Methyl tert-Butyl Ether Occurrence and Related Factors in Public and Private Wells in Southeast New Hampshire

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The occurrence of methyl tert-butyl ether (MTBE) in water from public wells in New Hampshire has increased steadily over the past several years. Using a laboratory reporting level of 0.2 μg/L, 40% of samples from public wells and 21% from private wells in southeast New Hampshire have measurable concentrations of MTBE. The rate of occurrence of MTBE varied significantly for public wells by establishment type; for example, 63% of public wells serving residential properties have MTBE concentrations above 0.2 μg/L, whereas lower rates were found for schools (21%). MTBE concentrations correlate strongly with urban factors, such as population density. Surprisingly, MTBE was correlated positively with well depth for public supply wells. Well depth is inversely related to yield in New Hampshire bedrock wells, which may mean that there is less opportunity for dilution of MTBE captured by deep wells. Another possibility is that the source(s) of water to low-yield wells may be dominated by leakage from potentially contaminated shallow groundwater through near-surface fractures or along the well casing. These wells may also have relatively large contributing areas (due to lower recharge at the bedrock surface) and therefore have a greater chance of intersecting MTBE sources. This finding is significant because deep bedrock wells are often considered to be less vulnerable to contamination than shallow wells, and in southeast New Hampshire, wells are being drilled deeper in search of increased supply.

Introduction

Contamination of groundwater in New Hampshire with methyl tert-butyl ether (MTBE) has occurred since its initial use, first as a substitute for tetraethyl lead (an octane booster) in 1979, and then as an oxygenate in reformulated fuel in the 1990s (1). The occurrence of MTBE in groundwater is greatest in New Hampshire counties where reformulated gasoline (RFG) usage is mandated (Figure 1). As of 2004, there is no Federal standard for MTBE in public water supplies, but a Federal Health Advisory of less than 20–40 μg/L was issued in 1997 (2). Several states have developed their own standards, including New Hampshire, which has a standard of 13 μg/L. The potential risk of exposure to MTBE through drinking water in New Hampshire may be greatest in southeast New Hampshire. As of 2003, Rockingham is the second largest county in the State in terms of population (280 500) but has the largest population served by groundwater (57 000 by community groundwater systems; 71 000 by community systems that use a combination of surface water and groundwater; and 135 000 by private domestic wells). Data from the New Hampshire Department of Environmental Services indicate that the percent of public wells with MTBE greater than 0.5 μg/L in Rockingham County has risen from 20.3% in 2000 to 23.1% in 2002 (Figure 1). This compares to an increase from 12.7 to 15.1% statewide for the same period (3).

The extent of low-level MTBE contamination in the State’s groundwater is not known (4). Although public water suppliers must monitor MTBE concentrations in their finished waters, their source waters are not routinely monitored. Moreover, because private wells are typically only tested at the discretion of the well owner, they are rarely sampled for MTBE contamination. Therefore the extent of MTBE occurrence in these wells is unknown.

The primary objective of this study was to determine the occurrence and distribution of MTBE in public and private drinking water sources in southeast New Hampshire. Rockingham County was chosen for this study because of the heavy reliance on groundwater from bedrock aquifers for both private and public supply and the frequent detection of MTBE in water supplies. Furthermore, we sought to identify physical, environmental, and anthropogenic factors associated with MTBE occurrence.

In 1990, over 75% of New Hampshire private wells were reported as drilled into fractured crystalline bedrock aquifers (5). The majority of public wells are also drilled into bedrock, although the largest withdrawals for public supply are often from unconsolidated aquifers. Water from bedrock aquifers moves through interconnected fractures occurring at various depths in the aquifer, and when these fractures intersect a well, water may be withdrawn for supply.

New Hampshire, and much of New England, is underlain by fractured crystalline bedrock that generally ranges in depth from a few meters to more than 100 m below land surface in deep glacial valleys. Fractured crystalline bedrock aquifers are dense, are relatively impermeable, have low porosity, range in age from Cretaceous to Precambrian, and are dominantly igneous and metamorphic rocks (6). Fractures were formed by stresses caused from erosion of overlying rock, tectonic activity, cooling associated with igneous intrusions, and unweighting due to the melting of continental ice sheets that once covered New England (7).

