MtBE AFTER THE BAN

James M. Tarr, CG, PG, LSP Regional Manager of Corporate Environmental Advisors Inc.

Adam M. Galonski, PG, LSP Senior Geologist, Corporate Environmental Advisors Inc.

ABSTRACT

Recent ground water contaminant concentration data from twenty-five active retail gasoline stations in New Hampshire were compared with historic data from the same sites to evaluate the overall impact of the State of New Hampshire banning the use of methyl tertiary butyl ether (MtBE) on January 1, 2007 as a part of its Oxygen Flexible Reformulated Gasoline (OFRFG) program. These data were statistically evaluated to determine the efficacy of eliminating MtBE from supply tanks. Preliminary findings will be discussed as well as outlining the long term study plans.

Introduction

This study examined the environmental results of the methyl-tertiary-butyl-ether (MtBE) and other ethers being deleted from use in New Hampshire. Specifically this paper investigated the presence of "MtBE after the Ban," in the ground water of 25 known MtBE gasoline contaminated sites located in New Hampshire. The investigation examined the relationship between the concentrations of MtBE and ethers and the various geologic settings found in New Hampshire.

Oxygenates, such as MtBE, were added to gasoline beginning in the late 1970's when leaded gasoline was phased out. In the mid 1990's with the passage of the Clean Air Act, MtBE was used in reformulated gasoline (RFG) in an effort to increase combustion and as a result, reduce air pollution resulting from vehicle emissions. MtBE was not specifically required, but the economics and characteristics of the chemical made it the additive of choice. Concentrations of MtBE in gasoline in New Hampshire have ranged from 11 % to 15 % by volume (Johnson et al., 2000). MtBE has impacted the ground water in the State of New Hampshire since the 1970's (Ayotte et al., 2005). Previous studies conducted by the U.S. Geological Survey (USGS, 2004) and the New Hampshire Department of Environmental Services (NHDES) also have determined that MtBE had been found in public water supplies throughout Rockingham County, New Hampshire. Rockingham County is one of four southern New Hampshire counties that utilized reformulated gasoline (RFG). It is for these reasons as well as alleged health concerns that MtBE and the other ethers were banned in the state of New Hampshire. We now know that New Hampshire has the highest reported concentrations of MtBE in groundwater amongst the New England states (Moran, 2007).

Effective on January 1, 2007 the State of New Hampshire law (RSA 146-G:12) prohibited the sale, delivery for sale or import into the state of gasoline containing MtBE, other gasoline ethers or tertiary butyl alcohol (TBA). The law reads as follows:

146-G:12 Elimination of Gasoline ethers and TBA from Gasoline Supplies. No person, as defined in RSA 146-A:2, VI, shall sell, deliver for sale, import, or cause to be imported into the state for sale any neat gasoline ethers or gasoline containing MtBE, other gasoline ethers, or tertiary butyl alcohol (TBA) in quantities greater than ½ of one percent by volume. Nothing in this subdivision shall be interepreted to prohibit the transshipment of MtBE, other gasoline ethers, or TBA content fuel through the state for disposition outside of the state including storage coincident to such shipment.

The New Hampshire ban is different than other New England States in that New Hampshire ban included MtBE, as well as other ethers and TBA. Many state governments have enacted or are considering mandatory phase outs primarily of just MtBE. These actions are not only based on health concerns but on the fact that, in even very small amounts, MtBE can make water taste and smell unpleasant. Note that while the ban in New Hampshire was effective as of January 1, 2007, nearly all retail gasoline facilities in New Hampshire had made the switch in early May 2006, before the 2006 summer driving season, as was reported by the Energy Information Administration (Shore, 2006). This was largely driven by the Energy Policy Act of 2005, which terminated the oxygen mandate as of May 6, 2006. In an effort to stave off potential liability due to the presence of MtBE, refiners used the May 6, 2006, date as the target to have the gasoline supply free of MtBE (McCarthy and Tiemann, 2006).

The NHDES completed small scale testing in the fall of 2006 to confirm that MtBE and other ethers were not being used in the gasoline (NHDES 2006).

