Arsenic Occurrence in New Hampshire Drinking Water

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Arsenic concentrations were measured in 992 drinking water samples collected from New Hampshire households using online hydride generation ICP-MS. These randomly selected household water samples contain much less arsenic than those voluntarily submitted for analysis to the New Hampshire Department of Environmental Services (NHDES). Extrapolation of the voluntarily submitted sample set to all New Hampshire residents significantly overestimates arsenic exposure. In randomly selected households, concentrations ranged from <0.0003 to 180 μg/L, with water from domestic wells containing significantly more arsenic than water from municipal sources. Water samples from drilled bedrock wells had the highest arsenic concentrations, while samples from surficial wells had the lowest arsenic concentrations. We suggest that much of the groundwater arsenic in New Hampshire is derived from weathering of bedrock materials and not from anthropogenic contamination. The spatial distribution of elevated arsenic concentrations (>50 μg/L) correlates with Late-Devonian Concord-type granitic bedrock. Field observations in the region exhibiting the highest groundwater arsenic concentrations revealed abundant pegmatite dikes associated with nearby granites. Analysis of rock digests indicates arsenic concentrations up to 60 mg/kg in pegmatites, with much lower values in surrounding schists and granites. Weak acid leaches show that approximately half of the total arsenic in the pegmatites is labile and therefore can be mobilized during rock–water interaction.

Introduction

The arsenic concentration of drinking water in the United States is regulated by the United States Environmental Protection Agency (USEPA), under the Safe Drinking Water Act. Reevaluation of the maximum contaminant level (MCL) for arsenic is underway due to recent risk assessments that suggest a link between exposure to low concentrations of arsenic and certain types of cancers (1, 2). The current MCL is set at 50 μg/L, and values being considered for the future MCL range from 2 to 20 μg/L (3). National surveys of arsenic occurrence in municipal water systems have identified states, primarily in the western and north central regions of the United States, that will be most significantly affected by regulatory changes (4, 5). The New England states, while ranking at the lower end of the national survey, have had occasional reports of arsenic in groundwater exceeding the USEPA MCL (6–9).

While changes in the MCL will directly affect towns and cities regulated by the USEPA, they have no regulatory consequences for domestic wells, which are defined as those serving less than 15 households or 25 individuals. Although domestic wells do not fall under federal jurisdiction, most people use the MCL as a benchmark figure. Almost 40% of the population of New Hampshire, and 15% of the U.S. population, obtains water from domestic wells (10). Most of these wells have not been tested for arsenic, and all are out of the sphere of regulatory control.

To quantify the arsenic exposure risks for domestic well users in New Hampshire and determine potential sources of arsenic in the groundwater, 992 household water samples were collected, analyzed, and compared to existing datasets of arsenic occurrence. The research objectives were to quantify the number of households that would be affected by the various regulatory arsenic MCL’s under consideration, determine the spatial trends of arsenic occurrence statewide, and suggest possible sources of arsenic in the groundwater systems.

Background

Arsenic Chemistry and Anthropogenic Arsenic Sources. The aqueous chemistry of arsenic has been reviewed by Cullen and Reimer (1989). High concentrations of arsenic in drinking water result from either anthropogenic contamination, or weathering of naturally occurring subsurface materials. The two primary anthropogenic sources of arsenic are agricultural chemicals and wood preservatives. Approximately 50% of the total U.S. consumption of arsenic was used in agriculture in 1980 (11). As a pesticide, acid lead arsenate (PbHAsO₄) was widely used in orchards until the development of DDT in 1947 (12). Smaller quantities of calcium arsenate and copper acetarsenite pesticide applications have also been noted (13). As a wood preservative, a formulation of copper arsenic arsenate (CCA) has been used for dimensional lumber since the late 1960s (14), and now accounts for approximately 40% of the U.S. consumption of arsenic. Wood preserved using this technique results in copper, chromium, and arsenic concentrations in the wood ranging from 1000–5000 mg/kg (15). Soils underneath decks constructed of CCA treated lumber have been found to contain up to 350 mg/kg arsenic, compared to concentrations in control soils of 2 mg/kg (15). In addition to the dispersed use of arsenical compounds, industrial manufacturing of sulfuric acid and leather tanning have also resulted in significant arsenic contamination (16).