Unconsolidated aquifers, by contrast, consist primarily of discontinuous sand and gravel deposits that overlie the bedrock; these were formed during the last glacial retreat and are also a major source of water for the region (6). These aquifers typically occupy valleys and plains and are generally less than 30 m thick but can exceed 100 m in deep valleys. Unconsolidated aquifers, where high transmissivity, often yield greater quantities of water than bedrock aquifers.

A number of U.S. Geological Survey and State studies have investigated MTBE contamination of groundwaters and surface waters (1, 4, 8–24). In a recent regional study in New England, MTBE concentrations greater than 0.2 μg/L were found in 38% of shallow, unconsolidated aquifer monitoring wells tested in emerging suburban parts of the Boston metropolitan service area (11). In another study on source water to public wells, MTBE was found in 11.3% of the wells...
sampled in the Northeast and Mid-Atlantic region (12). MTBE also was found at or above 0.2 µg/L in 15% of the public water supplies and domestic wells sampled in Maine in 1998 (23). Identification of the source(s) of MTBE contamination is valuable because it can be used to predict whether concentrations can be expected to increase over time, such as from point sources, or remain at relatively low levels, as with atmospheric and other sources (9).

**Study Design and Methods**

To determine the occurrence and distribution of MTBE in Rockingham County, this study incorporated both a random sampling design and low-level laboratory analytical methods (25). For contaminants such as MTBE, concentrations in drinking water sources are usually low or not detectable. By analyzing water samples to as low a detection level as possible, the number of samples with measurable MTBE is maximized and the distribution of MTBE concentrations can be better defined.

**Well Selection.** Wells sampled in this study were chosen randomly (26) from the entire population of public supply wells and from a database of private wells in the county. All private wells sampled were domestic water supplies drilled into bedrock aquifers. A total of 120 public supply wells and 103 private wells were sampled, and their locations are shown in Figure 2.

**Water Sampling.** Sampling was done according to USGS protocols (27–29) and was completed between May and August 2003. Private well and public system owners were
contacted to obtain permission to sample and to schedule sampling activities. All sampling sites were field-located using a global positioning system (GPS) to an accuracy of approximately 30 m. Water quality parameters measured in the field included temperature, pH, specific conductance, and dissolved oxygen concentration.

Samples were collected directly into 40-mL glass septum vials from a stainless steel flow-reducing port (to stabilize the flow and minimize sample contact with outside air) attached to existing plumbing as close as possible to the wellhead. In a small number of samples where this was not feasible, samples were collected from clean Teflon lines with stainless steel fittings or directly from existing plumbing.

Chemical Analyses. The New Hampshire Department of Environmental Services Water Quality Laboratory analyzed all water samples for MTBE using gas chromatography/mass spectrometry techniques via purge-and-trap procedures (GC/MS) according to a modification of the U.S. EPA Method 524.2 (30). No other compounds were analyzed. The laboratory reporting level (LRL) for the study was 0.2 μg/L. Samples were chilled immediately and analyzed within 14 d of collection.

Recent studies suggest that acidification for sample preservation may hasten the transformation of MTBE to TBA (31, 32), causing underestimates in the amount of MTBE in the environment. Because the rate of hydrolysis is dependent on the sample pH, temperature, and MTBE concentration (33), hydrolysis can be minimized by careful experimental design. We used ambient temperature (25 °C) purge-and-trap methods, and only enough acid was added to reach pH 2 (31, 33, 34). Additionally, because most samples (95%) had less than 5 μg/L of MTBE, it is unlikely that hydrolysis significantly affected measured concentrations of MTBE.

