L.U.S.T.LINE



A Report On Federal & State Programs To Control Leaking Underground Storage Tanks

Analytical Methods for Fuel Oxygenates

by Hal White, Barry Lesnik, and John Wilson

A Concise Background on Fuel Oxygenates

Fuel oxygenates are oxygencontaining compounds (e.g., ethers and alcohols) that are added to gasoline either to boost the octane rating, to make the fuel burn cleaner by increasing the oxygen content, or to achieve a combination of both. The most commonly used oxygenates are methyl tertiary-butyl ether (MTBE) and ethanol. Other oxy-

genates include tertiary-amyl methyl ether (TAME), ethyl tertiary-butyl ether (ETBE), diisopropyl ether (DIPE), tertiary-amyl ethyl ether (TAEE), tertiary-butyl alcohol (TBA), tertiary-amyl alcohol (TAA), and methanol. Some oxygenates have a long history of usage in gasoline. For example, ethanol has been used in automotive fuel blends since the 1930s. Ethers, and primarily MTBE, have been used increasingly since the late 1970s. Initially, MTBE was used to boost the octane rating of mid- and high-grade gasoline and was present at concentrations of about 4 to 8 percent by volume. These fuels were transported, stored, and used nationwide.

Amendments to the Clean Air Act in 1990 led to the implementation of the Oxygenated Fuel (Oxyfuel) and Reformulated Gasoline (RFG) programs in 1992 and 1995, respectively. While these programs stipulated a minimum oxygen content for gasoline sold in specific metropolitan areas to reduce air pollution, the choice of which oxygenate to use was

■ continued on page 2

Inside

- 8 Study Gives Thumbs Up on Direct-Push Technology
- 9 The Eleven Myths about MTBE
- 17() Collect Reliable Soil-Gas Data: Active Soil-Gas Method
- 23 Flexible Pipe Concerns
- 24 News from California
- 25() Pay for Performance: Does It Work? The Data
- 28 Square Operators, Round Tanks, and Regulatory Hammers
- 30 California Announces BP-Amoco Settlement
- 34 OUST Announces UST Cleanup Goals
- 35() UST Systems in China
- 36() U.S. Secures Pleas in Tanknology Case

■ Analytical Methods from page 1

left to the discretion of the petroleum refining industry. Primarily for economic and logistical reasons, the industry overwhelmingly opted for MTBE, and it is currently used in approximately 80 percent of oxygenated fuels at concentrations ranging from 11 to 15 percent by volume. Ethanol-containing fuel is used primarily in the midwestern United States and accounts for about 15 percent of the oxygenated fuel supply. The other oxygenates combined account for the remaining 5 percent.

The Down Side of Fuel Oxygenates

Releases of oxygenated fuel into the environment have occurred nation-wide from leaking storage tanks and pipelines, transportation accidents, refueling spills, unburned fuel present in the exhaust from watercraft, and/or consumer misuse. Even at very low concentrations, the presence of some of these oxygenates can



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render water unsuitable for a particular intended purpose (e.g., drinking, cooking, bathing, laundry, watering livestock) because it is either unsafe or unpalatable due to objectionable taste and/or odor.

Remediation of contaminated groundwater and treatment of contaminated drinking water is time-consuming and expensive. Detecting the presence of fuel oxygenates and delineating their extent in the environment is difficult for a variety of reasons. In fact, only a couple of states have even started to investigate the contamination of their groundwater with oxygenates other than MTBE. Thus, the extent and magnitude of oxygenate contamination in the United States is largely unknown.

Oxygenates easily dissolve into water and tend to migrate without significant retardation in flowing groundwater. MTBE plumes in particular may extend farther than is the case for the petroleum hydrocarbons benzene, toluene, ethylbenzene, and the three isomers of xylene (BTEX). Because they spread more extensively, oxygenate plumes are more difficult to detect and delineate. In LUSTLine #36 (2000), Jim Weaver and John Wilson discuss the difficulties of characterizing MTBE plumes in their article "Diving Plumes and Vertical Migration at Petroleum Hydrocarbon Release Sites."

A tremendous amount of oxygenate data from leaking UST sites have been generated over the past several years, yet there is understandable concern as to whether these data are valid. In general, these concerns are related to two issues:

- · Analytical obstacles, and
- Ether hydrolysis (particularly of MTBE to TBA).

In the following sections, we'll discuss these issues and present some new information that may help us in dealing with oxygenates in the environment.

Analytical Obstacles

One of the greatest impediments to understanding the extent of contamination caused by fuel oxygenates is the perceived lack of a single analytical method for the determination of fuel oxygenates as a group. Although the capability to conduct the analyses necessary to determine all of the fuel oxygenates at the concentrations of regulatory concern does exist in the current marketplace, the availability of this service is limited. It simply isn't standard operating procedure to calibrate for all of the oxygenates and, until now, no single method with this capability has undergone a rigorous demonstration of applicability. Conventional analytical procedures designed for petroleum hydrocarbons (i.e., BTEX) can also detect MTBE and the other ethers when properly calibrated for them, but they have very poor sensitivity for TBA and the other alcohols.

Of the several widely used determinative methods published in SW-846 (U.S. EPA, 1997), the two most appropriate for oxygenates are Method 8260 (Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry, GC/MS) and Method 8015 (Nonhalogenated Organics Using Gas Chromatography/Flame Ionization Detector, GC/FID). Other GC detectors (e.g., the electrolytic conductivity detector [ELCD] and the photoionization detector [PID]) are not designed to respond well to compounds that do not contain halogens (ELCD) or double bonds (PID). Therefore, methods using either of these detectors are not recommended for the analytical determination of oxygenates.

In particular, Method 8021 (PID detector) cannot be regarded as a consistently reliable analytical tool for the analysis of oxygenates because it is susceptible to both false positives (misidentifying the presence of an oxygenate) and false negatives (failing to identify the presence of an oxygenate). False positives often result in resources being wasted on unnecessary investigation and cleanup efforts. False negatives may result in the exposure of receptors to harmful levels of contaminants. The problems with Method 8021 are due primarily to coelution interferences and to the high ionization energies of many oxygenates.

Method 8021 uses a specialized light bulb (lamp) to ionize analytes of concern. The lamps typically used in a PID for Method 8021 operate at a maximum potential of 10 eV. The ionization potentials of ethanol and TBA are 10.2 eV and 10.25 eV, respec-

tively. As a result, ethanol and TBA are not ionized and cannot be detected by these lamps. The potential required to ionize MTBE is 10 eV, which is right at the maximum potential of these lamps. Although the PID may respond to MTBE when the lamp is new, the response becomes weaker as the lamp ages with use. If the calibration curve for Method 8021 is not current, the method can return false negatives for MTBE when MTBE is present at concentrations above regulatory action levels.

Method 8021 (PID) may also be subject to coelution interferences and generate false positive results when real-world samples contain significant concentrations of other contaminants such as petroleum hydrocarbons. Halden et al. (2001) found that when a sample contains petroleum contamination (as total petroleum hydrocarbon, TPH) of greater than about 1,000 μ g/L (1 part per million), Method 8021 is subject to false positive results for MTBE. He also found that the effect is concentration-dependent (i.e., the effect increases as the concentration of other contaminants in the sample increases). Most laboratory QA/QC procedures for MTBE are not set up to identify circumstances in which coelution and concentration effects compromise the reliability of the method. Without this information the analyst may have the mistaken impression that the analytical results are accurate, when in fact they are erroneous.

A more important concern inolves the unequivocal determination of the presence of oxygenates. Using either GC/MS (Method 8260) or GC/FID (Method 8015) with an appropriate GC column and an appropriate sample-preparation technique, it is possible to detect oxygenates at concentrations of 5 μ g/L or less. However, GC/MS provides positive confirmation of the chemical identity of the analyte that is detected, while GC/FID does not.

It is not necessary to modify existing conventional practice for chromatography to obtain data for all of the oxygenates; only the sample preparation and method calibration steps need to be modified. If calibration curves are run for all of the other ethers, then concentrations of all of these oxygenates can be determined for the same samples and in some of the same analytical runs used to determine BTEX and MTBE, provided that the concentrations of all target compounds fall within the operational calibration ranges of the detectors used.

It simply isn't standard operating procedure to calibrate for all of the oxygenates and, until now, no single method with this capability has undergone a rigorous demonstration of applicability. Conventional analytical procedures designed for petroleum hydrocarbons (i.e., BTEX) can also detect MTBE and the other ethers when properly calibrated for them, but they have very poor sensitivity for TBA and the other alcohols.

Another important concern is the method detection limit or the reporting limits of current analytical protocols for the alcohols, and TBA in particular. Analysis of the alcohol oxygenates is a more difficult challenge than analyzing for BTEX (or even MTBE). Many commercial laboratories set reporting limits for TBA that are much higher than reporting limits for BTEX and MTBE. Typical reporting limits for TBA may be as high as 100 or 1,000 μ g/L. These reporting limits are higher than the concentrations of TBA that are of regulatory interest to many states.

Overcoming Analytical Obstacles

Methods 8015 (GC/FID) and 8260 (GC/MS) are appropriate for determining the presence and concentration of fuel oxygenates and BTEX. sample-preparation Appropriate methods include Methods 5021 (static headspace), 5030 (purge-andtrap), or 5032 (vacuum distillation). TBA can also be recovered for analysis using the azeotropic distillation technique (Method 5031). If ethers are the only target analytes of interest, then using Method 5030 at ambient temperature (rather than heated) is adequate to determine concentrations of oxygenates that are greater than 5 μ g/L. However, if alcohols (or acetone) are analytes of concern, the water sample must be heated to attain adequate recovery of analytes. If the sample is not heated, the effective limit of quantitation for TBA using Method 5030 is near 100 μ g/L; when the water sample is heated to 80° C the limit of quantitation is near $10~\mu$ g/L.

In response to problems identified with current analytical practice, EPA conducted a study to determine the optimum conditions for purge-and-trap sample preparation of MTBE and the other fuel oxygenates in river water samples both with and without BTEX interferences in the form of gasoline spiked at $600~\mu g/L$. The compounds included in the study were MTBE, TBA, DIPE, ETBE, TAME, TAEE, and acetone. The target sensitivity was $5~\mu g/L$ (U.S. EPA, 2002).

The study was performed over a five-point calibration range of 2 μ g/L to 40 μ g/L for each target analyte. The analytes were purged at 80° C for seven minutes and trapped on a Supelco H trap¹, held at 35° C, dry purged, desorbed and baked for three minutes each, and analyzed on a standard VOA column and a wax column. Water samples were run both with and without BTEX present in the samples. An additional evaluation using purge-and-trap conditions at ambient temperature (20° C) and the standard VOA column was also performed.

The results of EPA's study demonstrate that the recoveries of low levels of MTBE and related oxygenates can be improved over current practice. The most consistent oxygenate recoveries were obtained using the following combination of methods: sample preparation using Method 5030 with a heated (80° C) purge-and-trap, then analysis by Method 8260 using a DB-Wax capillary column as the determinative method. Use of an RTX-Volatile capillary column with a heated purge did not significantly improve the

¹Performance with other brands of traps may vary from that of the present study. If a different trap is used, its performance must be demonstrated, not merely assumed to be comparable to the Supelco H trap. Silica gel is needed as a trapping material for the trap to perform properly.

■ Analytical Methods from page 3

overall oxygenate recovery compared to the DB-Wax capillary column. In addition, BTEX interferences did not adversely affect the chromatographic separation, quantitation, and recovery of oxygenates.

For samples with high concentrations of hydrocarbons and oxygenates, the samples will have to be diluted so that they are within the operating range of the instrument. As a general rule, analysts dilute and rerun samples when the concentration of any analyte exceeds 0.5 mg/L when using Method 8260 (MS detector) or exceeds 4 mg/L when using Method 8015 (FID). If the concentration of one of the BTEX compounds or oxygenates is much higher than the other analytes, then multiple runs will have to be made using diluted samples.

These methods must only be used by, or under the supervision of, analysts experienced in the use of gas chromatography for measurement of organic compounds at low concentrations (i.e., $\mu g/L$) and skilled in the interpretation of gas chromatograms and/or mass spectra. Each analyst must demonstrate the ability to generate acceptable results with these methods. This should be no different than current good laboratory practice.

To demonstrate that these methods work as well with real field samples as they do with laboratoryprepared samples, EPA recently participated in an interlaboratory comparison of the performance of methods for the BTEX compounds and the fuel oxygenates using static headspace as the sample preparation method. Water samples from monitoring wells in two fuel plumes on Long Island were sent to an EPA/ORD lab and two commercial labs. The agreement in the reported concentrations between the three laboratories was expressed as the percent relative standard deviation (%RSD) of the samples.

All three laboratories reported concentrations of MTBE above their detection limit in water from 23 of the 50 wells that were sampled. The %RSD for MTBE was 12.9. All three laboratories detected ETBE in water samples from six wells; the %RSD was 12.3. All three laboratories detected TAME in 12 wells; the %RSD was 5.3.

The EPA laboratory and one of

the commercial laboratories detected TBA in 10 wells; the %RSD was 21.4. The method detection limits for TBA in the EPA laboratory and the commercial laboratory were 2.4 and 5 μg/L respectively. The reported concentrations of TBA ranged from 6 to 154 μ g/L. The other commercial laboratory had a minimum reporting limit of 100 μ g/L and did not detect TBA in any of the water samples analyzed. The agreement between analyses of MTBE, TAME, ETBE, and TBA was good. The other oxygenates were not present in these plumes at concentrations that made it possible to make a comparison.

Ether Hydrolysis

Under normal environmental conditions ethers do not undergo hydrolysis at significant rates without enzyme catalysis; even in acidified (pH<2) groundwater samples, ethers are generally stable (Church et al., 1999). However, Wade (1998) reported evidence of decreasing MTBE concentrations in 91 acidified groundwater samples collected over a two-year period from a site known to have experienced a release of gasoline that contained MTBE. He postulated that acid-catalyzed hydrolysis of MTBE during sample storage could explain these observations.

Most protocols for the preservation of groundwater samples call for the addition of a sufficient volume of hydrochloric acid to adjust the pH of the sample to < 2. As a practical matter, more acid is added than is needed to preserve the samples. One standard drop of concentrated hydrochloric acid will adjust distilled water in a standard 40 mL VOA vial to pH = 1.8. Most field technicians add two or three drops of acid to each 40 mL VOA vial. Typically, it takes seven drops of acid to adjust a 40 mL VOA vial to pH=1. The majority of groundwater samples that have been preserved with acid probably have a pH of between 1 and 2.

As discussed in the preceding section, if purge-and-trap is used as the sample preparation procedure for TBA and the other alcohols, then it must be modified to increase method sensitivity, or an alternate high-temperature sample preparative procedure must be used. One straightforward approach to increase sensitivity is to heat the water sample

to 80° C during sample preparation. However, heating creates a problem with conventional practice for preserving groundwater samples.

If the sample is heated, the acid commonly added to preserve the sample can actually cause the hydrolysis of ether bonds. As a consequence, ether concentrations originally present in the sample may be underestimated, and the concentration of the hydrolysis products may be overestimated (e.g., TBA formed from the MTBE hydrolysis).

These analytical errors can cause errors in risk assessment, can lead to the implementation of a remedial technology that is not necessary, and can bias an evaluation of monitored natural attenuation (MNA). For example, the alcohol that corresponds to the ether is often the first product of biotransformation of the ether. Higher concentrations of the alcohol and lower levels of the ether may be interpreted erroneously as evidence for natural biodegradation in the plume. Consequently, the time required for MNA to achieve cleanup goals may be significantly underpre-

Recently, O'Reilly et al. (2001) published rate constants that can be used to calculate the effect of temperature on the rate of acid hydrolysis of MTBE in samples of groundwater. They measured the rate of MTBE hydrolysis at 26° and 37° C. As discussed above, a temperature of 80° C is necessary to promote efficient transfer of alcohols to the gas phase for sampling. If the rates published by O'Reilly et al. are extrapolated to 80° C, they predict that MTBE should be rapidly hydrolyzed to TBA during analysis.

EPA/ORD measured the rate of MTBE hydrolysis at 80° C at pH =1 and pH = 2; the results are presented in Table 1. The water samples in the heated headspace sampler are typically heated for 30 minutes before they are analyzed. After 30 minutes of incubation, 6 percent of the MTBE was hydrolyzed to TBA at a pH of 2, and 57 percent of MTBE was hydrolyzed at a pH of 1.

Data documenting the hydrolysis of MTBE during analysis of ground-water samples from an MTBE plume in California are presented in Table 2. The samples were preserved in the field with hydrochloric acid to pH < 2

Preserved with	Time of Incubation (minutes)	MTBE (µg/L)	TBA (μg/L)	Percent MTBI Hydrolyzed
HCL pH = 1	0	536	<3	
	30	196	255	57%
	60	88.5	343	77%
HCI pH = 2	0	495	<3	
	30	401	25.2	6.1%
	60	393	53.8	13%
1% trisodium	0	476	<3	
phosphate pH > 12	30	424	<3	<1%
	60	432	<3	<1%

Sample ID	Dilution	TBA (µg/L) corrected for dilution	MTBE (µg/L) corrected for dilution	Percent MTBE Hydrolyzed
ML-12-16	none	3,230		89%
	1:10	1,065	2,953	
ML-16-12	none	10,400		83%
	1:10	2,644		5.8%
AND STATE OF THE S	1:100	2,006	12,669	
ML-17-12	none	6,170		56%
	1:10	1,483		0.7%
	1:100	1,405	13,273	
ML-19-12	none	4,640		60%
	1:10	1,309		12%
	1:100	591	7,216	
ML-19-16	none	5,100		68%
	1:10	1,222		7.3%
	1:100	740	8,551	
ML-23-16	none	719	The second secon	22%
	1:10	260	2,550	

and shipped to EPA's R. S. Kerr Environmental Research Center for analysis using a static headspace sampler (Method 5021).

The water samples were brought to 80° C for 30 minutes prior to analysis of the headspace by GC/MS. Replicates of selected groundwater samples were diluted and then analyzed. The concentration of TBA reported for a sample was the sum of the concentration of TBA that was originally present plus the concentration of TBA produced from hydrolysis of MTBE.

For each tenfold dilution, the concentration of acid used as a

preservative was diluted tenfold, the rate of acid hydrolysis of MTBE was reduced tenfold, and the concentration of TBA produced from hydrolysis was reduced. The reported concentrations in Table 2 are corrected for dilution of the sample. The reported concentration of TBA in the undiluted samples was much higher than in the diluted samples.

The last column in Table 2 presents the fraction of MTBE that was hydrolyzed during analysis. The fraction was calculated by assuming that the reported concentration of TBA at the highest dilution was the true concentration of TBA that was originally

present in the sample and that the higher concentrations of TBA in the undiluted samples were produced by hydrolysis of MTBE.

