510N05001

New England Interstate Water Pollution Control Commission
www.neiwpcc.org/lustline.htm

Boott Mills South
100 Foot of John Street
Lowell, Massachusetts
01852-1124

Bulletin 49
March
2005

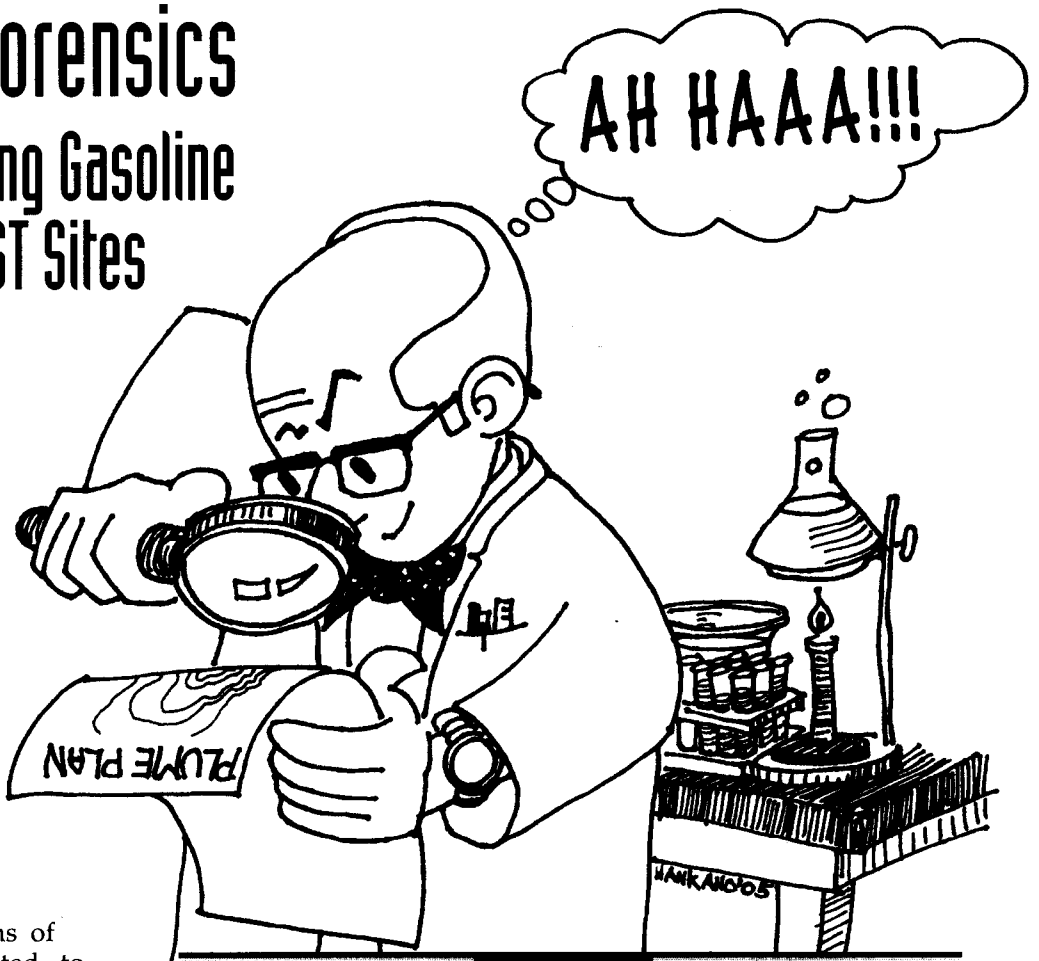
L.U.S.T.LINE

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

Environmental Forensics

Chemical Fingerprinting Gasoline and Diesel Fuel at LUST Sites

by Scott A. Stout, Allen D. Uhler, and Gregory S. Douglas



The need to identify, delineate, and differentiate petroleum-derived contaminants resulting from leaking underground storage tanks is often an important part of site investigations where knowledge of the source(s) of contamination is sought, and where an equitable settlement of the resulting remedial liability and damages is at stake. Significant advances have been made over the last 15 years with regard to detailed compositional analysis of petroleum in the environment—often referred to as "chemical fingerprinting."

