Methyl *tert*-Butyl Ether (MTBE) in Public and Private Wells in New Hampshire: Occurrence, Factors, and Possible Implications

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Methyl *tert*-butyl ether (MTBE) concentrations $\geq$0.2 μg/L were found in samples of untreated water in 18% of public-supply wells ($n = 284$) and 9.1% of private domestic wells ($n = 264$) sampled in 2005 and 2006 in New Hampshire. In counties that used reformulated gasoline (RFG), MTBE occurred at or above 0.2 μg/L in 30% of public- and 17% of private-supply wells. Additionally, 52% of public-supply wells collocated with fuel storage and 71% of mobile home park wells had MTBE. MTBE occurrence in public-supply wells was predicted by factors such as proximity to sources of fuel, land use, and population density, as well as low pH and distance from mapped lineaments. RFG use, land-use variables, and pH were important predictors of private-well MTBE occurrence. Variables representing sources of MTBE, such as the distance to known fuel sources, were not significant predictors of MTBE occurrence in private-supply wells. It is hypothesized that private wells may become contaminated from the collective effects of sources in high population areas and from undocumented incidental releases from onsite or proximal gasoline use. From 2003 to 2005, MTBE occurrence decreased in 63 public-supply wells and increased in 60 private-supply wells, but neither trend was statistically significant.

Introduction

MTBE has been found in groundwater in New Hampshire since its initial use in 1979 as an octane booster and then as an oxygenate in reformulated gasoline in the 1990s, but the extent of methyl *tert*-butyl ether (MTBE) contamination in drinking-water wells in the state is not well documented. A 2003 study in southeast New Hampshire identified widespread, low-level MTBE contamination in untreated water from public and private drinking-water supplies (*1*). Public water suppliers monitor MTBE concentrations in their finished water, but raw water (water prior to treatment) is not routinely monitored. Based on existing finished-water data from public water-supply systems, contamination of public supplies with MTBE concentrations greater than 0.5 μg/L in New Hampshire has risen from 12.7% in 2000 to 15.7% in 2005 (Table 1 in the Supporting Information (SI)).

MTBE contamination is greatest in the four counties where reformulated gasoline (RFG) use was mandated (Figure 1). In three of the four counties that were required to use RFG year-round since 1995, 20% of the public supplies had MTBE above 0.5 μg/L in 2004 and 2005 (SI Table 1). RFG contained about 11% MTBE by volume in New Hampshire. Currently there is no Federal drinking-water standard for MTBE; consequently, several states have developed their own drinking-water standards. New Hampshire has a standard of 13 μg/L (*2*). The New Hampshire Legislature stopped the use of MTBE as a gasoline additive as of January 1, 2007, although replacement of MTBE with ethanol was largely complete by June 2006.

New Hampshire is underlain by fractured crystalline bedrock, which can be more than 100 m below land surface. This Precambrian-to-Cretaceous-aged bedrock is relatively impermeable, has low porosity, and is dominantly igneous and metamorphic (*3*). Interconnected fractures transmit water to wells drilled into the bedrock (*4*). Unconsolidated aquifers, by contrast, are discontinuous glacial deposits that overlie the bedrock; these transmit water through primary porosity and are a major source of water for the state.

About 60% of New Hampshire's population uses public supply for which the source is either groundwater, surface water, or a combination of the two. Most of New Hampshire's public-supply wells are in bedrock aquifers, although large withdrawals are often from unconsolidated aquifers. Private wells serve the remaining 40% of the state's population. Private wells are only tested at the discretion of the well owner and are rarely sampled for MTBE. Over 75% of New Hampshire private-supply wells use fractured crystalline bedrock aquifers (*5*). The risk of exposure to MTBE through drinking water in New Hampshire is greatest in the four southeastern counties that, until 2006, used RFG with MTBE and have over 73% of the state's 1.3 million people. Nearly half of these people are served by groundwater supplies (*5*).

This study represents the first comprehensive evaluation of MTBE in untreated groundwater from public and private drinking-water wells in the state. National and regional studies show that redox, MTBE sources, biochemistry, and hydraulics are important to MTBE occurrence and that identifying factors to predict occurrence can help to understand trends (*6–9*). We identify physical, environmental, and anthropogenic factors associated with MTBE occurrence in public- and private-supply wells and report on preliminary trends in MTBE concentrations from paired well samples collected in 2003 and 2005.

