

# Relation of Arsenic, Iron, and Manganese in Ground Water to Aquifer Type, Bedrock Lithogeochemistry, and Land Use in the New England Coastal Basins

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## Abstract

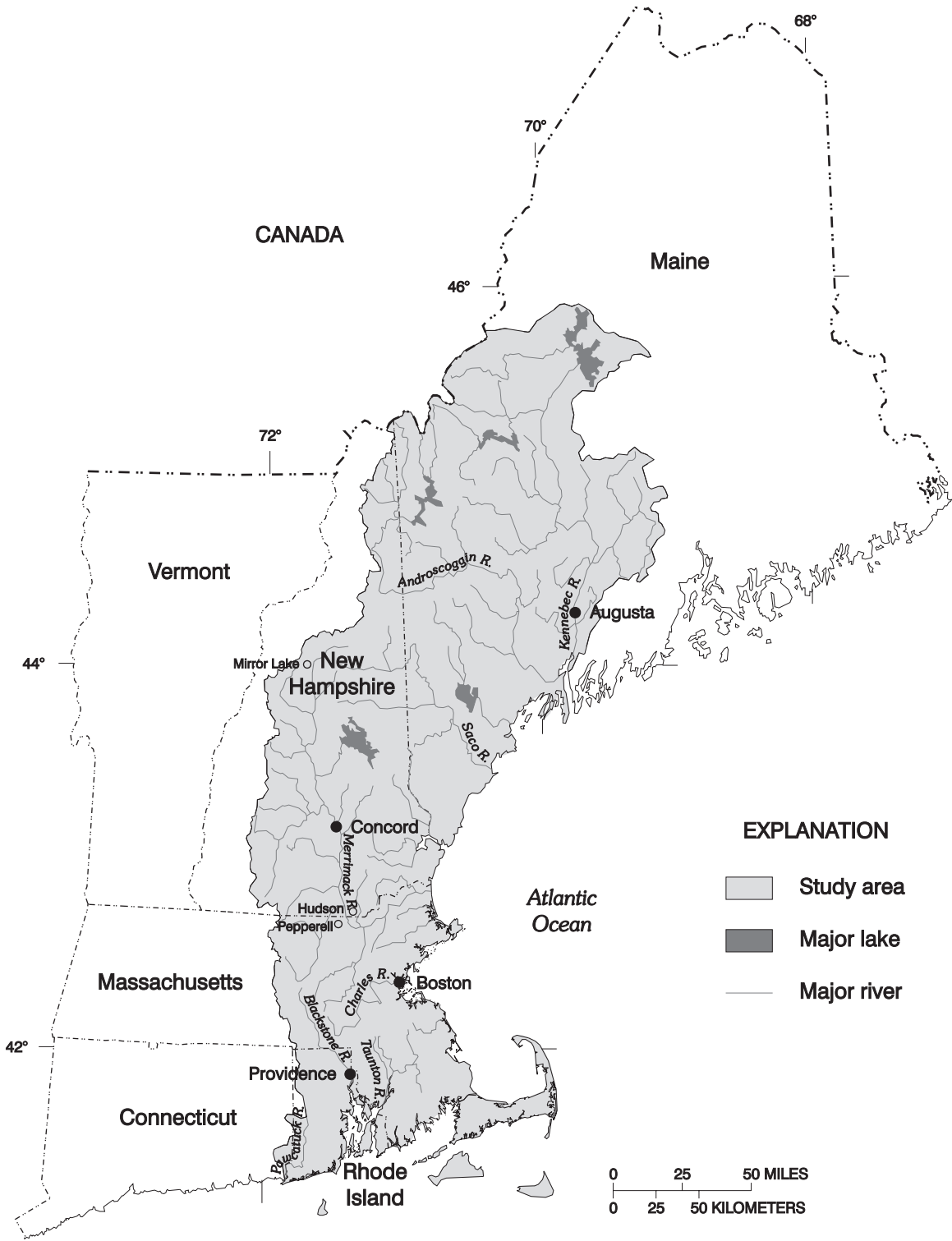
In a study of arsenic concentrations in public-supply wells in the New England Coastal Basins, concentrations at or above 0.005 mg/L (milligrams per liter) were detected in more samples of water from wells completed in bedrock (25 percent of all samples) than in water from wells completed in stratified drift (7.5 percent of all samples). Iron and manganese were detected (at concentrations of 0.05 and 0.03 mg/L, respectively) at approximately the same frequency in water from wells in both types of aquifers.