Some of the earliest applications of chemical fingerprinting were related to marine oil spills. The *Exxon Valdez* grounding, for example, was a situation in which knowledge of crude oil or residual fuel geochemistry was applied to identify and differentiate the spilled oil in Prince William Sound and to assess its environmental impacts (Bence et al., 1996). In the past few years, continued developments in the chemical fingerprinting of refined petroleum products, such as gasoline and diesel fuel (Kaplan et al., 1997; Stout et al., 2002), have aided in answering environmental forensic questions surrounding the source and/or age of contamination resulting from LUSTs (Beall et al., 2002; Kaplan, 2003).

■ *continued on page 2*

Inside

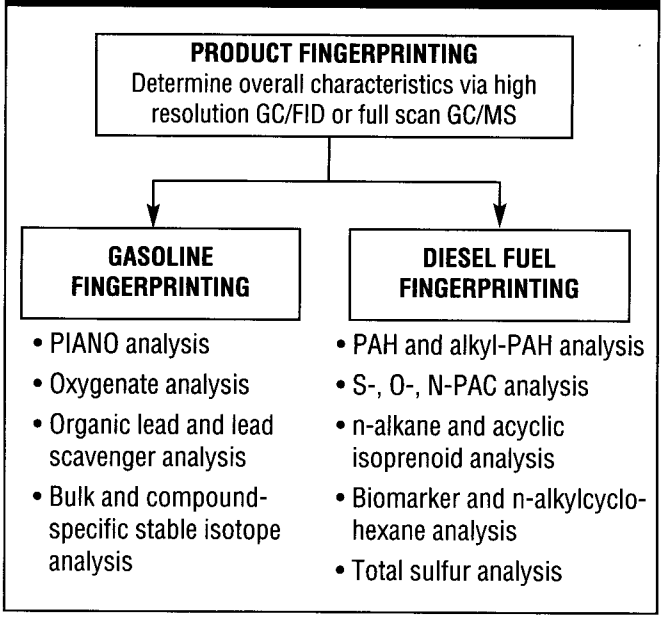
6 Age-Dating Releases at LUST Sites: Part II—Case Studies
10 Vapor Attenuation in Petroleum Hydrocarbon Sources
15 Maryland's MtBE Journey
17 USGS Study of MtBE in New Hampshire
18 Message from Cliff Rothenstein: Protecting the Environment
19 Second European Conference on MtBE
21 WanderLUST
24 Small Spills Count: The Spill Drill
27 Maine—The Way Sumps Should Be
29 FAQs from the NWGLDE
30 New Projects from PEI

■ Environmental Forensics
from page 1

Environmental forensic investigations at LUST sites are typically asking questions such as: What is the contamination? Where did it come from? When was it released? Answers to such questions are used to determine the responsible party. Definitive answers to these questions are not always achieved, but the questions are best addressed using a combined approach involving chemical fingerprinting, a good understanding of the site-specific geologic and hydrogeologic conditions, and the operational and regulatory histories for the site (Stout et al., 1998). This article focuses on the first of these—chemical fingerprinting.

We'll describe some of the advances in forensic chemistry that have been developed in the last five years and are routinely used in the chemical fingerprinting of dispensed and fugitive automotive gasolines and diesel fuels at LUST sites. The application of these techniques in environmental forensics investigations is demonstrated in two abbreviated case studies.

FIGURE 1. *General analytical approach and inventory of analyses conducted in the chemical fingerprinting of gasoline and diesel fuel. See Stout et al. (2002) for detailed descriptions.*



Analytical Strategies

Impacts at LUST sites can arise from non-aqueous-phase liquids (NAPLs), impacted soils with residual NAPL, and impacted groundwater with residual/entrained NAPL or dissolved-phase hydrocarbons. Regardless of the matrix, chemical fingerprinting data developed for such sites must provide sufficient specificity to recognize the particular type(s) of petroleum, characterize the degree(s) of weathering, and provide the diagnostic information necessary to distinguish and perhaps allocate among multiple source(s) of petroleum and/or assess their likely age(s).

A "turnkey" analytical program that utilizes standard methods of analysis (e.g., U.S. EPA Methods 8015, 8020, 8260, and 8270) usually will not produce the chemical detail needed to defensibly answer environmental forensic questions. The principal reason for this is that the conventional target analyte lists for compliance-driven measurement methods simply do not include the dominant and important hydrocarbon compounds that make up petroleum.