Study Design and Methods

Well Selection and Sampling. To determine the occurrence and distribution of MTBE statewide in New Hampshire, we used a random sampling design and low-level analytical methods. The population of private-supply wells is weighted toward southern New Hampshire, so an equal-area grid was superimposed on a map of the state to select private wells—one random well per cell. The public-supply well population is less skewed; therefore, a simple random design was used. All types of public-supply wells, including com-

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TABLE 1. Percent of Randomly Selected Private and Public Water-Supply Systems with MTBE ≥ 0.2 Micrograms Per Liter in Untreated Water in New Hampshire and by RFG Areas[a]

water-supply type	no. of samples	percent with MTBE ≥ 0.2 μg/L	95% confidence interval	no. (percent) with MTBE ≥ 5 μg/L	no. (percent) with MTBE ≥ 13 μg/L
			statewide		
public	284	18	13.5–22.4	1 (0.4)	0 (0.0)
private	264	9.1	5.6–12.6	1 (0.4)	0 (0.0)
χ^2 test for independence of occurrence rates, $p = 0.0025$.					
Wilcoxon rank sum test for independence of ranked concentration data, $p = 0.0014$.					
			RFG counties		
public	109	30	21.7–38.9	1 (0.9)	0 (0.0)
private	199	17	11.4–21.8	3 (1.5)	2 (1.0)
χ^2 test for independence of occurrence rates, $p = 0.0051$.					
Wilcoxon rank sum test for independence of ranked concentration data, $p = 0.0044$.					
			non-RFG counties		
public	175	10	5.8–14.8	0 (0.0)	0 (0.0)
private	165	7	2.9–10.5	0 (0.0)	0 (0.0)
χ^2 test for independence of occurrence rates, $p = 0.2325$.					
Wilcoxon rank sum test for independence of ranked concentration data, $p = 0.2047$.					

[a] Note that the statewide occurrence survey does not include the 100 additional wells randomly selected for sampling in the RFG areas so that the occurrence is not biased high; the extra wells are included in the intra-RFG comparisons.

munity wells (which serve at least 15 year-round connections or 25 people) and noncommunity wells (which serve smaller numbers of people or transient users) were selected. A total of 284 public-supply and 264 private-supply wells were sampled for the statewide survey (SI Figure 1 and Table 2). Most wells are in crystalline bedrock aquifers, but unconsolidated aquifer public and private wells were also sampled.

Four targeted surveys also were conducted. One hundred additional randomly selected private wells were sampled to more accurately determine MTBE occurrence in the four RFG counties. Another 100 private-supply wells were selected from areas of the highest population density (upper quartile of population density not served by public supply). Forty-one wells located on the same premises as gasoline storage tanks were sampled to assess the impact of collocation on MTBE concentrations. Lastly, 63 public and 60 private wells from a 2003 study (*1*) were resampled in 2005 to assess possible two-year trends in MTBE occurrence in southeast New Hampshire. Data for all wells are included in SI Table 2.

Sampling was done according to U.S. Geological Survey (USGS) protocols and in accordance with techniques used and described in the 2003 study (*1*). In a few wells, where specific MTBE treatment was installed, samples were collected prior to treatment. For most other wells (about 96%), samples were collected prior to any other form of treatment. The operational status of wells prior to sampling can affect measured concentrations (*4, 10*); thus, all wells, including those that were resampled, were currently active. Most wells, however, cycle over short time periods (minutes to hours) according to demand and pressure factors. Because cycling was relatively short, the samples were considered representative of contaminant occurrence. Wells were located with a global positioning system (GPS) to within approximately 30 m.

Chemical Analyses and Quality Control. The New Hampshire Department of Environmental Services Water Quality Laboratory analyzed water samples for MTBE using gas chromatography/mass spectrometry (GC/MS) ambient-temperature (25 °C) purge-and-trap, according to U.S. Environmental Protection Agency (USEPA) method 524.2 (*11*). No other compounds were considered. The laboratory reporting level (LRL) for the study was 0.2 μg/L.

Replicate, blank (from VOC-free water), and spike samples were collected throughout the investigation (every 10, 20, and 50 samples, respectively). Fifty-seven of 70 replicate samples had results below the LRL; relative difference for the 70 replicates ranged from 0 to 7% with a mean of 0.6%. One of 59 equipment blanks had a measurable MTBE concentration, as did the associated environmental sample, which was discarded. Seventy-one spiked performance-evaluation samples prepared with blank water had recoveries ranging from 55 to 145.2%, with a mean of 96.9%. Performance-evaluation samples prepared using environmental samples had recoveries ranging from 58.5 to 141.2%, with a mean of 97.8%. Seven ambient blanks (vials open to ambient air) were collected and one had measurable MTBE, as did the associated environmental sample, which was discarded. Overall, the QA/QC indicated that the environmental data were acceptable and that any potential bias would have no significant impact on our findings.

