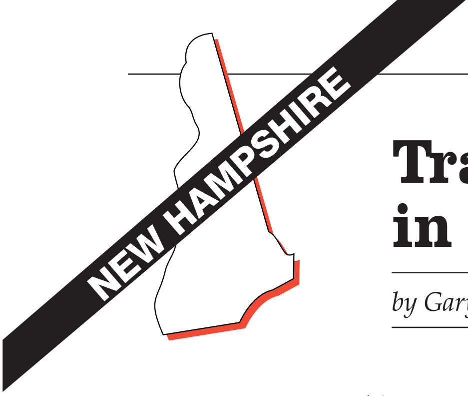

Tracking Troubling Vapor Releases in New Hampshire

by Gary Lynn

New Hampshire regulations require routine groundwater monitoring whenever groundwater quality standards are exceeded. Because of this requirement, the state has gained a considerable database of groundwater quality information at operating gas stations where releases have been identified. About four years ago, the Department of Environmental Services (DES) started to observe a trend at many operating gas station sites in which the concentration of MtBE was increasing and all other contaminants were stable or decreasing. DES concluded that an ongoing release of MtBE was occurring at these sites and impeding site remediation and closure. To help troubleshoot this problem, we began to track all of these ongoing release sites. We also began to investigate whether other states have observed and addressed this issue. (Also see LUSTLine *#46, March 2004, "Enhanced Leak Detection in California—What We've Learned," by Randy Golding.)*

Putting the Facts Together

Our review of existing studies and fieldwork turned up several very interesting investigations:

■ **Santa Clara Valley Water District** A pilot study was commissioned to determine whether there were undetected releases of MtBE present at 1998 upgrade-compliant gas stations. The Water District study (July 22, 1999) found MtBE contamination of groundwater at 13 of the 27 sites that were investigated. MtBE was the only petroleum constituent found in five of the 13 contaminated sites. The Water District attempted to statistically correlate the presence of contamination with the various types of UST system components present at each site. The analysis concluded that there was a statistically significant association between the occurrence of MtBE contamination and the presence of a vacuum-assist Stage II vapor-recovery system. DES believes this study is significant because the only plausible link between vacuum-assist Stage II equipment and MtBE groundwater contamination is the existence of vapor releases. (*http://www.scvwd.dst.ca.us/Water/Technical_Information/Technical_Reports/_Reports/USTMtBEStudyFinal.pdf.*)

■ **University of California at Davis and Tracer Research** A joint report on an UST System Field-Based Research Project was submitted on May 31, 2002, to the California State Water Resources Control Board. (*http://www.swrcb.ca.gov/cwphome/ust/leak_prevention/fbr/docs/FBR_Final_Report.pdf.*) The study evaluated the occurrence and environmental significance of very small releases from 1998 upgrade-compliant UST systems. The researchers tested 182 UST systems by inoculating the systems with tracers and then collecting subsurface vapor samples and analyzing them for the presence of the tracers.

Detectable levels of tracers were found at 61 percent of the tested systems. All but one of the tracer detections were judged to have been associated with a vapor-phase release. In addition, the study noted that none of the releases observed would likely have been detected by leak-detection systems that meet current performance standards of 0.1 gallons/hour. This study strongly indicates that vapor releases commonly occur but are infrequently detected by routine measures.

The study also draws a distinction between balance and vacuum-assist Stage II vapor recovery systems. Both types of systems are found to produce positive tank pressures during deliveries. According to the study, the assist system "is more likely to lead to pressurization of the UST ullage space for longer periods because of the tendency to return a larger volume of air to the tank than the volume of liquid product withdrawn." In fact, a number of Stage II vacuum-assist systems specify air-return to liquid-removal ratios of 1.0 to 1.2.

The study found a similar percentage of vapor-release detections for balance and assist Stage II systems, but the average detected concentration of tracer was approximately 2.6 times higher for the assist systems. The detection percentage should be approximately the same for balance and assist systems because there is little difference in the below-grade components of the two systems; however, the leak rate for the vacuum-assist system would be greater because of the greater operating pressure within the system.

