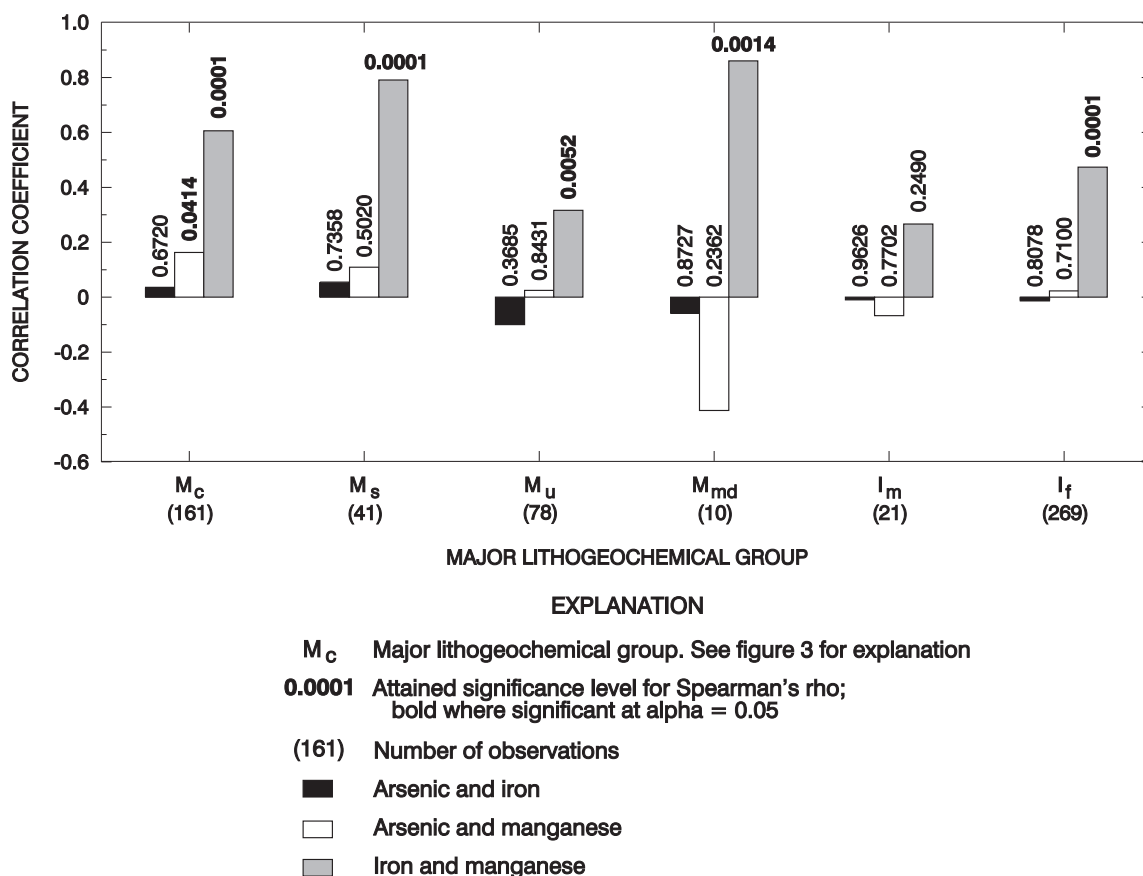


The variability of iron and manganese concentrations in ground water by lithogeochemical groups could be related to differences in iron and manganese concentrations in rock groups and the relative abundance of iron and manganese minerals that react with water. Sulfide-mineral oxidation and dissolution is identified as being a potential source for sulfate and metals concentrations in bedrock ground waters (Hem, 1985; Drever, 1988; Robinson, 1997). The Tukey analyses indicated that concentrations of iron and manganese were higher in water from the metasedimentary group  $M_s$  than in the other metasedimentary groups.

To test if arsenic concentrations are related to iron or manganese concentrations in the data set, Spearman's rank-correlation coefficients were calculated for the arsenic concentrations with iron

and manganese concentrations, as well as between iron and manganese. The arsenic concentrations are weakly correlated with iron concentrations in every lithogeochemical group; however, the correlation is positive for two of the groups of metasedimentary rocks and is negative for groups  $M_u$ ,  $M_{md}$ ,  $I_m$ , and  $I_f$  (table 6, fig. 9). Arsenic concentrations are also weakly correlated to manganese concentrations and the correlation is positive for three of the four metasedimentary groups. Iron and manganese concentrations are almost always strongly correlated, except for samples in the igneous group  $I_m$ , and these correlation were all significant ( $p = 0.0001$ ). Iron and manganese are strongly correlated in three of the four metasedimentary groups. The fact that the correlation coefficients in these metasedimentary categories are similar (table 6) and that arsenic concentrations differ



**Figure 9.** Correlation of arsenic and iron, arsenic and manganese, and iron and manganese concentrations in ground water by major lithogeochemical group in the New England Coastal Basins study unit.