Information and Statistics Used in Our Analysis. Geographic information system (GIS) and ancillary data used in our analyses includes data about (1) aquifer type, system size, water-supply establishment type, well depth, and reported safe yield; (2) population and housing density, and urban areas (*12, 13*); (3) land-use data (*14*); (4) soil data (*15*); (5) hydrogeologic data, including well-yield probability, lineament mapping, and lithology (*3, 16*); (6) road data (*17*); (7) RFG use, proximity to fuel sources (*18*); and (8) field water-sample temperature, pH, specific conductance, and dissolved oxygen concentration.

Between 50 and 90% of samples from the data sets for this study had MTBE concentrations less than the LRL. All statistical analyses (*19*) included the data below the LRL without modification (*20, 21*), and the significance level for all tests (α) was 0.05. Contingency-table analyses were used to measure the association of MTBE occurrence (presence or absence) with nominal grouping variables. The relative risk of one binary variable, while controlling for the effect of another, was computed to assess the relative importance of those variables. The Kruskal–Wallis test was used to determine if the means of the ranks of the data from various groups were significantly different (*22*). Spearman correlation coefficients were computed to measure the strength of the relation to explanatory variables (*22*).

Multivariate logistic regression, where the dependent variable is binary (i.e., presence or absence), was done to indicate factors associated with occurrence, source, and transport. The multivariate analyses were not intended to be predictive; therefore, predictive performance was not evaluated. Model fit, however, was evaluated using Akaike's

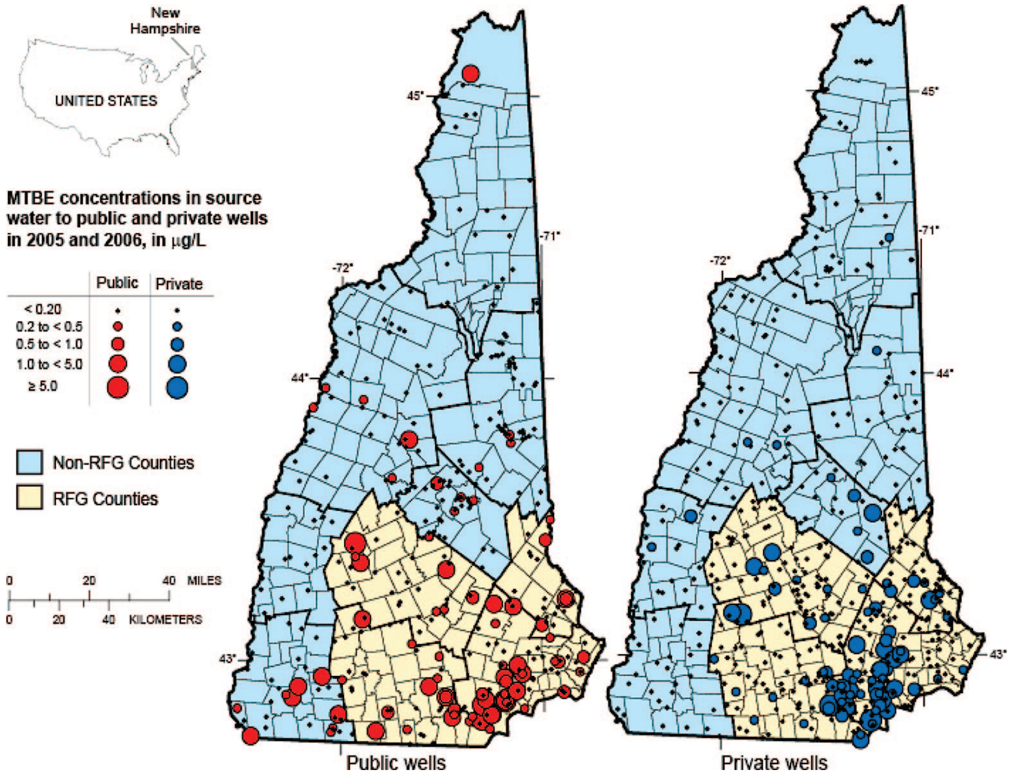


FIGURE 1. Locations of public and private wells and concentrations of methyl-*tert* butyl ether in untreated water samples. Counties required to use reformulated gasoline (RFG) are shown in tan. Number of public well samples shown = 364; number of private well samples shown = 516.