In 15 undiluted samples, the fraction of MTBE that was hydrolyzed during analysis varied from 22 percent to 89 percent, with a median of 62 percent hydrolyzed. The hydrolysis of MTBE in the undiluted samples increased the reported concentration of TBA by a factor of four to eight. When samples that were diluted 1:10 are compared to samples that were diluted 1:100, the extent of hydrolysis in the samples that were diluted 1:10 varied from 1 percent to 18 percent with an average of about 9 percent.

These data-quality problems associated with the hydrolysis of MTBE to TBA illustrate the importance of a quality assurance/quality control program. Any significant hydrolysis of MTBE can be detected easily if matrix spike samples are included in the analyses. The accuracy of the analysis is determined by measuring the concentration of the target compound present in a sample, then adding a known concentration of the target compound to a replicate sample of the same water (a matrix spike) and again determining the concentration of the target compound. The concentration in the matrix spike sample should equal the sum of the spiked concentration and the original concentration.

Therefore, if water samples are preserved with acid, there is an understandable concern as to whether or not any of these data are valid. Unfortunately, the answer to this can only be determined by reviewing the reports of analytical results from each site of interest. The things to look for are indications of sample-preservation methods, method operating parameters, quality assurance/quality control results, and whether or not confirmatory identification of analytes is provided.

The rate constants published by O'Reilly et al. (2001) can be used to estimate the stability of MTBE in water samples. Figure 1 (page 6) presents predictions for water samples that are preserved at pH=1 and pH=2 and stored before analysis at temperatures of 4° C, 10° C, and 20° C. If the samples were refrigerated at 10° C or lower, less than 5 percent of

■ Analytical Methods from page 5

the MTBE would be hydrolyzed in the first 30 days of storage. If samples were acidified to pH=1 and stored at 20° C, as much as 20 percent of the MTBE could be hydrolyzed in 30 days. If groundwater samples are refrigerated before analysis and all the sample preparation methods are carried out at ambient temperature (as opposed to an elevated temperature of 80° C), there is minimal opportunity for hydrolysis of the ether oxygenates.

Preventing Ether Hydrolysis Through Improved Sample-Preservation Technique

There are two widely used methods of preservation: refrigeration and chemical preservation (usually acidification). Often both methods are used on the same samples. If acid causes a problem with analysis of MTBE and TBA, one might be tempted to not use acid and rely on refrigeration alone.

It is essential, however, to use both a chemical preservative and refrigeration for groundwater samples, especially if they are to be analyzed for BTEX compounds. Groundwater samples from permanent wells typically contain microorganisms that are capable of degrading BTEX relatively quickly when oxygen is available. Contaminants may persist in groundwater because the plume is devoid of dissolved oxygen, but groundwater samples from wells invariably contain dissolved oxygen, particularly if samples were collected with a bailer. In samples that have not been preserved, BTEX compounds may be completely biodegraded in less than two weeks (Wilson et al. 1994) and MTBE and TBA may be completely degraded within two weeks of storage (Kane et al. 2001).

As good practice, samples should be packed in ice for shipment and refrigerated during storage. The temperature and general condition of the samples upon receipt by the laboratory should be indicated on the chain-of-custody. Samples should be cold (preferably close to 4° C upon arrival at the lab), they should be preserved, and they should be analyzed within prescribed holding times.

If samples arrived at the lab

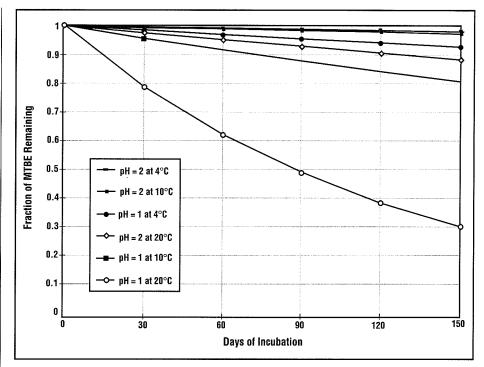


FIGURE 1. Predicted effect of pH and temperature on the stability of MTBE in samples of groundwater.

warm, if they weren't preserved, if they were analyzed past their holding time, or if acid-preserved samples were analyzed using a heated preparatory method, then there is a chance that some of the MTBE was hydrolyzed to TBA. If hydrolysis is a possibility, then examine the quality assurance/quality control data provided with the analytical report. If the recovery of MTBE (or other ether oxygenate) from spiked samples is near 100 percent, then hydrolysis of MTBE during analysis was minimal and should not be of concern.

We must reiterate that both a chemical preservative and refrigeration should be used to preserve sample integrity. Refrigeration by itself may slow the rate of biological degradation, but not to a useful extent. A conventional refrigerator is often near 10° C and refrigerated storage for samples is usually near 4° C.

The temperature of groundwater in the northern half of the United States ranges from 10° C to 15° C. As a consequence, the microorganisms collected along with a groundwater sample are already adapted to cold conditions. Storage of samples without a chemical preservative at 10° C to 4° C will only slow the rate of biological degradation of BTEX by a factor of two to four at most. Although refrigeration is only minimally effective in retarding biodegradation of

the sample, it is effective at inhibiting the chemical deterioration of the sample.

Kovacs and Kampbell (1999) developed an alternative procedure for chemically preserving groundwater samples that avoids hydrolysis of ether oxygenates. Instead of using an acid to lower the pH, samples are preserved with a base to a pH greater than 11. The elevated pH effectively prevents the biodegradation of organic compounds in the sample. The ethers are not subject to base-catalyzed hydrolysis, and a basic pH has no adverse effect on BTEX or the alcohol oxygenates (O'Reilly et al. 2001). The pH is elevated by adding a salt of a weak acid (trisodium phosphate dodecahydrate, or TSP), instead of a solution of a strong base such as potassium hydroxide. Table 1 compares MTBE hydrolysis in samples that were preserved with acid to samples preserved with TSP. There was no evidence of MTBE hydrolysis to TBA in the samples that were preserved with TSP.

The Kovacs and Kampbell (1999) procedure is safe and convenient. In the laboratory, between 0.40 and 0.44 gram of TSP is added to each 40 mL sample vial. Because it is more convenient to measure the required amount of TSP on a volume basis rather than by weight, staff of the R.S. Kerr Center use a precalibrated

spoon (Hach # 907-00 or equivalent). In the field, each vial is filled with the groundwater sample and sealed without headspace (the same as is done if the sample is preserved with acid).

The salt is added to excess. If a portion of the salt is washed out of the vial as the vial is filled with sample, enough TSP will remain to preserve the sample. As the salt dissolves, it buffers the sample to a pH greater than 11.

No special handling of the samples is required prior to analysis, although they should be stored in a refrigerator at 4° C. Water samples preserved with TSP are 1 percent salt by weight. If purge-and-trap (Method 5030) is used to prepare the water samples, it is particularly important to prevent the transfer of aerosols from the purged water to the trap and GC column. This should be no different than current good laboratory practice.

It is prudent to check the pH of the sample with indicator paper to ensure that the pH is greater than 11 prior to introducing it into the purge vessel or the headspace sampler for analysis. If it is necessary to analyze samples that have already been preserved with acid, the acid can be destroyed with TSP prior to analysis. An amount of TSP sufficient to raise the pH of the sample to greater than 11 is added to the sample vial, which is quickly resealed without headspace and shaken gently to dissolve the salt. Generally, about 0.7 gram of TSP is sufficient for a 40 mL VOA vial, but sometimes (depending upon the pH of the sample) more must be added to elevate the pH to greater than 11.

Recommended Protocol

The protocol described in this article enables us to determine the presence and concentration of all of the common oxygenates and BTEX at levels of regulatory interest. Routine use of this protocol will greatly improve the quality of the data that are reported, which in turn will enable us to make better decisions, which will ultimately result in more effective utilization of available resources.

Because MTBE (and potentially any other oxygenate) may be present at any petroleum UST site, whether the release is new or old, virtually anywhere in the United States, it is also important to respond promptly to any petroleum release. The sooner all of the contaminants in a plume are identified and their subsurface extent determined, the sooner a remedy can be selected and implemented. Because a contaminant plume is smaller and more easily managed early on, the magnitude of the impact and the overall cost of the cleanup should be less than if the plume is allowed to expand.

The protocol described in this article enables us to determine the presence and concentration of all of the common oxygenates and BTEX at levels of regulatory interest. Routine use of this protocol will greatly improve the quality of the data that are reported, which in turn will enable us to make better decisions, which will ultimately result in more effective utilization of available resources.

Consequently, it is prudent to analyze samples for the entire suite of oxygenates as identified in this protocol (i.e., MTBE, TAME, ETBE, DIPE, TAEE, TAA, and TBA). Samples should be prepared for analysis, preferably using EPA Method 5030 heated to 80° C (although either Method 5021 or Method 5032 may be used if the laboratory can demonstrate appropriate performance with these methods).

The determinative method (e.g., Method 8260, 8015, or other appropriate method) should be calibrated for the entire suite of oxygenates, and these analytes should be reported for every sample analyzed. With the understanding that ethanol and methanol are potentially present at fuel release sites, it is also advisable to have samples analyzed for these alcohol oxygenates using appropriate preparative and determinative methods.

EPA Method 8260 (or another method that provides *confirmatory identification* of all of the fuel oxygenates and can be demonstrated to meet project data quality objectives) is the preferred determinative analyt-

ical method for fuel oxygenates (and other contaminants of concern) when the analyses will be used to (1) characterize the three-dimensional extent of a contaminant plume, (2) determine whether a site requires active remediation, (3) select an active remedy, (4) design an active remedy, (5) determine whether a site has met site-specific cleanup objectives, or (6) determine if it is no longer necessary to continue monitoring a site.

After all of the oxygenates (and other contaminants of concern) present at a site have been identified and their concentration and extent determined, future analyses might then be conducted using a less expensive determinative method (e.g., 8015). Situations that might not require confirmatory analysis would include routine long-term performance monitoring as part of a MNA remedy or exposure management strategy.

To properly implement this protocol, groundwater samples should be collected from locations where oxygenates are most likely to occur, based on their chemical and physical behavior. Because oxygenates are more soluble than petroleum hydrocarbons and can be more recalcitrant, oxygenate plumes may be longer than typical BTEX plumes.

Oxygenate plumes may also "dive" beneath conventional monitoring wells and migrate undetected until a drinking water source is impacted. (See Weaver and Wilson's article in LUSTLine #36.) To ensure that such plumes aren't migrating undetected, samples should be collected from a series of discrete sampoints draw that pling groundwater only over short vertical intervals. There should be a sufficient number of sampling points to cover the entire vertical distance over which an oxygenate plume may migrate. Generally this means that additional sampling points are required at progressively greater depths below the water table as the downgradient distance from the source increases. Increasing the length of monitoring well screens is not appropriate as this will only dilute the concentration of contaminants in the sample and mask the true concentration in the plume.

To prevent constituents in the samples from being biodegraded

■ Analytical Methods from page 7

during storage and transport, samples should be preserved. To prevent chemical hydrolysis of the ether oxygenates during storage, the samples should be preserved with a base delivered as a salt (TSP), rather than as a strong acid, and also refrigerated. Preservation with TSP will also eliminate the possibility that ethers will be hydrolyzed during sample preparation. Stored samples should be refrigerated at 4° C and analyzed within the holding period. ■

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For More Information

For additional information about analytical methods, call the Methods Information Communication Exchange (MICE) hotline at 703-676-4690, or visit the MICE web site at http://www.epa.gov/SW_846/mic e.htm. For information about the Underground Storage Tank program, visit http://www.epa.gov/oust. For information about either this article or the soon-to-be-released EPA Fact Sheet, e-mail Hal White (EPA/OUST) at white.hal@epa.gov.

Disclaimer

This article was written by staff of the U.S. Environmental Protection Agency who are assigned to the Office of Underground Storage Tanks, the Office of Solid Waste, and the Office of Research and Development. It has been subjected to the Agency's peer and administrative review and has been approved for publication. The article has not been subjected to Agency policy review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products in EPA methods is for illustrative purposes only, and does not constitute an endorsement or exclusive recommendation for use by EPA. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in these methods may be employed provided that method performance appropriate for the intended application has been documented.

Monitoring-Well Comparison Study Gives Thumbs Up on Direct-Push Technology

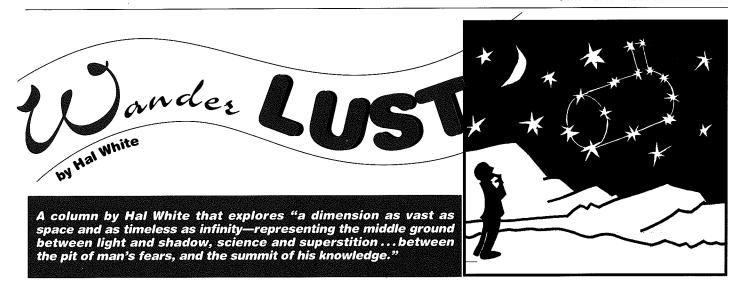
The U.S. EPA Region 5 and Region 4 UST programs, together with BP Amoco and LUST programs in Georgia and Ohio, initiated a study several years ago to evaluate the performance of direct-push monitoring wells compared to conventional monitoring wells. Many state agencies have been reluctant to accept data generated from direct-push wells because of uncertainties about their accuracy or reliability. The resulting peer-reviewed report, released in May 2002, shows that for most of the parameters included in the comparison, the direct-push wells performed just as well as conventional wells, provided the wells are properly developed.

This study, titled Monitoring Well Comparison Study: An Evaluation of Direct-Push Versus Conventional Monitoring Wells, is available at

www.epa.gov/reg5rcra/ wptdiv/tanks/. A separate but very similar study that confirms these results was recently completed by the Naval Facilities Engineering Center in California (www.clu-in.org/techdrct/ techpubs.asp).

Technical questions about the EPA/BP Amoco report can be directed to Gilberto Alvarez of U.S. EPA Region 5 at (312) 886-6143 (alvarez.gilberto@epa.gov) or David Ariail of U.S. EPA Region 4 at (404) 562-9464 (ariail.david@epa.gov).

Feedback on this report is welcome. ■



The Eleven Myths about MTBE

myth: a fiction or half-truth, esp. one that forms part of the ideology of a society. (Webster's Dictionary)

In an article in a recent issue of Contaminated Soil, Sediment, and Water (Spring, 2001—which was just released this past spring) authors Dick Woodward and Dick Sloan outline 11 so-called myths, misconceptions, and assumptions about MTBE. The article, titled "Common Myths, Misconceptions and Assumptions about MTBE: Where Are We Now?" is based on presentations from a series of seminars sponsored by Lyondell Chemicals (a major producer of MTBE) through the consulting firm of Tighe and Bond, Inc. The seminars, many of which were led by Woodward and Sloan, were presented in dozens of cities across the United States (and also around the world). These myths have also been immortalized in a giant, full-color, wall-sized poster.

But with all of the resources that have been poured into this information dissemination effort on behalf of Lyondell, can we safely assume that we've been presented with the truth, the whole truth, and nothing but the truth about MTBE? I decided to explore this question by taking a closer look at the 11 MTBE myths put forth in Woodward and Sloan's article. For consistency and ease of comparison, I present each myth in the same order and with the same title as it appears in the article. (See my references for a URL). My critiques consist of a brief summary of the major points from the article that purportedly support their classification as a myth, a comprehensive analysis of each major point, and finally a conclusion as to whether or not the alleged myth is in fact a myth. After examining each of the myths and determining its status as a myth, I tally up the results.

Note: In each "Major points" section below, I have quoted the text exactly as published in *Contaminated Soil, Sediment, and Water.* It has not been edited for grammar or clarity of content.

MYTH #1: MTBE DEGRADES STORAGE/HANDLING FACILITIES

Major points: (1) "MTBE has been an important component of unleaded gasoline and subsequently reformulated gasoline (RFG) for more than 20 years. MTBE containing formulations have been successfully shipped nationwide in a variety of truck transports, pipelines and rail transfer facilities. Historically, the materials of these gasoline-handling facilities have been compatible with MTBE and have tested tight."

(2) "Several detailed reviews over the last three years have not revealed any specific instances where MTBE in gasoline caused premature failure of systems components or resulted in material incompatibility."

Analysis: (1) At face value there's no

dispute with this point. However, despite the title of this myth, this point explicitly mentions "gasoline-handling" facilities (i.e., truck transports, pipelines, and rail transfer facilities), not "storage" facilities. The claim that any gasoline-handling facility has "tested tight" is not necessarily an indication that there hasn't been a release. UST systems are not air-tight, and vapor releases in particular are not detected by most leak-detection devices.

(2) Admittedly, definitive examples of compatibility-related UST system failures are rare. But it is due more to the fact that this type of information is difficult to ascertain and rarely collected, and not because such problems never occur. Virtually all UST-system compatibility studies to-date have been conducted in the laboratory and not in the field.

Couch and Young (1998) conducted a comprehensive evaluation of MTBE-UST compatibility issues. Although their review of available literature found no significant threat to most UST materials from fuels containing up to 20 percent MTBE, published data indicate that the service life of some elastomer products is shortened due to swelling, softening, and permeation when in contact with fuel containing 15 to 20 percent MTBE or when in contact with MTBE vapors.

Couch and Young (1998) also concluded that despite the fact that numerous compatibility studies had been conducted, none were long term, most were qualitative rather than quantitative in nature, and most of the investigators were industry purveyors or materials suppliers.

■ **Myths** from page 9

Due to this "lack of objective, independent, and quantitative research," Couch and Young (1998) suggest that further investigation is warranted, especially with regard to elastomer performance.

Davidson (1998) also reviewed the available knowledge regarding the compatibility of MTBE with UST systems in an article for LUSTLine (Bulletin #28). Although he concluded that there were no obvious compatibility problems, he also noted that available information was either limited or contradictory. He recommended that more research be conducted, especially in the areas of seal and gasket material compatibility with MTBE and the effect MTBEof enriched vapors and condensates on UST system components.

Conclusion: It's no myth—there are compatibility concerns with some UST components, at least at present. Even if all of the other UST system components are eventually shown to be compatible with gasoline that contains MTBE, some data indicate that certain elastomeric materials that are in use today are degraded to some extent when in contact with MTBE (and especially vapors) and could potentially fail sooner than anticipated. Until these materials are no longer in use in UST systems, there is still a potential for a release.

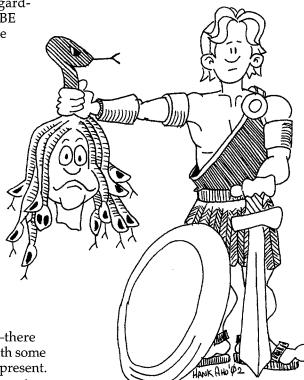
MYTH #2: MTBE ALONE LEAKS FROM GASOLINE TANKS

Major points: (1) "when an [UST] fails, all of the chemical components of the fuel are released into the subsurface soils and likely into the underlying groundwater..."

(2) "Typically, gasoline may contain 6% MTBE by volume, which means that 94% of what leaks into the soil and groundwater is other gasoline components..."