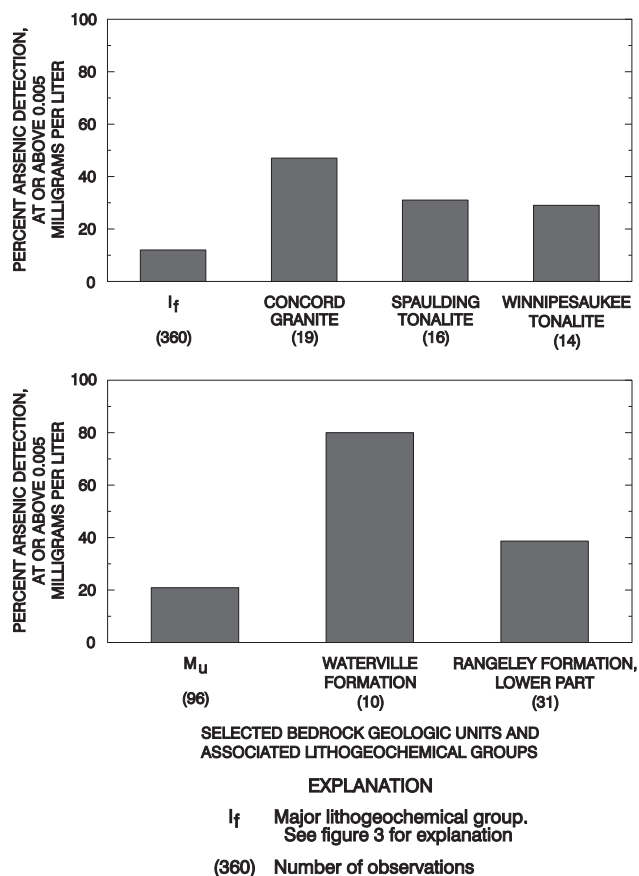
widely among water samples from these same categories indicates that high iron and manganese concentrations are not good indicators of high arsenic concentrations in ground water from these public-supply wells. These relations suggest that simple dissolution of arsenic-bearing iron sulfides and hydroxides probably does not account for arsenic concentrations in ground water from bedrock.

### Anomalous Concentrations of Arsenic By Bedrock Geologic Unit

The lithogeochemical associations discussed above show strong correlations of arsenic to the metasedimentary lithogeochemical group  $M_c$ ; however, some variation at the geologic formation scale from State geologic maps is present. The six lithogeochemical groups used in this report to analyze arsenic occurrence and distribution were defined on the basis of existing rock unit data on State bedrock geologic maps of Maine (Osberg and others, 1985), New Hampshire (Lyons and others, 1997), Massachusetts (Zen and others, 1983), and Rhode Island (Hermes and others, 1994) in the study unit. In two lithogeochemical groups that show statistically low concentrations of arsenic in water, wells in five rock units, as shown on the State bedrock geologic maps, yield water with high arsenic concentrations. Three of these rock units are in the igneous group  $I_f$  (fig. 3) and include the Concord Granite, Spaulding Tonalite, and the Winnepesaukee Tonalite (Lyons and others, 1997); and two, the Waterville Formation, in Maine (Osberg and others, 1985), and the Rangeley Formation, lower part, in New Hampshire (Lyons and others, 1997), are part of the metasedimentary group  $M_u$  (fig. 3). This section describes those geologic units where greater than 25 percent of wells in the unit yield water with detectable arsenic concentrations at or above 0.005 mg/L.