Concentrations of arsenic in public-supply wells drilled in bedrock (in the National Water-Quality Assessment Program New England Coastal Basins study unit) vary with the bedrock lithology. Broad groups of lithogeochemical units generalized from bedrock lithologic units shown on state geologic maps were used in the statistical analyses. Concentrations of arsenic in water from public-supply wells in metasedimentary bedrock units that contain slightly to moderately calcareous and calc-silicate rocks (lithogeochemical group  $M_c$ ) were significantly higher than the concentrations in five other groups of bedrock units in the study unit. Arsenic was detected, at or above 0.005 mg/L, in water from 44 percent of the wells in the lithogeochemical group  $M_c$  and in water from less than 28 percent of wells in the five other groups. Additionally, arsenic concentrations in ground water were the lowest in the metasedimentary rocks that are characterized as variably sulfidic (group  $M_s$ ). Generally, concentrations of arsenic were low in water from

bedrock wells in the felsic igneous rocks (group  $I_f$ ) though locally some bedrock wells in granitic rocks are known to have ground water with high arsenic concentrations, especially in New Hampshire.

The concentrations of arsenic in ground water also correlate with land-use data; significantly higher concentrations are found in areas identified as agricultural land use than in undeveloped areas. There is, however, more agricultural land in areas overlying the metasedimentary rocks of lithogeochemical groups  $M_c$  and the minimally-deformed clastic sediments of group  $M_{md}$  than in areas overlying other lithogeochemical groups. This correlation complicates the interpretation of sources of arsenic to ground water in bedrock. A test of this association revealed that relations between arsenic concentrations and the metasedimentary rocks of group  $M_c$  are not weakened when data associated with agricultural land use is removed; the reverse is true, however, if the data associated with the group  $M_c$  are removed from the analysis.

The occurrence and variability of arsenic in water from bedrock supply wells could be related to several factors. These include (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. Strong relations between agricultural land use and the



Base from U.S. Geological Survey digital data, 1:2,000,000, 1972  
 Albers Equal-Area Conic projection  
 Standard parallels 29°30' and 45°30' and central meridian

Figure 1. Location of the New England Coastal Basins study unit.

metasedimentary rocks of group  $M_c$  complicate the interpretation of arsenic source to water in these bedrock aquifers. This is due in part to the past use of arsenical pesticides; additionally, few whole-rock geochemical data are available for the rock types in the lithochemical groups of aquifers that contain ground water with elevated concentrations of arsenic. Without such data, identifying specific bedrock types as arsenic sources is not possible. In southern Maine and south-central New Hampshire, and in northern Massachusetts, the few available whole-rock analyses suggest, at least for these local areas, a connection between known bedrock chemistry and ground-water arsenic levels.

Although the lithochemical group and land-use category variables individually describe much of the variance in the concentrations of arsenic in ground water, the lithochemical relation is statistically stronger than the land-use relation. Low concentrations of arsenic in water from bedrock public-supply wells are associated with the metasedimentary rocks of group  $M_s$  (characterized as variably sulfidic). This association could reflect a variety of factors and suggests that simple dissolution of arsenic-bearing iron phases, such as sulfides, may not explain concentrations of arsenic in water in this bedrock aquifer group. Whole-rock geochemical data and more complete water-chemistry data, as well as studies of historical variation of arsenic concentrations (time-line studies), and site-specific studies, will be critical in addressing the arsenic source issue.

## INTRODUCTION

The New England Coastal Basins study unit is one of 59 study units in the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program (fig. 1). The NAWQA program began full implementation in 1991 to (1) describe water-quality conditions for the nation's major freshwater rivers and aquifers, (2) describe how water quality is changing over time, and (3) to improve our understanding of the primary natural and human factors that affect water-quality conditions (Leahy and

others, 1990). Information obtained from these study units can be used to help manage, regulate, or make decisions about water resources in the United States. The New England Coastal Basins study unit is one of several NAWQA studies that began in 1997 (Ayotte and Robinson, 1997).