For example, the PAH and BTEX target compounds measured using standard EPA 8270 and 8260 typically make up less than 5 to 8 percent of the total PAHs and volatiles in most petroleum products, and as such the data have little or no diagnostic value (Douglas and Uhler, 1993). Instead, methods suitable for environmental forensics investigations are performance-based modifications to existing EPA SW-846-series methods that target a greater suite of compounds in gasoline and diesel fuel that are useful for source identification and differentiation.

For LUST site investigations of gasoline or middle-distillate releases, we advocate the use of a tiered analyticial strategy that captures a full spectrum of chemical compositional information (Figure 1). Such a stratagy allows for the quantitative measurement of a large number of gasoline-range (volatile) and diesel-range (semi-volatile) hydrocarbons and non-hydrocarbons.

In gasoline investigations this strategy involves measurement of nearly 100 of the so-called "PIANO" compounds (paraffins, iospaaffins, aromatics, naphthenes, olefins), oxygenates, alkyl lead additives, halogenated lead scavangers, and volatile sulfur compounds. In diesel-fuel investigations it involves the measurement of n-alkanes, acyclic isoprenoids, parent and alkylated PAH, low-boiling biomarkers (e.g., sesquiterpanes), and total sulfur concentrations. Detailed descriptions of the analyses used in measuring these compounds have been published elsewhere (Stout et al., 2002; Uhler et al., 2003; Douglas et al., 2004).

Gasoline Fingerprinting

Automotive gasolines are complex fuels blended from a variety of intermediate refinery streams, each with different physical and chemical properties (Stout et al., 2001). Historic gasolines were blended primarily to achieve physical specifications for

L.U.S.T.Line

Ellen Frye, *Editor*
Ricki Pappo, *Layout*
Marcel Moreau, *Technical Adviser*
Patricia Ellis, Ph.D., *Technical Adviser*
Ronald Poltak, *NEIWPCC Executive Director*
Lynn DePont, *EPA Project Officer*

LUSTLine is a product of the New England Interstate Water Pollution Control Commission (NEIWPCC). It is produced through a cooperative agreement (#T-830380-01) between NEIWPCC and the U.S. Environmental Protection Agency.

LUSTLine is issued as a communication service for the Subtitle I RCRA Hazardous & Solid Waste Amendments rule promulgation process.

LUSTLine is produced to promote information exchange on UST/LUST issues. The opinions and information stated herein are those of the authors and do not necessarily reflect the opinions of NEIWPCC.

This publication may be copied. Please give credit to NEIWPCC.

NEIWPCC was established by an Act of Congress in 1947 and remains the oldest agency in the Northeast United States concerned with coordination of the multi-media environmental activities of the states of Connecticut, Maine, Massachusetts, New Hampshire, New York, Rhode Island, and Vermont.

NEIWPCC
Boott Mills South, 100 Foot of John Street
Lowell, MA 01852-1124
Telephone: (978) 323-7929
Fax: (978) 323-7919
lustline@neiwpcc.org

LUSTLine is printed on Recycled Paper

FIGURE 2. *Normalized PIANO distribution for two premium reformulated gasolines (RFGs). Gasoline from Refiner A achieved octane primarily from the blending of MtBE and iso-octane whereas Refiner B achieved octane from MTBE and toluene.*