Wells in three rock units in the igneous group  $I_f$  yield water with anomalous (greater than 25 percent detection at 0.005 mg/L) arsenic detections; arsenic was detected in water from 47 percent of the wells in the Concord Granite, from 31 percent of wells in the Spaulding Tonalite, and from 29 percent in the Winnepesaukee Tonalite; wells in these bedrock units yield water with arsenic detections at more than twice the overall detection rate of 12 percent for igneous

group  $I_f$  (fig. 10). Wells in the Concord Granite yield water with a detection rate for arsenic (47 percent) similar to the overall rate for wells completed in the metasedimentary group  $M_c$  (44 percent detection rate) (fig. 6). Thus, the detection rate for arsenic in water from the Concord Granite is approximately three times the detection rate for water from the entire  $I_f$  group. Peters and others (1998) also found anomalously high arsenic concentrations in domestic bedrock wells completed in the Concord Granite. These concentrations are attributed to natural sources of arsenic in the bedrock based on geochemical analysis of whole-rock samples and geochemical leach tests of several rock types (Peters and others, 1999).



**Figure 10.** Percent detection of arsenic concentrations, at or above 0.005 milligrams per liter, in ground water, by selected bedrock geologic units and their associated lithogeochemical groups.

Within the  $M_u$  group, 80 percent of the wells in the Waterville Formation and 39 percent of the wells in the lower part of the Rangeley Formation, yielded water with detectable arsenic concentrations; the Waterville Formation had a rate of more than twice the overall detection rate (28 percent) from well water from the  $M_u$  group (fig. 10). The Waterville Formation, with 8 of the 10 wells in this lithology having water with detectable arsenic, has the highest rate of detection of all bedrock geologic units in the study unit. This rate (80 percent) is more representative of detection rates of arsenic in water from geologic units in the  $M_c$  group (fig. 7) than rates of detection in the  $M_u$  group.