Quality Control. Quality control samples including blanks, spikes, and replicates were collected (total of 15%) according to USGS protocols (25). None of the 22 blanks had concentrations of MTBE above the LRL of 0.2 μg/L. Percent recoveries for performance evaluation samples ranged from 87.8 to 151% for the four samples analyzed, with a mean of 119%. Thus, in some cases, MTBE concentrations could be reported higher or lower than actual. Percent recoveries for two field-spiked samples were 85.5 and 94.4%. Replicate samples had concentration differences ranging from 0 to 17%, with five out of the six sample pairs differing by less than 0.1%. All statistical analyses in this study were performed on the ranks of the data rather than the actual concentrations; therefore, any potential bias would have no significant impact on our findings.

Explanatory Variables. Specific Geographic Information Systems (GIS) and ancillary data used in the analysis of MTBE occurrence include (i) aquifer type—bedrock or unconsolidated, system size, water supply establishment type, well depth, and reported safe yield; (ii) population statistics (35, 36); (iii) high-resolution land-use data (37); (iv) Soil Survey Geographic (SSURGO) database (38); (v) lithology and lithochemical character of near-surface bedrock in New England (39); (vi) Topologically Integrated Geographic Encoding and Referencing (TIGER) road data (40); (vii) proximity to underground storage tanks and related tank information (41); and (viii) water sample temperature, pH, specific conductance, and dissolved oxygen data.

Statistical Analyses. Nonparametric group comparison tests were used to examine the relations of MTBE to environmental factors because the data are highly skewed—that is, a large proportion (about 60% of public wells and 80% of private wells) of the samples have MTBE concentrations that are less than 0.2 μg/L and, thus, are reported as “less than the LRL.” For this study, all statistical analyses included the data reported as below the LRL, and the significance level (α) was 0.05.

Contingency table analysis (Pearson’s χ² test for independence) were used to measure the association of the rate of occurrence of MTBE (presence or absence) with a nominal grouping variable of two or more categories (42). Group comparison tests such as the Wilcoxon and the Kruskal–Wallis tests also were used to determine if the means of the ranks of the data from two or more groups were significantly different (42). Where multiple comparison tests showed independent populations exist, the Tukey test was used on the ranks of the data to identify group means that were significantly different (42, 43). Although other methods exist for estimating the distribution of missing data and comparing groups, such as substitution and distributional methods, nonparametric methods offer several benefits including (i) no assumption of normally distributed data; (ii) better statistical power; and (iii) data below the LRL are used without fabrication, resulting in an accurate portrayal of the less than the LRL information (42, 44).

For analysis of environmental and other factors related to MTBE concentrations, Spearman correlation coefficients were computed to measure the strength of the relation to explanatory variables (42). Multivariate analysis of variables identified as significant in the correlation analysis was done on the public wells using logistic regression (43) where the dependent variable can be analyzed as a binary response variable (i.e., greater than or equal to 0.2 μg/L or less than 0.2 μg/L).

Results and Discussion

The analysis of groundwater sampled for this study shows that 40% of public wells and 21% of private wells have MTBE concentrations greater than 0.2 μg/L. The locations of wells and MTBE concentrations are shown in Figure 2. Public and private wells have significantly different MTBE occurrence rates (Table 1, p = 0.0028), and public wells have higher MTBE concentrations than private wells (Table 1, p = 0.00012). A cumulative distribution function plot (Figure 3) for public and private well data further illustrates the difference between the two groups.

### Table 1. MTBE Occurrence Rates by Well Type*  

<table>
<thead>
<tr>
<th>Well Type</th>
<th>Aquifer Type</th>
<th>No. of Samples</th>
<th>Wells with MTBE &gt; 0.2 μg/L (%)</th>
<th>95% Confidence Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>Public</td>
<td>Bedrock</td>
<td>103</td>
<td>21.4</td>
<td>13–29</td>
</tr>
<tr>
<td>Public</td>
<td>All</td>
<td>120</td>
<td>40.0</td>
<td>31–49</td>
</tr>
<tr>
<td>Private</td>
<td>Bedrock</td>
<td>97</td>
<td>7.2</td>
<td>0–14</td>
</tr>
<tr>
<td>Private</td>
<td>All</td>
<td>103</td>
<td>16.5</td>
<td>0–33</td>
</tr>
</tbody>
</table>

*χ² test for independence of occurrence rates, p = 0.0028. Wilcoxon rank sum test for independence of group data, p = 0.0012.