■ **Vermont** Over the last two years, the Vermont UST program has been routinely assessing the presence, source, and significance of vapor releases at operating UST facilities with ongoing remedial groundwater monitoring. The methodology utilizes a hand-held, direct-read vapor measuring instrument, typically a photo-ionization detector (PID), to measure vapor concentrations in the vicinity of readily accessible tank-top fittings. Measurements are usually conducted as part of a routine UST compliance inspection.

The vapor-concentration readings can help pinpoint potential vapor-release source locations. Volatile organic compound (VOC) concentrations ranging from 2.0 to 200 parts per million (ppm) have been measured in the vicinity of tank-top features under normal operating conditions. Under pressurized (delivery event) conditions, VOC emissions concentrations show a significant increase. Based on this information, the Vermont UST program has determined that the primary vapor-release sources from operating USTs are vent lines, ancillary risers, caps, in-tank monitor wiring fittings, and Stage I vapor-recovery poppets. In general, any tank-top component that could allow the emission of

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VOCs under primary-tank pressurization is considered a potential source of hydrocarbon vapors that could contribute to groundwater contamination.

■ **New Hampshire** MtBE concentrations found in reformulated gasoline (RFG) are typically 9 to 11.5 percent in New Hampshire. The MtBE concentration in gasoline vapors is even higher because the vapor composition emanating from a mixture of chemicals like gasoline is dependent on the mole fraction of each component in the liquid phase and the pure-phase vapor pressure of each component. MtBE has a pure-phase vapor pressure that is much higher than other key constituents of concern (e.g., BTEX compounds).

The combination of high MtBE vapor pressure and high MtBE content in RFG results in a vapor-phase composition that is significantly enriched in MtBE. There is a good discussion of this phenomenon and calculation of the anticipated concentration of MtBE in an article by Blayne Hartman in *LUSTLine* #30, "The Great Escape."

DES also found a Finnish analysis that compared the composition of regular gasoline and vapors in equilibrium with the gasoline that indicated a nearly three-fold increase in the concentration of MtBE in the vapor phase compared with the liquid phase. *(http://www.uku.fi/vaitokset/2002/isbn951-802-491-X.pdf.)* The take-home message from these data is that the composition of a vapor release of MtBE-based reformulated gasoline will include a very substantial MtBE component.

Vapor Releases and Tank Pressurization

Based on the information we reviewed, we decided that vapor releases could potentially explain the data trends that were being observed at our LUST monitoring sites. We decided that further investigation was necessary to evaluate vapor releases from active USTs and set out to explore the effects of tank pressurization on vapor-phase releases.

A working hypothesis was developed postulating that a combination of the physical properties of MtBE, the operating pressures found in Stage II tank systems, and leaks in tank tops and tank-top fittings was creating the elevated MtBE levels in groundwater at our monitored LUST sites. We conducted an investigation to evaluate this hypothesis and establish the relationship between vapor releases, UST system operating pressures, and MtBE groundwater contamination.

To conduct this investigation, DES installed pressure-monitoring equipment and a data logger on five operating UST systems. The pressure was then monitored continuously and recorded in each of the UST systems for approximately one week. The UST systems monitored included a balance and four vacuum-assist Stage II installations. DES confirmed a number of the results and conclusions found in the California field-based study, including the following:

- The monitored UST systems routinely showed positive operating pressures ranging from just above atmospheric to three inches of water column (the pressure-relief setting of the tank vent).
- The vacuum-assist tank systems in two of the four systems monitored showed significantly higher pressure levels than the balance system. The other two vacuum-assist systems had relatively low operating pressures and additional follow up is required to determine whether the vacuum-assist systems were fully operational or operating at very low air-to-liquid ratios. The low level of pressure (except during deliveries) in the UST with a Stage II balance system was expected because balance systems use the slight positive pressure generated by adding fuel to a car's gas tank and a low-level vacuum in the UST system to recover vapors created during car fueling.
- The two Stage II vacuum-assist systems that showed positive pressures showed daily cycles (accumulated pressure during the day because of fueling activities and lost pressure at night, presumably because of vapor releases). Both of these systems had six-figure MtBE contamination in groundwater.
- All observed delivery events resulted in strong pressure oscillations.