Figure 1 depicts the MtBE and other contamination sites in New Hampshire (NHDES, 2004). We looked at the distribution of these sites and it was quite apparent that the largest occurrence is associated with the greater population centers along the seacoast and major highway I-93 corridor south from Nashua through Manchester and Concord to the north.

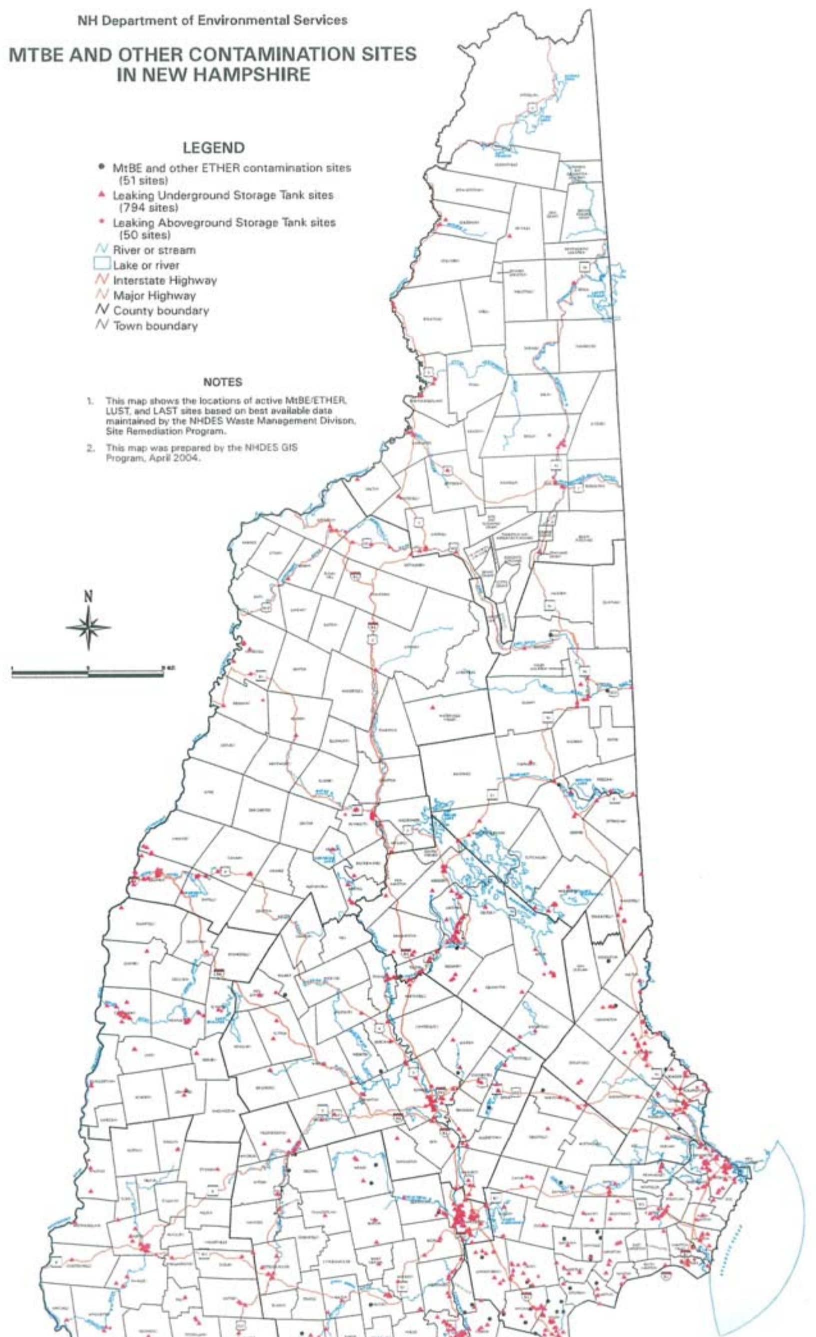


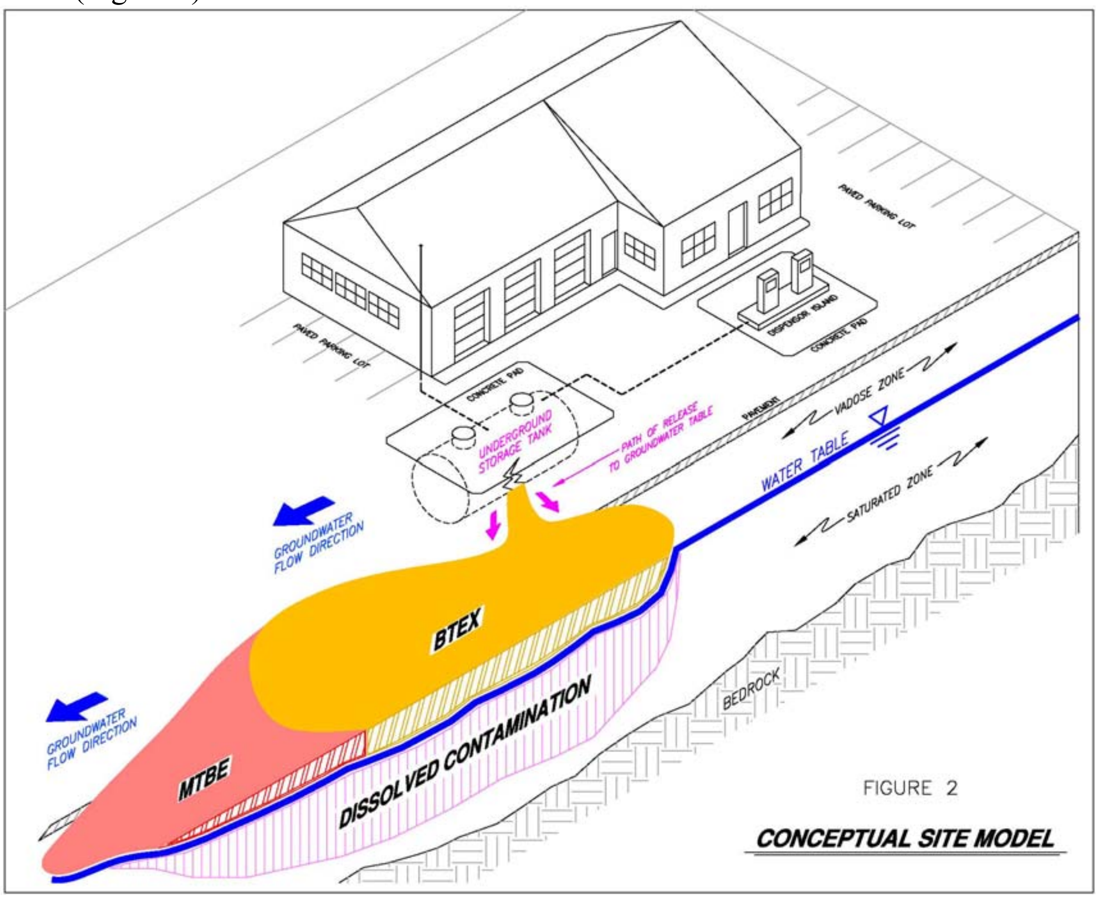
FIGURE I

One key source of MtBE contamination in ground water is the leaking underground storage tanks (LUSTs). In 2002, MtBE was detected in 60% of ground water samples collected in association with gasoline releases in New Hampshire. The average MtBE plume length ranges from approximately 100 to 250 feet (Weston Solutions, 2006). It is this source (LUSTs) that this paper focuses on.

The regional geographic areas are; the seacoast, the lakes and mountains, the inland areas in between and the most northern locations. We examined the correlation between the surficial geology and MtBE concentration/trends were apparent and if so, what the trends indicated. We examined the fate and transport of MtBE in the various geological settings. For general purposes, we have included a brief description of the characteristics of MtBE.

Characteristics

After MtBE is released from a leaking UST, it will migrate horizontally and vertically with time (Figure 2).



Although most of us are quite familiar with the fate and transport of MtBE, we have included a brief description for understanding the general background of it in this paper. Within the saturated zone the dissolved phase the major processes that occur are; dissolution, advection, dilution, dispersion, sorption, diffusion, and biodegradation (ITRC 2005). The primary attenuation mechanism for MtBE is dispersion. It is well understood that MtBE may be regarded as recalcitrant under site-specific conditions. If MtBE resists biodegradation, then these plumes will eventually attenuate to regulatory concentration goals due to dispersion, although in contrast to benzene, toluene, ethylbenzene, and xylenes, (BTEX compounds), the mass would not be depleted and significantly longer distances and time frames would be required. Although a number of laboratory studies indicate that microorganisms isolated from various environments can degrade MtBE, this study attempted to determine if MtBE has degraded or the banning of MtBE and its discontinuing use of has caused a reduction in measured concentrations.