Analysis: (1) This point assumes that all releases from USTs are liquid

releases that are the result of tank failure. However, the majority of releases from UST systems are low-volume, chronic releases, not catastrophic tank failures. There is an increasing body of evidence that indicates that *vapor* releases from UST systems may be a significant source



of groundwater contamination. For fuels oxygenated with MTBE, vapor releases are composed almost entirely of MTBE, which readily diffuses in soil moisture and begins a downward migration toward groundwater. BTEX, on the other hand, tends to sorb to organic carbon in soil, therefore traveling a shorter distance, and often degrading relatively close to the source area (though there are lots of exceptions).

Even when a liquid release does occur, and components other than MTBE are released into the subsurface, MTBE will be preferentially depleted from the residual fuel source and dissolve into soil moisture and groundwater. As a result of the relatively lower solubility of BTEX, MTBE will end up in the groundwater more quickly than will BTEX.

(2) MTBE may be present in oxygenated fuels at volumes from 11 to 15 percent (much higher than the 6 percent stated in the article). While

this still means that 85 to 89 percent of the total volume of the fuel is composed of other chemical constituents, it also means that for every seven to nine gallons of oxygenated gasoline released into the environment, one gallon of MTBE is also released. If this one gallon of MTBE is evenly distrib-

uted in groundwater at a concentration of 20 ppb, a volume of more than 4 million gallons of water would be polluted.

Another point that the article doesn't make is that MTBE is increasingly found in fuels other than gasoline (e.g., diesel fuel, heating oil, and jet fuel). Since these fuels consist primarily of heavier, less-soluble constituents than gasoline and sorb to soils more readily, it is entirely possible that a plume originating from one of these releases could be composed solely of MTBE.

Conclusion: It's no myth. It is possible that MTBE may be the only fuel component released to the environment in any significant quantity, especially in the case of vapor-only releases or releases of fuels other than gasoline.

MYTH #3: MTBE TRAVELS FAR BEYOND BTEX PLUMES

Major points: (1) "Dissolved chemicals cannot travel faster than the groundwater but they may travel slower if their movement is retarded by adsorption to the soil."

(2) "The net result is that MTBE will tend to exist on the leading edge of a typical groundwater plume, however the other gasoline components, e.g. BTEX, will tend to exist immediately behind the leading edge of the plume."

(3) "Several recent studies of groundwater plumes associated with gasoline releases have confirmed that MTBE and BTEX plumes generally

coincide."

Analysis: (1) No hydrogeologist would say that dissolved chemicals travel faster than groundwater. What can be said, however, and what may be misinterpreted as meaning the same thing as the preceding statement, is that some dissolved chemicals travel faster than the *average*

linear velocity of the groundwater. As groundwater flows through the aquifer matrix, water molecules twist around individual grains and pass through interconnected pore spaces at differing velocities. Some water molecules, therefore, reach a given point faster than others.

Dissolved chemical molecules also travel at differing velocities but none faster than the fastest water molecule. At any given point in space, a breakthrough curve—a plot of concentration versus time—has the shape of an elongated "S." The inflection point of this curve represents the hypothetical arrival time of an undiluted slug of contaminant that is moving at the average linear groundwater velocity. The upper and lower tails of the "S" represent the effect of dispersion—the lower tail represents molecules that travel faster than the average linear groundwater velocity, the upper tail represents molecules that travel slower.

For a perfectly nonreactive chemical (i.e., one whose movement is not "retarded"), the breakthrough curve would be a step function; that is, the concentration would be zero until first arrival and then it would jump (step) to 100 percent concentration instantaneously. While the movement of BTEX is retarded, the movement of MTBE is relatively unimpeded such that its movement through the aquifer is generally at a velocity that is higher than that of BTEX, although no faster than groundwater.

(2) All other conditions being equal, if BTEX and MTBE are released into flowing groundwater at the same time, MTBE will almost certainly jump out ahead of BTEX in the plume that forms and be present as the leading edge. Because of its greater solubility, MTBE will be preferentially depleted from the residual source sooner than will BTEX. Once the source is exhausted, both BTEX and MTBE plumes may detach and continue to migrate downgradient as slugs of contaminants rather than as an attached plume. However, BTEX sources tend to persist for longer periods of time than do MTBE sources because the MTBE is depleted more quickly from the source, and BTEX source areas tend to be anaerobic, so biodegradation is

slower. In groundwater environments that are not conducive to biodegradation of MTBE, given enough time the MTBE slug will eventually migrate farther downgradient than will BTEX.

(3) The degree of plume separation is dependent upon many other factors in addition to time. One factor that is frequently overlooked is the adequacy of the monitoring network from which groundwater data are derived. Because MTBE behaves differently than BTEX, MTBE often will not be detected in the same wells as those with BTEX, especially with increasing downgradient distance from the source.

Perhaps the best-recognized example of MTBE moving independently of BTEX is the plume at East Patchogue, New York. The MTBE plume is about 20 feet below the water table with a leading edge ("toe") that is over 6,000 feet from the source; the trailing edge ("heel") is nearly 4,000 feet from the source. On the other hand (or perhaps a better word in this case would be "foot"), the toe of the benzene plume is over 5,000 feet from the source and still attached to the source area. LUSTLine #36 (November 2000, pp.12–15) contains an article by Jim Weaver and John Wilson (EPA/ORD) that presents this example along with a comprehensive discussion of plume diving and the inadequacy of conventional monitoring well networks for detecting MTBE plumes.

Conclusion: It's no myth. MTBE does have the potential to migrate farther (and faster) than BTEX. There are numerous examples from around the country that support this observation. For example, several MTBE plumes on Long Island are up to several thousand feet ahead of BTEX plumes. From the 2000 NEIWPCC survey, 27 states reported that MTBE plumes were often or sometimes longer than BTEX plumes, and 19 states indicated that they had MTBE plumes in excess of 1,000 feet in length. But it is also important to realize that this won't necessarily be the case at every site.

MYTH #4: MTBE PLUMES SINK (OR DIVE)

Major points: (1) "MTBE and the other components of gasoline have a

specific gravity of less than 1, consequently free phase gasoline, with MTBE or without, floats on the groundwater water table."

- (2) "If recharge occurs from the surface, older aquifer water and its dissolved constituents may be pushed downward in the formation."
- (3) "Likewise, pumping of an aquifer at depth may pull the water table and constituents dissolved in the groundwater to deeper locations in the formation."
- (4) "...it is important to conduct complete, three-dimensional characterization of plumes prior to remedial action."

Analysis: (1) No disagreement here. Free-phase LNAPLs will certainly float on the water table. But it's the dissolved phase, not the free phase, that's of concern with regard to MTBE plumes.

- (2) No disagreement here. This is one of the three mechanisms by which MTBE plumes have been observed to sink (or "dive").
- (3) No disagreement here either. This is the second of the three mechanisms by which MTBE plumes have been observed to sink (or dive). The third mechanism can be referred to as "stratigraphically" or "structurally" induced. In this situation, preferential pathways that occur in the subsurface act as conduits that allow contaminants to migrate deeper into the aquifer than they might otherwise have were the aquifer composed of media that was homogeneous and isotropic.
- (4) Absolute, 100 percent agreement with this statement, especially in the context of the article as a whole, which is that there is essentially no difference between an MTBE site and a BTEX site—both need a comprehensive, three-dimensional site characterization.

Conclusion: It's no myth. Curiously, the arguments made in the journal article fully support the observation that MTBE plumes *do* sink (or dive), thus this behavior is no myth. (Regardless of whether or not I agree with any of the other arguments presented in the journal article, I couldn't agree more with their statement: "...it is important to conduct complete, three-dimensional characterization of plumes...")

■ **Myths** *from page 11*

MYTH #5: MTBE CAUSES CANCER

Main points: (1) "Several studies have shown the formation of tumors in animals exposed to high concentrations of MTBE."

- (2) "However, there is some doubt about the relevance of these data to assessing the carcinogenicity of MTBE to humans and whether the doses are environmentally realistic."
- (3) "Furthermore, human epidemiology studies failed to support the classification of MTBE as a carcinogen."
- (4) "No national or inter-national regulatory agency has classified MTBE as a human carcinogen, and the available genotoxicity data suggest that MTBE is not mutagenic."
- (5) "The weight of evidence suggests that ingestion of water [containing MTBE] below or close to the taste threshold is unlikely to result in adverse health effects.
- (6) "...MTBE has been used to treat gall stones both in the UK and the US..."

Analysis: (1) Oddly, this first point succinctly refutes the argument that MTBE does not cause cancer—MTBE does cause cancer. Both benign and malignant (cancer) tumors have been observed in two animal species at multiple organ sites in long-term studies. Generally this is sufficient for a substance to be classified as a potential human carcinogen at the very least.

(2) The relevance of animal carcinogenicity studies to humans is always uncertain. But, in the world of toxicological testing, the use of animals under strict protocols is a necessity for a variety of reasons. First, and probably foremost, is that it's generally prohibitively expensive to use human subjects. It is also difficult to get human volunteers to be willingly exposed to substances that stand a chance of giving them cancer. Humans also live considerably longer than laboratory animals and the time required for cancer to manifest is generally a significant portion of the lifespan of an organism. To compensate, lab animals with shorter life spans are given higher doses of toxicants in the hope of inducing cancer in them before they would die

naturally. So while it's easy to belittle animal studies, there are good reasons why they are conducted the way they are. The fact remains, MTBE is an animal carcinogen.

(3) While no known studies of human MTBE epidemiology have conclusively demonstrated that MTBE is a human carcinogen, neither have they removed all doubt as to whether or not it is in fact carcinogenic in humans. EPA presented cancer slope factors associated with MTBE in the 1997 publication: "Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on MTBE." The National Science and Technology Council (NTSC) concluded that MTBE is an animal carcinogen and has carcinogenic potential for humans (National Toxicology Program 1998).

Considering the fact that the best possible (least likely to cause cancer) rating on the scale used by the International Association of Research on Cancer (IARC) is Group 4, which indicates that a substance is "probably not carcinogenic to humans," even extremely long-term studies are unlikely to completely vindicate MTBE or any other potentially hazardous chemical. Human studies take decades to complete, and the wise course of action in the interim is to assume that a chemical is dangerous rather than expose entire populations (especially our children) and wait to see what happens. Have our experiences with lead, arsenic, mercury, asbestos, cigarette smoke, coal dust, and silica dust (to name but a few) taught us nothing?

(4) The same points made in #3 apply here. But, the half of the story that is not being told is that such decisions are done by committee vote and that generally the votes are not unanimous—they're usually a narrow majority. For example, when the National Toxicology Program voted on whether or not to list MTBE as reasonably anticipated to be a human carcinogen, the final vote was six to five against listing after two subgroups split four to three in favor of listing and three to four against listing.

The fact that a committee as a whole has not supported a resolution declaring that MTBE is reasonably anticipated to be a *human carcinogen* obscures the fact that there is a great deal of disagreement about MTBE

not being classified as a potential human carcinogen. Further, these votes have been against declaring that MTBE is a human carcinogen because there is insufficient evidence that it is positively a human carcinogen, not because there is evidence that MTBE is a noncarcinogen.

This is a very important distinction, as such rulings are a far cry from concluding that MTBE is noncarcinogenic. In fact, the body of data is sufpersuasive for some regulatory bodies. For example, the California Office of Environmental Health Hazard Assessment (OEHHA) concluded in March 1999 that the data on the carcinogenicity of MTBE were sufficient to propose a Public Health Goal (PHG) of 13 ppb for MTBE, based on the carcinogenic effects observed in animals. And, as indicated in the analysis of point #3 above, the NTSC has concluded that MTBE has carcinogenic potential in humans.

(5) It is unclear which taste threshold Woodward and Sloan are talking about here. Several studies have been conducted, and there has been a wide range of results. But, let's play it safe and assume that the taste threshold we're talking about is the one that Campden Food and Drink Research Association of Chipping Campden, England, conducted in 1993 at the request of Arco Chemicals.

This study (which only grudgingly became part of the public record as a result of the lawsuit that South Lake Tahoe Public Utility District recently won against the petroleum industry) established a taste threshold of between 0.04 and 0.06 ppb!!! That's right, parts per billion! This threshold is nearly three orders of magnitude lower than EPA's current drinking water advisory (which is based on policy, not science). So, I'd tend to agree with this point at face value-if concentrations in our drinking water are lower than 0.04 ppb, then there probably wouldn't be any adverse health effects.

But, I'm only comfortable with this concession if there is absolutely nothing else in the water. There have been no studies published that present incontrovertible evidence that small (even minute) amounts of MTBE (or any other potentially toxic chemical) in drinking water are safe to consume if any other potentially toxic chemicals are also present. Study of the toxic effects of mixtures has largely been ignored, and the data do not exist (at least not in the public record.)

(6) Whether the pure phase of an environmental contaminant has been used for medical purposes isn't really germane to this debate. Doubtless, countless examples could be presented where toxic compounds have been used (not wholly without risk) to remedy an ill that may be imminently debilitating (if not fatal) if not treated immediately. Obviously in such a case the mere chance of contracting cancer (or manifesting other long-term adverse effects) is greatly outweighed by the necessity of treatment with the potentially toxic substance.

Conclusion: It's no myth. MTBE is an *animal* carcinogen, and while there is disagreement over its classification as a potential human carcinogen, the best that can be said right now is that we just don't know for sure. But, in deference to the "precautionary principle," if a substance is known to cause cancer in animals, why in the world would human beings want to be unnecessarily exposed to it?

MYTH #6: MTBE IS A THREAT TO DRINKING WATER RESOURCES

Main points: (1) "Any chemicals, metals or other toxic substances are a potential threat to drinking water supplies..."

(2) "MTBE is not toxic to human beings."

(3) "The presence of MTBE in spilled or leaked gasoline does not increase the treat [sic] that the gasoline poses to drinking water resources."

Analysis: (1) General agreement with this point; however, any substance present in water can be considered to be a "contaminant." Whether or not the substance is a "pollutant" (and therefore a "threat") depends on the concentration and the question of whether the usability of the water has been diminished. The presence of any pollutant that renders a drinking water supply undrinkable for *any* reason is most certainly a threat. And even low levels of MTBE render

water supplies undrinkable.

(2) This statement is false. MTBE exhibits quite a number of toxic effects on human beings; just check any Material Safety Data Sheet (MSDS) or EPA's Drinking Water Advisory (U.S. EPA 1997). Documented symptoms include irritation of the eyes, nose, and throat; dizziness; nausea; weakness; and potential kidney damage. The carcinogenic potential of MTBE in humans has not yet been definitively established. (See the discussion of Myth # 5.) Whether any of these effects will occur depends on the concentration, length of exposure, route of exposure, and sensitivity of the receptor. And, let's not ignore metabolites of MTBE; in particular TBA and TBF (tertiarybutyl formate). Both of these are toxic substances with known toxic effects on humans.

(3) This statement is also false. Let's look at it from two different perspectives: (a) water resources, and (b) drinking water supplies.

(a) MTBE has had an impact on water resources—both groundwater and surface water—at tens of thousands of sites nationwide. In fact, anywhere MTBE is detected in water in the environment is an impact (and not a positive one). At a significant number of sites, no gasoline constituent except MTBE has been detected. This is directly attributable to the properties of MTBE that enable it to move more rapidly through the environment than other non-ether gasoline constituents.

(b) Consider the financial impacts to drinking water supplies: conservatively hundreds of millions of dollars have been spent nationwide remediating and treating MTBE-contaminated groundwater. At all of the major, headline-grabbing MTBE cases (e.g., Santa Monica; Lake Tahoe; Long Island—too many sites to list; Pascoag, RI; and most recently Roselawn, IN) MTBE is the only significant contaminant detected in the drinking water.

The U.S. Geological Survey (U.S.G.S.) reported (2001) on the occurrence and distribution of MTBE and other volatile organic compounds in drinking water in the Northeast and Mid-Atlantic regions. From 1993 to 1998, MTBE was detected in nearly seven times as many drinking water supplies as was benzene. A recent

U.S.G.S. study of 30 public water supplies in Delaware found four wells with benzene detections and 17 with MTBE detections. Two of the MTBE detections were above regulatory levels, but none of the benzene levels were above the MCL.

Conclusion: It's no myth. Clearly, the statement that MTBE in gasoline poses no additional threat to drinking-water resources is false.

MYTH #7: MTBE CAN'T BE REMEDIATED

Main points: (1) "MTBE responds to the same types of physical, chemical and biological treatment processes effective with other hydrocarbon contamination. Gasoline plumes containing MTBE can be managed by traditional approaches of hydraulic control, impermeable barriers, reactive barriers and excavation. The same *in-situ* chemical oxidation or bioremediation processes used for other hydrocarbons can destroy MTBE."

(2) "Indeed, the physical properties and resulting behavior of MTBE expedite remediation by conventional, physical processes. Classic treatment technology like pump and treat is particularly effective at removing MTBE from the saturated zone due to the high solubility, low Henry's constant and low adsorption coefficient of MTBE in groundwater. In the unsaturated zone, the low vapor pressure of MTBE makes soil vapor extraction (SVE) a particularly effective approach to removing the components of gasoline and MTBE."

(3) "A variety of processes including, air stripping, adsorption of activated carbon or resins, biological treatment and advance [sic] oxidation have been used to remove MTBE from groundwater brought to the surface."

Analysis: (1) As MTBE is seldom the remediation driver, it is often treated along with other petroleum constituents in systems designed for treatment of the other constituents alone. Of the four "traditional" approaches listed in the article as being effective in managing MTBE plumes, only one, reactive barriers, is anything more than a containment method, and it is hardly "tradi-

■ **Myths** *from page 13*

tional." Permeable reactive barriers (PRBs) are cutting-edge science and the optimization of these systems for MTBE in all subsurface environments is a long way off.

There's no dispute that chemical oxidation and bioremediation (see also the discussion of Myth #8) may be effective in remediating MTBE contamination. The problem with bioremediating MTBE is the rate of the reaction and the question of whether it will be fast enough to achieve remediation objectives in a reasonable period of time. In many environments, even where the contaminant source has been removed, bioremediation can be expected to take years, even decades, to meet regulatory levels.

(2) These statements are deceiving, as almost all of MTBE's properties make it more difficult and expensive than BTEX to remediate, not easier and less expensive. While pump-and-treat may be very effective in pumping MTBE out of the ground (assuming that the plume is captured by the extraction wells), the process generates large volumes of groundwater that must be treated. Technologies that force MTBE out of the dissolved phase and into the vapor phase (e.g., air-stripping) generally require multiple passes through the system, plus off-gas treatment, and these expenses may significantly increase the overall cost of remediation. Let's look at how MTBE's properties would affect remediation costs in both the saturated and unsaturated zones.