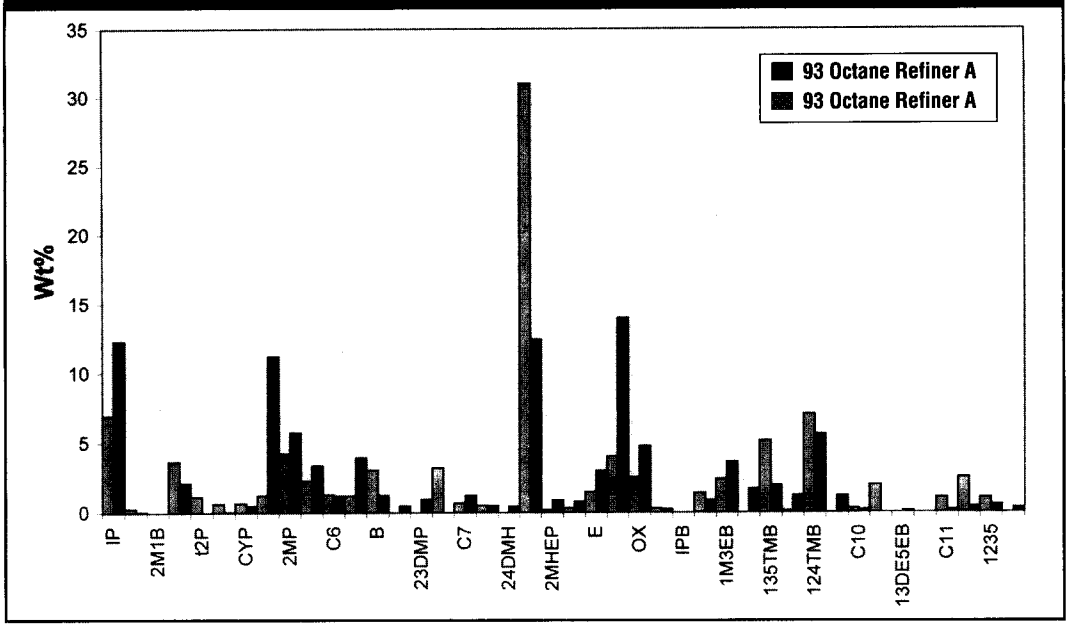
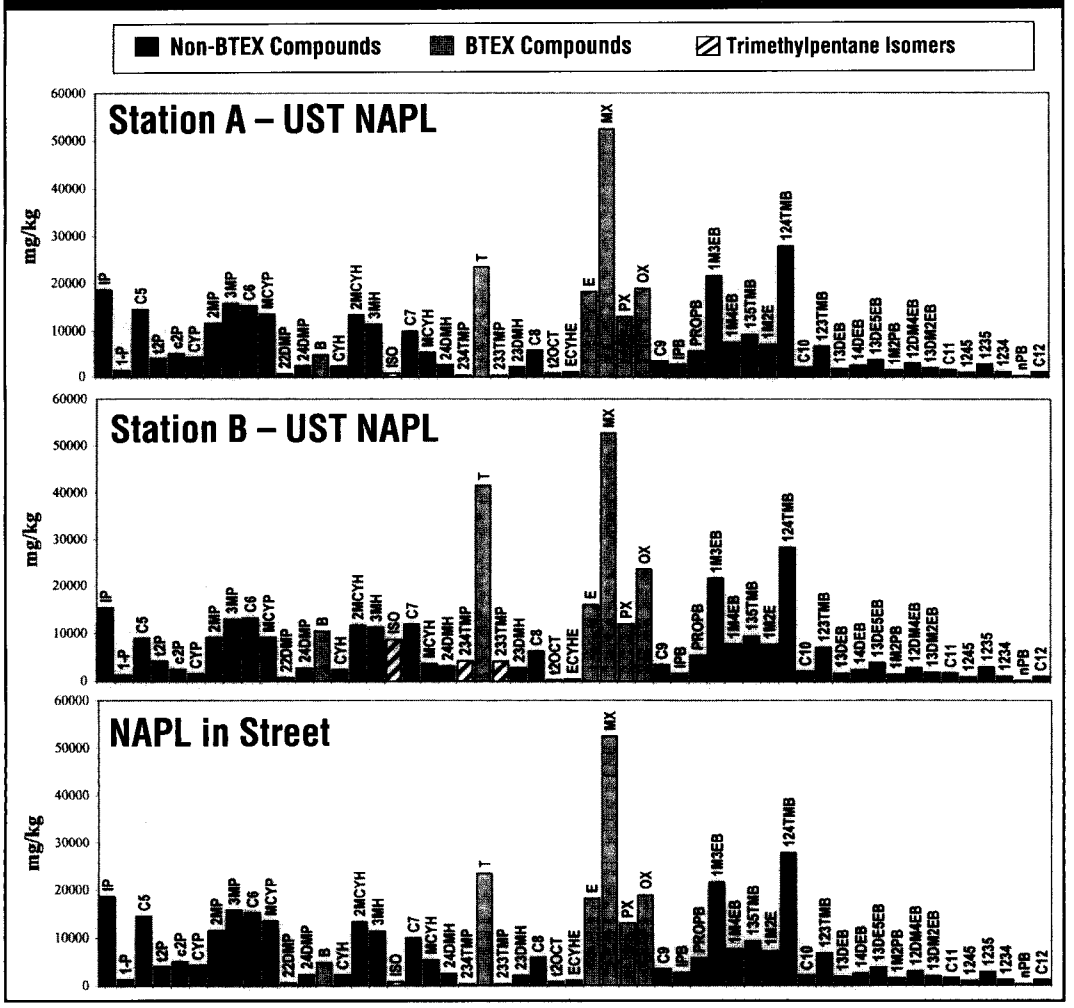