FIGURE 3. Percent of wells with MTBE less than the concentration shown, by well type, in Rockingham County, NH.
Wallis test for independence of group data, \( p \leq 0.05 \) rank sum test for independence of group data, \( p \leq 0.05 \)

D

serving at least 1000.

establishment type

<table>
<thead>
<tr>
<th>no. of samples</th>
<th>wells with MTBE concn greater than 0.2 ( \mu g/L ) (%)</th>
<th>95% confidence interval</th>
<th>Tukey grouping</th>
</tr>
</thead>
<tbody>
<tr>
<td>residences</td>
<td>38</td>
<td>63.1</td>
<td>48–78</td>
</tr>
<tr>
<td>commercial</td>
<td>27</td>
<td>40.7</td>
<td>22–59</td>
</tr>
<tr>
<td>schools/recreation</td>
<td>16</td>
<td>31.3</td>
<td>9–54</td>
</tr>
</tbody>
</table>

None of the 103 private bedrock wells has an MTBE concentration that exceeded either the State drinking water criteria of 13 \( \mu g/L \) or the State action level for notification of adjacent well owners of 5 \( \mu g/L \). For the public wells, however, 4 exceeded both the 5 \( \mu g/L \) and the 13 \( \mu g/L \) levels.

### MTBE Occurrence in Public Wells

The occurrence rates and concentrations of MTBE in public wells were not significantly different for bedrock and unconsolidated aquifers (Table 2). However, rates of MTBE occurrence \( (p = 0.0042) \) and concentrations \( (p = 0.0017) \) varied significantly by type of water supply establishment. Public wells that were used for residential supply (including apartment complexes, condominiums, and mobile-home parks) had the highest rate of occurrence (63% were above 0.2 \( \mu g/L \)). Public residential well MTBE concentrations were significantly higher than for schools (Table 3); commercial wells, including those at restaurants and service stations, and large community systems were not significantly different from any of the other establishment types.

Wells from the three categories of public supply systems were compared: community water systems, which serve at least 15 year-round service connections or 25 year-round residents; nontransient, noncommunity water systems, which serve more than 25 of the same people for more than 6 months per year but are not community supplies; and transient noncommunity systems, which are water systems that do not serve over 25 of the same people for at least 6 months per year. MTBE occurrence in public wells also varied significantly by U.S. EPA-defined water system category \( (p = 0.0315) \), but the difference in the means of the ranks of the concentrations by category was not statistically significant \( (p = 0.1177) \) (Table 4).

Community water systems had the highest rate of MTBE occurrence at 53%; followed by transient noncommunity; and nontransient, noncommunity at 35 and 27%, respectively (Table 4). Unlike the other categories, owners of transient noncommunity supplies are not required to submit routine monitoring samples for MTBE, although data from this study (35% greater than 0.2 \( \mu g/L \)) show that these supplies have similar occurrence rates to other public well categories.

### MTBE, Urban Factors, Well Characteristics, and Chemistry

MTBE concentrations in water from public and private wells sampled in this study are related to urbanization and other factors. Because Spearman correlation coefficients are computed using the ranks of the actual data, all of the samples, including the ones with concentrations below the LRL, were used in the computation (Table 5). Only wells greater than 500 m apart were used in the correlation analysis. The full correlation matrix is shown in Table 2 of the Supporting Information.

#### Private Wells

MTBE concentrations in water samples from private wells are correlated strongly and positively to population density and housing density and to the percentages of urban land use and roads within a 500 m buffer around the well. Because many of the factors are themselves correlated, they collectively point toward increasing concentrations with increasing urbanization. In addition, MTBE concentrations are positively correlated to the specific conductance of the water sample, which may be another indication of urbanization (45).

#### Public Wells

MTBE concentrations in the water samples from public wells also correlated strongly and positively with some urban factors (such as population density, housing density, and specific conductance) but not with others (such as percent urban or percent of developed land). In addition, several other correlations were observed that are significant for the public wells but that were not present for the private wells.