In the saturated zone, the high solubility of MTBE is one of the primary reasons it creates such difficult (and expensive) groundwater remediation problems in the first place. MTBE plumes may be significantly larger than BTEX plumes, meaning a larger volume of water must be treated, and more wells will probably be required to capture the plume. MTBE's low Henry's law constant means that once dissolved in water, MTBE will tend to stay in the water air sparging and air stripping are not nearly as effective for MTBE as they are for BTEX. And its low adsorptive coefficient means that although MTBE will move virtually unretarded through the subsurface, treatment by

granular-activated carbon is much less cost-effective because MTBE exhausts carbon much more quickly than does BTEX, so the carbon must be changed more frequently.

In the unsaturated zone, the effectiveness of SVE is dependent upon properties other than just vapor pressure. If a release is acted on immediately, while it is still in the vadose zone, and if the vadose zone has relatively low soil moisture, then SVE can be very effective. But, MTBE's affinity for soil moisture and it's low Henry's law constant mean that MTBE will tend to dissolve quickly in soil moisture where it isn't as amenable to SVE. In fact, SVE performance is significantly reduced by high soil moisture.

(3) The term "removal" is misleading, as it is probably very rare indeed that contaminants are actually completely removed from groundwater as opposed to merely "reduced in concentration." For example, if a treatment system is 99 percent effective at "removing" MTBE, then to achieve a final concentration of 10 ppb, the influent water cannot have a concentration greater than 1 mg/L. As stated in #2 of this section, air stripping, adsorption, and biological treatment all have limitations. Advanced oxidation techniques may be highly effective, but some of them aren't without significant risk. For instance, use of Fenton's Reagent on gasoline releases has resulted in catastrophic explosions and loss of life. Advanced oxidation processes also generate degradation products (e.g., tertiary-butyl alcohol, tertiary-butyl formate, formaldehyde) whose toxicity is greater than that currently ascribed to MTBE.

Conclusion: It is a myth. MTBE *can* be remediated. However, the situation is not nearly as rosy as the journal article (and poster and seminars) would have one believe.

MYTH #8: MTBE DOESN'T BIODEGRADE

Main points: (1) "Increasing evidence is being found and reported on the biological natural attenuation of MTBE in gasoline contaminated aquifers."

(2) "While defined biodegradation pathways are predominantly aerobic, recent evidence indicates that some organisms indigenous to the subsurface can utilize MTBE as a carbon and energy source by reducing iron in the presence of humates or under methanogenic conditions."

Analysis: (1) No disagreement here. The body of literature supporting biodegradation of MTBE is indeed increasing in volume. This is not to say, however, that MTBE will biodegrade in every subsurface environment at a rate that is sufficient to achieve remediation objectives in a reasonable period of time. It is important to note that MTBE-degrading microorganisms are not nearly as ubiquitous as are BTEX degraders (Deeb and Kavanaugh 2002).

In some environments, MTBE biodegradation occurs very quickly, as quickly as benzene biodegradation (this is usually in situations where the groundwater is sufficiently oxygenated such that oxygen is not the limiting factor). In other environments, the rate is so slow as to be almost nonexistent. The problem is that researchers are currently unable to predict a priori for any given environment whether MTBE biodegradation will be fast or slow. Such a determination can only be made in real time (a posteriori) and with field data, not laboratory data.

(2) There is no disagreement as to whether MTBE biodegrades anaerobically. Kolhatkar et al. (2000) studied MTBE (and TBA) plumes at 74 gas stations in the U.S. They found that natural biodegradation of MTBE could be demonstrated only under conditions strongly anaerobic (methanogenic with or without sulfate) but not weakly anaerobic/ anoxic conditions (weakly methanogenic and sulfate available, or nitrate depleted and sulfate available).

This study also presents a compilation of MTBE biodegradation rates from the literature. It points out that MTBE biodegradation under ironreducing conditions in the field is very slow, and biodegradation under sulfate-reducing conditions had not yet been demonstrated.

Deeb and Kavanaugh (2002) cite four more recent studies of anaerobic biodegradation under a variety of conditions. These studies support the observation that anaerobic biodegradation of MTBE is highly site-specific and that microorganisms capable of

degrading MTBE in the absence of oxygen have not yet been cultured. Therefore, the mechanisms of anaerobic biodegradation have not yet been identified and hence can't be optimized until cultures have been isolated for study.

Conclusion: It is a myth. MTBE *is* biodegradable; however, not in all environments and not always at rates that are fast enough for remediation objectives to be met in a reasonable period of time or within a reasonable distance from the source so that receptors are protected.

MYTH #9: MTBE WON'T NATURALLY ATTENUATE

Main points: (1) "...the process of natural attenuation includes both destructive (mass reduction) and nondestructive processes. Destructive processes include biological degradation and abiotic chemical degradation. Nondestructive processes include dilution, adsorption, dispersion and volatilization."

(2) "Aerobic biodegradation of MTBE occurs when the concentration of other degradable substrates becomes limited and sufficient dissolved oxygen is present. Consequently, biologically based natural attenuation at the leading edge of the plume has been used to explain many mature, static plumes."

(3) "Recent investigations into biological degradation of MTBE under anaerobic conditions have verified biodegradation by ferric iron reduction in the laboratory and by methanogenic conditions...in the field."

Analysis: (1) For petroleum hydrocarbons, biodegradation is the most important (and preferred) attenuation mechanism because it is the only natural process that results in actual reduction in the mass of petroleum hydrocarbon contamination. Neither dispersion nor dilution are particularly effective since many documented MTBE plumes are several thousand feet in length and at concentrations that are high enough to cause adverse impacts on drinking water supplies. In the subsurface, there are no significant abiotic transformation processes for MTBE. MTBE does not sorb well to soil organic carbon nor mineral surfaces,

and once dissolved into water it doesn't tend to volatilize readily, so neither of these mechanisms are very helpful *in-situ*.

(2) Aerobic biodegradation consumes available oxygen, resulting in anaerobic conditions in the core of the plume and a zone of oxygen depletion along the outer margins. The anaerobic zone is typically more extensive than the aerobic zone due to the abundance of anaerobic electron acceptors relative to dissolved oxygen (Weidemeier et al. 1999). For this reason, anaerobic biodegradation is typically the dominant process.

For both aerobic and anaerobic processes, the rate of contaminant degradation is limited by the rate of supply of the electron acceptors, not the rate of utilization of the electron acceptors by the microorganisms. As long as there is a sufficient supply of the electron acceptors, the rate of metabolism does not make any practical difference in the length of time required to achieve remediation objectives.

(3) So as not to reiterate, see the analysis of point #2 in myth #9. It is also extremely important to realize that laboratory-derived rates of biodegradation are almost never comparable to rates observed in the field. Almost without exception, laboratory rates are much higher, and estimations (or simulations) of the time required to reach remediation objectives should never be based on laboratory-derived rates.

Conclusion: It is a myth. However, this entire point is really a continuation of the preceding myth about biodegradability of MTBE. It is not a discussion of other natural attenuation mechanisms. And, in fact, biodegradation is the only significant natural attenuation process for MTBE in most subsurface environments.

MYTH #10: MTBE REMEDIATION COSTS SIGNIFICANTLY MORE THAN BTEX REMEDIATION

Main points: (1) "It is true that some gasoline spills and leaks were ignored in the past, but today all leaks and spills must be assessed and remediated."

(2) "...gasoline does not belong in groundwater."

- (3) "Numerous case studies over the last few years have confirmed that the presence of MTBE in gasoline does not significantly impact the cost for assessment and remediation."
- (4) "The site assessment, design and remediation are generally independent of the gasoline components."

Analysis: (1) In theory anyway, this should be the case. But, the fact of the matter is that we're leaving ever larger masses of contaminants in the ground at increasing numbers of sites. And in many cases, site characterization data are too sparse, and of such poor quality, that the real magnitude of the problem at the site isn't adequately defined. Comprehensive three-dimensional site characterization hasn't been universally implemented and not all states routinely require appropriate sampling and analysis for MTBE (and even fewer for the other common oxygenates).

(2) I agree 100 percent with this point. The trouble is that UST systems do leak, and they will continue to leak. With a leak detection threshold of a mere 0.1 gallon per hour, a "tight" system could potentially leak about 900 gallons of fuel per year, which means about 50 to 135 gallons of MTBE would be released into the environment.

(3) One of the many factors affecting cleanup costs is target cleanup standards. In the survey that NEIWPCC conducted in 2000, 16 states that had (at that time) groundwater standards or cleanup and/or action levels for MTBE reported that MTBE had made a noticeable impact on the cost of remediation; seven of these states indicated that cost increases at some sites were 20 percent to more than twice as expensive. Of the 25 states that indicated that MTBE had no noticeable impact on the cost of remediation, 15 either had no cleanup standards for MTBE or didn't require analysis for MTBE. Undoubtedly the picture has changed somewhat over the past two years. More states have cleanup standards, action levels, or require analysis for MTBE (and other oxygenates).

(4) Hopefully, the days of longscreened, three- to four-well site characterizations are gone (and just as hopefully not simply replaced by

■ **Myths** *from page 15*

the drive-by site/risk assessment). The presence of MTBE in groundwater has opened up our eyes to the fact that "conventional" monitoring wells are particularly poorly suited for three-dimensional site characterization. Far more data, and data analysis, are required to adequately characterize contaminant plumes, especially those made up of MTBE, which can be deeper and longer than previously envisioned for BTEX (although the vision of relatively well-behaved BTEX plumes is in serious need of "revision"). And, none of this is cheap. So, site characterization costs more, remediation costs more, and performance monitoring is generally required for a longer period of time and, hence, costs more. The bottom line is that dealing with MTBE plumes appropriately will cost more than dealing with BTEX plumes.

Conclusion: It's no myth. The assessment and remediation of an MTBE plume has the potential to cost significantly more than a BTEX-only plume.

MYTH #11: MTBE ALWAYS DRIVES REMEDIATION DESIGN, PROGRESS, AND COST

Main points: (1) "...remediation technology selection; progress and costs are very site specific."

- (2) "Remediation progress and costs are primarily driven by the: A. Amount and duration of the release, B. Physical nature of the subsurface, C. Concentrations of the gasoline components in the soils and groundwater, D. Rates and direction of chemical migration, E. Nearest receptors and exposure pathways, F. Required cleanup objectives."
- (3) "However, benzene, due to its toxicity, has driven progress and costs at some sites."

Analysis: (1) I agree 100 percent. This point is too often glossed over. It is folly to assume that, if the same type of remediation technology were implemented at multiple sites without first conducting comprehensive, three-dimensional site characterization, each of the systems would operate optimally. Remediation *is* sitespecific.

- (2) All of the listed factors certainly affect remediation costs. A couple of critical factors that are not on this list are contaminant "treatability" and system performance. If an inappropriate treatment technology is selected for a specific site, then it will operate inefficiently, if at all. The remediation time frame will be extended, and long-term performance monitoring costs will increase. Likewise, if the system isn't designed optimally for the site, it will operate inefficiently and ineffectively, thereby increasing the cost of remedi-
- (3) According the NEIWPCC (2000) MTBE survey, 37 states indicated that BTEX and free product are the two factors that are their primary remediation drivers. However, 10 states indicated that MTBE drives remediation at greater than 20 percent of their LUST sites.

As more states establish action levels and cleanup levels or MCLs, this percentage will probably increase.

Conclusion: It is a myth, though perhaps only because of the word "always," which covers a lot of bases. It should also be noted that regulatory levels for MTBE in groundwater (and drinking water) have been decreasing, and that it is possible that MTBE *will* drive many more cleanups in the future, especially as more states adopt regulatory levels.

The Score

Now that we've analyzed each of the 11 myths, what's the score? I count 4 myths and 7 nonmyths. Thus, more than half of what Woodward & Sloan's article claims are myths, are, in fact, not myths. Or stated another way, the article presents "half-truths" and as a whole the article itself can, by definition, be considered a myth! Hmm, does that make it 12 myths? ■

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How to Collect Reliable Soil-Gas Data for Risk-Based Applications

Part 1: Active Soil-Gas Method

by Blayne Hartman

n July 2002, I attended a conference held by the Indiana L Department of Environmental Management (IDEM) in Indianapolis with special emphasis on the upward-vapor risk-assessment pathway. Issues raised repeatedly during the conference pertained to the advantages of using soil-gas data in making risk assessments and the need for having established protocols and guidance for soil-gas surveys to ensure high-enough quality data. After making a brief statement to the audience and then being swarmed by interested parties, it was clear to me that the environmental community would be well served by an article addressing this topic.

Contrary to Popular Belief...

Before diving into the meat of the topic, let me make three points to address some of the misconceptions raised at the IDEM meeting:

- Contrary to popular belief, soil-gas techniques that yield reliable data have been in existence for many years, and published regulatory protocols do exist. (I list applicable Web sites later.)
- Contrary to the prevailing opinion that soil-gas data is so variable that it can not be trusted for risk-assessment purposes, soil-gas data collected in a careful, consistent manner typically show reproducibility of +/- 25 percent. This margin of error is on the same order as indoor air measurements and is a much smaller error than that introduced by many of the assumptions in the Johnson-Ettinger (J-E) model using groundwater data.
- Contrary to popular belief, soil-gas data should be significantly less expensive (by at least a factor of two) than indoor air measurements.

Why Use Soil-Gas Data for Upward-Vapor Risk Assessment?

As was pointed out repeatedly at the Indianapolis conference, even by Dr. Paul Johnson himself, the use of actual soil-gas values, rather than values calculated from models, is preferred. The reason for this is that the measured values account for processes that are currently hard to quantify with risk models, such as volitalization from groundwater, transport across the capillary fringe, and bioattenuation. In addition, measured values will take into account the presence of vapors in the vadose zone from sources other than groundwater, such as contaminated soil or lateral vapor transport (i.e., vapor clouds).

Experience has documented that the potential error in calculated soilgas values versus measured soil-gas values can be several orders of magnitude. If calculated soil-vapor values can differ from actual values by factors of 10 to 1,000, then the calculated vapor fluxes and in turn, the calculated room concentrations using any version of the J-E model, will be off by a similar factor. In other words, the error introduced by using calculated soil-vapor data is likely to be far greater than the errors introduced by all of the other parameters used in the model (e.g., porosity, advection, multi-layers).

Some History and Current Status of Regulatory Soil-Gas Guidance

Historically, soil-gas surveys have been used primarily for site assessment purposes to identify soil and groundwater contamination. Part of the motive for employing such surveys was that the methods were inexpensive and quick. In the absence of published U.S. EPA methods, soilgas surveys were conducted using a variety of protocols, depending on

the operator. Indeed, in their simplest form, soil-gas surveys have been conducted by hammering a piece of galvanized water pipe into the ground and hooking up a hand-held meter. No wonder soil-gas methods got such a bad rap for data quality.

In the early 1990s, the Los Angeles Regional Water Quality Control Board (L.A. Water Board), under contract to U.S. EPA Region 9, began investigating the sources of chlorinated solvent contamination in groundwater in parts of the Los Angeles Basin. The board preferred to use soil-gas surveys as its initial investigatory method on the basis that the technique had a greater chance of detecting vadose-zone contamination.

Recognizing the lack of published protocols and noting a wide variability in techniques by firms offering the service, the L.A. Water Board, with input from many of the soil-gas firms, wrote a set of analytical guidelines for soil-gas surveys for the purpose of bringing some consistency to the data. The original document, written in 1992, has been revised several times by the L.A. Water Board (most recent version: February 1997), and adapted as recently as 2000 by the San Diego County Department of Environmental Health (DEH) for its site assessmanual (http://www.co. ment sandiego.ca.us/deh/lwq/sam/pdf_ files/SoilGas.PDF).

As years passed, these protocols became the "standard" for most of southern California and parts of northern California. However, they focused primarily on the analysis of soil-gas samples and gave little information on the collection of these samples. Since collection methods are also extremely varied among operators and can introduce large errors, the San Diego County DEH decided that additional guidelines were needed to bridge this gap, especially

■ Active Soil-Gas Method from page 17

in light of the increased emphasis on health risks resulting from vapor intrusion.

In 2001, the DEH commissioned a technical work group to write a set of collection guidelines for all soil-gas applications, including upward vapor risk. Those guidelines were completed in August 2002 and are now available in the San Diego County Site Assessment Manual (http://www.co.san-diego.ca.us/cnty/ cntydepts/landuse/env_health/lwq/sam/pdf_files/presentations/soilvapor_guide.pdf).

These guidelines are not step-bystep protocols, but they present general topics/issues that need to be considered and fulfilled. Currently, CA-EPA, in conjunction with the L.A. Water Board and many of the local soil-gas firms, is finalizing a set of step-by-step collection protocols. These should be available on-line before the end of this year, perhaps as early as November.

Which Soil-Vapor Method to Use?

Three methods are commonly employed to measure soil-vapor/gas contamination: active, passive, and surface-flux chambers. A full discussion of the various measurement techniques is beyond the scope of this article; however, some summary thoughts will be presented here. Helpful overviews can be found in the San Diego County Site Assessment Manual and the Standard Encyclopedia of Environmental Science, Health & Technology, Chapters 11.8 and 11.9 (ISBN# 0-07-038309-X).

Active soil vapor methods consist of the withdrawal of the soil vapor from the subsurface and subsequent analysis of the vapor. These methods give concentration data (e.g., μ g/m³), which are required for calculating the contaminant flux using Fick's first law or with various versions of the Johnson-Ettinger model. Vertical profiles of the soilvapor concentrations can be obtained to aid in determining the direction and magnitude of the flux. Active soil-vapor data can be collected and measured in real time, enabling decisions to be made in the field. The problem most often raised with active soil-vapor data is whether the concentrations measured at any given time and day are representative of normal conditions (i.e., how "stable" are active soil-vapor data?). We'll tackle this issue in the sections ahead.

Passive soil vapor methods consist of the burial of an adsorbent in the ground with subsequent retrieval and measurement of the adsorbent. These methods give a time-integrated measurement and therefore reduce the uncertainty caused by temporal variations. However, passive soil-vapor methods only yield soil-vapor data in terms of mass (e.g., micrograms $[\mu g]$ or some other form of relative units), not concentration, because the amount of vapor that comes into contact with the adsorbent is unknown. To mitigate this problem, a "conversion" of the data from mass units to concentration units is sometimes attempted, which requires knowledge of the volume of vapor that passed by the buried adsorbent during the burial time period. There is no practical way to estimate this volume; therefore passive soil-vapor data cannot be used for quantitative upward vapormigration assessment. For this reason, this method will not be discussed further in this article.

Surface-flux chambers are enclosures that are placed directly on the surface (e.g., ground, floor) for a period of time (generally a few hours to a few days), and the resulting contaminant concentration in the enclosure is measured. By dividing the measured concentration by the incubation time, a direct value for the flux is determined. This method offers advantages over the other two methods because it yields the actual flux of the contaminant out of the ground, which eliminates some of the assumptions required when calculating the flux with a model. However, this technique is not as fast or easy to implement as the other two, it is subject to near-surface effects (i.e., are the measured fluxes "stable"?), and it gives us no idea of what may be "hiding below."