The two bedrock units with the highest concentrations of arsenic in well water (the Concord Granite and the lower part of Rangeley Formation are located primarily in central New Hampshire) and are adjacent to each other (fig. 11).

### Relation of Arsenic in Ground Water to Land Use and Lithology

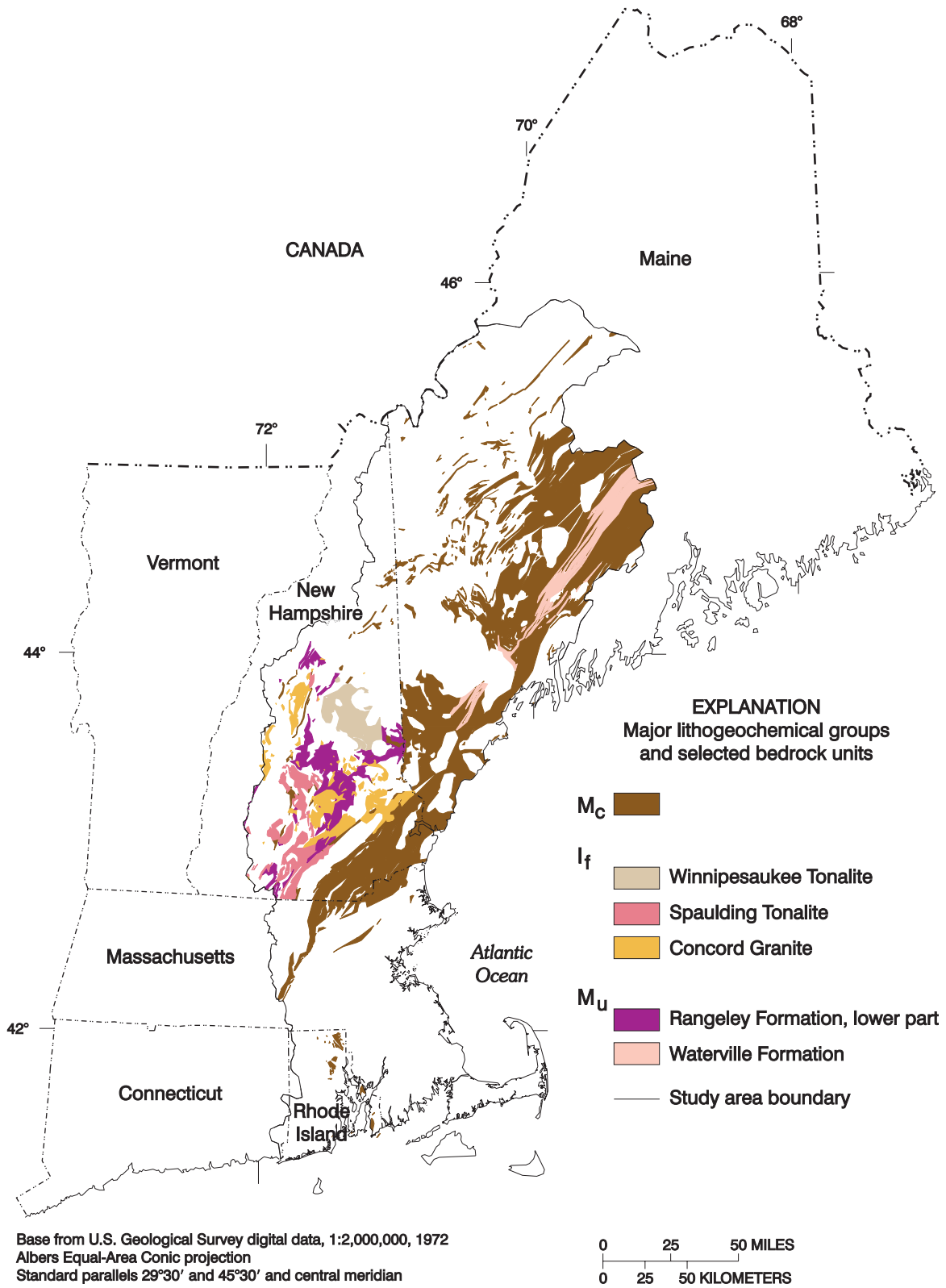
Previous studies (Boudette and others, 1985; Marvinney and others, 1994; Zeuna and Keane, 1985) have suggested a possible link between land use, specifically the historical application of large amounts of arsenical pesticides in agricultural areas, and arsenic detections in ground water. The present study used a land-use coverage (scale 1:250,000) compiled from high-altitude aerial photographs from the late 1960's and early 1970's (fig. 12), when the use of arsenical pesticides was being phased out, to try to determine whether there is a relation between that pesticide use and the water-quality data compiled for this report. The land-use data are classified into Level I and II land-use categories (Anderson and others, 1976). These data were obtained in digital form in a Geographic Information Retrieval and Analysis System (GIRAS) described in Hitt (1994). Level I data include broad categories such as Urban, Agriculture, and Undeveloped. Level II further classifies land use; for example, agriculture is classified into categories such as cropland and orchards. The bedrock-well arsenic data were compared by major categories of land use (Anderson Level I) including urban, agriculture, and undeveloped land uses (fig. 13). A Kruskal-Wallis test of arsenic concentrations by land use alone is significant ( $p = 0.0128$ ), although this was not as strong as the lithogeochemical relation. Results of a subsequent multiple comparison of means test of ground-water-