Strongest and perhaps most surprising is the positive correlation \( (0.37, \alpha = 0.0004) \) of well depth with MTBE concentrations in public wells (Table 5, Figure 4a). Well depths for all public wells sampled in this study ranged from 5 to 287 m, with a median of 7.5 m. Eighty-two percent of the public wells sampled are in bedrock aquifers and ranged in depth from 38 to 287 m.

Several factors were inversely correlated with MTBE concentrations, including distance to fuel underground storage tanks (USTs), the pH of the water sample, and, although not statistically significant \( (p = 0.19) \), the reported safe yield of the well (Table 5). The “safe yield” of a well in this study is a reported value representing the yield associated with near maximum drawdown in a well as determined from hydraulic testing; in cases where hydraulic tests were not available, this value may be estimated from drillers’ reported yields or from well operator information (46). MTBE concentrations in public wells generally decrease with increasing distance from the nearest UST (Figure 5a). This significant but weak correlation \( (p = 0.2274, \text{ Table 5}) \) is consistent with findings in a New Hampshire study, where the presence of gasoline sources within the Source Water Protection Area of a well was related to MTBE concentrations in public wells (17). There is no apparent correlation, however, to UST distance for private wells (Figure 5b).

#### Multivariate Analysis of MTBE in Public Wells

For MTBE concentrations in the public wells, the correlations to depth, pH, and distance to fuel USTs, among other urban factors,
make the interpretation complex; we used multivariate logistic regression analysis to further examine MTBE occurrence in this well type (47).

Two constraints were placed on the data set for the logistic regression model. First, wells had to be at least 500 m apart to help ensure independence among observations (18). Second, all observations were required to have a full set of independent variables; this reduced the total number of wells available for the analysis to 86. Thirty-five percent of these (30 out of 86) had MTBE concentrations greater than 0.2 μg/L.

The significant factors identified in the correlation analysis (Table 5) were used in the preliminary model. Model diagnostics (Tables 6 and 7) such as the Wald $p$-value, and tests for multicollinearity (48) were used to evaluate various models before final selection (43, 49). Estimated coefficients are also reported as standardized coefficients according to methods described by Menard (50) so that the relative contribution of each variable can be compared. The final model is not intended for use in prediction but rather to identify factors related to MTBE occurrence that may, in turn, be related to source and transport; therefore, model predictive performance was not evaluated.

Well depth was the most significant variable associated with the occurrence of MTBE, as indicated by the standard-
be supplied by numerous fractures (may be supplied by one major fracture whereas others may intersect open boreholes at any location, and some wells have casings that seal off the unconsolidated deposits above, terminating 1–10 m into the underlying bedrock. Fractures can intersect open boreholes at any location, and some wells may be supplied by one major fracture whereas others may be supplied by numerous fractures (52–54). Direct leakage from the overburden to the well may be a dominant source of water to low-yield bedrock wells. Most of the public bedrock wells (77%) in this study are in metamorphosed marine sediments, and 23% are in igneous rocks. The degree of bedrock fracturing may vary by formation type for the rocks in the study area (52), and it is possible that this could affect MTBE concentrations; however, based on state-scale geologic data (39), MTBE concentrations did not vary by geologic formation or groups of formations.

Bedrock wells are increasingly being drilled deeper in search of adequate water supplies. Mean well depth has increased from 99.5 m in 1985 to 124.8 m by 1998 (55). In this region, bedrock well drilling is typically stopped when an adequate supply is found; if an adequate supply is not found, drilling often continues (to exploit available drawdown of water in the well), and relatively deep wells with relatively low yields often result. The apparent, though weak, inverse relation between depth and yield for the public bedrock wells is shown in Figure 6a and is consistent with other studies of bedrock well yield in New Hampshire and elsewhere (7, 55–56).