Which method to use on a given site depends upon your site-specific goals and the logistical limitations. The active soil-vapor method offers less uncertainty and more versatility than the surface-flux chamber

method for most situations. For this reason, we'll start with the active soilgas method and tackle the surface-flux chamber method in the next issue of *LUSTLine*.

Collecting Active Soil-Gas Samples

Reported soil-vapor data depends greatly on the collection protocols. This section presents a brief description of the primary factors that can influence the measured results. Refer to the previously referenced documents for more details.

Volume of Sample Withdrawn In my opinion, this is perhaps the most important issue influencing the integrity and composition of soil-gas samples, so I will address it first. In a nutshell, the larger the quantity of soil vapor that is withdrawn, the greater the uncertainty about the exact location from which the soil vapor came. For example, if near the surface, large extraction volumes increase the potential that atmospheric air might be drawn down the outside of the probe body. If at depth, large extraction volumes increase the potential that samples might be from a different depth or location. In addition, large purge volumes can create vacuum conditions that cause contaminant partitioning from the soil into the soil gas. All of these issues increase the potential that the collected soil-gas sample is not representative of in-situ soil vapor at the target depth. Lastly, the larger the sample volume required, the larger and more complex the sample collection system required (e.g., vacuum pumps, larger sample containers). For all of these reasons, sampling systems with small, internal dead volumes offer advantages over systems with larger, internal dead volumes, although reliable samples can be collected with the latter.

Sample Collection Through a Driven Rod versus Burial of Tubing Two techniques are most commonly used to collect samples:

- Driving a hard rod to a given depth (e.g., using hand equipment, direct-push systems) with the subsequent removal of the rod.
- Burying a small-diameter (1/8" to 1/4" outer diameter) inert tube to a given depth with subsequent

sampling after a short "equilibration" time period (20 to 30 minutes). The tubing may be buried in holes created with hand-driven rods, direct-push systems, hand augers, or drill rigs.

Both methods have been shown to give reliable, reproducible data. If the drive-rod method is used, the sample integrity is optimized if the rod is drawn through small-diameter inert tubing that runs down the center of the drive rod, as opposed to the drive rod itself.

Purge Volume The sample-collection equipment has an internal volume that is filled with air or some other inert gas prior to insertion into the ground. This internal volume, often called the dead volume, must be completely purged and filled with soil vapor to ensure that a representative soil-vapor sample is collected. Different opinions exist on the optimum amount of vapor to be purged. Some believe that, at a minimum, enough vapor should be withdrawn prior to sample collection to purge the probe and collection system of all ambient air or purge gas (one purge volume). Others believe that a minimum of three system volumes should be purged, similar to a groundwater monitoring well. Most experienced soil-vapor personnel purge a minimum of one and a maximum of five system volumes before collecting a sample. CA-EPA requires that a site-specific purge volume test be conducted at the start of a survey. In my opinion, this test is only necessary when large volumes are being collected (>500 cc). Most important is that the purge volume is consistent for all samples collected from the same site.

Excessive Vacuums Applied During Collection Soil-vapor samples that are collected under high-vacuum conditions or under a continuous vacuum may contain contaminants that have partitioned from the sorbed and dissolved phase into soil gas created by the collection process, rather than the contaminants present in the undisturbed soil vapor. For collection systems employing vacuum pumps, the vacuum applied to the probe should be kept to the minimum necessary to collect the sample and should be measured and recorded.

Probe Seals For collection systems that have large purge volumes or that are designed to collect large sample volumes, it is often necessary to seal the probe at the surface. Seals may also be necessary for small-volume systems if the soils are extremely porous and the sampling depth is close to the surface (<3 feet). Most common sealing techniques involve packing the upper contact of the probe at the surface with grout or using an inflatable seal. Seal integrity can be tested easily by allowing a tracer gas (e.g., propane or butane) to flow around the probe at the contact with the ground surface and then analyzing the collected soil-vapor samples for the tracer gas. CA-EPA requires tracer-gas tests on at least 50 percent of the probes. In my opinion, this test is only necessary at very shallow depths (<3 feet bgs), or when larger volumes are being collected (>500 cc) at <5 feet bgs, or when it is visually apparent that the surface seal is poor.

Systems with Vacuum Pumps Soilvapor samples from collection systems that employ vacuum pumps should be collected on the intake side of the pump to prevent potential contamination from the pump. Further, because the pressure on the intake side of the pump is below atmospheric, soil-vapor samples must be collected with appropriate collection devices, such as gas-tight syringes and valves, to ensure that the samples are not diluted by outside air.

Sample Containers and Sample Storage The rule of thumb here is the shorter the time between collection and analysis, the better. While on-site analysis is advantageous to ensure sample integrity, soil-vapor samples can be collected and analyzed off-site. To minimize potential effects on the sample integrity, follow these recommended practices:

- Maximum storage time should not exceed 48 hours after collection.
- Samples should not be chilled during storage, as is common with soil and water samples.
- Gas-tight vials or canisters may be used if stored samples are to be subjected to changes in ambient pressure (e.g., shipping by air).
 Tedlar bags are not advised.

- For fuel-related compounds (e.g., TPHv, BTEX) and biogenic gases (e.g., CH₄, CO₂, and O₂), allowable containers include Tedlar bags, gas-tight vials (glass or stainless steel), and Summa canisters.
- For halogenated compounds (e.g., TCE, TCA, PCE), allowable containers should be gas tight and also dark to eliminate potential effects due to photodestruction. Tedlar bags are generally not considered to be reliable for low-contaminant levels for storage times exceeding a few hours. For higher-contaminant levels (>1 µg/L-vapor), storage in Tedlar bags for up to 24 hours may be okay.

Collection of Soil Vapor Samples with Summa Canisters Because Summa canisters are typically largevolume containers (e.g., three to six liters) under high vacuum, extra care should be exercised during sample collection to ensure that air from the surface is not being inadvertently sampled or that desorption of contaminants from the soil does not take place. The possibility of breakthrough from the surface increases the closer to the surface the samples are collected (i.e., less than five feet below grade). To minimize the potential of surface breakthrough, there should be seals around the probe rod at the surface. To minimize the potential desorption of contaminants from the soil, Summa canisters should be filled at a rate that minimizes the vacuum applied to the soil and the turbulent flow at the probe tip. CA-EPA's guidance requires this rate to be less than 200 mL/min, although the technical basis for this specific value is unclear.

Transient Effects Influencing Measured Soil-Gas Values

There are four transient effects that can influence soil-gas values: temperature, barometric pressure, precipitation, and gravitational effects. So let's look at each of these.

- Temperature This can have an effect on soil vapor concentrations, since both the vapor pressure and water solubility of compounds are temperature dependent. However, temperature variations decrease with depth in the soil column and
 - continued on page 20

■ Active Soil-Gas Method from page 19

are unlikely to have large influences on concentrations at five feet below grade or greater. In areas with large seasonal temperature variations, the most conservative values will be collected in the warmer months. Measurement of temperature at collection depth is easy and can help to quantitate any expected variation. In areas with small temperature variation, the variation at typical collection depths (>3 feet bgs) is typically less than 2° C. This level of temperature variation will not create a measurable effect.

- **Barometric Pressure** Changes in barometric pressure can lead to a pressure gradient between the soil vapor and the atmosphere, creating a flow of soil vapors out of the vadose zone during barometric lows and into the vadose zone during barometric highs. The potential effects decrease with increased sampling depth and are generally less than a factor of two at depths of five feet below grade or greater. Measurement of barometric pressure is advised for samples collected at depths shallower than five feet below grade for riskbased applications.
- **Precipitation** Infiltration from rainfall can potentially impact soil vapor concentrations by displacing the soil vapor, dissolving volatile organic compounds, and by creating a "cap" above the soil vapor. In practice, infiltration from large storms only penetrates into the soil on the order of inches. Hence soil-vapor samples collected at depths greater than three feet below grade are unlikely to be significantly affected. Soil vapor samples collected closer to the surface (<3') may be affected, and it is recommended that measurements of percent moisture of the soil be taken if shallow sampling is performed during or shortly after significant rainfall (>1").
- Gravitational Effects (Earth Tides) Earth tides (movement of soil vapor in response to variations of the earth's geometric shape due to gravitational pull) have been

promoted as a factor on soil-vapor movement. However, in reality, fluctuations in water levels during periods of maximum gravitational pull (new and full moons) are less than 0.1 foot. Hence, earth tides do not have a significant effect on soil-vapor movement and concentration.

Analysis of Active Soil-Gas Samples

As stated previously, regulatory guidance for soil-gas samples has existed since 1992. This guidance is similar to the U.S. EPA analytical methods for water and soils in SW-846 and yields equivalent-quality data. The largest modification from SW-846 methods is the limited number of target compounds (22 in total) chosen to cover the most common aromatic and solvent compounds. The San Diego County version expands and divides the target compound list into three different groups: fuels, solvents, or mixed-use (http://www.co.san-diego.ca.us/deh/ lwq/sam/pdf_files/SoilGas.PDF).

Primary analysis-related factors that can have an effect on soil-vapor data are:

- **Instrumentation** The typical instruments used for the analysis for most compounds are gas chromatographs that are equipped with a variety of detectors. VOCs are detected and quantified with photoionization detectors (PIDs), electron capture detectors (ECDs), electrolytic conductivity detectors (ElCDs), and mass selective detectors (GC/MSs). In some cases, depending on the project goals, simple flame ionization detectors (FIDs) may be suitable. The GC/MS provides more selectivity and is advantageous at sites where a variety of compounds may be present and cause interferences. At gasoline sites, the GC/MS is the preferred instrument for risk assessments due to the high potential for the alkanes to interfere with benzene and the oxygenates.
- On-Site versus Off-Site Analysis On-site analysis offers significant advantages over off-site analysis, especially for risk assessments since the real-time data enables additional locations to be

- added, either spatially or vertically. Laboratory-grade instruments, including mass spectrometers, are capable of being transported into the field, and they can fulfill the analytical protocols referenced previously.
- **Detection Limits** Most analytical instruments can readily reach detection levels of 0.1 μ g/L (100 $\mu g/m^3$) in the vapor (beware, 1 μg/L-vapor is not equivalent to 1 ppbv) using 10 cc to 40 cc of sample. Programs requiring lower detection limits (1 to 10 μ g/m³) typically require larger sample volumes (>1000 cc) and are usually performed by collecting samples in a Summa canister, with subsequent analysis off-site by an air-concentration method (e.g., TO-14 or TO-15). Because soil-gas concentrations can be 1,000 to 100,000 times higher than indoor air concentrations, the potential for carryover from "hot" samples is much greater. To avoid this, every Summa canister used for soil-gas samples should be cleaned and verified clean by analysis when used for risk assessments. An alternative approach for very low detection limits that eliminates the use of Summas is to use on-site analysis with the GC/MS in SIM mode or, depending on the VOCs of concern, by Method 8021 (PID/EICD/ECD).

Issues Specifically Related to Risk Assessments

Sample Location and Spacing Enough samples should be collected to allow a representative estimate of the average flux to the base of the existing or future structure. At a minimum, samples should be collected at the location of highest vadose-zone contamination near or under the structure and at each corner, or along each side, of the structure (inside if logistics allow, immediately outside if not). Real-time results can be extremely advantageous, because additional locations can be added around or inside the structure to better define the most reasonable value to use in the risk calculation. How the sample results are averaged (e.g., straight average, average plus two standard deviations) needs to be specified by the regulatory group

that has jurisdiction.

Sampling Depths For sites where near-surface sources are not suspected (e.g., fuel sites with USTs), I recommend that samples initially be collected at a depth of five feet below the structure/basement or ground surface. The logic here is two-fold: (a) this depth is generally deep enough to minimize any near-surface and transient effects on the soil-vapor values as discussed previously and (b) measured soil-vapor values at this depth will be more representative of values near the enclosure than deeper samples.

At sites where there is reason to suspect shallower contamination (e.g., dry cleaners, sites with solvent usage at the surface), or where conditions don't allow deeper samples (e.g., high water table or gravelly soils), or where the data from five feet fail the risk calculation, the collection of shallower samples (<5 feet) may be appropriate. If soil-vapor data from depths less than five feet below grade are collected, additional sampling events may be appropriate to ensure representative values, especially if the measured values yield risks that are near acceptable levels. In such cases, the burial of minivapor monitoring probes (implants) is an easy and inexpensive way to get repetitive data (see below).

I want to point out that the latest version of the U.S. EPA vapor-intrusion guidance implies a preference for deeper samples (i.e., 15 feet). My recommendation is not in agreement with this preference. If deeper samples are desired, all the collection methods/issues described in this article apply. In addition, it is important that you remember that the potential for vacuum stripping of contaminants out of the pore water/groundwater will increase as the percent water content goes up (i.e., in the capillary fringe and near the water table).

Sample Frequency/Reproducibil- ity of Data Typically, a single sampling event should be sufficient to assess this risk pathway, especially if collected at deeper depths (>5 feet bgs). In some situations, additional sampling events may be appropriate; for example, where the calculated risk from the first sampling event is close to acceptable levels, or for shal-

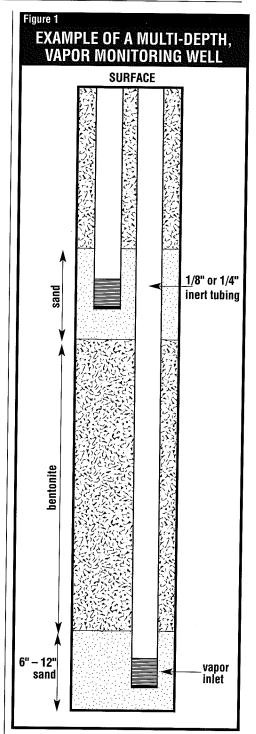
low sampling depths, or if sampling takes place during the winter in areas with large seasonal temperature variations. In such situations, the burial of mini-vapor monitoring probes (implants) is an easy and inexpensive way to get repetitive data (see below). One simple and inexpensive approach is to measure the soil-gas values in the morning and again at the end of the day. If the results match up well, then you can conclude the sampling. If not, return the next day and repeat the procedure until the variability can be assessed.

Mini-Vapor Monitoring Probes/ **Implants** Mini-vapor monitoring probes (implants) consist of small diameter (e.g., 1/8" or 1/4" outer diameter) inert tubing with a perforated tip at the bottom (refer to Figure 1). The tubing allows for a seamless installation to depths of hundreds of feet and low internal dead volumes for easy sampling. Mini-vapor probes can be emplaced using hand augers, hand soil-vapor equipment, or direct-push systems, or can be lowered down the open drill pipe of hollow-stem and percussion drilling rigs. Several choices of perforated tips are available, including stainless-steel screens, slotted PVC pipe, and aluminum or ceramic

The tube and tip are emplaced to the target depth, buried with 6 to 12 inches of sand, and then sealed to the surface with bentonite. The small tubing enables multiple tubes to be buried in the same borehole when vertical vapor gradients are desired ("nested vapor wells"). The surface end of the vapor tube is capped with a gas-tight Swagelok nut and cap or with a gas-tight valve as desired. The mini-vapor probe can be terminated at the surface with a variety of completions, such as locking well covers.

Recommended Sampling Protocol for Determining Upward Vapor Migration Risk

I recommend the following procedure for collecting near-surface soilgas data with the intent of determining the upward-vapor flux into an existing or future room/building. This protocol is based upon the approach we have been using in Southern California for some time:



1. Collect active soil-vapor data at five feet below grade at enough sampling points under or near the building to give a reasonable estimate of the subsurface soil-gas concentration under the building footprint. At a minimum, samples should be collected at the corners or sides of the existing or future building and the location of highest contaminant concentration under the building (if determined previously). If the location of the future building is unknown,

■ Active Soil-Gas Method from page 21

collect soil-vapor data at five feet below grade spatially across the site to identify the location of highest concentration. If a surface source of contaminants is suspected, collect at least one or two samples closer to the base of the building (one to two feet below) to validate that the five-foot samples are representative of the subbuilding soil-gas concentration.

- 2. Determine the health risk from the soil-vapor value using the method allowed by the local oversight agency (e.g., J-E model, default attenuation factor). If the risk calculation indicates that upward vapors pose no threat to human health, then submit a formal request for closure to the governing agency.
- **3.** If the risk calculation indicates that upward vapors may pose a threat to human health, then either add more sampling locations spatially under the building or repeat steps 1 and 2 at a shallower depth. The logic behind this recommendation is that additional spatial samples under the footprint will yield a more representative subbuilding value, and shallower samples might show lower concentrations due to bioattenuation- and trans-

- port-related factors (especially in the case of nonchlorinated compounds). Alternatively, consider an approach such as collection of indoor-air data or direct measurement of flux with surface-flux chambers.
- **4.** If soil-vapor data are to be collected at depths less than five feet below grade, or if the risk calculation from the initial set of data is borderline, repeated measurements may be appropriate to ensure that the measured soil-gas values are representative.
- **5.** Vertical profiles of the soil gas may be useful to document bioattenuation and to reduce near-surface variability. In such situations, it is recommended that data be collected at a minimum of three locations vertically from one foot to five feet to ensure that vertical variations are characterized adequately. Measurements of oxygen and carbon dioxide should be included if bioattenuation is being assessed.

For subsurface enclosures, such as basements or utility trenches, the same protocol can be used; however, soil gas samples should be collected from three to five feet below the floor (rather than bgs). Additionally, it may be necessary to also consider the potential flux through the walls in

addition to the floor. Assuming a contaminant source deeper than the enclosure, the most conservative assumption is to assume the flux through the walls is equal to the flux through the floor. In this case, the total flux into the room would be equal to the flux through the floor times the combined surface area of the floor and the walls.

For near-surface sources, this assumption is not safe as horizontal permeability is often much greater than vertical permeability. In such situations, a soil-vapor measurement should be made on each side of the wall (i.e., three to five feet away) and the flux through the wall should be computed separately. The total flux into the room would then be computed by summing the individual fluxes through the floor and walls.

Blayne Hartman, Ph.D., is a principal of HP Labs and the founder of TEG. He has lectured on soil-vapor methods and data interpretation to over 20 state agencies and to all of the U.S. EPA regions. Blayne has contributed numerous articles to LUSTLine and authored chapters in three textbooks on soil-vapor methods and analysis. For more information, either e-mail Blayne directly at

bhartman@hplabsonsite.com or check out his web page at www.hplabsonsite.com.

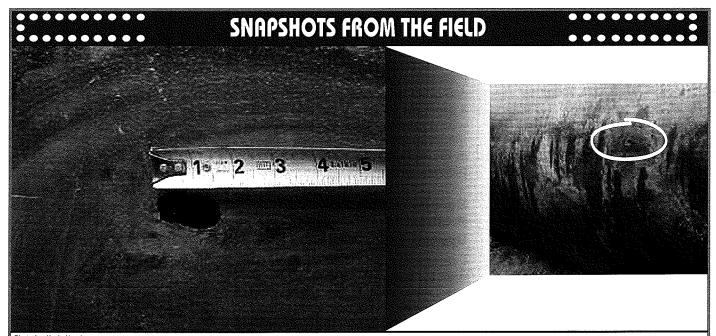


Photo by: Kevin Henderson

Uh Oh! Striker plate's out of line with the drop tube. The dip stick punched a hole in this tank.