TABLE 2. Comparison of Selected MTBE Occurrence Rates from Selected Aquifer Studies in the Eastern United States

study	sample category	aquifer type	% of samples with MTBE ≥ assessment level	assessment level, μg/L	number of samples	reference
Maine	statewide public	Mixed	14.9	0.2	793	*24*
Maine	statewide private	Mixed	15.0	0.2	946	*24*
Maine	statewide public	Crystalline bedrock	16.2	0.1	569	*24*
Pennsylvania	near-source	Mixed	22	0.2	86	*25*
Pennsylvania	ambient	Crystalline bedrock	18	0.2	73	*25*
Pennsylvania	near-source	Crystalline bedrock	57	0.2	21	*25*
12-state northeast and mid-Atlantic	finished drinking water	Mixed, includes surface sources	9	0.2	985	*26*
Boston, MA metropolitan area	ambient, suburban	Shallow unconsolidated	38	0.2	29	*27*
New Jersey	ambient, urban	Shallow unconsolidated	44	0.1	72	*28*
this study	statewide public	mixed	18	0.2	284	
this study	statewide public	Crystalline bedrock	14.9	0.2	181	
this study	RFG-use public	Crystalline bedrock	27.5	0.2	69	
this study	statewide private	Crystalline bedrock	9.1	0.2	264	
this study	RFG-use private	Crystalline bedrock	17	0.2	199	
this study	wells at fuel storage sites RFG areas	Mixed, mostly bedrock	52	0.2	21	
this study	mobile home parks	Mixed, mostly bedrock	71	0.2	17	

Information Criteria, Wald p-values of model parameters, model discrimination (c-statistic), the Hosmer−Lemeshow statistic, and classification tables. Two-year trends, from 2003 to 2005, were tested using the nonparametric sign test, one pair per well, using a correction for ties for nondetects in the data (*20, 23*).

Results and Discussion

MTBE Occurrence. In the statewide survey, MTBE concentrations were ≥0.2 μg/L in untreated groundwater samples from 18% of public- and 9.1% of private-supply wells. The locations of wells and MTBE concentrations are shown in Figure 1. Public and private wells had significantly different MTBE occurrences (Table 1, $p = 0.0025$), and public wells had higher MTBE concentrations than private wells (Table 1, $p = 0.0014$). Exceedence plots of the public and private well data illustrate the differences in the data distributions (SI Figure 1). By comparison, MTBE was ≥0.2 μg/L in 15% of public and private water supplies sampled in Maine in 1998 (Table 2), in a population-based survey (*24*).

In the statewide survey, 1 of the 284 randomly selected public-supply wells (0.4%) and 1 of the 264 private wells (0.4%) had an MTBE concentration that exceeded the state action level for notification of adjacent well owners, which is 5 μg/L. None of the MTBE concentrations from the statewide survey exceeded the state drinking-water criteria of 13 μg/L (Table 1); however, two wells from the private well survey in the RFG counties exceeded 13 μg/L. MTBE occurred in 30% of public- and 17% of private-supply wells in the four New Hampshire counties where RFG use was required. The concentrations of MTBE in public-supply wells were significantly higher than in private-supply wells in the RFG counties but not in non-RFG counties (Table 1). MTBE occurrence was highest in the targeted surveys. For private wells randomly selected in the highest population density areas, 3% exceeded 5 μg/L and 2% exceeded 13 μg/L (SI Table 3). Occurrence was similar in the 100-well random and high-density random networks. However, occurrence in Rockingham County remained the highest in the state for several categories, including 48% of private wells with MTBE ≥ 0.2 μg/L in the high population density survey area (SI Table 7). In public wells collocated with fuel storage facilities (generally transient noncommunity wells), 52% of wells in the RFG counties had measurable MTBE (≥0.2 μg/L) whereas 19% exceeded 13 μg/L and 29% exceeded 5 μg/L. None exceeded these state limits in the non-RFG counties (SI Table 3). Currently, the USEPA does not require VOC analyses for transient public-supplies, and most states do not require more stringent testing than that imposed by USEPA.

MTBE occurrence in public-supply wells varies by water-supply system category (SI Table 4). The largest MTBE occurrence was 71% for mobile-home park wells, which is well above the occurrence for the other categories. Large community water systems (CWS) and day-care facilities had occurrences of about 40%, whereas schools and single-family residences had the lowest at about 8% (SI Table 4). The reasons for these differences are not clear, although a combination of factors is likely responsible.

Concentrations of MTBE detected in this study were not significantly different by aquifer type for public- or private-supply wells in New Hampshire. For public-supply wells, the occurrence and concentrations were slightly, but not significantly, higher in unconsolidated wells than in bedrock wells in both RFG and non-RFG counties (SI Table 5). Private-supply wells had a slightly, but not significantly higher, occurrence in bedrock than in unconsolidated aquifers (SI Table 5a). This implies that the bedrock aquifer may be similarly vulnerable to contamination from MTBE and other similarly mobile contaminants. This may have implications for future water development in the state where there is increasing reliance on the bedrock aquifer for water supply (*16*).