Whereas we are not suggesting that deeper groundwater is more contaminated with MTBE, the finding of higher MTBE concentrations in deeper wells may be explained by several possible hydraulic conditions. Einarson and Mackay (59) suggest that contaminant concentrations in wells under constant pumping decrease with increasing pumping rate. This is because the ratio of clean water to contaminated water increases and the contaminated water that reaches the well is diluted. The same concept can be applied to low-yield wells. For the deep, low-yield, public bedrock wells in this study, MTBE captured by the well has less opportunity for dilution than in high-yield wells.

Another explanation may involve the source(s) of water to the wells. In some cases, the transmissivity of the bedrock may be so low that the dominant contribution of water (and MTBE) to the well is leakage from overlying unconsolidated materials near the casing/bedrock boundary. Thus, although the well is deep, the bulk of the water may come from near-surface sources that are most vulnerable to contamination.

A third possible explanation involves the size of the contributing area to deep, low-yield wells. In a Massachusetts study, Lyford et al. (60) note that contributing areas to deep wells are sensitive to the vertical transmissivity of the aquifer—lower transmissivity at the recharge boundary (bedrock surface) results in a decrease in the recharge rate and a corresponding increase in the size of the contributing area to the well. For a given pumping rate, low-yield wells would have a larger contributing area and, thus, a greater chance of intersecting an MTBE plume than a high-yield well and would therefore be more vulnerable to contamination (59, 61).

There are several other factors, not evaluated in this study, that may relate to contamination of wells with MTBE including the cumulative effects of minor spills, the urban atmosphere (61, 62), well pumping style, and subsurface vapor releases of MTBE to groundwater associated with gasoline UST air vapor recovery systems (63, 64). Also, average linear groundwater velocities in fractured crystalline bedrock may be relatively high as compared to unconsolidated aquifers causing contaminants to move more quickly through the bedrock aquifer system (16). This would, in turn, result in relatively short aquifer contact time, potentially affecting processes such as biodegradation, adsorption, and dispersion and diffusion (16).

In southeastern New Hampshire, population growth continues at a rapid rate, and there is an increasing demand for groundwater resources from bedrock aquifers. Low dilution potential coupled with potentially large contributing areas and direct overburden source water suggest that low-yielding public bedrock wells in the southeast New Hampshire may be at greater risk for MTBE contamination than other wells.

### TABLE 7. Logistic Regression Diagnostics and Classification Table for Multivariate Analysis

<table>
<thead>
<tr>
<th>model</th>
<th>$-2 \log \text{likelihood}$</th>
<th>intercept only</th>
<th>intercept and covariates</th>
<th>specificity (%)</th>
<th>sensitivity (%)</th>
<th>total correct (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>well depth, pH, log population density</td>
<td>86</td>
<td>109.94</td>
<td>86.24</td>
<td>48</td>
<td>89</td>
<td>76</td>
</tr>
</tbody>
</table>

Implications for Sources and Transport. As in other studies (16, 23), several urban factors were found to be correlated with the occurrence of MTBE. However, the positive correlation between depth of public wells and MTBE concentration was not anticipated. In interpreting this result, some background on well construction in fractured crystalline bedrock should be considered. Most bedrock wells have concentration was not anticipated. In interpreting this result, several urban factors were found to be correlated with the occurrence of MTBE. However, the positive correlation between depth of public wells and MTBE concentration was not anticipated. In interpreting this result, some background on well construction in fractured crystalline bedrock should be considered. Most bedrock wells have more likely to be relatively old and may predate the introduction of MTBE to the local groundwater system.

Population density was also significant in the model and appears to account for urban effects (sources) not addressed by the physical and chemical variables. Many studies have associated population density and RFG use with the occurrence of MTBE (8, 20, 23). Another study has also associated MTBE with other factors including groundwater recharge and, to a lesser extent, with leaking USTs and aquifer properties (16).

FIGURE 6. Relation between reported safe yield and depth of well for public (a) bedrock and (b) unconsolidated wells in Rockingham County, NH.
Acknowledgments

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Supporting Information Available

Table of data including MTBE concentrations, field parameters, and ancillary data; full correlation matrix of MTBE with urban and physical variables, including numbers of samples. This material is available free of charge via the Internet at http://pubs.usgs.gov.

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