NAWQA ground-water studies focus on water-quality conditions in major aquifers, primarily by using aquifer-wide surveys (termed subunit surveys) and land-use studies designed to assess the effect of specific land uses on aquifer water quality. Subunit surveys are designed to assess the water quality of the major aquifer systems of each study unit. Land-use studies focus on recently recharged shallow aquifer systems so that the influences of land-use practices and natural conditions can be assessed for selected subunit aquifers.

During the planning period of NAWQA studies, locally important water-quality issues are identified through meetings with Federal, State, and local agencies, as well as universities and the private sector. Existing data, and results from previous studies, are simultaneously reviewed to understand the primary physical, chemical, and biological factors that affect water quality in the study unit and to identify gaps in the current data. In the New England Coastal Basins study unit, a major concern related to ground-water quality is the concentration of trace elements, particularly arsenic, in ground water from the major aquifers. Many trace elements pose potential health risks if they are present in drinking water and, as such, are regulated by Federal and State safe-drinking water programs. Other trace elements are not a health risk but can result in additional maintenance or repair to water-using systems in homes.

## Purpose and Scope

This report describes the occurrence and distribution of arsenic, iron, and manganese in the bedrock and stratified-drift aquifers in the New England Coastal Basins NAWQA study unit. Results from this work will be used to help design regional-scale studies of ground-water quality in the study unit. Included in this analysis is a classification of geologic data according to geochemical considerations (Robinson, 1997).

This report includes a description of the sources of the data used; the approach used for screening the

data; a description of the methods used to group geologic data by general geochemical characteristics (lithogeochemical maps); and statistical and graphical presentations of the data by aquifer type, major lithogeochemical group, and major land use.

## **Health and Regulatory Concerns Related to Arsenic, Iron, and Manganese in Ground Water**

Arsenic in public drinking water is regulated by the U.S. Environmental Protection Agency (USEPA) because health risks are associated with exposure to arsenic. On the basis of an increased risk of cancer due to low-level arsenic exposure, the National Academy of Sciences (1999) has recommended that the arsenic standard for drinking water be lowered. Although evidence that arsenic causes cancer in animals and humans is limited (International Agency of Research on Cancer, 1987), the National Institute of Environmental Health Sciences (NIEHS), an institute of the National Institutes of Health (NIH), Superfund Basic Research Program is currently (1999) supporting cancer-risk research from long-term, low-level exposure to arsenic through drinking water in New Hampshire. Recent studies indicate that levels of arsenic in drinking water, which are lower than the current drinking-water standard, could be related to an increased risk of cancer (National Institutes of Health, 1998).

The USEPA has identified arsenic as a “known” human carcinogen based on occupational and drinking-water exposures: “arsenic is the only known carcinogen for which exposure through drinking water has been demonstrated to cause human cancer” (U.S. Environmental Protection Agency, 1998a). The USEPA has set enforceable exceedence levels or maximum contaminant levels (MCLs) that must be met to ensure public health and safety. For arsenic, the current MCL is 0.05 mg/L. The USEPA, as specified in the Safe Drinking-Water Act amendments of 1996, is currently reviewing options for revising the MCL for arsenic to a lower concentration (U.S. Environmental Protection Agency, 1998b).

The occurrence of arsenic in public water supplies is a concern with respect to the proposed regulation of arsenic in drinking water (U.S. Environmental Protection Agency, 1998c). An assessment of the distribution of arsenic levels in public water

systems will provide a basis for estimating the number of systems exceeding various MCL options and, therefore, the populations exposed to different levels of arsenic. This will likely mean that a percentage of the public-supply wells in the New England Coastal Basins will either require treatment to reduce concentrations of arsenic in the water or an alternative source of supply will be needed.

Historically, arsenic has been detected in bedrock ground waters in local areas of this study unit. Studies of arsenic in water from domestic bedrock wells in Maine (Marvinney and others, 1994), parts of New Hampshire (Boudette and others, 1985; Peters and others, 1999), and in Pepperell, Massachusetts (Zuena and Keane, 1985) have shown arsenic detection rates, at concentrations above 0.005 mg/L, of more than 50 percent. A sample population of domestic well data in New Hampshire (Peters and others, 1999), as well as data from previous studies in Maine, New Hampshire, and Massachusetts, indicates that arsenic concentrations above 0.05 mg/L in domestic well water occur in about 10-15 percent of the samples analyzed (Marvinney and others, 1994; Boudette and others, 1985; Zuena and Keane, 1985).