If you have any UST/LUST-related snapshots from the field that you would like to share with our readers, please send them to Ellen Frye c/o NEIWPCC.

From the Editor

Flexible-Pipe Concerns Drive Home the Need for Tank-Owner Vigilance

It probably comes as no surprise to any of our readers that piping and associated sumps have been and continue to be the sticklers in our quest to achieve UST-system integrity nirvana. Over the past year, several states, particularly Mississippi and Florida, have reported that certain types of flexible-piping systems have been failing and with increasing frequency—and we don't hear that about tanks.

John Mason, U.S. EPA Region 4 UST Program Manager, says he has received reports from several states regarding several different generations of polyethylene flexible piping exhibiting unusual physical changes. "Some of the changes appear to be an 'elongation' of the pipe resulting in torn containment sump boots, compressed test boots, contorted flex connectors, and splitting of the pipe as it grows over metal fittings. There are other reports where the outer layer has wrinkled, softened, and split," says Mason.

"The reports described changes that occurred sometimes within weeks, or even days of installation," notes Mason. "There seem to be more and more reported incidents as inspectors and owner/operators become more familiar with what to look for in the piping and dispenser sumps. The majority of the piping incidents have been detected in time, and within secondary containment; however, there have been some catastrophic failures resulting in releases to the environment of several thousand gallons of product."

Now I know there has been some discussion about the definition of "failure." And the federal UST rule does not specifically define what constitutes a failure. So, for the purpose of this discussion, let's say that a product that fails to perform according to reasonable customer expectations is a failure. I don't think there is a regulator (or tank owner) out there who reasonably expects that as a "normal" occurrence, flex pipe will swell and tear out penetration fit-

tings, thus destroying the integrity of the secondary containment system. Fortunately, most of the flex-pipe failures that have been reported recently have not resulted in releases into the environment.

Although a thorough assessment of the facts has not yet been made, the New England Interstate Water Pollution Control Commission, the organization that produces this publication, feels it is important that we give our readers a heads-up on this issue, so that steps can be taken to avoid any potential releases to the environment and threats to human health and safety. It is likely that most systems will not have a problem, but vigilance is always well advised with any UST system.

Failure Modes

Tom Schruben, an independent risk-management consultant who has reviewed reports of close to 200 failures in double-walled flexible pipe systems in 11 states, says that there are two distinct failure modes, which sometimes operate in tandem:

- The most common failure mode is one where the outer layers of the primary pipe soften, swell, and split. The pipe often feels sticky and spongy. The swelling can cause the pipe to grow several inches in length. This growth sometimes tears the secondary containment boot at the sump wall. Swelling can also seal off the interstice of the coaxial pipe against the coupling ferrule, masking a leak in the primary pipe.
- The second mode of failure involves the end fittings of the primary pipe. The swaged fittings sometimes split or loosen, allowing the pipe to slip off of the end fitting. This can happen at either end of the pipe run.

"These failures are not limited to a particular manufacturer or even a particular generation of pipe," says John Mason. He explains that the total amount of pipe in the ground of each brand is not known, so it is impossible at this point to determine if a particular brand of pipe is failing more frequently than another. The amount of flexible piping being used in new installations has increased by 50 percent since 1995. Mason says it is not clear whether the failures are the result of installation error, shipping damage, poor quality control, design flaws, fuel incompatibility, or poor maintenance and monitoring of sumps—or a combination of these things.

Preemptive Actions

One aspect of the failures that is clear to regulators and owners alike is that the piping failures are too often compounded by leaks in sumps. Not only do sump leaks allow the petroleum to discharge to the environment, they can also defeat the release-detection system because the product does not fill the sump to the trip level of the liquid sensor.

UST owners, state regulators, and state fund administrators are approaching this problem in different ways around the country. Several states are looking into the problem to determine what actions will be appropriate. Pipe vendors are working with the states and tank owners to try to resolve these issues.

One conclusion is clear, however—both UST regulators and tank owners need to increase their vigilance for potential failures of flexible piping, and they should be ready to take swift action when failed (or failing) piping is discovered. The good news is that many of the piping abnormalities are easily visible if you know what to look for and where to look. Here are some preemptive actions that we have gleaned from discussions with regulators, consultants, and flex-pipe vendors.

- Inspect the piping sumps for any of the following signs of compromised integrity:
 - continued on page 34

NEWS FROM CALIFORNIA

New Legislation Requires New UST Systems to be Vapor Tight and Fully Contained!

On September 28, 2002, California Governor Gray Davis signed into law Assembly Bill (AB) 2481, strengthening the law related to USTs in that state. The findings of the Field-Based Research Project (see related article below), which revealed vapor releases at 80 percent of facilities tested, were a major driving force for the new construction and testing standards in the bill.

Major provisions of AB 2481:

- Allow local agencies to prohibit fuel delivery to USTs that have significant violations by affixing a red tag to the fill pipe.
- Require USTs installed after July 1, 2003, to be liquid and vapor tight.
- Require licensed tank testers to sign tank or piping integrity-test reports under penalty of perjury.
- Modify enhanced leak-detection (ELD) testing requirements to include a one-time testing requirement for double-walled UST systems within 1,000 feet of a public drinking water well. (Previous legislation required that all singlewalled facilities within 1,000 feet of a public drinking water perform ELD every three years. This is above and beyond all other required routine monitoring. The new bill expands this requirement to include a one-time ELD test for double-walled systems.)
- Create a single, consistent, administrative enforcement authority (orders and/or penalties) for Certified Unified Program Agencies' (CUPA's) use in enforcing UST requirements and other CUPA requirements.
- Permit a claimant to be eligible for reimbursement from the UST Cleanup Fund despite having acquired the site from an ineligible person, as long as the claimant is not affiliated with the ineligible person.

ELD is a method of leak detection that we have defined to be able to detect both vapor and liquid

releases and it is thirdparty certified to detect a leak rate of 0.005 gallons per hour. AB 2481 requires that all UST systems installed after July 1, 2003, be constructed in a manner that is both liquid and vapor tight. Additionally, the bill requires that a post-installation test be conducted to verify that the system meets these requirements before it is placed in service.

Currently, the only third-party approved leak-detection method currently available for this purpose is the Tracer-Tight[®] test method at a detection sensitivity of 0.005 gallons per hour. The bill allows for alternative test methods that are approved by the California State Water Resources Control Board.

The new construction standards also require that all UST components, including vapor return lines, risers, and tank-top connections, be secondarily contained. Note that according to current California law, all secondary containment components must be tested upon installation, six months after installation, and every three years thereafter.

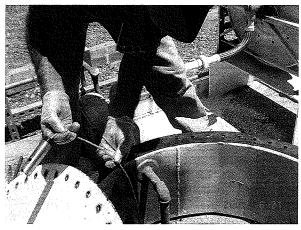
For more information about this new law, contact Shahla Farahnak at farahnas@cwp.swrcb.ca.gov.

Vapor Releases from UST Systems

California's Field-Based Research Findings Put the Blame on Vapors

A recent study completed for the California State Water Resources Control Board (SWRCB), known as the Field-Based Research (FBR) Project, indicates that liquid leaks from underground storage tank systems are rare; however, vapor leaks are abundant. Results from the FBR Project suggest that the 1998 UST upgrade requirements were effective at reducing liquid leaks from UST systems.

The research focused on UST systems at 55 randomly selected UST facilities in three areas of California—Sacramento and Yolo Counties, San Diego County, and the City of



Service technician removes a sump sensor for testing.

Temecula. The systems were tested using the Enhanced TracerTight® test, a very sensitive leak-detection method offered by Tracer Research Corporation. The method is capable of detecting both liquid and vapor leaks as small as 0.005 gallons per hour. Results of the 182 UST systems evaluated indicated more than 60 percent of the systems had vapor releases, while approximately 1 percent of the systems indicated a liquid release.

The majority of vapor releases identified were associated with tanktop fittings and connections. In contrast to the liquid releases of the past, which were typically associated with product piping, the vapor releases were identified near the tanks. The two liquid releases found as part of the FBR Project were associated with single-walled piping.

To obtain a copy of the FBR Project report, please visit the SWRCB Web site at http://www.swrcb.ca.gov/cwphome/ust/docs/fbr/index.html. For more information about the project, contact Erin Ragazzi at ragazzie@cwp.swrcb.ca.gov.

California's Field Evaluation of Leak-Detection Sensors

The California State Water Resources Control Board's (SWRCB) UST program staff have conducted a comprehensive evaluation of the effectiveness of leak-detection sensors, which are the primary form of leak detection in double-walled UST systems. Leak-detection sensors are typically located in tank interstitial spaces, piping sumps, under-dispenser containment, and monitoring wells within excavation liners. They

may also be located in groundwater monitoring wells or soil-vapor monitoring wells surrounding the tank system, although no such facilities were included in this field evaluation. California regulations require that all leak-detection equipment be functionally tested and certified by an authorized service technician on an annual basis. The field evaluation was based on data collected from 789 sensors at 124 UST facilities during routine annual testing and certification.

The data collected in this field evaluation demonstrate that sensors can be a reliable form of leak detection only when properly installed, programmed, maintained, and operated. Most problems observed in this field evaluation were due to improper installation and programming of sensors, poor or infrequent maintenance at UST facilities, ignoring alarms, and tampering with monitoring equipment. Poor design, construction, and maintenance of secondary containment systems were also common.

Approximately 12 percent of the sensors had one or more problems at the time of testing. The most common problems observed were sensors raised from the low point of the secondary containment, sensors failing to alarm when tested, and sensors failing to shut down the turbine pump in the event of an alarm (when programmed to do so). Secondary containment must be kept clean and dry in order for sensors to perform properly; however, water was found in over 10 percent of the secondarycontainment systems. Liquid product was present in an additional 3.5 percent of the systems. Overall, 31 percent of the facilities visited in this field evaluation had water or product in one or more areas of the secondary-containment system. One can only assume that the problems identified in this field evaluation would be significantly more common if there were no requirement for annual certification of monitoring equipment.

Based on the findings of this evaluation, SWRCB UST program staff have concluded that the effectiveness of sensors as a leak detection method can be improved with periodic visual and functional inspection of sensors and secondary contain-

■ continued on page 27

Pay for Performance: Does It Work? The Data

by Robert S. Cohen

Pay for Performance¹ (PFP) has produced remarkable results in many states with faster and less expensive cleanups. Yet, there has been a lack of comparative data to "prove" the case. I have experienced this frustration many times in the course of moderating over a dozen PFP workshops and two dozen training sessions. At each event the same questions were raised: Does it really work? Where's the data? The questions come from regulators and consultants, both of whom are reasonably skeptical of change.

At the Florida Department of Environmental Protection's (FDEP's) 16th Annual Storage Tanks/Preapproval Program Meeting (August 2002, St. Petersburg), two papers were presented with unequivocal results comparing PFP

with Time and Materials (T&M):

- A Comparative Study of the Relative Success of Site Cleanups Under Preapproval and Pay for Performance Contracting. Draft. August 2002 by Brian Dougherty and Ferda Yilmaz of the Florida DEP, and
- Comparison of Price and Time in Pay for Performance and Time and Materials Cleanup Contracting. (South Carolina and Florida) Draft. April 2002. By Dana Hayworth of U.S. EPA Region 4, with major contributions by William Foskett of the U.S. EPA Office of Underground Storage Tanks.

What follows is a discussion of the results of these papers along with my own private-sector observations. In discussing the Florida program, I use the terms T&M and preapproval interchangeably. The Florida petroleum cleanup program currently operates under a variant of T&M in which costs are preapproved for a specific scope of work. The preapproved costs are paid in a lump sum, and the basis of the costs is traditional time and materials build-ups. In contrast, PFP is a market-based lifecycle cost to completion, which may be determined by bidding or negotiating. A key element to PFP is the fixed price—no change orders are allowed. After presenting the data, I'll briefly discuss why PFP provides such dramatic results. A future article will explore the reasons for success in more detail.

The Data

As the data in Table 1 and Figures 1a and 1b demonstrate, PFP cleanups are considerably less expensive (28, or 64%) and remarkably faster (39, or 67%). That is, the environmental results are achieved faster, with a greater leveraging of the financial resources. These studies are significant in that they cover a large number of sites with a variety of geological settings. The factors that could affect the results were considered and normalized.

Discussion of Data

The Florida DEP study compared 57 preapproval sites with 57 PFP sites. The EPA study (Florida and South Carolina) compared 28 PFP sites with

35 T&M sites. Some of the differences in results between the studies may reflect the smaller sampling of the EPA study. In Florida, both preapproval and PFP are active programs. In South Carolina, PFP has fully replaced T&M, and therefore the South Carolina comparison includes two generations of data. The PFP data represents the more recent cleanup efforts.

The EPA study shows more dramatic differences between PFP and T&M than the DEP study; however, the Florida study, being of contemporaneous sites, may be a more accurate statement. Nevertheless both studies show the same trends at the same order of magnitude.

¹ Pay for Performance is a contractual mechanism by which the cleanup consultant is paid upon achieving agreed-upon environmental milestones. The cleanups are typically faster and cheaper than the ordinary time and materials approach. PFP has been described in previous LUSTLine articles and more information is available at the EPA Web site: http://www.epa.gov/swerust1/pfp/index.htm

■ PFP from page 25

Data I collected on a recent Florida PFP bidding project (see *LUSTLine* #39) produced savings of a similar degree on 70 sites. Using PFP bidding techniques, an owner/operator was able to save at least \$3 million over the anticipated preapproval cleanup costs.

Florida has one of the nation's largest cleanup programs and has for many years studied the most effective measures for cleanup, based on cost and environmental results. The Florida study concluded that PFP cleanups consistently produce better results than those performed under preapproval when those results are measured by the amount of contamination removed, time for that removal, and cost.

The EPA study looked at similar T&M and PFP sites in Florida and South Carolina. The study concluded that PFP cleanups are significantly faster and less costly than the customary T&M cleanups in the study's sample of ordinary UST cleanups. By reviewing sites in both Florida and South Carolina, the EPA study covered a range of lithologies (e.g., coastal plain to bedrock), depths to water, and standards. The study concluded that the most significant factor for determining the speed and cost of cleanup is the contractual mechanism (i.e., PFP vs. T&M).

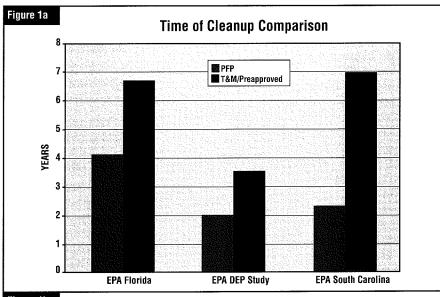
Factors Considered

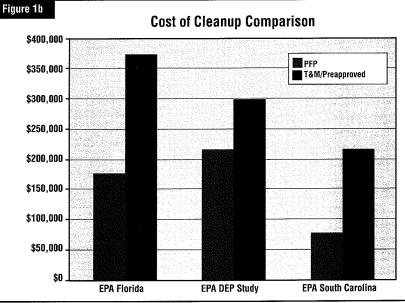
The EPA study posed two key questions: Could other factors account for speed and low prices of PFP cleanups? Could the superiority of PFP over T&M in the cleanups studied be due to something other than PFP (e.g., lower baseline concentration levels, smaller plumes, less stringent goals, less difficult hydrogeological conditions)?

The study determined that none of these factors seems likely to account for the differences in PFP and T&M cleanup prices and time frames. PFP site baseline-concentration levels averaged 16 percent higher than those at the T&M sites to which they were compared. South Carolina PFP sites dealt with the same size plumes on average as did the T&M sites.

Within each state, goals for PFP and T&M cleanups were set follow-

Table 1	COMPAR	ISON OF COS	T AND TIN	ME OF PFP V	S.T&M	
	EPA South Carolina		EPA Florida		Florida DEP Study	
	Average Cost	Average Time (Yrs.)	Average Cost	Average Time (Yrs.)	Average Cost	Average Time (Yrs.)
PFP	\$78,351	2.3	\$176,021	4.1	\$215,427	2
T&M/ Preapproval	\$215,110	7	\$376,308	6.7	\$300,255	3.5
Difference Between T&M and PFP	64%	67%	53%	39%	28%	43%





ing similar procedures, essentially requiring that all key wells at PFP sites reach the goals set for the site. Within each state, the hydrogeological differences between individual sites varied somewhat, but overall, T&M and PFP sites in each state were hydrogeologically similar to each other and relatively ordinary.

Both studies analyzed the following factors:

- plume size
- hydrogeological conditions/soil type
- treatment technology
- cleanup standards

- plume concentration (BTEX)
- depth to groundwater
- · size of consulting firm
- operating vs. nonoperating facility
- cleanup progress (most of the sites are work in progress)

Each of these items was examined and compared to assure that the distribution of PFP versus T&M sites were comparable in difficulty. The comparisons were demonstrated to be unbiased in any significant manner. The Florida study included extensive statistical analysis of the risk factors for time and cost, which is too voluminous to include herein.

Why Does PFP Work So Well?

The data in the Florida study clearly show that sites do get cleaned up under both PFP and preapproval. Therefore the knowledge and ability to do so is obviously present in the industry. The key difference between the two types of cleanup is incentive. Under a preapproval cleanup there is no incentive to succeed and no penalty for failure. A contractor is paid regardless of progress made toward meeting the cleanup goal. Under PFP, only success toward the cleanup goal meeting rewarded, and therefore an incentive is provided to ensure the greatest possible success in the least amount of time. This study demonstrates that if the right incentive is provided, then the sites will be cleaned up faster and for a lower cost.

The Florida study also looked at a common question regarding PFP: Are some companies too small to take the risk associated with PFP? The study data suggests that a PFP cleanup is not as risky a venture as it is sometimes portrayed to be. The majority of the PFP sites (39, or 68%) in this study achieved the 90 percent contamination reduction milestone in a year or less, compared with only 10 sites (18%) under preapproval. This milestone corresponds to a 75 percent payment of the total cleanup price. Not all PFP cleanups proceed this well, and there are some PFP cleanups in this data set that are not going well, but overall it is possible to succeed under a PFP cleanup and to do so on a regular basis regardless of company size.

The studies both concluded that PFP motivates consultants to achieve results while simultaneously providing the latitude to do so. Successful PFP consultants understand the nature of risk and spread that risk over groups of sites. They also take advantage of the "volume discount" of LUST sites and reuse equipment, coordinate field events, template reports, and incorporate various other cost-saving devices that are not encouraged in the T&M approach.

Thumbs Up!

PFP cleanups are superior to those performed under T&M (or the preapproval variety of T&M). This was demonstrated by all reasonable criteria of concern—the time and the costs to achieve targets. Could other factors account for these phenomena? Based on the 175-plus sites reviewed in these studies, the results of PFP are genuine and are not due to sampling prejudice.