Because the application of arsenical pesticides precedes any systematic record keeping, it is unclear where and in what quantity they were applied. However, in New Hampshire, most of the orchard agriculture was located in the southern half of the state around the turn of the century, with intensive centers in Londonderry, Wilton, and Milford (Figure 1) (17). CCA-treated lumber is used throughout the state in renovations and new building construction.

Natural Sources. In its geological occurrence, arsenic is found at high levels in primary sulfide minerals such as arsenopyrite (FeAsS), pyrite (FeS₂), pyrrhotite (Fe₁₋₂Sₓ), orpiment (As₂S₃), and realgar (AsS). Additionally, its ionic radius...
and valence allow arsenic to substitute in trace amounts for many elements in silicate rock-forming minerals (18). The chemical similarities of arsenate ($H_2AsO_4^-\cdot$) and phosphate ($H_2PO_4^-\cdot$) lead to anion solid solutions between such minerals as pyromorphite ($Pb_5(PO_4)3Cl$) and mimetite ($Pb_5(AsO_4)3Cl$) (19). Combining both primary minerals and trace substitution in other minerals, arsenic has an estimated average concentration in the upper crust of 1.5 mg/kg (20).

In surficial water systems, arsenic can be dissolved either directly from weathering of geological materials (21) or through mixing with high-arsenic geothermal waters (22). In groundwater systems, arsenic can also be derived from the dissolution of arsenic-bearing iron oxides in unconsolidated aquifers (23). Aqueous arsenic concentrations are controlled by anion exchange and coprecipitation with iron and manganese oxyhydroxides, and are therefore a function of Eh and pH. Arsenate anion exchange dynamics are analogous to phosphate, with competition for exchange sites favoring phosphate over arsenate. Competitive exchange reactions show that arsenic can be stored in soils, and then inadvertently released with the addition of a high phosphate source, such as fertilizer (12).

**New Hampshire Geology.** The bedrock geology of New Hampshire can be broadly separated into three composite accretionary terranes: the Grenville, Central Maine, and Nashoba–Casco–Miramichi (Figure 1) (24). Most of the state is dominated by the Central Maine terrane and is characterized by complexly folded Siluro-Devonian metasediments with associated syn- and post-tectonic plutons. Silurian sediments were deposited in an anoxic marine basin, with

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**FIGURE 1.** Map of arsenic concentration in New Hampshire groundwater. Sampling coverage indicates little or no arsenic present in the northern half of the state, or west of the CMT. Concord age granites (24) are shown because we have implicated them as possible sources of arsenic-bearing pegmatites. Inset shows towns with two or more water sample analyses over 50 µg/L arsenic. The historical orchard agricultural centers of Londonderry, Wilton, and Milford are included for reference.
compositions ranging from sulfidic schists to quartz metasandstones and pebble conglomerates. During the early Devonian, sediment provenance switched from west to east, and bedded turbidites were deposited in anoxic basin. Compositions are predominantly metapelites and metawackes with the Silurian/Devonian boundary marked by metasiltstones and layered calc-silicate metapelites (24). To the southeast, the Nashoba–Caso–Miramichi terrane is characterized by folded Ordovician-Silurian calc-silicate metaseasiments, with associated Devonian plutons. To the west, the Grenville terrane is predominantly composed of Ordovician volcanic rocks and granitic gneisses associated with the Bronson Hill Anticlinorium (24).