There was no significant difference in MTBE contamination in wells grouped by USEPA-defined public-supply system categories, although community water-supply wells had a 2-fold higher occurrence than noncommunity wells in both RFG and non-RFG counties (SI Table 5b). The statewide public and private occurrence data and the additional targeted private, RFG-county occurrence data are tabulated by county in SI Tables 6 and 7.

Overall, our data indicate that MTBE occurrence is high throughout New Hampshire, especially in the RFG-use counties, and that the occurrence rates are similar to other studies in the northeast (Table 2). In 1998, Maine reported that 15% of private and 14.9% of public wells sampled in a statewide survey had MTBE concentrations above 0.2 μg/L compared to 9.1 and 18%, respectively, in this New Hampshire study. In 2003, near-source samples from wells in crystalline bedrock in Pennsylvania had a 57% occurrence rate (*25*). Targeted surveys from shallow unconsolidated-aquifer wells (Boston and New Jersey) also had high occurrence. Targeted samples from our study at sites with fuel storage and at mobile home parks had among the highest occurrence rates (52 and 71%, respectively).

Factors Related to MTBE Occurrence. Many factors correlate with MTBE in water-supply wells sampled for this study, including population density, RFG-use areas, and distance to known sources of fuel (for public wells) (SI Tables 8 and 9). The importance of population density, RFG use, and distance to known sources of fuel were assessed in this section using contingency-table analysis, whereby continuous variables were treated as a binary categorical variables based on their median values (*24*). The relative risk (RR) is the ratio of the probability of having MTBE present for a given risk factor to the probability of having MTBE present in the absence of that risk factor. Others factors such as land use, well depth, well age, and dissolved oxygen concentration are discussed in later sections.

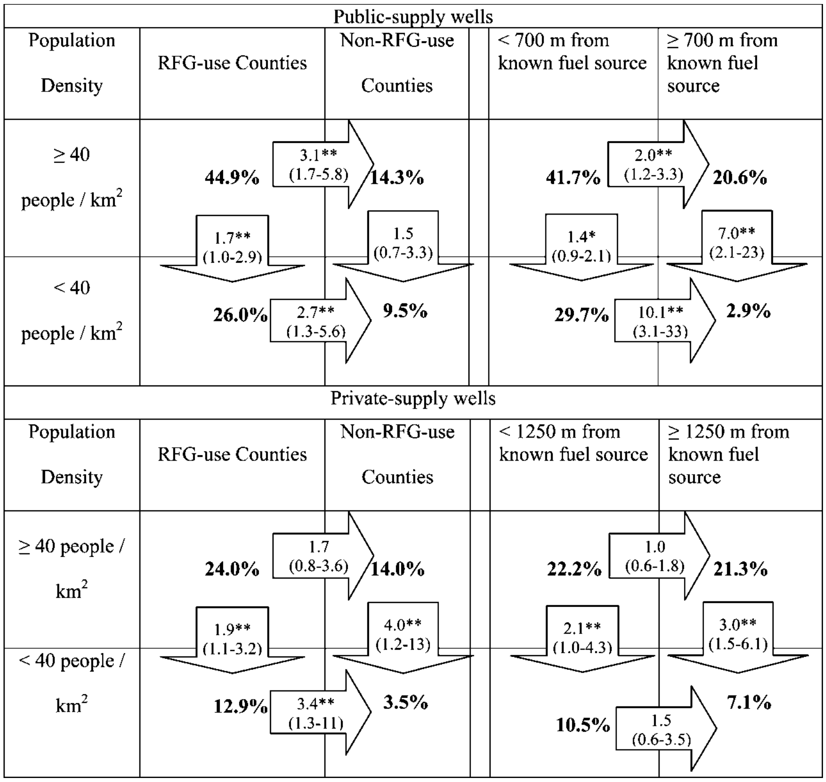
For public-supply wells, MTBE occurrence within RFG-use categories and fuel-source distance categories is compared over two population-density categories (Table 3). The RR of MTBE occurrence is nearly two times higher between the RFG-use categories (horizontal arrows) than between the population-density categories (vertical arrows), implying that RFG use is a stronger predictor than population density for MTBE occurrence. Also, the RR for RFG use compared to non-RFG use is about 3 in both population density categories, suggesting that the RFG-use variable is independent of population density.