arsenic concentrations by land-use category indicated that concentrations of arsenic in the agricultural land-use category [a] are significantly higher than concentrations in the undeveloped category [b], but are not significantly different from the urban category [ab] (fig. 13). Land use was determined by identifying the particular land-use polygon in which the well was located.

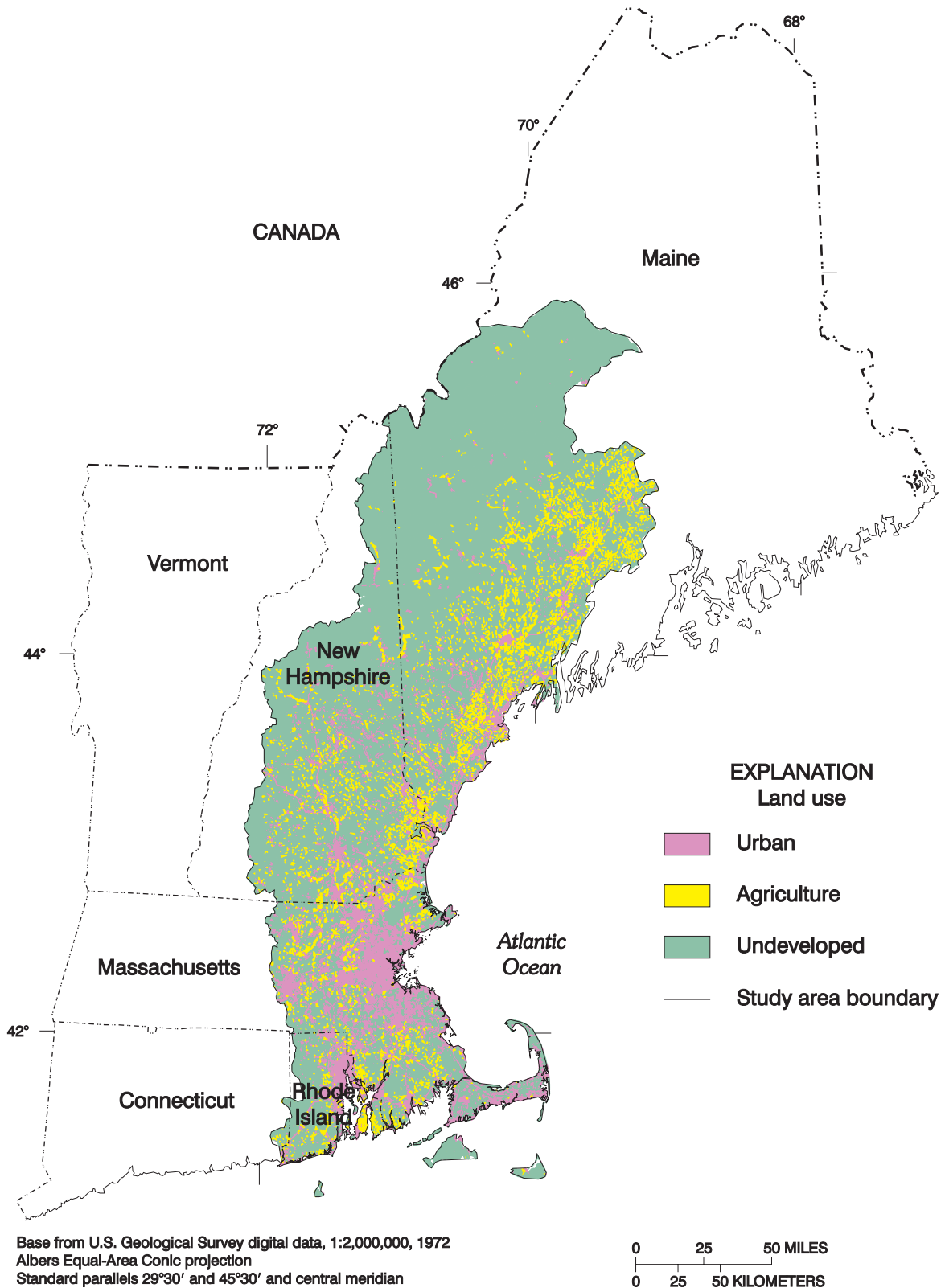
The GIRAS data was used because no earlier land-use coverage was available, but that data base may not accurately represent agricultural land use between 1920 and 1950 when arsenical pesticides were used on orchards and potatoes in the study area. Agricultural lands could have been urbanized or reverted back to forests by the time of the GIRAS photography and thus would not be represented by this data set.

Another point to consider when comparing historical land-use data with ground-water-quality data representing current conditions is that the ground water may have travelled significant distances from the land use that affected the water quality. Ground water with high arsenic concentrations derived from a specific land-use activity could now be located under a different land-use type. This could also account for a weaker relation between ground-water arsenic concentrations and land use than between ground-water arsenic concentrations and lithogeochemical data.

A qualitative test was done to assess the significance of the land-use arsenic relation: the detection-rate bar graph by lithogeochemical category was recomputed with and without the water-quality data from the agricultural land-use category (fig. 14a). The percentages of detection of arsenic at the 0.005 mg/L level by lithogeochemical group for all of the data is virtually identical to the percentages without the data in the agricultural category. This indicates that if the effect of land use is removed, the geologic (lithogeochemical) relation still holds. Similarly, the land-use category comparison was also redone without the data from the wells in the metasedimentary group  $M_c$  and these bars were plotted with the original data (fig. 14b). This plot shows that the frequency of detection of arsenic is significantly less in all three categories; however, it is still higher in the agricultural category than in the urban and forested category. This relation indicates that a significant amount of the variance in arsenic concentrations is probably the effect of the lithogeochemical group  $M_c$  rather than agricultural land use; however, some amount of the variance can be attributed to land use.



**Figure 11.** Areal distribution of selected bedrock geologic units, and their associated lithogeochemical groups that have anomalous arsenic concentrations in ground water. [Lithogeochemical groups are explained in figure 3. Bedrock units are from Lyons and others, 1997; Hermes and others, 1994, Osberg and others, 1985; and Zen and others, 1983.]