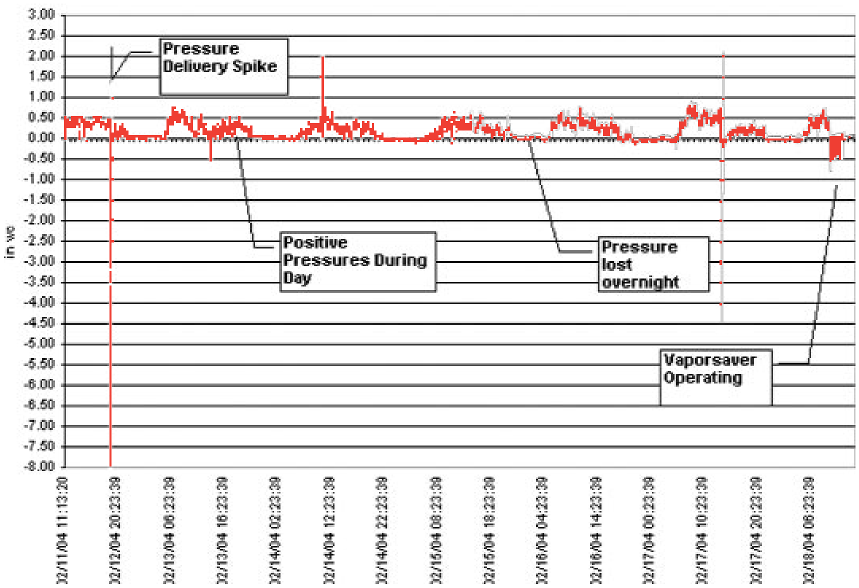
Figure 1 is an example of a vacuum-assist system pressure chart that was generated during the research. The data indicate that the pressure gradients that are integral to the operation of this Stage II vacuum-assist system, in combination with the significant vapor-phase concentration of MtBE, are a plausible explanation for the MtBE contamination observed in groundwater for this LUST site. Note: Each tank-system pressure profile is different. The other vacuum-assist system with a known MtBE release exhibited much larger daily pressure cycles (ranging from atmospheric to 3.5 inches of water column), possibly because the tank system was tighter.

The Vapor Release/ Groundwater-Contamination Connection

We decided that it was important to go beyond showing that vapor releases were a plausible explanation for what was being observed. We decided to closely study one of our ongoing release sites to see whether manipulating the pressure in the UST system would affect the MtBE concentration in the groundwater outside the UST system. We chose to investigate an existing operating gas station site with a well-established, increasing MtBE concentration trend. Pressure-monitoring information showed that the vacuum-assist system was causing positive tank pressures. Daily pressure cycles seemed to indicate that the system lost pressure overnight due to leakage. Note: A review of multiple pressure-decay tests conducted at the facility revealed that the facility lost an average of 0.4 inches of water column of pressure in just 10 minutes (each test passed, but typical tests passed by just 0.1 inches of water column).

The enhanced Tracer Tight testing method was used on the tank system to evaluate its tightness. A different tracer was added to each grade of gasoline and the release of tracer was evaluated by sampling soil

FIGURE 1. ***Vapor Release Research, New Hampshire UST pressure (in inches of water column) vs. time***



vapor adjacent to the storage system and testing it for the presence of hydrocarbons and the tracer compounds. Concentrations of tracer indicated that the super gas tank had the most significant release, and the regular tank also showed a release, although almost an order of magnitude less than the super tank. We compared the characteristics of the release with the criteria used to evaluate the vapor-versus-liquid releases in the California field-based research study. The release exhibited the characteristics of a vapor release (i.e., relatively low ratio of total volatile hydrocarbons compared to tracer).