When gasoline chemical components, including MtBE, contact ground water, these chemicals will dissolve based on their respective solubility limits and site-specific conditions. The chemicals will then migrate with the ground water. Dissolved chemicals cannot travel faster than the ground water but they may travel slower if their movement is retarded by adsorption to the soil. Several processes occur when ground water plumes migrate; the chemicals in the water are diluted and dispersed; the chemicals may absorb onto the soil particles or the chemicals may desorb from soil particles; the chemicals may be aerobically or anaerobically biodegraded (Sloan et al.). The net result is that MtBE will tend to exist on the leading edge of a typical ground water plume; however the other gasoline components; for example, BTEX, will tend to exist immediately behind the leading edge of the plume (Reisinger II, et al., 2000).

Increasing evidence has been found and reported on the biological natural attenuation of MtBE in gasoline contaminated aquifers. The capacity to biologically degrade ethers, like MtBE, is widespread in nature (Ramsden, 2000). Numerous organisms, with the capability to biodegrade MtBE along with other components of gasoline, have been identified from surface soils, and aquifers. Oxygenate plume stabilization may be more related to population density and site conditions than to the innate biological capabilities on site (Sloan et al.).

Johnson et al., estimates that typically at least 10 years will be required for MtBE from a typical LUST to reach acceptable ground water regulatory levels. In New Hampshire the regulatory level is 13 (μg/L) micrograms per liter. It is worth noting that the majority of the sites used in our study have been remediated using "Monitored Natural Attenuation," (MNA) as the preferred remedial method. In many cases soil remediation (removal) has occurred followed by MNA.

Geology

It is important to understand the surficial geology of New Hampshire when discussing the relative distribution of MtBE contaminated sites. During the last glacier advance in New Hampshire approximatley 14,000 years ago most of the state was covered with ice. As a result of the glaciers, two major types of glacial deposits were left in the state, glacial till and stratified drift. The till consists of unsorted sediments deposited in place directly by melting ice. Sediment sizes generally range from very small to very large-clays to boulders. Today till is commonly seen at or near upland areas throughout the state and has generally a low transmissivity associated with it. The other major type of glacial deposit, stratified drift, began to form during the late stages of the Great Ice Age, (USGS 1995). At that time, the glaciers had melted back to the north. The various stratified deposits were a result of this melting. The stratified-drift deposits are the major source of aquifers found in the state. These deposits consist of mainly layers of sand and gravel, parts of which are saturated and yield significant amounts of ground water. About 14 %

or 1,299 of 9,282 miles of New Hampshire are underlain by stratified-drift aquifers (USGS 1995).

In general, most transmissive aquifers are found in the central and southern parts of the state. The general distribution of stratified-drift aquifers are depicted on Figure 3. When comparing Figure 1 the distribution of MtBE contaminated sites and Figure 3 it shows that the greatest occurrence of MtBE sites are located along major population areas of the southeast coastal region and along the major I-93 highway. The some of the major aquifers also lie within these areas, particularly in the regions from Nashua, Manchester, and Concord. Ayotte et al., found that MtBE concentrations correlated strongly with urban factors such as population density.

Twenty-five sites that were investigated for this paper are superimposed over the USGS figure and are depicted on Figure 3. The 25 sites are distributed in various regions. We examined sites in glacial till areas as well as within stratified-drift aquifers.