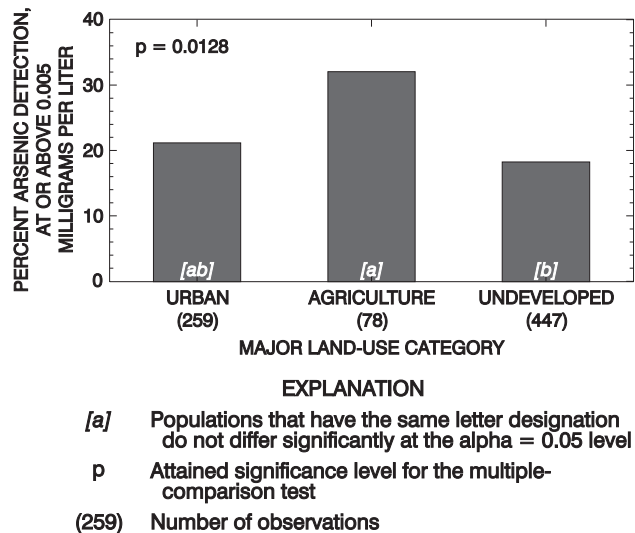
**Figure 12.** Areal distribution of major land-use categories. (From Flanagan and others, 1999)

To test for independence between geology and land use, a contingency table test was computed as a measure of association between the two variables. The results show that the variables (three land-use and six lithogeochemical variables) are not independent ( $p = 0.001$ ). The analysis showed significantly more agricultural land use in the metasedimentary groups  $M_c$  and  $M_{md}$  than in the other groups. Agricultural land use was significantly lower in group  $M_s$  than in the other lithogeochemical groups. These associations indicate that geology and land use are related and, therefore, should not be treated as if they were independent variables.

### Possible Sources of, and Controls on, Arsenic in Ground Water

Two categories of sources for arsenic in ground water in New England are (1) natural geologic sources, including arsenic-containing sulfide minerals, or arsenic contained in trace amounts in other minerals present in rocks, and (2) anthropogenic sources, primarily considered to be from past (early 1900's to the 1960's) arsenical-pesticide use.

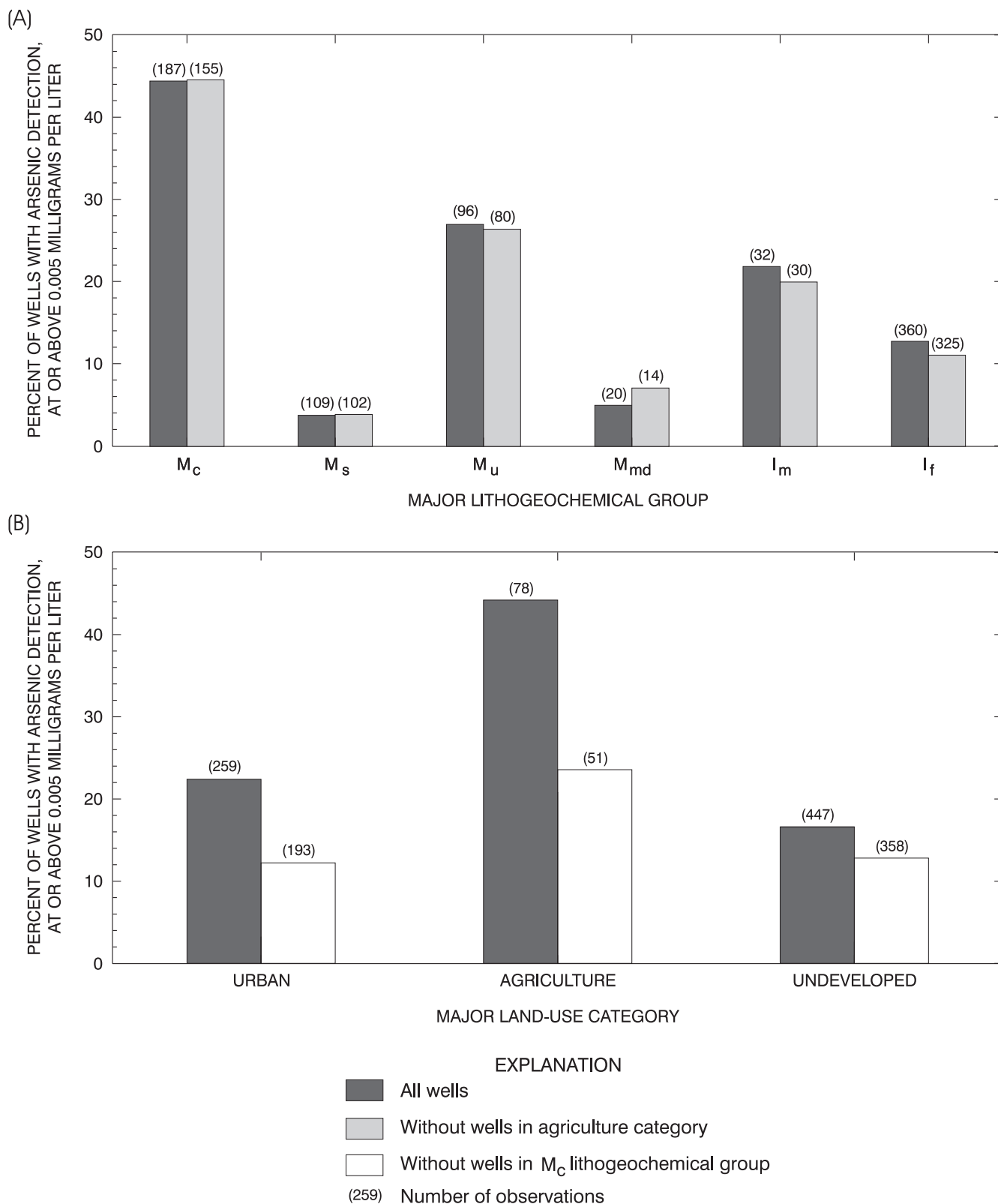
Some investigators in this region have suggested relations between likely geologic sources of arsenic and ground-water-arsenic concentrations; none, however, have found a relation between arsenic concentrations in ground water and the presence of calcareous and calc-silicate rocks. Stream sediment chemistry data (Grossman, 1998) from the National Uranium Evaluation Program (NURE), for the Massachusetts portion of the NECB study unit, show higher concentrations of arsenic in stream sediments in small drainage basins underlain by the metasedimentary group  $M_c$  compared to other lithogeochemical groups. Whole-rock arsenic concentrations are commonly higher in sulfidic rocks than in other rock types, and high arsenic concentrations are commonly associated with sulfidic rocks in New England (U.S. Environmental Protection Agency, 1981). Hitchcock (1878) noted many localities in New Hampshire where occurrences of arsenic minerals (arsenopyrite) have been reported. Arsenopyrite is reported as occurring throughout Rockingham County, which is largely underlain by rocks of the  $M_c$  group. Hitchcock also noted several other towns that are reported to have occurrences of arsenopyrite, but many of these towns do not have known arsenic problems in ground water. Some studies have suggested possible relations between