DES next evaluated the leakage rate of the tracer after manipulating tank-system pressures. For the purpose of the research being conducted, DES elected to utilize a commercially available system designed to continuously maintain the pressure inside storage systems at or slightly below atmospheric pressure. The technology, supplied by OPW, and known as a Vaporsaver, uses membrane separation technology to concentrate and condense gasoline vapors in the storage tank, essentially filtering the gasoline out of the air in the tank. The gasoline-free air is exhausted to the atmosphere, thus controlling the tank pressure, while liquid gasoline is returned to the tank. The vapor processor is automatically controlled by a pressure sensor to create an average net negative pressure in the tank. No repairs or other changes in the UST equipment or operations were made; all of the changes observed in tracer releases from the storage system were the direct result of controlling tank-system pressures.

The tracer test was repeated with a different tracer after the Vaporsaver system was installed. There was a significant reduction in the tracer concentrations observed in soil gas in the vicinity of the tank system. The reduction in tracer levels was observed at nearly every sample point. It should be noted that the Vaporsaver minimized but did not eliminate the development of positive pressures during tank delivery (it kept up with normal operations but not the spike in pressures that occurs during a delivery) and that there were periods of system downtime caused by a combination of belt and electrical problems. As a result, DES did not observe a total elimination of the release of tracer; however, a significant reduction in tracer and total volatile hydrocarbons in the vicinity of the USTs was observed.

DES is evaluating the long-term reliability of the Vaporsaver technology. DES believes that eliminating the pressure in tank ullage spaces will eliminate the driving force for vapor releases and minimize gasoline vapor leakage rates—based on the immediate impact in soil-gas contaminant levels surrounding the tank system observed at our test site after the pressure was controlled.

Groundwater at the experiment site is being monitored to determine whether the changes in tank-system operating pressures will also reduce the high levels of MtBE groundwater contamination observed in nearby wells. As can be seen in Table 1, dramatic reductions in MtBE concentrations were observed in samples taken approximately two months after the Vaporsaver unit reduced UST system operating pressures (February 18, 2004 was the date of system start-up). All overburden wells near the USTs had significant MtBE concentration reductions; the only wells near the tank system that did not see reductions were the two deep wells that are screened in bedrock. DES believes these wells will respond more slowly than the overburden wells.

Table 1 **Groundwater trends in wells adjacent to the tank installation**

Monitoring Well Number	Concentration of MtBE in ppb (11/13/03)	Concentration of MtBE in ppb (1/27/04)	Concentration of MtBE in ppb (3/24/04)	Concentration of MtBE in ppb 2 months after start-up (4/21/04)
JB-13/MW	45,300	12,000	18,400	714 (96% reduction)
JB-14/MW	160,000	176,000	159,000	4,320 (97% reduction)
JB-16/MW	471,000	277,000	276,000	91,400 (66% reduction)

The concentrations of MtBE detected in wells JB-13/MW and JB-14/MW were the lowest detected in those wells since they were installed in 1998. It should be noted that these reductions were achieved during a time period when the Vaporsaver unit was not operating full time due to operational difficulties that have since been resolved. DES believes that the data establish an extremely strong relationship between tank-system operating pressures, vapor releases, and groundwater contamination, since MtBE groundwater

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contamination reductions occurred solely because of the reduction in tank-system pressure.

Follow-Up Analysis of Ongoing Release Sites

Upon review of the data generated by this research project, we decided that it would be valuable to review our list of ongoing release sites (based on upward trends in groundwater contamination by one or more of the contaminants) versus the type of Stage II system present at the facility. We compared the distribution of Stage II systems for all of our LUST sites at operating gas stations with the distribution of systems believed to be ongoing release sites.

requested that the consultant collect a sample of the vapors from the influent of the SVE system when the PID readings spike after a gasoline delivery. MtBE was detected at 415,000 μg/m^3 in the sample. The next highest concentration detected was nearly an order of magnitude lower (toluene at 52,700 μg/m^3).