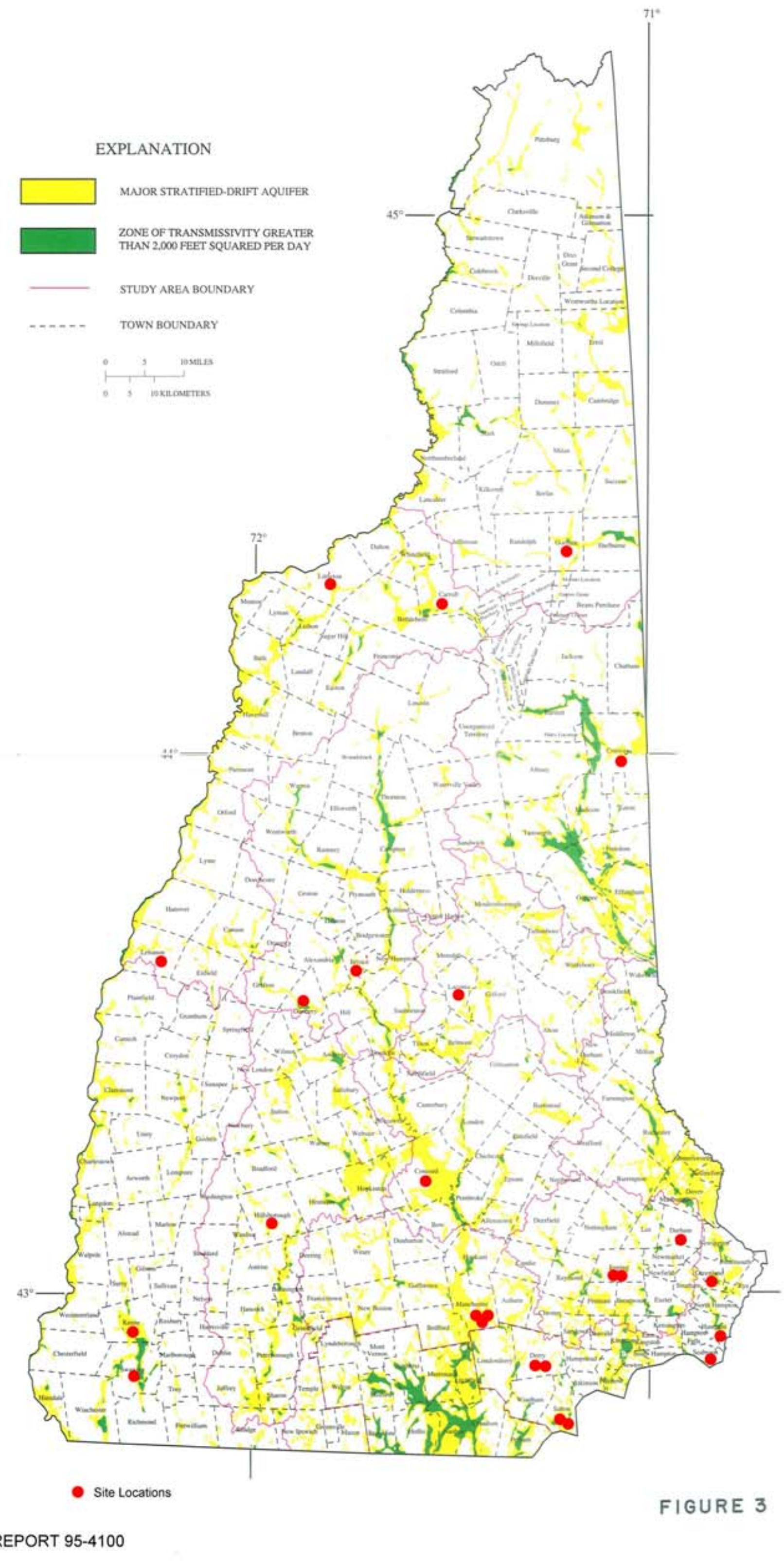


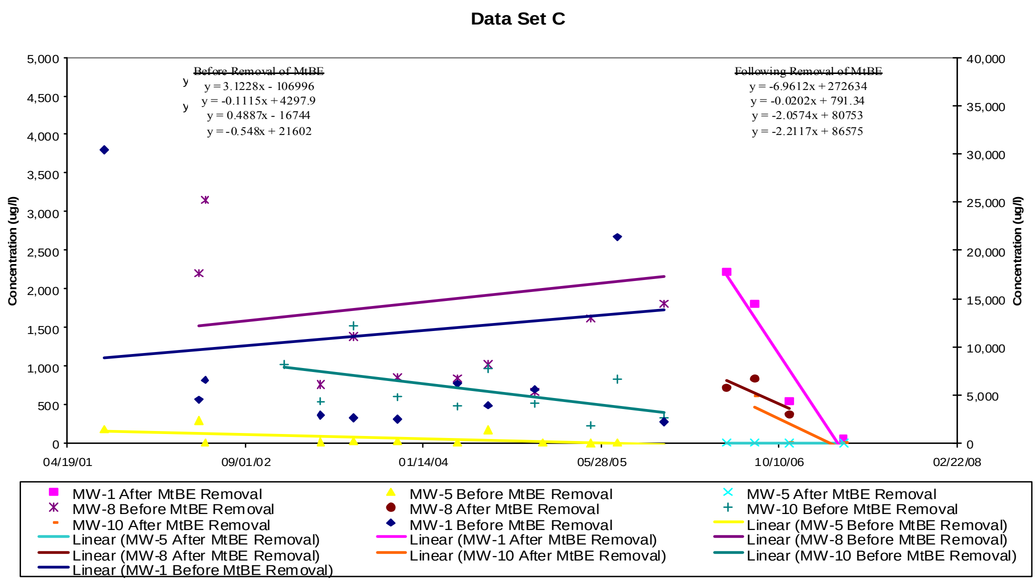
FIGURE 3

FROM USGS REPORT 95-4100

Data Analysis

As indicated previously, the study consisted of data from 25 sites across New Hampshire. The sites were randomly chosen based on location, suitability of the MtBE data, and historical extent of temporal data available. At a given site monitor wells were selected based on whether the target wells had detections of MtBE both prior to and subsequent to the time when MtBE was removed from the gasoline supply. A total of 78 monitor wells located at the 25 sites were selected for this study.

After the concentration data had been compiled, the first step was establishing the trends of MtBE in the ground water prior to its removal from the gasoline supply. Therefore, the pre-removal data was plotted against time and a regression analysis was performed based on this data. Similarly a regression analysis of each well using the post-MtBE removal data was performed. The following chart illustrated the process.



This analysis was completed for each of the 25 sites and the above chart was selected based on the typical results of the analyses. It is hypothesized that the rate of decrease of MtBE has accelerated following removal of it from the gasoline supplies. It is primarily thought that this is as a result of the lack of continued releases of MtBE to the subsurface, whether from UST system failures, vehicle overfills, or vapor releases which are suspected of causing some of the MtBE spikes observed in the ground water data at many sites.

In analyzing the trends observed in the 78 pairs of data the paired t-test was used as the primary statistical tool. This test determines if the sum of the change between the before and after MtBE removal data sets is significantly different from zero. Therefore, the null hypothesis in this study is that there is no difference in the rates of degradation before and after the MtBE removal from the gasoline supply. The alternate hypothesis is that the difference will be negative indicating an increase in the rate of degradation of MtBE following its removal. Both individual populations (pre- and post- MtBE removal) are approximately normal, and as a result, the difference between the two is also approximately normal, however for this test, normality is not necessarily required.