**Figure 13.** Percent detection of arsenic concentrations in ground water, at or above 0.005 milligrams per liter, by major land-use category.

rusty-weathering schists (associated with sulfidic rocks) (Boudette and others, 1985) and natural sulfides in rocks (Zeuna and Keane, 1985) and high ground-water arsenic concentrations in New England. More recently, data show that arsenic-bearing minerals are found in granite pematites within the Concord-type granite in central New Hampshire in areas of elevated arsenic in bedrock ground water (Peters and others, 1999; Peters and others, 1998).

The presence of arsenic in water from wells in bedrock aquifers, and the variation of these arsenic concentrations among major lithogeochemical groups of bedrock units, indicates bedrock could be a source for at least some of the arsenic; anthropogenic sources of arsenic are also possible in some instances, but the relative importance and the interrelation of the two sources are not clear. Few whole-rock geochemical data exist for the rock types in the lithogeochemical groups where elevated arsenic concentrations are present in ground water. Without such data, the effect of the specific bedrock types on arsenic concentrations in ground water cannot be determined. In northern Massachusetts, central New Hampshire, and in Maine, a few whole-rock geochemistry analyses detected concentrations of arsenic ranging from 30-700 ppm. These analyses indicate that the rocks could provide a natural source of arsenic to ground water, and some of the rocks with elevated arsenic concentrations occur near areas with elevated concentrations of arsenic in ground water.



**Figure 14.** Percent detection of arsenic concentrations in ground water by lithogeochemical group and major land-use category; (a) major lithogeochemical group with and without wells in the agricultural category, and (b) major land-use category with and without wells in the M<sub>c</sub> lithogeochemical group. (Major lithogeochemical groups are described in figure 3.)