Iron and manganese in drinking water do not pose a health risk. The USEPA, however, has established non-enforceable exceedence levels or secondary maximum contaminant levels, (SMCLs) that are designed to limit ‘nuisance’ levels of these constituents. The SMCL for iron is 0.3 mg/L and for manganese is 0.05 mg/L. People who obtain their water from private and public stratified-drift or bedrock wells, however, are affected economically by the presence of iron and manganese in ground water. The most notable effects of these metals in water are the staining of clothes and household fixtures such as clothes washers, dishwashers, and bathtubs. Iron and manganese can also impart a metallic taste to the water. A less obvious effect of iron and manganese in well water is the accelerated deterioration of pipes, water heaters, and home heating systems. In addition, many homes require installation of water treatment systems to remove iron and manganese as it enters the home. Iron and manganese in water also support the growth of iron and manganese bacteria. These bacteria are not considered a health risk, but can cause clogging or restriction of pipes, pumps, valves, and other water-system parts by precipitation of metal hydroxides.

## Previous Investigations

Since the late 1970's, there has been an awareness that the concentrations of arsenic in ground water in some areas of eastern New England are above the MCL. Boudette and others (1985) indicated that the presence of elevated concentrations of arsenic (above the USEPA MCL of 0.05 mg/L) in southeastern New Hampshire's ground water had been known since 1977. In Pepperell, Mass., 12 percent of 301 private wells tested for arsenic yielded water with concentrations of arsenic greater than the MCL (Zeuna and Keane, 1985), and 32 percent yielded water with concentrations greater than 0.005 mg/L. Marvinney and others (1994) found that approximately 10 percent of all wells in Maine tested for arsenic yielded water with concentrations greater than the 0.05 mg/L MCL, and 46 percent of the wells tested yielded water with concentrations exceeding 0.005 mg/L. Causes for the elevated arsenic levels in New England ground water have been investigated, but, to date, a definitive regional source has not been identified. The USEPA concluded that the spatial pattern of elevated arsenic concentrations in New Hampshire was random and could not be attributed to land use, and, therefore, was assumed to be attributed to natural sources, such as the dissolution of arsenic-bearing sulfide minerals (U.S. Environmental Protection Agency, 1981). The study by Boudette and others (1985), however, concluded that arsenopyrite and arsenical pyrite were probably not the source of the elevated arsenic concentrations and that anthropogenic sources, specifically arsenical pesticide use and domestic septic leachate, were more probably the cause. After elevated levels of arsenic were found in wells in Pepperell, Mass., Zeuna and Keane (1985) found evidence of arsenical pesticide usage in the area and high levels (49-227 ppm) of arsenic in the soil. They also found high levels (21-710 ppm) of arsenic in bedrock cores collected during domestic-well installation in the same area. Although Zeuna and Keane (1985) did not specifically demonstrate a pathway for the high concentrations of arsenic in soils of the many orchards in the area to reach the ground water, they did demonstrate that arsenic could leach from samples of the local bedrock and produce concentrations exceeding the MCL in the leachate solution.

In Maine, Marvinney and others (1994) studied ground-water arsenic concentrations statewide with a focus on southwestern Maine. Through analysis of

more than 5,000 ground water samples, elevated arsenic concentrations were found in many geologic settings. In the Maine study, bedrock wells yielded water with statistically higher concentrations of arsenic than did wells completed in the surficial aquifer. Marvinney and others concluded that if bedrock was the source for the elevated arsenic levels found in ground water, "multiple models for its origin are required to explain its occurrence across such diverse geology;" furthermore, anthropogenic sources could not be ruled out. Chormann (1985) concluded, in a study of arsenic occurrence in stream sediments and soils in Hudson, N.H., that, for some orchard sites, anomalously high soil arsenic concentrations were likely the result of the use of arsenical pesticides. Chormann also concluded that combined arsenic/phosphate anomalies in stream sediments were associated with agricultural land uses but not with residential uses. A more recent study in New Hampshire (Peters and others, 1999) found that arsenic concentrations greater than 0.002 mg/L were measured in water from domestic bedrock wells (35 percent of the 218 bedrock wells sampled) more often than in water from surficial aquifer wells (1 percent of the 54 surficial wells sampled). In addition, they found that arsenic was readily leached by weak acid from some pegmatite rocks in the region. Concentrations of arsenic in whole-rock samples of the pegmatites were as high as 60 ppm and were much less in surrounding rocks. They concluded that arsenic in ground water in this region came from the weathering of bedrock and not from the use of arsenical pesticides or other anthropogenic sources.