Public-supply wells within 700 m of a known fuel source (the median distance for public wells in this study) are more likely to have MTBE contamination than those that are more than 700 m away. The RR is 2-fold in high population-density areas and 10-fold in low density areas. By contrast, for wells within 700 m of a fuel source, the RR from low to high population density is about 1.4 (marginally significant). For wells more than 700 m from a known source, there is a 7-fold increase in RR from low to high population density, indicating that population density is a strong risk factor for MTBE occurrence when wells are far from known fuel sources. One explanation is that there may be point sources in high population density areas that have not been identified, which lead to MTBE contamination. Alternatively, this increased risk is associated with the cumulative effects of nonpoint sources commonly associated with high population density areas.

For private wells, the RR's between RFG-use categories are only slightly smaller than between population density categories, suggesting that both RFG use and population density significantly influence MTBE occurrence. Private wells within 1250 m of a known fuel source (the median distance for private wells) are no more likely to have MTBE contamination than those that are more than 1250 m away, for both population-density groups (RR = 1 and 1.5, respectively). However, wells in high population densities are 2−3 times more likely to have MTBE. This suggests that private and public wells may become contaminated as a result of different factors, possibly due to differences in pumping stresses and (or) well yield. In general, the public and private wells in the bedrock aquifer in this study are similar in well depth and construction, but public wells are generally constructed to meet volume requirements, whereas, private wells are more often sited to fit the house-lot configuration.

Multivariate Analysis of MTBE in Public- and Private-supply Wells. Logistic regression was used to identify additional factors that predict the probability of MTBE occurrence in public- and private-supply wells. Variables for the regression models were compiled in a GIS and evaluated initially with backward selection and then individually before developing the final models. All wells were at least 500 m apart and were required to have a full set of independent variables. The number of public and private-supply wells available for this analysis was 361 and 481, respectively. The binary dependent variable cut-point was 0.2 μg/L.

TABLE 3. Percent of Public- And Private-Supply Wells with MTBE ≥ 0.2 μg/L, By Population Density, Reformulated-Gas (RFG) Use, and Distance to Known Fuel-Source Categories in New Hampshire[a]



[a] Binary categories based on median values for respective factors. Values inside arrows indicate relative risk (risk ratio) between the factors shown (*24*); values in parentheses are 95%-confidence intervals. ** indicates significant at alpha = 0.05 level; * indicates significant at alpha = 0.1.

TABLE 4. Parameters of Multivariate Logistic-Regression Models for Public Unconsolidated and Bedrock-Aquifer Wells, and Private Bedrock-Aquifer Wells

model	parameter	parameter type: units	parameter type: type	estimated coefficient (β)	Wald p-value	exp(β) (odds ratio)	95% CI
public, unconsolidated aquifer wells, $N = 114$	intercept			1.1754	0.1673		
	distance to known source	$m^{0.5}$	source	−0.0547	0.0130	0.947	0.91–0.99
	RFG area	binary	source	0.9552	0.0534	2.599	0.99–6.9
	forested land use (%)	percent	source	−0.0270	0.0493	0.973	0.95–1.0
H-L statistic = 0.5783; c statistic = 0.783; Sensitivity = 11/27 = 41%; Specificity = 84/87 = 97%							
public, bedrock aquifer wells, $N = 247$	intercept			4.3950	0.0377		
	specific conductance	μs/cm	source	0.0013	0.0040	1.001	1.00–1.002
	distance to known source	$m^{0.5}$	source	−0.0669	0.0003	0.935	0.90–0.97
	density of high risk sources	no./km^2	source	0.3589	0.0022	1.432	1.14–1.80
	pH	standard units	transport	−0.8263	0.0040	0.438	0.25–0.77
	RFG area	binary	source	1.3601	0.0019	3.897	1.65–9.20
	lineament within 100 m	binary	transport	−2.1767	0.0007	0.113	0.03–0.40
	Population density	continuous	source	0.00231	0.0263	1.002	1.000–1.004
H-L statistic = 0.8398; c statistic = 0.889; Sensitivity = 36/60 = 60%; Specificity = 174/187 = 93%							
private, bedrock aquifer wells, $N = 481$	intercept			−4.1091	<0.0001		
	wells <80 m from any road	binary	source	1.0573	0.0163	2.879	1.22–6.82
	road density	km/km^2	source	0.3412	0.0007	1.407	1.15–1.71
	RFG area	binary	source	0.7355	0.0491	2.086	1.00–4.3
	pH <7.75	binary	transport	−0.9101	0.0033	0.402	0.22–0.74
	Berwick Fm	binary	transport	1.5622	<0.0001	4.769	2.57–8.85
H-L statistic = 0.4763; c statistic = 0.817; Sensitivity = 23/83 = 28%; Specificity = 378/398 = 95%							