The statistical analysis developed in this report measures the degree of spatial association between arsenic in ground waters used for public drinking-water supply and landscape features such as bedrock geology and land use. The causes and processes responsible for controlling arsenic concentrations in ground water are not well defined for the region. In addition, all the factors underlying the statistical associations presented are unclear, but probably include the following four elements: (1) the distribution and chemical form of arsenic in soils and rocks that are part of the ground-water-flow system, (2) the characteristics that influence the solubility and transport of arsenic in ground water, (3) the differing degrees of vulnerability of ground-water supplies to surface contamination, and (4) the spatial associations between land use, geology, and ground-water-flow patterns. In addition, the use of data from public water-supply wells eliminates analytical data from non-potable ground waters (with higher dissolved solid loads or with water that does not meet regulatory standards) that may differ with respect to spatial and chemical association patterns from the potable ground waters in the region.

The application of the observed spatial-association patterns toward a predictive model for the occurrence and distribution of arsenic in drinking water from bedrock aquifers will benefit from an understanding of the chemical, physical, and land-use factors and processes that control and significantly influence the solubility of arsenic in ground water.

### **Arsenic in Water from Public-Supply Wells and Future Drinking-Water Standards**

The National Academy of Sciences recommends that the current standard for arsenic in drinking water be lowered in order to protect public health (National Academy of Sciences, 1999). The 1996 Safe Drinking Water Act requires the USEPA to revise the existing drinking-water standard (0.05 mg/L) for arsenic. Currently (1999), the USEPA is evaluating lowering this level and must have a proposal to revise the MCL by 2000 and a final rule by 2001 (U.S. Environmental Protection Agency, 1998b). Data from the 804 public bedrock supply wells used in this study indicate that 4 percent of all wells have arsenic concentrations above 0.02 mg/L, 9 percent

have arsenic concentrations above 0.01 mg/L, and 19 percent have arsenic concentrations above 0.005 mg/L. This indicates that for a subset of public-supply wells used in this study, depending on the limit in the final rule, the drinking-water standard would be excluded.

The percent of wells that will potentially exceed the drinking-water standard, however, is likely to vary significantly depending on the lithogeochemical group of the aquifers in which the well is drilled. For wells drilled in the metasedimentary group  $M_c$ , 8 percent of wells yield water with arsenic concentrations above 0.02 mg/L, 20 percent yield water with arsenic concentrations above 0.01 mg/L, and 41 percent yield water with arsenic concentrations above 0.005 mg/L. The percent of wells exceeding 0.005, 0.01, and 0.02 mg/L, respectively, by lithogeochemical groups of bedrock aquifers and for the bedrock aquifers of the entire study unit are shown in table 7.

**Table 7.** Percent of wells yielding water with arsenic concentrations exceeding 0.005, 0.01, and 0.02 milligrams per liter by lithogeochemical group in the New England Coastal Basins study unit

[mg/L, milligrams per liter]

Major lithogeochemical group	Percent of wells with arsenic exceeding		
	0.005 mg/L	0.01 mg/L	0.02 mg/L
$M_c$	41	20	8
$M_s$	4	2	0
$M_u$	24	10	4
$M_{md}$	5	5	0
$I_m$	22	9	9
$I_f$	11	6	3
Overall (all groups— 804 wells)	19	9	4

This study focused primarily on water-quality data for samples from public-supply wells in the bedrock aquifer; however, past studies of arsenic in bedrock ground water in the study area focused primarily on domestic-well data. Arsenic data from privately-supplied ground water from domestic bedrock wells needs to be considered because of the large amount of drinking water that these wells supply (approximately 36 percent of all ground-water use). Additionally, this self-supplied ground-water use is not subject to regulation by USEPA and many of these



users do not test for, or treat for, arsenic in their water. Peters and others (1998) show, in graphical form, that about 25 percent of domestic bedrock wells tested for arsenic in New Hampshire yielded water with arsenic concentrations that exceed 0.005 mg/L, 17 percent yielded water with arsenic concentrations that exceed 0.01 mg/L, and 11 percent yielded water with arsenic concentrations that exceed 0.02 mg/L.

Some states recommend testing for arsenic in water from all private domestic bedrock-supply wells. The State of New Hampshire (New Hampshire

Department of Environmental Services, 1998) recommends that water from bedrock wells be tested for arsenic and radon. In Massachusetts, local Boards of Health can require testing to determine if water meets drinking-water standards (Massachusetts Department of Environmental Protection, 1998). The Maine Bureau of Land and Water Quality issued a 'Safe Home' fact sheet that similarly recommends that home owners test their wells for contaminants including trace inorganic constituents (Maine Bureau of Land and Water Quality, 1998).