Robert S. Cohen, BS, MS, is a professional geologist specializing in LUST cost-containment issues. He is a consultant to both the public and private sectors. He has conducted over 30 PFP workshops and studies on behalf of the EPA and various states. For more information, contact Bob at bobcohen@ivs.edu

A PFP Toolbox Update

EPA's Office of Underground Storage Tanks (OUST) has developed an online resource for people interested in performance-based contracting for LUST cleanups. OUST's Pay for Performance (PFP) Toolbox contains valuable information provided by states and others using performance-based contracting. The PFP Toolbox is designed to assist state regulators in developing and maintaining a PFP program in their state. After six months online, OUST is now revising and editing some portions of the toolbox. In the coming weeks, OUST will be interviewing states currently using PFP to include their experiences in a "Making Your Opportunity" section of the toolbox. In addition, an online user questionnaire has been posted so that OUST can receive feedback on the usefulness of this tool. The PFP Toolbox can be seen at www.epa.gov/oust/pfp/toolbox.htm.

From Our Readers

"We've Shown 'Em Our Backs Long Enough!"

I found the excellent article by G. Scott Deshefy, "We've Shown 'Em Our Backs Long Enough!" in the June 2002 *LUSTLine* extremely well written, and coming from someone who's been around this program long enough to appreciate the history and evolution of the UST effort. I think Scott is absolutely correct in many of his observations. I imagine the concerns Scott expressed resonated with many veteran UST regulators.

As Scott points out, greater involvement of UST operators will prove particularly challenging for us, S.1850 notwithstanding. S.1850 mandates that implementing agencies address the operator training issue, albeit four years after S.1850 finally becomes law. That time frame seems extremely long to me. S.1850 doesn't help define the "operator" for whom implementing agencies are to provide a strategy for training.

Perhaps, as Scott suggests in his article, agencies should focus on who should be accountable for an UST operation. In some cases it might be the owner, in other cases the operator, while still in others an owner/operator, and for some locations, a trained UST professional might be the "accountable party." The journey should prove interesting.

Lamar Bradley Assistant Director Tennessee Division of UST

■ CA News from page 25

ment. Many of the problems observed in the study can be addressed with more thorough training of personnel who install, service, and operate UST leak detection equipment. Manufacturers should also continue to improve sensor design and field-testing procedures.

A complete report of the sensor field evaluation, including detailed findings and recommendations, can be found on the SRWCB Web site at http://www.swrcb.ca.gov/cwphome/ust. For more information about this study, contact Scott Bacon at bacons@cwp.swrcb.ca.gov.

Square Operators, Round Tanks, and Regulatory Hammers: A Petroleum Marketer's Perspective

by Ron Marr

USTLine Bulletins 40 and 41 are interesting reading to anyone involved with underground storage tanks. Marcel Moreau's article, "Of Square Pegs and Round Tanks," dealing with the lack of involvement by UST owners in operating their tanks, and G. Scott Deshefy's article, "We've Shown 'Em Our Backs Long Enough," expressing frustration with getting USTs into compliance, pretty much detail both ends of today's UST environment. But interestingly, neither writer is addressing the compliance issue from the underground tank owner's perspective.

As the state executive of the Petroleum Marketers and Convenience Stores of Iowa, I have been involved in the UST regulatory and lawmaking process since its inception in the early 1980s, both as a marketer and as a representative of Iowa's regulated tank owners. In Iowa, as in most other states, tank owners have witnessed extremes in the enforcement of the regulations that govern their underground storage systems.

Over the past 20 years, I have learned that it takes an awful lot of heavy regulatory hammer blows to force many of our "square" operators to operate their "round" tank systems properly. But I have also come to realize that there is a "lubricant" out there that really eases the regulator's hammer blows and helps get the square operators into operating their round tanks properly. Surprisingly to many regulators, that lubricant is called enforcement of the financial responsibility (FR) requirements in the UST regulations, or, as it's more commonly referred to in our industry, underground storage tank insur-

As nearly any reader of LUST-Line will concede, business owners are motivated by economic incentive. Show a business owner a way to increase sales, decrease costs, or increase profits, and he or she'll bite—you've got a player. Frankly, just trying to be environmentally friendly doesn't cut the mustard. The only thing that most tank operators saw when faced with the federal UST regulations was increased operating costs.

The shiny new, environmentally friendly USTs weren't going sell more product, and they weren't going to increase sales and profits. But, and this is the big but, if the tank owner could find a way to reduce the costs associated with the tank system and comply with the regulations at the same time, he or she would be much more likely to get on board. That's a way to increase profits.

The FR Hitch

Most states provide some form of the needed financial responsibility to their UST owners through a state fund program. At first blush, this seems to be a logical approach because it ensures that sites will be cleaned up sooner than later. In reality, however, I believe that providing tank owners with a financial responsibility option that leaves them pretty much off the hook with regard to cost and responsibility is the Achilles' heel in terms of getting them to operate their UST systems properly.

Think about it for a minute. If you are getting FR coverage at little or no cost for simply being in "substantial compliance" or in some cases for doing nothing, what is your incentive to do more? If you have a leak, who cares? The state fund will clean it up. And how's the program financed? Typically through some sort of per gallon or per barrel fee that is passed on to the gasoline consumer.

Now keep in mind that I represent private Iowa UST owners. And I've been through the legislative dogfights and the stress (applied by our petroleum marketers) of dealing with cleaning up leaking underground storage tanks and upgrading existing USTs and finding government funding solutions for both. And I've found two things to be true: "You can

lead a horse to water, but you can't make it drink" and you need both a carrot and a stick to get the horse to drink, or in this case, to get the tank owner to comply with the regulations. And, as I'll explain, here in Iowa we've found that insurance is the carrot and the threat of losing that insurance or having higher premiums is the stick.

Covering the Future

In 20-20 hindsight, Iowa's initial decision to split out the leaking underground storage system scenario into two distinct pieces—one to clean up past leaks and the other to provide the required financial responsibility for future leaks—has been a blessing not only for the environment but also for the regulated tank community.

In 1989 the Iowa legislature and the governor created Iowa's LUST cleanup fund. They called for two funding programs-a distinct cleanup assistance program (past leaks), funded through a one cent per gallon environmental fee placed on product deposited into regulated USTs and paid for by the consumer, and a financial responsibility program (future leaks), funded by tank owner fees and "insurance" premiums. The initial few years of premiums were at rates prescribed by the state.

Iowa's law also required that the premiums to be actuarially sound and reflect the exposure of the UST system to the environment. By October 1990, all owners and operators of regulated USTs had to conduct soil and groundwater tests at their facilities to discover any contamination in order to access state cleanup assistance. If a contaminated site was not reported to the Iowa Department of Natural Resources (IDNR) by this date, that UST site was ineligible for cleanup assistance from the state. Furthermore, the insurance program would not provide coverage for future releases if the site had not been tested for contamination. This testing deadline for determining eligibility

for the Iowa cleanup program became the single critical keystone of Iowa's UST program.

By creating this deadline, a demarcation point of prior existing contamination and future contamination caused by a new release was created. This allowed Iowa's cleanup program to begin to get its arms around the potential cost of remediating existing contamination. The creation of the demarcation point also helped draw a line in the sand between past and future for future financial responsibility program liability. Releases discovered prior to the October 1990 were the responsibility of the state cleanup program; releases after that deadline were the responsibility of the insurance program. The owners wrote checks for the insurance. Suddenly owners were more concerned about stopping future leaks and became more effective at doing so than the regulators were.

Foiling the Raiders

During the late 1990s the Iowa legislature, like many other state legislatures, began scooping cleanup monies from existing fund balances in order to meet budget demands. Tired of the seemingly endless struggle to prevent the Iowa legislature from raiding money from the insurance fund—a fund that the UST owners were financing—the Petroleum Marketers and Convenience Stores of Iowa, along with other interested parties, began the process of privatizing the state-run UST insurance fund.

In 1995 legislation had been passed that allowed the insurance portion of Iowa's program to privatize itself if and when the state-sponsored insurance program could meet the requirements of a fully state-admitted nonprofit mutual insurance company. A new nonprofit, marketer-owned mutual insurance company was proposed.

Boiler Insurance

As part of the proposed business plan, the proposed insurance company adopted a loss-control philosophy usually associated with boiler insurance. Part of the philosophy of boiler insurance is that frequent equipment inspections are required to make sure that the insured equipment (originally boilers) is maintained and operating properly. If the insured equipment is operated and maintained correctly, the chance of loss is greatly reduced, and insurance premiums reflect this decreased loss.

This new UST insurance company is called the Petroleum Marketers Mutual Insurance Company (PMMIC), and policy owners are the owners of the company. The owners have dictated through their representatives on the Board of Directors of PMMIC that compliance with technical regulations is to be the foundation of the PMMIC's loss-control inspection program.

Iowa tank owners are now experiencing frequent loss-control inspections of their UST equipment by the UST insurance company that they own. IDNR's UST equipment and operating regulations provide the baseline for these inspections. But what is different about these inspections is the climate in which they are conducted.

In fact, the legislature took
\$30 million from the insurance
fund in 2002, and the governor
has proposed taking \$99 million
from the revenue source, which
would put the fund at zero balance.

The Inspection Climate

PMMIC inspections are conducted with the owner or operator of the tank as an educational and informational experience for the owners and are as detailed as a regulatory inspection. Instead of issuing a notice of violation (NOV), as a regulator would if the system were out of compliance, PMMIC allows the owner up to 60 days to correct any deficiency identified. If the deficiency is not addressed, insurance can be cancelled or premiums increased. If the insurance is cancelled, then the regulatory agency can shut down the operator for not maintaining FR coverage.

Compliance is a business issue. PMMIC members meet the standards because they have to and because it is their money that is spent on cleanup if any of the tanks leak. By taking tax

dollars and politicians out of the picture, PMMIC is able to obtain compliance at every site it insures and its rates are less than \$1,000 per site. PMMIC is protecting its members' money and focusing its efforts on leak prevention. The system works.

The Owners Reap the Benefits

PMMIC is currently evaluating a rating program that will eventually offer UST operation credits to insured's premiums for the best systems and the best operators if the operator demonstrates that state-of-the-art, environmentally safe equipment or enhanced daily operation of the system is in place.

The real beauty of the system today is that owners know they have coverage for a new release while their policy is in effect. They don't find out after the fact that they were not in compliance and therefore the cleanup won't be covered. The inspections document compliance with the terms of the policy.

Theoretically, Iowa tank owners insured by PMMIC may reap another benefit. If their UST equipment fails, PMMIC has the ability to address UST equipment manufactures through legal avenues in order to recoup cleanup costs expended by the insurance company.

Finally, if PMMIC encounters a tank owner who fails to meet IDNR's baseline standards for equipment and operations, PMMIC will cancel his or her UST insurance policy. In Iowa, it's the law that an owner must have viable FR to operate an underground tank system.

If Regulators Could Choose?

When the only avenue a regulator has to enforce UST regulations is to catch a noncompliant operator, a huge game of cat and mouse begins. In states that provide "free" FR for owners in "substantial compliance," the tank owner doesn't have an economic risk position in operating the UST improperly. They might think: "If I'm not caught, or even if I have a release, it is someone else's problem. My tank premium won't be going up. There is no economic hardship. What's my incentive to properly operate my UST?"

■ Square Operators from page 29

I'm sure that that many regulators welcome the idea of a force of private UST inspectors who have hard money on the line in doing their job. If you wonder how accurate or effective these private inspections are, remember that the inspector's primary mission is to ensure that they prevent losses from occurring—losses that eat up hard-earned premiums whenever a cleanup takes place.

Looking over the shoulder of PMMIC is the Iowa Insurance Commissioner, who is responsible for making sure that proper capital reserve levels are kept in place, underwriting standards adhered to, and so on. That level of supervision and the assurance to the public that the insurance company is indeed solvent is surely better than dealing with most state legislatures that are simply looking at budget expense numbers.

Getting Installers on Board

One more tidbit we've picked up in our journey: Obtaining a petroleum equipment installer's technical insight is crucial when assisting owners to become better tank managers. Again, financial incentives are the key. In Iowa, every installer is required to have a license and to demonstrate pollution liability coverage.

If the installer installs a system improperly, or if a component of an existing system leaks due to improper installation, PMMIC represents the owner in subrogation claims against the installer. Since they are truly responsible for their work product, Iowa's installers have established a high standard of care, which is evident in the reduced frequency of leaks found in the insured population.

If Ya Can't Take the Heat...

The Petroleum Marketers and Convenience Stores of Iowa, as an organization, has realized that any owner who cannot afford to upgrade his or her UST system or to operate it in compliance with all technical operating standards should not stay in business. Members demand a level playing field when dealing with regulators and the cost of complying

with those regulations. Society cannot afford to pay the costs associated with environmental damage caused by those who cannot meet, or refuse to meet, minimum technical standards.

Requiring owners and operators to obtain and maintain FR coverage is the most cost-effective method to obtain compliance throughout the industry. The provider of FR has a significant incentive to reduce leaks or to shut down those sites that are too risky. As soon as states stop providing free FR coverage that absolves tank owners and operators of responsibility, the owners and operators will become better educated as to what is required to maintain private FR and continue to operate their UST systems properly.

Ron Marr is Executive Vice President of the Petroleum Marketers and Convenience Stores of Iowa, a trade association that represents about 1,000 members that distribute, wholesale or retail, about 85 percent of the diesel and about 70 percent of the gasoline used in the state. Ron can be reached at ron@pmofiowa.com.

LEGAL UPDATE

by Patricia Ellis

California Announces BP-Amoco Settlement

In June, 2002, California officials announced a \$45.8 million settlement in a case against Atlantic Richfield Company (ARCO). (Note: BP-Amoco merged with ARCO in April 2000 and is now called BP, and is California's largest gas seller with about 20 percent of the market share.) The company was accused of failing to make required safety improvements in underground tank systems at 59 service stations throughout the state.

The first signs of trouble for ARCO came in mid-1998 from San Joaquin County. County regulators suspected inadequate tank improvements at five or six stations. In digging up systems at eight stations, each of the stations had some tanks and piping that were found to be substandard. According to David

Irey, the lead deputy in the environmental prosecution unit of the county district attorney's office, "Eight for eight stations had problems. We thought that it would be highly unlikely that there wouldn't be similar problems throughout the state."

The district attorney's office filed a lawsuit in 1999, which ARCO settled in 2000. The San Joaquin officials contacted the state, prompting agencies to begin looking for similar problems in Los Angeles and Sacramento counties. They found the same pattern of inadequate tanks or pipes. Ultimately, inspectors found substandard components at 59 ARCO stations in 13 counties. ARCO had about 1,000 stations operating in California during the 2000–2001 investigation.

Unfair Competition

In preparing the case, the attorney general's office used the state's Unfair Competition Act. ARCO had a financial advantage, the state alleged,



because it kept selling gas while other companies shut down to replace tanks, pipes, and other parts of the system.

The state also used the 1988 law that required tank systems to be upgraded by December 22, 1998. State law, after the deadline, prevented oil companies from delivering fuel to stations that did not have a blue-and-white upgrade placard. Violators faced fines of \$5,000 per tank.

In the late 1990s, when the tank upgrade deadline approached, then-Governor Pete Wilson signed a bill that allowed oil companies to selfcertify completion of the upgrade work. The bill was in response to industry concerns that delays in government inspection of the upgrades could result in service station closures. ARCO sponsored the legislation allowing self-certification, and in 1998, the oil company sued several local regulatory agencies in California who would not issue the upgrade certification without actual site inspections.

The state's investigation found that ARCO falsely self-certified some of its own stations, claiming that they had fiberglass tanks and piping when, in fact, they had bare steel. Prosecutors argued that ARCO's actions provided the company with an unfair business advantage. While other companies were shutting down service stations to meet the deadline for underground tank improvements, ARCO continued selling gasoline at 59 stations, postponing upgrade costs and hiring contractors to do the work after the rush by other companies seeking to meet the state deadline.

The suit does not allege that ARCO "falsified" its applications for the upgrade certificates it needed to stay in business. The suit says local agencies issued the certificates based on "incorrect" information from ARCO, which does not imply criminal intent or constitute a violation of state law.

The Settlement

About \$18 million of the settlement money will go to a state water pollution fund for cleaning up spills where no responsible party is found liable. The remaining money will go to reimburse state and local agencies for the cost of the ARCO investigation and to state environmental enforcement training and actions. Technically, the settlement totals \$45.8 million—\$25 million in cash, plus \$20.8 million that the state will credit BP for tank system improvements that exceed state requirements. The company says it had made such improvements at dozens of stations since April 2000. BP must demonstrate that the work was done, or pay the difference. As further assurance, BP agreed to give state inspectors access to ARCO stations and to immediately close stations with tank violations until improvements are made.

The settlement does not affect local enforcement actions against BP in Orange County or the case settled in San Joaquin County, where the pattern of alleged noncompliance was first uncovered. State Attorney General Bill Lockyer said that the enforcement action was necessary even though investigators found no evidence that gasoline had leaked from the substandard storage tanks and pipes. "They were obligated to replace these kinds of steel pipes that would corrode underground, and they didn't. The goal (of the \$25 million cash settlement) was to compel ARCO to disgorge profits that they made because they didn't...make improvements at these sites."

Despite the settlement, state officials say that some of the 59 sites have been or are still contaminated. Nothing in the settlement "closes the book" on ARCO's potential liability if leakage is found to have occurred from delays in tank improvements at the 59 sites. According to Bill Rukeyser, spokesman of CalEPA, "The complaint was about failure to upgrade. We didn't have to prove leaks, and the settlement does not let anyone off the hook if there are leaks."

Lake Tahoe Suit Finally Settled

In August, a settlement with Shell Oil Company ended nearly a year-long trial in which the South Lake Tahoe Public Utility District sued oil companies, refiners, MTBE manufacturers, gas stations, and distributors for concealing the dangers of MTBE when they marketed it as a gasoline additive. The agreement includes Shell Oil Co., Shell Products Co., Equilon Enterprises LLC, and Texaco, Inc.

Shell reached its settlement as the jury was about to decide the company's share of damages to the utility. Damages resulted in the closure of 13 of the utility's 34 wells, which were tainted or immediately threatened by the fuel additive. Fourteen companies settled with the district before the trial began, including Exxon and Chevron, which agreed to pay \$12 million and \$10 million, respectively.

Lyondell Chemical Company agreed to a \$4 million settlement in July after a jury said Lyondell and Shell knew about the dangers of MTBE-blended gasoline but withheld that information.

David Harpole, a Lyondell spokesman said "We feel that it is in the best interest of our shareholders to settle at this time, as mistrials, retrials, and appeals could create costs larger than this settlement."

In all, the 16 settlements totaled just over \$69 million. Shell agreed to pay \$28 million to cover the costs of cleaning up eight drinking water wells contaminated by MTBE. The companies maintain that they aren't liable, despite the settlement. According to Shell spokesman Cameron Smyth, "We felt that settling now was the best thing to do to no longer deal with protracted litigation costs."