Public-Supply Wells. The public-supply well models (Table 4) indicate that source and transport variables are significant predictors of MTBE in groundwater. The most significant source variables include RFG use areas, distance to known fuel sources, density of potential sources, population density, and land use factors. Many of these factors, such as population density, RFG use, and various land uses have been reported in other studies in the United States (*29–31*). The models show that unconsolidated- and bedrock-aquifer wells in RFG-use counties have 2.6- to 3.9-fold higher odds of having MTBE than in non-RFG-use counties (Table 4). Also, the probability of MTBE occurrence is inversely proportional to the distance from a known fuel sources and positively proportional to specific conductance (SC). SC is indicative of urban effects on the groundwater system (such as roadway deicing or sewer and septic-system leakage) and may be a proxy for the effects of nonpoint sources of MTBE (*32*). Other factors, such as pH, mapped lineaments, and to some extent, the distance to known sources, indicate possible mechanisms that affect the transport of MTBE for public bedrock wells. Low pH indicates recent recharge of groundwater to the bedrock aquifer and (or) relatively short residence time (*1*), and therefore, the inverse relation of MTBE to pH suggests that MTBE is associated with recent recharge. Wells within 100 m of lineaments identified on 1:20000-scale photography had a 9-fold reduced odds of MTBE contamination ($\mathrm{EXP}(\beta) = 0.113$). Mapped lineaments are linear ground-surface features identified on aerial or satellite imagery that can indicate fractures in the underlying bedrock aquifers and are indicative in some areas of high-yielding water wells (*16*). One explanation is that MTBE may be diluted by high groundwater fluxes commonly associated with lineaments. This is consistent with VOC dilution resulting from increasing pumping rates (*33*). This finding is inconsistent with a risk-analysis study where MTBE occurrence in some wells was associated with lineaments shared by the public-supply well and known remediation sites (*31*). However, this difference could be attributable to transient effects associated with high-conductivity fracture zones. Such zones may rapidly transport contaminants such as MTBE to supply wells and thus are an important pathway. Over time, however, high-conductivity fractures may ultimately reduce contamination as the source is diminished and increasing proportions of clean water are captured.

Notably absent in the bedrock well model were variables such as well depth, well yield, and dissolved oxygen, which have been reported in other studies as related to MTBE occurrence (*6, 9, 30*). Well depth and yield correlate weakly with MTBE concentrations as in a previous study (*1*) in Rockingham County, but were not significant statewide. In the four RFG counties in southern New Hampshire, well yield had a marginally significant inverse relation. The finding that well depth is not significant may be due in part to the generally narrow range of well depths common to bedrock wells (interquartile range, IQR, of public well depths ranged from 67 to 146 m for wells in this study; the private well IQR was 60–152 m) and that individual fracture locations in wells are unknown. Dissolved oxygen is variable (IQR was 0.3−3.5 mg/L in both public and private wells sampled) but the reason for the lack of correlation is unclear.

Private-Supply Wells. The private-supply well regression model (Table 4) includes primarily nonpoint source terms such as RFG use, proximity to roads, and road density. Wells located near roadways (<80 m) and RFG use increase the odds of MTBE occurrence by about 3- and 2-fold, respectively. Road density results in a 41% increase in the odds of MTBE occurrence per unit increase in density (km km^{-2}). This suggests that wells located near roadways and in higher roadway density are particularly sensitive to MTBE contamination. The effect of pH is similar to the effect in the public bedrock well model, whereby the odds of MTBE occurrence increase 2.5-fold for wells in the low pH category.

Variables representing sources of MTBE, such as the distance to fuel sources, were not significant predictors in the private-well model. This is not unexpected because private wells withdraw less water, have smaller contributing areas, and may be located on the fringes of high population density areas, compared to public wells. Public wells may therefore have a greater opportunity to capture multiple MTBE plumes. A subset of private wells had well-construction date data which is discussed in a later section.

Unexpectedly, the geologic units of Berwick Formation in the southeast part of the state were significant predictors of MTBE occurrence in private wells. Private-supply wells in the Berwick Formation had 4.7-fold higher odds of MTBE occurrence than wells in other lithologies in the state (3-fold higher odds in just the RFG counties). Although the mean population density for wells in the Berwick Formation is high (234 people km^{-2}), attempts to explain this relation with population density, well depths, yield, and other factors were not successful. Whether there is an effect from the properties of the Berwick Formation or this relation is a surrogate for some other factor is unresolved.