The intrusive history of the Central Maine terrane is complex, but can generally be broken down into three major intrusive suites. The oldest are syenitic anatectic granites that were emplaced about 410 million years ago at the peak of the Acadian metamorphism, and include the Bethlehem, Spaulding, and Kinsman plutons (25). Approximately 370 million years ago, the anatectic Concord Granites were emplaced in the late stages of regional metamorphism. These granites are thought to have little or no mantle component, having been formed by the melting of the metasedimentary country rocks (26). In contrast, the White Mountain magma series, which occurs in the northern 60% of the state, is comprised of a series of plutons with a significant mantle component that were post-tectonically emplaced through the Jurassic and Cretaceous periods (27).

Pegmatites of various ages are found as dikes and small bodies throughout and adjacent to the syen- and late-tectonic granites. Pegmatites are formed from late-stage residual magmas during granite crystallization, and are enriched in incompatible elements such as lithium, cesium, beryllium, and rare-earth elements (REE) (28). Because arsenic is an incompatible element, it is also likely to be concentrated into pegmatites.

**Previous Studies.** In 1981, the USEPA Region 1 office released a report examining the occurrence of elevated arsenic in the groundwaters of Hudson, NH (9). Arsenic analyses of 100 groundwater samples from domestic wells were found to be inconsistent with a contaminant plume from either a hazardous waste or pesticide source. It was hypothesized that sulfide minerals, such as pyrite or pyrrhotite, in fractures were causing the elevated groundwater arsenic levels and that the random subsurface distribution of these fractures accounted for the observed variations from well to well.

As a followup to the USEPA report, the United States Geological Survey (USGS) investigated this hypothesis through detailed analysis of waters sampled from 24 bedrock wells with arsenic concentrations in excess of 50 μg/L (8). No apparent correlation was found between arsenic and sulfate concentrations in well water, casting doubt on the sulfide source of arsenic. A weak correlation was found with phosphate concentration, leading the authors to suggest that either fertilizer-induced release from contaminated soils, or outfall from washing machine detergents was associated with the high arsenic levels.

A similar problem was encountered in the towns of Buxton and Hollis, ME, where elevated arsenic concentrations in the public school drinking water prompted officials to investigate possible sources (6). Intensive water sampling throughout the town resulted in a detailed map of arsenic concentration in groundwater samples. There appeared to be no correlation with any particular geologic unit, although water from bedrock wells contained more arsenic than water from surficial wells. A compilation of the statewide database estimated approximately 10% of all of the wells in the state had arsenic concentrations in excess of 50 μg/L (6).

### TABLE 1. Characteristics of Data Sets Discussed in This Study

<table>
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<th></th>
<th>this study</th>
<th>NHDES</th>
<th>USGS</th>
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<td>240</td>
<td>24</td>
</tr>
<tr>
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<td>self-selection</td>
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</tr>
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<td>analysis method</td>
<td>ICP-MS</td>
<td>GFAA</td>
<td>ICP-ÖES</td>
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<tr>
<td>detection limit</td>
<td>0.0003 μg/L</td>
<td>5 μg/L</td>
<td>5 μg/L</td>
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</tbody>
</table>

*Abbreviations: NHDES, New Hampshire Department of Environmental Services; USGS, United States Geological Survey; ICP-MS, online hydride generation magnetic sector inductively coupled plasma mass spectrometry; GFAA, graphite furnace atomic absorption; ICP-ÖES, inductively coupled plasma optical emission spectroscopy.*

The USGS has recently compiled the results of water analyses conducted throughout Massachusetts, Rhode Island, Vermont, New Hampshire and Maine as part of the National Water Quality Assessment (29). Of the 800 public and 190 private wells analyzed, 23% contained arsenic above the detection limit of 5 μg/L. Domestic bedrock wells contained the highest average arsenic concentrations, with 10–15% exceeding 50 μg/L. Bedrock wells in calcareous metasedimentary rocks had the highest probability of containing arsenic above the detection limit of 5 μg/L. Water from bedrock wells drilled in noncalcareous metasediments, felsic and mafic igneous rocks, and clastic sediments contained significantly less arsenic.

