The resulting adjusted detection limits for each constituent were 0.005 mg/L for arsenic, 0.05 mg/L for iron, and 0.03 mg/L for manganese. A few samples were reported with higher reporting limits than the adjusted reporting limit used in this study (less than 0.30 or less than 0.010 mg/L for arsenic), and thus were deleted from the data set.

Statistical Analyses

Helsel and Hirsch (1992) note that water-quality data cannot be normally distributed because the data

are bounded at zero or censored at one or more lower reporting levels. These data commonly are skewed and often have unknown distributions. For these reasons, robust statistical methods must be used to avoid potentially large errors associated with using parametric tests on non-normally distributed data (Helsel and Hirsch, 1992). Normality tests were performed on the arsenic, iron, and manganese data, and on the logs of these data. The constituents analyzed for this report were neither normally nor lognormally distributed. Therefore, nonparametric methods, which do not require assumptions about the distribution of the data, were used in this study.

Tests for differences in chemical distributions by aquifer type, major lithogeochemical group, and land use were performed using contingency-table analysis, Kruskal-Wallis and multiple-stage Kruskal-Wallis tests. To compare the rates of arsenic, iron, and manganese detection in the bedrock and surficial aquifers, the data were transformed into categorical values of “above” or “below” the detection level (data for this test were available from Maine, New Hampshire, and Rhode Island only). Contingency-table analysis was used to determine whether any of the constituents occurred at different frequencies in either of the aquifers at the $\alpha = 0.05$ level. Contingency-table analysis was also used to test for independence between the two explanatory variables, lithogeochemical group, and major land-use category, which were used to analyze the bedrock-well water-quality data. The null hypothesis for this test is that the distribution of the data in the categories of one variable is not affected by the classification of another