Null Hypothesis: $H_o = X - Y = 0$

Alternate Hypothesis: $H_A = X - Y < 0$

Test Statistic: $$t_{paired} = \frac{\mu_d}{s_D/\sqrt{(n)}}$$

MONITOR WELLS

Data Set	Trend Prior to Removal of MTBE	Trend Following Removal of MTBE	Data Set	Trend Prior to Removal of MTBE	Trend Following Removal of MTBE
1	-0.2688	-1.2751	48	-0.0843	-0.035
2	0.0238	-0.4853	49	-43.65	-0.4891
3	0.1121	-0.1573	50	-0.8894	-0.0072
4	-0.5379	-0.0508	51	-0.2763	-0.2871
5	-2.0432	-4.2764	52	0.5403	-4.0424
6	-0.0055	-0.0353	53	0.308	-0.7681
7	-1.3317	-0.0756	54	0.3646	-0.3194
8	-15.899	-0.3289	55	-0.694	-0.4066
9	3.1228	-6.9612	56	-0.0158	-0.1376
10	-0.1115	-0.0202	57	3.3024	-0.1721
11	0.4887	-2.0574	58	-0.8168	-0.0496
12	-0.548	-2.2117	59	-0.1717	-0.0231
13	0.0182	-44.533	60	-0.0266	-0.0064
14	-0.8473	-70.386	61	-7.5662	2.3074
15	-2.585	-55.49	62	-0.0579	-0.3251
16	-3.5038	-6.4681	63	-0.0611	-1.6833
17	-12.534	-4.5477	64	-2.0976	-0.0542
18	-75.321	-150.99	65	0.2538	-0.4773
19	-57.968	-256.34	66	-2.0062	0.1203
20	-0.4617	-0.6795	67	-0.3966	0.0265
21	-33.108	0.1764	68	-0.183	-0.6321
22	-37.525	54.399	69	0.2831	-0.4888
23	-0.0458	-0.9854	70	0.1147	-0.1481
24	0.8823	-10.132	71	-0.1455	-0.9091
25	-0.1436	-0.4147	72	-0.7289	-1.303
26	0.0216	0.0256	73	0.1638	-3.4091
27	0.1114	-0.1488	74	-0.932	0.4545
28	1.0907	-40.703	75	-0.5971	-8.5606
29	0.0775	-0.2691	76	-0.9713	0.0032
30	-0.1533	-0.1399	77	-0.0455	-0.0306
31	-0.0894	0.0021	78	-0.0172	-0.0146
32	-0.0607	-0.0496			

Data Set	Trend Prior to Removal of MTBE	Trend Following Removal of MTBE	Data Set	Trend Prior to Removal of MTBE	Trend Following Removal of MTBE
33	0.0019	-0.0197			
34	0.0043	-0.8408			
35	2.8677	-3.3102			
36	0.892	-3.0537			
37	-12.738	-10.632			
38	0.4083	-0.0055			
39	127.46	-1.9239			
40	-11.406	-5.3883			
41	-0.0563	-0.1519			
42	-0.0472	-6.2955			
43	-2.5285	1.72			
44	-0.7447	0.1752			
45	-0.0713	0.9865			
46	3.2711	-7.3242			
47	-15.782	-25.361			

In general, the above data exhibit some interesting characteristics. Prior to the removal of MtBE from the gasoline supply, approximately 68 % of the wells had declining MtBE trends as compared to 85 % after the MtBE removal. Forty-seven wells of the 78 analyzed indicate an acceleration of the rate of decline of MtBE concentrations, while the balance remained consistent or a slightly decreased rate of decline, and even a few increases were noted.

Using the above raw data in the paired t-test yields the following results:

The mean of the differences, (μ_d), is: $\mu_d = -6.208$
The standard deviation of the differences, (s_D) is: $s_D = 32.780$
The sample size, (n), is: n = 78
The test statistic, (t_{paired}), is then calculated to be:

$$t_{paired} = (-6.208)/(32.780/(\sqrt{78})) = -1.6726$$

The rejection region for an α of 0.05 with (n – 1) degrees of freedom, (77), based on a standard t table is:

$$t_{\alpha,n-1} = t_{.05,77} \leq -1.6649$$

Therefore, we reject the null hypothesis that the difference in rates of degradation from both before and after the removal of MtBE from the gasoline supply is zero. The alternate hypothesis, that the difference is less than zero is accepted, at a 95% level of confidence.

Qualitatively, the geologic formations were compared with respect to the rates of decrease of MtBE. As expected, areas with higher transmissivities exhibited the higher rates of attenuation of MtBE prior to its removal. However, subsequent to the removal these data suggests that higher rates of attenuation were independent of the transmissivity, which is counter-intuitive and may warrant further investigation.

Future Considerations

The post-removal trends are based on two to four sampling events and when compared to the years of data available from the time prior to the MtBE removal the data sets are quite limited. As more data become available, the post removal trends will be monitored to determine if they will continue at this pace. Although MtBE is quite soluble in water, it is possible that adsorbed constituents in the vadose zone still contain MtBE which may be desorbed with time and fluctuations in the water table. This would then contribute to concentration fluctuations creating small spikes in the data that would alter the trends calculated herein. It is our opinion, that the concentrations of MtBE will remain in the groundwater of New Hampshire for several more years to come before it eventually reaches the acceptable drinking water standards in the state.