### Methods

**Water Samples.** A total of 992 water samples from households throughout the state of New Hampshire were collected as part of an epidemiological study (30). Sampling and analytical techniques for this study are summarized in Table 1. Acid-cleaned 125-mL low-density polyethylene bottles were used to sample water from the kitchen tap using strict trace element protocols (30, 31). Total arsenic concentrations were determined by online hydride generation coupled to a magnetic sector inductively coupled plasma mass spectrometer (ICP-MS). Using online hydride generation eliminates the interference between ArCl+ and As+ and allows for rapid analysis (<3 min/sample) on small samples (<1 mL). Elimination of the ArCl+ interference allows operation of the mass spectrometer at low mass resolution (M/AM =300), thus maximizing signal intensities. Optimization of the instrumental parameters and reagents for this technique are discussed in detail elsewhere (32). Briefly, the instrument was linearly calibrated from 0.010 μg/L to 10 μg/L with six standards, yielding a minimum R2 of 0.9999. Higher concentration samples were diluted into the operating range and reanalyzed. Typical analytical uncertainty for all analyses was less than 5%, with a mean uncertainty of ~3%. Field blanks measured regularly during the study were all at or below 0.005 μg/L. Randomized blind replicate sampling of about 10% of the households agreed with an intraclass correlation of 0.91 throughout the range of results (30).

**Rock Samples.** Twenty-one rock samples were collected from bedrock outcrops in the towns of Bow and Dunbarton, NH, because they had the highest density of wells with elevated arsenic concentrations. Each sample was sawed into 1-cm slabs, and a ~1-kg subsample was crushed to less than 2 mm. Care was taken to ensure representative sampling, especially from the pegmatites. After the sample was crushed, a 0.5-g sub-sample was leached in 5 mL of 1 M HNO3 at room temperature for 24 h on a rocking shaker table, and the leachate separated by centrifugation. The remaining residue was totally digested in a mixture of hot HF and HClO4. Following digestion, samples were dried and redissolved in 1 M HNO3 for analysis. After diluting into the working range of the ICP-MS, arsenic concentrations were determined using the same methods described for water samples.
Results and Discussion

Analysis of Arsenic Concentration Data. To analyze the distribution of arsenic concentrations in water, a cumulative probability distribution function was plotted (Figure 2). For any given percentage of sampled households plotted on the y axis, a maximum arsenic concentration can be read off the graph. The shape of the curve shows the distribution of concentrations, with steeper slopes indicating a narrower spread of concentrations, while an offset in the x direction indicates a difference in the median concentration. The data are divided into households served by municipal wells and households served by domestic wells. None of the municipal water system users have arsenic concentrations above the current MCL of 50 μg/L, compared to 2% of domestic well users. Approximately 2% of municipal users have water with over 10 μg/L of arsenic, compared to 13% of domestic well users. At the lowest arsenic MCL under consideration (2 μg/L), more than 25% of the domestic wells in the state would be above the recommended level. In general, domestic water supplies have higher arsenic concentrations than municipal systems due to a concentration of 0.1 μg/L, where the curves in Figure 2 converge. This is especially important in suburban and rural areas, where a large proportion of residents obtain water from domestic wells. When evaluating the health impacts of regulatory decisions, this needs to be considered, because regulation will not directly reduce the risk to those populations who rely on domestic water supplies.

Also plotted in Figure 2 are 240 analyses from the NHDES data set, and the USEPA estimated national average (5). The NHDES curve is truncated at 5 μg/L, because this is the detection limit for the analytical method used in the NHDES lab. Results below the detection limit are included in the percentage calculation. While the slope of the data matches that of the other samples, there is a significant offset in the intercept. The distribution of samples indicates that there is a significant self-selection bias in the NHDES database, due to the fact that samples were volunteered. This appears to oversample residents from areas known to have high arsenic concentrations in groundwater. We conclude that extrapolating to the general population from volunteered sample sets will likely overestimate the number of people with excessive arsenic in their drinking water.