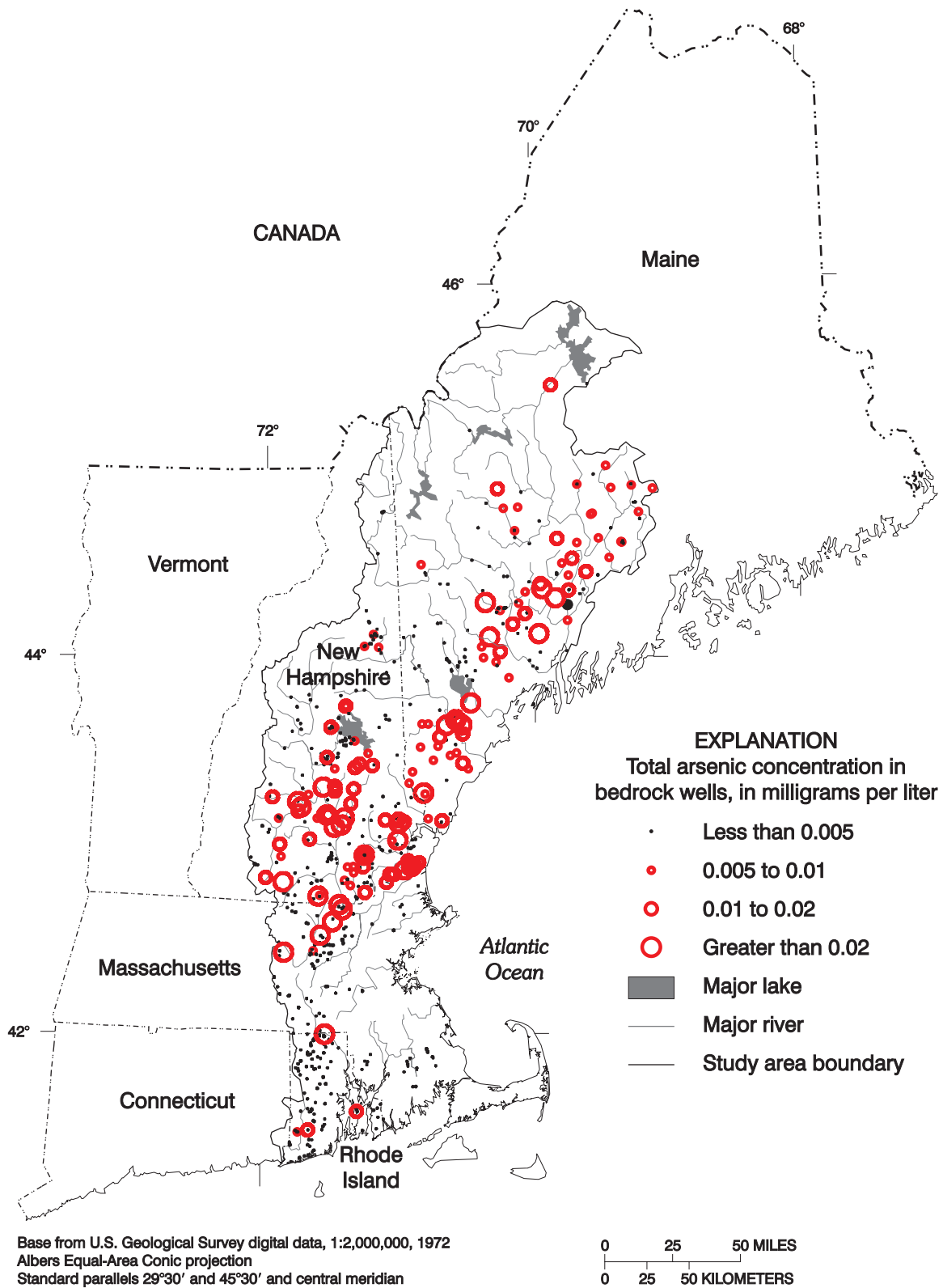


Figure 4a. Areal distribution of arsenic concentrations in water from selected bedrock wells.