According to South Lake Tahoe Public Utility District spokesman Dennis Cocking, "When we started out down this road, we set out to recover enough money to fix the system and pay the bills, so our customers didn't have to pay for it out of their pockets. With the total settlement (\$69 million), we are able to do that." Estimates of cleanup costs range from \$35 to \$45 million.

What the Industry Knew

During the discovery phase of the trial, thousands of documents revealed that the oil industry knew of the dangers of MTBE before it became heavily used to make gasoline burn cleaner.

A 1981 ARCO document shows that the company learned that 20 percent of USTs leak, leading to the "possibility of groundwater contamination by MTBE."

A 1983 Shell document showed that Shell found a taste and odor threshold of 7–15 ppb, and that "even if not a factor to health, it still had to be removed below detectable amount in order to use the water."

A 1983 API report indicated ineffective remediation of MTBE. API members indicated in 1984 that MTBE had potential for rapid migration and noticeable taste and odor, and an Exxon researcher predicted that fate, transport, remediation, and taste/odor issues would lead to higher cleanup costs and "adverse public exposure."

In 1985, an Exxon researcher recommended that "MTBE not be con-

■ Settlement from page 31

sidered an additive to Exxon gasoline on a blanket basis throughout the United States because of "environmental risk."

In 1986, ARCO told the Interagency Testing Committee that MTBE is "slightly soluble... minimal possibility of spills,...extremely small losses." By 1987, EPA found that "MTBE contamination found in four states.... problem could mushroom."

Komex H₂O Science, a consulting company that has assisted on a number of the MTBE litigation cases, has created a timeline of MTBE information, much of it based on documents submitted during the discovery phase of the trial. During this period, thousands of confidential company records were unearthed, showing that America's biggest oil companies knew about MTBE's risk to drinking water years before domestic refiners more than tripled the amount of the additive in gasoline.

The timeline tracks regulatory action, industry developments, major spills, and research developments. The timeline reveals that oil companies knew of the environmental risks of MTBE but fought efforts to correct it. The chronology, a display of who knew what and when, is titled "From Tank to Tap: A Chronology of Methyl Tertiary Butyl Ether (MTBE) in Groundwater." The chronology can be viewed at http://www.blue waternetwork.org/reports/rep_ca_ mtbe_history.pdf. An available-forpurchase computer-based version of the timeline allows you to click on an event in the timeline and view an electronic version of the original document, report, or memo.

Lessons Learned?

The water utility's attorney, Duane Miller of Sacramento, said, "It's going to set a precedent. The oil industry has to continue getting MTBE out of gasoline sooner rather than later unless they want to face a jury again with these issues." Miller, who also represents officials in Dinuba, California, who have a similar case pending against Unocal, Tosco (now Phillips), and Chevron Corp., said "I think it's very clear to defendants that if they go to trial, there's a real risk of losing."

Oil companies say that the Lake

Tahoe settlement does not mean that other similar cases will turn out the same. According to Unocal spokesman Batty Lane, "We evaluate every lawsuit on its individual merits."

The South Lake Tahoe trial began in October 2001, in Superior Court in San Francisco. In the mid-April verdict in the product liability case, the jury said Shell Oil Company, Lyondell Chemical Co. (formerly Atlantic Richfield Chemical Co.), and Tosco Corp. (now part of Phillips Petroleum) had placed a defective product on the market when they began selling gasoline with MTBE.

The jury also found that Shell and Lyondell acted with malice when they withheld information about the chemical. Tosco was found liable for pollution, but not for withholding information. The verdict in the first part of the trial came after seven weeks of deliberation in a five-month trial.

The penalty phase of the trial began in April 2002, when the Tahoe utility district sought tens of millions of dollars in cleanup costs and punitive damages. It wanted to force the companies to "disgorge" profits made from MTBE manufacturing and sales. The settlement was reached with Shell before the court had completed the penalty phase of the trial.

According to Scott Summy, a Texas lawyer who is handling MTBE cases in a number of states, "Very similar evidence presented to the jury in Tahoe will be presented in these other cases. The jury was presented with ample evidence that these companies had early knowledge that predicted these problems. They failed to disclose the information they had and also promoted the additive in gasoline despite the fact that it had inherent problems."

Michael Hawley, the jury foreman, said he found the records of early knowledge among the most compelling evidence that he recorded in 635 pages of handwritten notes. "There were lessons to be learned, but [Shell] didn't [learn them] because it saw money to be made in selling the product."

Wouldn't you love to know what kind of dollar settlement that the jury had in mind for each of the defendants?

The South Lake Tahoe Public Utility District recently held an open

house at the Arrowhead well in Meyers to allow neighbors a tour of the well, which is equipped with an innovative \$1.4 million water treatment system being paid for with part of the settlement money. The system is an ozone and hydrogen peroxide system that has been online since the end of June, treating drinking water at 800 gallons per minute.

Santa Monica Settles with Chevron Texaco and ExxonMobil

Six years after Santa Monica discovered MTBE in its drinking water wells, the Santa Monica City Council has approved a proposed settlement with two oil companies that the city said were partly responsible for contaminating its municipal water supply. (The court still has to agree to accept the settlement.)

Under the settlement agreement, Chevron Products Co., a subsidiary of Chevron Texaco Corp. and Exxon-Mobil Corp. will pay to design, build, and operate a facility to treat the city's water—a venture that is expected to cost more than \$200 million over the years.

The companies will also pay the city \$30 million in cash to cover damages. In 1996, Santa Monica detected MTBE in 7 of its 11 drinking water wells. The city had to scramble to find replacement water. Two years ago, Santa Monica sued seven major oil companies and 11 other manufacturers, suppliers, refiners, and pipeline operators, claiming that they had tainted much of the city's drinking water with MTBE.

Chevron Texaco, Shell Oil Co., and ExxonMobil voluntarily agreed to help the city deal with the contamination, but the agreement expired in January 2000. Five months later, the city sued. In the interim, Shell had been paying Santa Monica \$3.25 million per year to cover the cost of importing water, because federal and regional environmental officials had designated Shell as the company primarily responsible for the contamination.

As part of its settlement, the city has agreed to cease legal action against ExxonMobil and Chevron Texaco. If the city is successful in litigation against companies not

involved in the settlement, then ExxonMobil and Chevron Texaco might be able to recover a portion of the money they have agreed to spend to restore the city's drinking water. It is expected to take five years before the facility to treat all the city's water opens, according to Craig Perkins, city director of environmental and public works management.

According to Rod Spackman, Chevron Texaco manager of government and public affairs in the Los Angeles area, "It is our strong belief that our facilities have in no way contributed to the contamination. Protracted litigation around these issues we think is unproductive, and you draw resources away from fixing the problem."

NAFTA Rejects Methanex Free-Trade Complaint

On August 7, 2002, a North American Free Trade Agreement (NAFTA) tribunal rejected most of the claims of the Canadian methanol producer Methanex over California's decision to ban MTBE. The panel said it needed more evidence to support Methanex's claim that it was the victim of a political deal between California Governor Gray Davis and ethanol producer Archer Daniels Midland Company.

Methanex claimed that California violated free-trade rules when it banned MTBE. Methanex claimed that the governor imposed the ban to eliminate a competitor of ADM and pointed to a \$200,000 campaign contribution from ADM to Mr. Davis as evidence. The tribunal expressed skepticism that the governor was aiming specifically at Methanex when he imposed the ban. It said that the tribunal could not "identify a single or predominant purpose," such as targeting Methanex, in what Mr. Davis did. The tribunal offered Methanex a final chance to prove its claim by submitting a new legal brief within 90 days.

NAFTA prohibits unfair protection of domestic industries, and Methanex's original complaint alleged U.S. officials acted improperly to protect the U.S. ethanol industry, which competes against MTBE as a fuel oxygenate. Methanex later

amended its complaint with the claim that Davis and ADM officials held a secret meeting during the 1998 campaign at ADM's Illinois head-quarters and ADM made over \$200,000 in contributions to his campaign.

Aids to the governor scoffed at the charges and said that the dangers of MTBE were clear. Davis spokesman Davi Chai also argued that ADM and the ethanol industry have not won any special favors in California. He said that Davis has fought attempts to make ethanol the preferred clean-air additive in the nation. He said, "It is extremely clear that ethanol has found no friend with California and the Davis administration."

In the lawsuit, filed in June 1999 against the U.S. government, Methanex demanded \$970 million in damages. The State Department defends the United States in NAFTA cases. If Methanex were to win, the federal government would have to pay the claim, or California could be forced to revoke the ban.

Methanex has announced it will file a new trade complaint against California, arguing that a backroom deal had been cut between Davis and ADM.

Well Cleanup Class-Action Status Denied

A Southern District judge ruled in July 2002 in a suit in which it was charged that the major oil companies polluted groundwater. The judge rejected the arguments of plaintiffs from New York and three other states who sought class-action status to obtain an injunction that would ensure the safety of their well water. Judge Shira Scheindlin said that the individual circumstances of each case, and several other factors, made certification impractical improper in the Methyl Tertiary Butyl Ether (MTBE) Products Liability Litigation.

The plaintiffs wanted class-action status to seek an injunction on well cleanup that costs billions of dollars, with individual trials on damages to follow. The judge said that the plaintiffs, despite making "every conceivable argument to persuade this Court that class-action treatment is appro-

priate in this hybrid environmental/products liability action," did not meet the standards for certification under Rule 23 of the Federal Rules of Civil Procedure. "Such treatment would stretch the decidedly elastic class-action device beyond its breaking point—causing it to snap."

The plaintiffs, some of whom lived adjacent to or near gas stations, claimed the oil companies conspired to mislead the public and the EPA as part of an effort to increase concentrations of MTBE in gasoline and block demands for additional testing and safety measures.

The judge ruled that the claims failed to meet the requirement of "typicality." The judge stated that "while the named plaintiffs made the same legal arguments as the proposed class, their claims must also derive from the same course of conduct. Yet, the contamination of each plaintiff's well comes through a factually unique set of circumstances, such as a burst pipeline or a leaking container." The plaintiffs were also unable to show that the proposed class action would "adequately and fairly protect the interests of the class."

An additional concern of the judge was that the named plaintiffs' stake in the action was substantial enough "to prosecute this action vigorously on behalf of absent class members. The named plaintiffs actually claim no personal injury," adding they complain instead of badtasting or bad-smelling water.

The judge said that "this case presents a novel issue: whether a hybrid environmental/products liability class seeking mandatory injunctive relief in the form of clean water and well remediation may be certified" where class members are geographically diverse, a large group of actors made the product, the effect of the contamination is dramatically different among classes, and the contamination stems from diverse causes.

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■ Flexible Pipe from page 23

- Sticky and deformed pipe in the sumps and cracked or loose end fittings
- Misaligned piping tees, ells, and riser pipes
- Pipe that is bent at an unusual angle where it is terminated into the submersible pump housing or metallic fittings underneath the dispensers
- Pinched, buckled, or elongated piping
- Any signs of swelling or growth of the secondary jacket of coaxial piping over the coupling ferrules
- Compression, swelling, or distortion of the rubber boots that may be installed on the pipe in coaxial systems where the metallic fitting is installed at the pipe terminations
- Stretching or tearing of the rubber boots that are installed in the walls of the containment sump, or boot clamps that are out of place
- A visible crack or leaking fuel at the swaged area of the end fitting
- Fractures or cracks in the outer layers of the primary pipe
- rest the secondary containment and release-detection system to confirm that it is working properly. As with all pressurized piping, release detection is critical to preventing releases to the environment. Properly functioning secondary containment and rapid response to release alarms have kept a number of flex-piping failures from becoming major releases to the environment.
- Check that sumps are liquid-tight and that sensors and alarms are working.
- Consider adding additional, redundant piping release-detection systems to minimize any release that might occur from a failure of the primary pipe. There are a variety of release-detection systems that can be used in combination with pressurized piping, including liquid sensors in the sumps, mechanical line-leak detectors, or electrical interlocks from the leak-detection system to the

pumps.

- Do not allow any fuel to remain in the secondary containment system for any length of time. For purposes of this discussion, secondary containment refers to the outermost jacket of the coaxial pipe, secondary containment conduit pipe, sumps, and the various boots. What is not clear to investigators is exactly how long an exposure to product constitutes too long.
- If you find compromised flexible piping, take it out of service immediately. Investigate and preserve the evidence of the failure so that an effective examination of the failure can be made and we all can gain a better understanding of the causes of the failures. Have an independent expert at the site when removing failed equipment or investigating suspicious releases. Many state inspectors, insurance adjusters, and installation experts, such as installers, have the experience and the qualifications for this task. Notify the manufacturer and other parties concerned and work closely with them to investigate the causes of the failure. The manufacturers

and marketers of flexible piping need to be involved in the investigation if the owner intends to make a warranty claim. Many owners are preserving samples of failed piping for independent testing. Document the condition of the system as it is being uncovered and removed with photographs.

Vigilance, Vigilance, Vigilance!

The bright spot in this flexible-pipe situation is that many of the failures have been discovered and caught by vigilant UST owners and regulators before they resulted in releases to the environment. With further analysis of these failures and improved communication, we can gain a clearer understanding of the root causes of these failures and manage the risks.

EPA's Office of Underground Storage Tanks (OUST) has work underway to collect quality data to determine the cause, scope, and magnitude of the problems described above. OUST intends to work with Underwriters Laboratory (UL), the manufacturers of flexible pipe systems, the states, and EPA's Office of Research and Development to gather needed information on flexible pipe issues.

EPA HQ UPDATE

OUST Announces LUST Cleanup Goals

On October 1, 2002, OUST announced new national and regional annual LUST cleanup goals. OUST established a national goal of completing between 18,000 and 23,000 cleanups each year for fiscal years 2003–2007. The aim is to reduce the current (FY02) national backlog of petroleum release sites by one-half or more in the next five years and improve the overall performance of the UST cleanup program.

OUST has provided each U.S. EPA region with a range of goals that are based on historical and recent cleanup performance data and the existing cleanup backlog. Each region has been encouraged to consider state-specific circumstances when planning for cleanup progress with each of its state UST programs. The regions have also been encouraged to maintain or exceed the FY02 level of cleanups initiated at 90 percent of all confirmed release sites.

To step up the pace of cleanups, OUST highlighted the importance of encouraging the use of a wider array of programmatic tools, such as multi-site cleanup agreements, pay-for-performance contracting, and risk-based decision making. OUST indicated that it would support efforts to obtain a better understanding of the progress being made to clean up leaking tank sites. (For more information, contact Richard Mattick at (703) 603-7154.) ■

Field Notes &

from Robert N. Renkes, Executive Vice President, Petroleum Equipment Institute

UST Systems in China—Yesterday, Today, and Tomorrow

Tattended China's Petroleum Distribution and Retail Summit on August 27–28, 2002, in Beijing, China. It was hard to turn down the invitation, since China is the most dynamic retail petroleum market in the world today. With 1.4 billion people and only 80,000 service stations, China will soon be a force to be reckoned with.

Today, only one person in one hundred owns a motor vehicle in China. But that's about to change, as the middle class grows and vehicle ownership increases. And change is definitely in the air—the number of new driver's licenses in China has quadrupled since the beginning of the year.

Throughout China, thousands of new stations are either planned or awaiting government approval. So far, most of the new stations are the result of joint ventures with Western oil company giants like BP, Shell, and ExxonMobil. Thousands more will be modernized in the next few years as Chinese oil companies and their Western partners attempt to build a network of "world-class" retail refueling sites.

Some of the newer stations I visited in the Beijing area appear similar to newer service stations in the United States from the ground up—electronic dispensers, good lighting, uniformed attendants (full-service only in China). And in metropolitan areas where air pollution is a substantial problem, Stage I and Stage II vapor recovery equipment will soon be required to clean up the air.

You begin to get a good feeling about where China is headed with their refueling stations until you ask about what's underground. It's then that you think you are back to the United States in the early 1960s, when we buried bare steel tanks and forgot about them. All tanks and almost all product lines in China are bare steel. I couldn't find a person at the conference who knew of a fiberglass or cathodically protected tank that was buried on the mainland.

The big question regarding China's underground storage systems is what kind will be installed in the future? Will the Western oil company partners demand systems similar to those they now install in North America and Europe, will they do only what Chinese governmental regulators require (whatever that is), or will they take the easy way out and bury bare-steel tanks and forget them? I hope it's a decision the Chinese are willing to live with for decades to come.

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U.S. Secures Pleas to 10 Felony Counts in Tanknology Case

On July 24, 2002, U.S. EPA and the Department of Justice jointly announced that the United States had filed criminal charges against Tanknology-NDE International, Inc. On the same day, the United States also filed a plea agreement wherein Tanknology agreed to plead guilty to 10 felony counts of presenting false claims and making false statements to federal agencies. The guilty pleas were for false USTtesting services performed by Tanknology employees at federal facilities located in the states of Texas, California, Arizona, Illinois, Florida, South Carolina, New Jersey, and the Commonwealths of Pennsylvania and Massachusetts.

In pleading guilty at the federal Western Texas District in August 2002, Tanknology admitted that the investigation provided evidence to a number of improper and/or fraudulent practices carried out by its employees at federal facilities across the country, including U.S. postal facilities, military bases, and a NASA facility.

Under the plea agreement, Tanknology has agreed to pay a criminal fine of \$1 million and pay

EPA HQ UPDATE

restitution of \$1.29 million to the United States for the cost of retesting the tanks. In addition, Tanknology will serve five years probation and implement a quality management system to ensure that false and improper testing practices do not occur again. Tanknology is the largest UST testing company in the United States, with four regional offices and six field offices located across the country. Its corporate headquarters are in Austin, Texas.

The case was filed under the criminal provision of 18 U.S.C. Sections 287 and 1001 (false claims and false statements) subsequent to the federal government conducting an investigation from July 1998 through December 1999. During this period, federal agents observed Tanknology testers at federal facilities across the country. Investigators found evidence that Tanknology employees failed to properly perform tank tightness testing and leak detection testing at U.S. Department of Defense, U.S. Postal Service, and National Aeronautics and Space Administration (NASA) facilities.

The false tests ranged from failing to follow required test protocols

to "drive-by" tests, where a Tanknology tester was videotaped driving up to a federal facility, driving away after a few minutes, and then submitting false data.

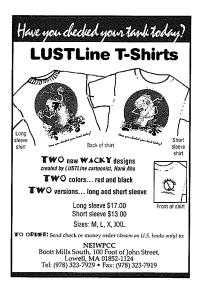
The investigations were conducted by the U.S. EPA Criminal Investigation Division along with the investigative arms of seven other federal agencies with the assistance of personnel from the Texas Natural Resources and Conservation Commission (TNRCC) and the Pennsylvania Department of Environmental Protection. The United States has no evidence that the environment was harmed due to the company's violations.

For more information on this case, visit the EPA OUST Web site at www.epa.gov/oust.



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