Two-Year Trends in MTBE Occurrence. Two MTBE measurements were made at 60 private- and 63 public-supply wells in southeast New Hampshire. All private wells and 51 of the 63 public wells were in fractured crystalline bedrock. Most of the wells with measurable MTBE in 2003 and a subset of wells that did not have MTBE in 2003 were resampled in 2005 (SI Table 2). The measurements made in 2005 show a slight increase in MTBE occurrence for private wells (from 33 to 37%) and a slight decrease for public-supply wells (from 60 to 48%). The nonparametric sign test, however, corrected for ties, showed no significant trends for either public- or private-supply wells ($p = 0.7759$ and 0.9998, respectively). This suggests that the two-year period between samples or the number of samples may be inadequate for detection of trends or that there currently are no trends.

Available well-construction data for private-supply wells showed that MTBE occurrence decreased with increasing decade of construction, from about 20 to 5% from before 1980 to 2000 (SI Figure 2). For private wells in the RFG counties, the construction date of wells with MTBE is significantly earlier than wells without MTBE (mean = 1987 and 1992, respectively; $p = 0.0051$). It is unclear whether newer wells have lower MTBE occurrence because insufficient time has elapsed for contaminants to be transported along flow paths to the well, or if factors such as long-term well integrity play a role. Considering the generally low rate of groundwater flow, it was not surprising that no significant trends were discernible after two years; however, periodic monitoring on a similar interval, in the wake of the legislative ban on MTBE, may be useful in understanding MTBE fate in crystalline-bedrock aquifers. Specific geologic formations and variation in fracture hydraulic conductivities may affect rates of dilution and, thus, MTBE trends.

Implications. The occurrence of MTBE in untreated water from public and private water-supply wells in New Hampshire is controlled by factors related to sources, transport, and fate of MTBE in unconsolidated and fractured crystalline bedrock aquifers in the state. Some factors for MTBE in public and private-supply wells are shared among well types in this study, such as RFG-use areas, distance to known sources (unconsolidated and fractured bedrock public-supply wells), and pH (fractured bedrock private- and public-supply wells). Others were unique to a particular well type, such as the association of MTBE with mapped lineaments for fractured bedrock public-supply wells or MTBE and specific geologic units for fractured bedrock private-supply wells.

The finding that older private wells have more MTBE than younger ones suggests that MTBE may take years-to-decades to move through the groundwater system, and the transport of MTBE may be affected by large-scale hydraulics of fractured crystalline bedrock. For example, at dimensions of 10−100 m, bedrock fractures can support very high flow velocities, but at dimensions of 100−1000 m or more, flow velocities diminish rapidly, due to a bottleneck effect of intermittent low-conductivity fractures (*4, 34*). Fractures that are low conductivity may contain MTBE or similar contaminants for long periods of time. Private wells are generally drilled for home construction, and the age of a well may be a surrogate for the beginning of incidental releases of gasoline associated with home use and maintenance. Although for private wells there was no relation of MTBE occurrence to known fuel sources, it is hypothesized that undocumented releases from on-site or proximal gasoline and (or) fuel-oil use may contribute to private-supply well contamination. Whether there are cumulative effects from small releases over time is not clear. However, once contaminated, small releases may have a comparatively large and long-term effect on private-supply wells due to lack of dilution, particularly in low-yielding portions of bedrock (*34*).

Biochemical degradation may decrease contamination. MTBE can degrade in groundwater under anaerobic conditions such as near MTBE sources (*9*), but these conditions are generally not present at drinking-water wells with low-level MTBE contamination in New Hampshire. MTBE also can degrade under aerobic and subaerobic conditions (*9*), which are more typical of conditions in drinking-water wells in this study. MTBE was completely mineralized under aerobic conditions in a microcosm study using starting MTBE concentrations of 150 μg/L (*35*). However, microbial degradation of MTBE in groundwater may be mass dependent, requiring relatively high environmental concentrations of MTBE for productive biodegradation (*36*). The timing and effectiveness of biodegradation of low-level MTBE contamination in fractured-bedrock aquifers is unknown.

Crystalline bedrock aquifers also are an important source of water supply in other areas of the United States, such as major parts of New England and parts of the Piedmont and Blue Ridge region. Results from this study provide information about factors that may control MTBE contamination and possibly other contaminants, such as deicing chemicals and nitrate, in crystalline bedrock aquifers. Factors such as proximity to mapped lineaments, specific geologic formations, and various land uses may play a role in the transport and fate of these and other contaminants.

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Supporting Information Available

Tables including wells sampled, concentrations, ancillary data, occurrence frequencies, correlations, and data descriptions. Figures including plots of concentration data and percent of wells with MTBE by construction date. This material is available free of charge via the Internet at http://pubs.acs.org.

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