The consultant is slated to return to the site for the next gasoline delivery to develop an accurate estimate of the mass released via the potential vapor leak during gasoline delivery. Although the fast response time seems inconsistent with a delivery-induced liquid release, DES intends to evaluate this possibility by conducting an in-depth inspection and evaluation of the tank system. We hope to identify the cause of the release and learn more about the potential for vapor releases during deliveries. Although the mass released is likely to be small, DES notes that it was sufficient to threaten nearby private drinking water wells and forced the state fund to pay for the installation of the SVE system.

Table 2 New Hampshire LUST sites vs. ongoing release sites

Stage II system	% of active LUST sites	% of ongoing release sites
Exempt	47% / 253 sites	14% / 12 sites
Balance	11% / 61 sites	9% / 8 sites
Vacuum Assist	42% / 225 sites	77% / 79 sites

As shown in Table 2, gas stations that are exempt from Stage II system requirements are significantly less likely to experience ongoing releases, and the vacuum-assist system sites are much more likely to do so. This is strong evidence that vapor releases are responsible for the increasing concentrations of MtBE observed in groundwater at ongoing release sites. DES believes that this is because vacuum-assist systems are more likely to have higher average tank-system pressures, based on our observations at two of the four systems evaluated and an understanding of vacuum-assist system operation.

Although our analysis of available data indicates that most of the exempt systems do not exhibit increasing MtBE groundwater contamination trends, DES does not believe that the Stage II-exempt systems are immune from vapor releases. We have a Stage II-exempt-tank system that is surrounded by a soil vacuum extraction (SVE) system with an extraction point located in the tank-system backfill. The consultant has observed spikes in PID readings at the SVE system immediately following gasoline deliveries. DES

These data indicate that there are at least small, episodic releases of vapors from any system that is not vapor tight, since all observed systems had tank-system pressure spikes during gasoline deliveries. It should be noted that these spikes are brief in duration (approximately 5 to 15 minutes) and thus do not constitute a release of the same volume of vapors as when a system is continuously operating under positive pressures. The much lower mass that is released results in much lower concentrations of MtBE in groundwater, making DES reviewers less likely to associate these spikes with ongoing releases.

The Pressure of It All

Based on a review of existing studies and DES data, it appears that vapor releases are common at operating gas stations. Additionally, DES data indicate that this class of release poses a groundwater contamination threat when MtBE is present in significant concentrations in the gasoline. The environmental significance of these releases depends on a number of factors, including the size of the release, gasoline composition, site-specific geology, hydrogeology (e.g., depth to groundwater, groundwater flow velocity), and the presence of sensitive receptors. New Hampshire is particularly vulnerable with its high water table, its heavy use of groundwater, and the relatively high concentration of MtBE in gasoline supplied to much of the state.

The potential for releases is dependent on tank-system installation practices and other factors; however, the vapor release rate is highly dependent on tank-system operating pressures. Vapor releases should be evaluated as a source of ongoing releases at all active gas stations with Stage II systems, especially vacuum-assist Stage II systems, and tank pressurization should be minimized to the extent practicable. Minimization of tank pressures will reduce vapor release rates.

None of the releases at ongoing release sites were detected using conventional leak-detection equipment and technology. In fact, at most of the sites where DES requested the identification and elimination of observed leaks, the source of the release was not identified using the traditional leak-detection methods, such as pressure decay and line-leak detection testing. This strongly suggests that the existing leak-detection methods do not detect vapor releases and that the allowable leak rates specified in the UST rules are larger than the releases that are typically present. The data strongly indicate that significant MtBE plumes can result from these undetected releases and that better leak-detection methods are required to prevent MtBE contamination of groundwater.