Domestic water sources are categorized as either deep bedrock drilled wells or shallow wells in surficial deposits. Comparison of the arsenic concentrations in the two well types illustrates that bedrock wells are much more likely to contain high concentrations of arsenic. For example, only 1% of the surficial wells contain arsenic in excess of 2 μg/L, compared to 35% of bedrock wells. If anthropogenic contamination were the primary source of elevated arsenic concentrations, the highest concentrations would be expected at the NHDES analytical detection limit of 5 μg/L arsenic. Open circles are USEPA estimates for arsenic in groundwater supplies nationwide (5).

FIGURE 2. Cumulative probability curve for arsenic concentrations in NH household drinking water. Domestic households are subdivided into those served by bedrock and surficial wells, then replotted as dashed lines. NHDES data are shown for comparison. Data truncates at the NHDES analytical detection limit of 5 μg/L arsenic. Open circles are USEPA estimates for arsenic in groundwater supplies nationwide (5).
expected in surficial wells. This observation argues strongly against a primarily anthropogenic source for arsenic contamination in New Hampshire, and instead points to the possibility of a natural bedrock source.

Spatial Patterns. The geographic distribution of our sample locations approximates population density throughout much of the state (Figure 1), with a relatively constant sampling rate of 1 per ~370 households (Table 2). The NHDES dataset covers a similar overall region, but sample density varies widely depending on the voluntary submission rate. While this bias significantly skews the statistical data as shown above, it does not affect the relationship to subsurface source material.

The occurrence of elevated arsenic concentrations is constrained to approximately four clusters located in the southeastern and south central part of the state (Figure 1), within which there are extreme variations in arsenic concentrations. Bedrock wells located in the southeast and south central regions of the state are most susceptible to elevated groundwater arsenic. Eight of New Hampshire’s 261 towns contain at least two samples above 50 μg/L and are constrained to approximately four clusters. Most of the arsenic in household drinking water is derived from sample density as ρ = (sample households/total households) for each county.

TABLE 2. Distribution of Sample Sites by County for NIEHS and NHDES Data Sets

<table>
<thead>
<tr>
<th>county</th>
<th>tested households</th>
<th>sample rate (1/μ)</th>
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</thead>
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<tr>
<td></td>
<td>households this study</td>
<td>NHDES total households</td>
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<tr>
<td>Coos</td>
<td>35 6</td>
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<td>Grafton</td>
<td>98 23</td>
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<tr>
<td>Carroll</td>
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<td>Sullivan</td>
<td>62 13</td>
<td>14,873</td>
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<tr>
<td>Cheshire</td>
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<td>Hillsborough</td>
<td>303 31</td>
<td>124,567</td>
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<tr>
<td>Merrimack</td>
<td>159 76</td>
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</tr>
<tr>
<td>Belknap</td>
<td>82 15</td>
<td>30,306</td>
</tr>
<tr>
<td>Rockingham</td>
<td>186 55</td>
<td>89,118</td>
</tr>
<tr>
<td>Strafford</td>
<td>64 6</td>
<td>37,744</td>
</tr>
<tr>
<td>total:</td>
<td>1132 237</td>
<td>422,653</td>
</tr>
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</table>

* Note the high variance of the NHDES data as a result of self-selection bias. Sample rate is derived from sample density as ρ = (sample households/total households) for each county.

An analysis of the statistical and spatial patterns of arsenic concentration in New Hampshire drinking water reveals trends that are important to current regulatory decisions. A comparison of bedrock and surficial wells indicates that water from bedrock wells contains significantly more arsenic than water from surficial wells. Geologic relationships support a hypothesized mechanism whereby pegmatite-hosted arsenic minerals release arsenic into groundwater. Research is underway to elucidate the details of water–rock interactions that lead to elevated arsenic levels in these groundwater systems. Most of the arsenic in household drinking water is delivered by domestic wells, and lowering the MCL may not directly alleviate the health risk to this sector of the population. We have identified towns that are the most susceptible to water quality problems in this regard and should be targeted for water testing and education concerning treatment alternatives. Similar databases exist for many states and can be evaluated to locate regions susceptible to high groundwater arsenic concentration.
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