In southern Maine, analyses of whole-rock and ground-water samples from an area near a landfill indicates a local connection between known bedrock chemistry and background ground-water arsenic levels. Concentrations of arsenic in rocks near Saco were as high as 120 ppm (J.A. Colman, U.S. Geological Survey, oral commun., 1998). Ground-water arsenic levels of 0.3 mg/L from an uncontaminated bedrock well, up-gradient of the landfill site, were also measured.

As noted in previous studies (Zeuna and Keane, 1985; Boudette and others, 1985; Marvinney and others, 1994), the historical application of arsenical pesticides on orchard and potato crops in New England could be contributing to arsenic concentrations in ground water. Few data exist on the amounts of lead arsenate and calcium arsenate and other inorganic

pesticides that were applied to New England crops between the early 1900's and the 1960's, before they were phased out of use. The amounts are believed to be large but are difficult to quantify (D'Angelo and others, 1996). In Maine, arsenic pesticide use on apple orchards was greatest between 1928 and 1943. Up to "15 lead arsenate cover sprays of 100 gallons per tree per year" could have been applied during this period (D'Angelo and others, 1996). By 1958, the recommended usage had been revised downward considerably. Estimates for the total amounts of lead arsenate applied in an orchard sprayed for 40 years was 200 lbs/acre (D'Angelo and others, 1996). Applications of calcium arsenate on potato crops, which are less common than are orchard crops in the New England Coastal Basins study area, are estimated to have been up to 20 lbs/acre/yr (D'Angelo and others, 1996). Contamination of ground water by arsenic in Pepperell, Mass. (Zeuna and Keane, 1985), was found near old apple orchards where elevated concentrations of arsenic were measured in the soils. The use of inorganic arsenic compounds in pesticides was largely discontinued in the study unit by the late 1960's, however, and subsequently has been banned since the 1980's and 1990's (A.H. Welch, U.S. Geological Survey, written commun., April 1999).

Elsewhere, studies have been published about the occurrence of elevated concentrations of arsenic in ground water in Arizona (Robertson, 1989), Ohio (Masitoff and others, 1982), the western United States (A.H. Welch, written commun., April 1999); Maest and Wing, 1986), the Midwestern United States (Korte, 1991), and Montana (Nimick, 1998). Most of these studies indicated that local bedrock or alluvium was the ultimate source of the elevated arsenic levels. Nimick (1998) concluded that multiple causes were responsible for elevated arsenic concentrations in the study area in Montana. He found that a combination of percolation of river water high in arsenic, leaching from bedrock, and the release of sorbed arsenic under reducing conditions in the aquifer, all contributed to high dissolved arsenic concentrations in the aquifer water. He also concluded that agricultural practices in the area (irrigation with river water high in arsenic) were of much less importance than earlier investigators had concluded.

In many parts of the country, arsenic in ground water has been attributed to geologic sources, anthropogenic sources, and combinations of geologic sources and a particular land use. In New England, many studies (Zeuna and Keane, 1985; Boudette and

others, 1985; Marvinney and others, 1994) have attempted to associate arsenic concentrations in ground water with either geologic or anthropogenic sources but have not definitively linked ground water arsenic to either source. Other studies have shown a relation to geology. Peters and others (1998, 1999) have shown that concentrations of arsenic in ground water from bedrock wells can be attributed to bedrock associated with the Concord Granite; this bedrock unit, however, is of limited extent and does not explain other significant areas with high concentrations of arsenic in ground water. No previous work has described the occurrence of arsenic in ground water on a regional scale and the sources of, and controls on, ground water arsenic in this region are still poorly understood.

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