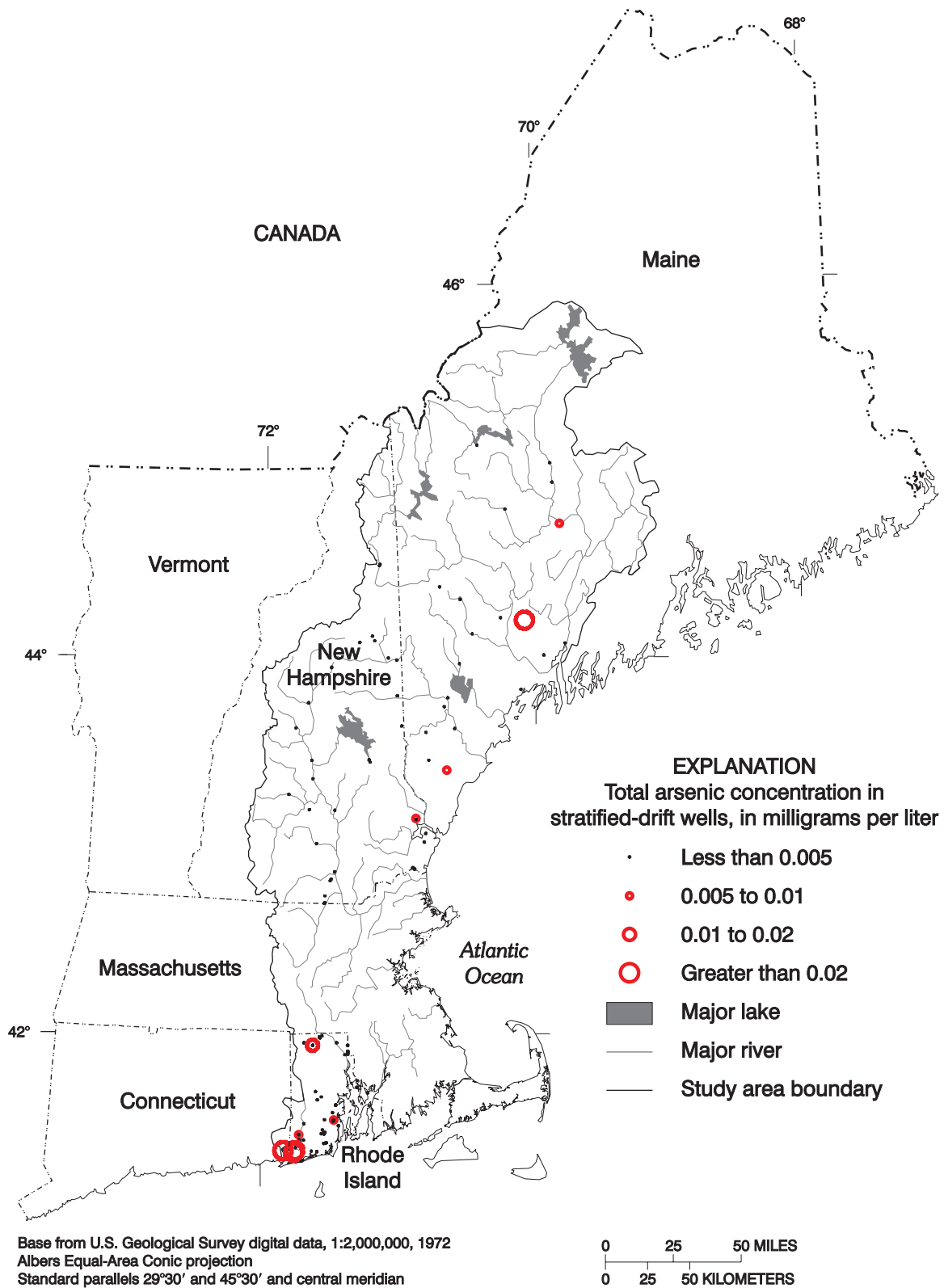


Figure 4b. Areal distribution of arsenic concentrations in water from selected stratified-drift wells.

variable (Helsel and Hirsch, 1992). Rejection of the null hypothesis indicates that the variables are dependent.

Kruskal-Wallis tests on the ranks of the data were run to test the null hypothesis that the water-quality data from all the lithogeochemical groups or land-use categories are from the same population. The null hypothesis is that there is no significant difference between the means of the ranks of the concentrations of a chemical constituent among the major lithogeochemical or land-use groups. This test does not indicate, however, which groups have higher or lower values of a constituent than others. To detect specific significant differences between populations in pairs of lithogeochemical groups, a subsequent multiple-stage Kruskal-Wallis test was used. This multiple-stage test is valid only if the null hypothesis was rejected by the initial Kruskal-Wallis test.

The general linear model (GLM) procedure (SAS Institute Inc., 1990) provides a method of testing each mean from each group against all other means in a non-parametric test, the Tukey test. This test is equivalent to a multiple-stage Kruskal-Wallis test when performed on the ranks of the data and is valid for unequal sample sizes in each group (Helsel

and Hirsch, 1992). This test controls for experiment-wise errors rather than comparison-wise (pair-wise) errors; the comparison-wise error rate is dependent on the number of means (number of independent variables) being compared, and will be much less than the overall error rate. The ability to detect significant differences in the means of the ranks of data for three or more groups of explanatory variables is maintained at the desired alpha level by controlling the experiment-wise error rate; if comparison-wise errors were controlled, the overall experiment-wise error rate would increase and could lead to a false sense of confidence in the results. Methods for computing the comparison-wise error rates are given by Helsel and Hirsch (1992). For all possible pair-wise comparisons, the Tukey test uses the within-group variance to calculate the minimum difference in mean rank that is necessary to consider groups significantly different (SAS Institute Inc., 1990). For all hypothesis tests in this study, rejection of the null hypothesis requires that the attained significance level (p) is less than 0.05. Lastly, rank-order correlation (Spearman's rho) was used to determine if the concentrations of arsenic, iron, and manganese were associated.