FIGURE 3. *Histograms showing the PIANO distribution for NAPLs from three locations in a study area. The absence of trimethylpentane isomers (ISO, 234TMP, and 233TMP) in the Street NAPL indicated it is more closely related to the gasoline from Station A. Supply history research demonstrated that Refiner B blends alkylate (enriched in trimethylpentanes) into their gasolines while Refiner A does not. Note that the BTEX compounds' (gray) distribution, as might only have been measured by conventional EPA Method 8260, could not have been used to distinguish these NAPLs from one another.*



boiling range, vapor pressure, oxidation stability, and octane with the goal of suitable engine performance, such as cold/hot starts, acceleration, knock, resistance to vapor lock. How these physical specifications were achieved was largely left up to the individual refiners. Consequently, historic gasoline compositions were quite variable in chemical composition in both a temporal and spatial sense.

Modern reformulated and oxygenated gasolines must now meet stricter physical and chemical specifications. The latter include restrictions on the content of olefins, sulfur, benzene, total aromatic hydrocarbons, and oxygen. These specifications have reduced the compositional variability that had existed within the gasoline pool; nonetheless, on a molecular level chemical differences between different "types" of gasolines persist depending on the refining process (Beall et al., 2002; Stout et al., 2001). This is exemplified in Figure 2, which shows the normalized PIANO distribution for two premium-reformulated gasolines (RFGs) sold in the mid-Atlantic region (an ozone nonattainment area) during the winter of 1999.

In this example, both gasolines (presumably) met federal RFG and ASTM and performance requirements, yet each exhibits distinct hydrocarbon distributions. It is apparent that the RFG from Refiner A achieved octane primarily from the blending of MtBE (RON 115) and iso-octane (RON 100), whereas Refiner B achieved octane from MtBE and toluene (RON 124). This probably reflects a difference in refining

■ *continued on page 4*

■ Environmental Forensics
from page 3

capabilities. For example, Refiner B does not employ an alkylation unit and must rely upon aromatics (toluene) to achieve the necessary octane.

So let's see how we use this information on gasoline variability to conduct a gasoline-fingerprinting investigation.

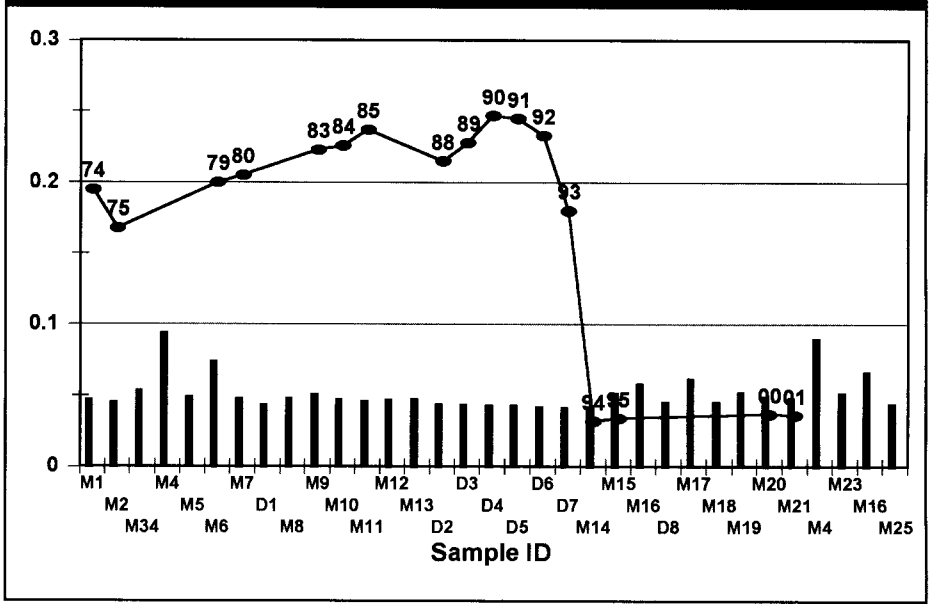
■ **Case Study #1** The objective of this investigation was to determine if NAPL encountered under a street separating two service stations was correlated to free-phase gasolines found on two adjacent service station properties. Detailed gasoline analysis was conducted on free-phase product samples from each property and from beneath the street (Figure 3). Weathering had affected the samples differently; therefore, some differences were apparent. In spite of weathering differences, the gasolines recovered from each station revealed genetic differences related to refinery blending. Station B's gasoline contained an abundance of particular isoparaffins, namely, 2,2,4-, 2,3,4- and 2,3,3-trimethylpentane (Fig. 3), which indicate that Refiner B blended alkylate into its gasolines. Station (Refiner) A apparently did not use alkylate in production of its gasoline(s). The relative absence of these isoparaffins in the 'Street' indicated it was consistent with the gasoline from Station (Refiner) A.