Although it appears that New Hampshire's recent legislative MtBE ban could address much of the vapor release problem, as a state, we must deal with our current situation because the ban will not take effect unless U.S. EPA approves of the state's efforts to opt out of reformulated gasoline. Additional research

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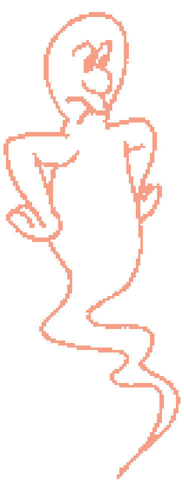
Sugar? Cream? MtBE?

It's Time to Close the Gap Between Water Supply and UST Programs

by Kara Sergeant

I don't drink coffee on a regular basis, but I do know that the last thing you want in your coffee is a splash of MtBE. Yet this is exactly what was occurring at a Dunkin' Donuts operated in conjunction with a Mobil gasoline station in Rutland, Massachusetts. The discovery of 2,200 ppb MtBE in the facility's well in February opened the eyes of environmental regulators and industry to the potential for other such cases of public drinking water contamination. Officials do not know how long the well has been contaminated.

The well was identified during a larger investigation of food service establishments located near hazardous waste facilities to make sure the establishments have the necessary permits. State officials discovered that the Dunkin' Donuts had been operating at the gas station for two years without having obtained a water supply permit from the state.



The facility is classified as a transient non-community (TNC) public water supply, because its well provides water to more than 25 people at least 60 days a year. Other examples of TNCs include restaurants, motels, and rest stops. TNCs are required to meet federal and state regulations, which in Massachusetts include enforcing a 100-foot protective radius around the well and sending monitoring reports to the state.

The 2,200 ppb MtBE level exceeds the state's guideline level of 70 ppb. The facility owner also did not maintain a protective zone around the well. The Dunkin' Donuts was immediately shut down, and local private wells were tested for contamination. One home adjacent to the station had trace amounts of MtBE.

The facility owner hired a licensed site professional to perform preliminary tests on the site, including a soil-gas survey, borings, monitoring wells, and tank-tightness tests, including spill bucket and dispensers checks. Although MtBE was detected, the source was not located. All USTs tested tight, and there was no apparent upgradient source. The state is waiting for the consultant to submit the findings of the site assessments, at which time the state will propose Immediate Response Action plans (the next step required by DEP). Dunkin' Donuts, based in Randolph, Massachusetts, has cooperated fully with the state's investigation.

It is important to realize that this is a water supply issue. In most cases a business may operate a food establishment in conjunction with a gas station even if it has onsite wells, but it must be registered with the appropriate state authorities so that public health can be adequately protected.

The good news is that some states are working to improve communication between the UST/LUST and drinking water programs. The New England Interstate Water Pollution Control Commission (NEIWPCC) held a meeting with New England and New York state and federal program staff in May to discuss ways to improve the partnerships between the programs in an effort to better protect drinking water supplies.

The Dunkin' Donuts case was one of the issues that came up at the meeting. As a result, several states are attempting to identify food establishments located in conjunction with gasoline stations. One idea states had was for UST inspectors to note on their inspection form if a food service, such as a convenience store or coffee service, is present on the site and to pass this information along to their drinking water counterparts. Inspectors could even go so far as to ask operators if they know if they're hooked up to the municipal system or whether they have an onsite well. Also, industry representatives should determine the source of drinking water at their sites and check with their state drinking water program to see what regulations apply. ■

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might lead to information on measures that can be taken—apart from national or state policy decisions on fuel content—to mitigate vapor releases. For example, research on Stage II systems should be encouraged and information made available that compares the amount of pressurization caused by the various Stage II systems. Stage II system designs should be evaluated to determine whether equipment changes can be made that would allow a reduction in air-to-liquid ratios and increase onboard refueling vapor-recovery (ORVR) compatibility with Stage II systems. Finally, new methods of vapor-release detection should be developed and implemented.■

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