References

Ayotte, Joseph D., Denise M., and McGarry, Frederick J., USGS, 2005, *Methyl tert-Butyl Ether Occurrence and Related Factors in Public and Private Wells In Southeast New Hampshire, Environmental Science and Technology,* 39 (1), 9-16,.

Giunta Anthony P. and the New Hampshire Department of Environmental Services, December 11, 2006, *Elimination of MtBE, Other Gasoline Ethers and TBA from Gasoline Supplies, Letter.*

ITRC (Interstate Technology and Regulatory Council). 2005 *Overview of Ground water Remediation Technologies for MTBE and TBA.* MTBE-1. Washington, D.C.: Interstate Technology and Regulatory Council, MTBE and Other Fuel Oxygenates Team. Available on the Internet at http://www.itrcweb.org.

Johnson, Richard, Pankow, James, Bender, David, Price, Curtis, and Zogorski, John, May 2000, MTBE: *To What Extent Will Past Releases Contaminate Community Water Supply Wells?* Environmental Science and Technology.

McCarthy, James E. and Mary Tiemann, 2006. *MTBE in Gasoline: Clean Air and Drinking Water Issues.* CRS Reports, National Council for Science and the Environment, obtained from www.ncseonline.org.

Moran, Michael J. USGS, 2007, *Trends in the Occurrence of MtBE in Drinking Water in the Northeast United States,* National Groundwater Association, Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Assessment, and Remediation Conference, November 5-6, 2007.

Ramsden, D. 2000, *MTBE Bioremediation Studies: Are we learning anything? Soil, Sediment and Ground water Journal, MTBE Special Edition*, Pg 34-40.

Reisinger II, H.J., J.B. Reid, and P.J. Bartolomae, 2000. *MTBE and Benzene Plume Behavior: A Comparative Perspective. Soil, Sediment and Ground water Journal,* MTBE Special Edition Pg 43-46.

Shore, Joanne, 2006, *Eliminating MTBE in Gasoline in 2006*, Energy Information Administration, obtained from www.eia.doe.gov.

Sloan Richard L. Chickadee Remediation Co., Humble, Texas, and Helena, Montana 2006, WEB Page *Common Myths, Misconceptions and Assumptions About MTBE: Where Are We Now?*

Lynn Gary S., P.E New Hampshire Department of Environmental Services April 17, 2007, *Life After MtBE*, BIA/NHDES Waste Management Seminar.

New Hampshire Department of Environmental Services, April 2004, *MtBE and Other Contamination Sites in New Hampshire.*

New Hampshire Department of Environmental Services, One Stop List On-Line.

U.S. Geological Survey, 1995, *Ground-Water Resources in New Hampshire*: Stratified-Drift Aquifers Water-Resources Investigations Report 95-4100.

Weston Solutions, Inc. New Hampshire Department of Environmental Services, August 2006, *Final Phase 1 Report Statewide Methyl Tertiary Butyl Ether Risk Analysis For The State Of New Hampshire.*

Williams, P.R.D, 2001, *MTBE in California Drinking Water: an analysis of patterns and trends.* Environmental Forensics 2:75-85.

Biographical Sketches

James M. Tarr is the Regional Manager of Corporate Environmental Advisors, Inc. (CEA) office in Concord, New Hampshire. He has more than 20 years as a geologist and hydrogeologist in New England. He specializes in hydrocarbon and hazardous waste investigation and remediation in bedrock and unconsolidated aquifers. Mr. Tarr has completed investigations through out New England, Quebec, Canada, and several other states. Mr. Tarr is a Massachusetts Licensed Site Professional, a New Hampshire Professional Geologist and a Maine Certified Geologist. Mr. Tarr holds a Bachelor of Science Geology, Regents College, Albany New York.

Adam M. Galonski is a Senior Project Manager for Corporate Environmental Advisors, Inc. office in Concord, New Hampshire. He has more than 12 years as a certified geologist. In addition, he has performed hundreds of commercial and industrial environmental site assessments and underground storage tank removals. Mr. Galonski is a Massachusetts Licensed Site Professional, New Hampshire Professional Geologist and a Certified New Hampshire Hazardous Waste Coordinator. Mr. Galonski holds a Bachelor of Science in Geology from the University of New Hampshire. CEA is located at 2 Whitney Road, Concord, NH 03301.