Diesel-Fuel Fingerprinting

Diesel fuel #2, used in on-road vehicles, belongs to the distillate family of fuels. As the name implies, the production of distillate fuels involves vaporizing and recondensing, which distinguishes these fuels from the higher-boiling-range residual fuels (e.g., fuel oil #6). With minor exceptions, diesel fuel #2 generally boils within the range of approximately 100°C to 400°C, which roughly corresponds to a carbon range of C_7 to C_{25}.

The specific characteristic of any given diesel fuel #2 depends on: (a) the specific "recipe" by which it was refined and/or blended (e.g., hydrotreated versus straight-run), (b) the nature of the crude-oil feedstock (e.g., sweet versus sour crude), and (c) the intended market (e.g., on-road- versus off-road-grade diesel fuel; Stout et al., 2004). Each of these factors can introduce considerable variability in the detailed molecular composition of distillate fuels. This variability provides an opportunity for the environmental forensic investigator to unravel issues, such as the source(s) of diesel fuel-derived contamination at LUST sites.

FIGURE 4. *Histogram showing the concentration of total sulfur (ASTM D4294) measured in 25 NAPLs (M#) and 8 dispensed diesel fuels #2 (D#). Superimposed on the histogram is the historic trend in total sulfur (averaged by year) in the northeastern U.S. showing the significant reduction in 1993 following the new federal regulations. Most NAPLs and all dispensed diesel fuels from this site fall below the 0.5 wt% (500 ppm) limit (horizontal dashed line) established in 1993, indicating most NAPLs were released after 1993.*



Due to the detrimental effects (e.g., corrosion, wear, deposit build-up) sulfur has on engine and furnace parts, and the implications for deleterious air quality impacts, sulfur content of most distillate fuels has been long specified (Gruse, 1967). The first U.S. specification for diesel fuel #2, dating from 1922, required <1.5 percent volume sulfur (< 15,000 ppm; Gruse, 1967). However, it was quickly learned that the higher the sulfur content, the greater were the maintenance problems encountered in diesel engines.

Thus, in practice, most historic diesel fuels contained <5000 ppm sulfur. In 1993, owing to concerns surrounding air emission (not engine maintenance), U.S. EPA required that "low-sulfur," on-road varieties of diesel fuel contain < 500 ppm sulfur. Prior to 1993, on-road diesel fuels #2 contained an average of 2,500 ppm sulfur (U.S. EPA, 2000) (i.e., five times higher than the current limit). Even more stringent sulfur specifications for on-road diesel fuels are planned for the future. U.S. EPA has proposed a rule that would require refiners to further reduce the sulfur maximum in 80 percent of the on-road diesel fuels sold from the current maximum, 500 ppm, to 15 ppm (0.0015 % vol) by June 1, 2006. (The remaining 20 percent of the on-road diesel would need to meet the 15 ppm limit by 2010.)

This difference in sulfur content, with time, can prove useful in certain environmental forensic investigations at LUST sites where the "age" of diesel fuel determines liability. So let's look at how we can use this information to conduct a diesel-fuel fingerprinting investigation.

■ **Case Study #2** The objective of this study was to determine the age(s) of NAPL at a truck stop that changed owners in December 1993, with the agreement that existing contamination was the responsibility of the former owner and any new contamination was the responsibility of the new owner. In 1997, NAPL thick-

ness was observed to increase dramatically despite ongoing recovery, prompting the previous owner to suspect that a recent (post-sale) UST release had occurred.

Because each operator had received diesel fuel from a variety of sources over the time of operation, the conventional fingerprinting data (e.g., isoprenoid ratios, PAH distributions, and low-boiling biomarkers), which might normally recognize distinct types of diesel, yielded ambiguous results, most likely due to the long-term nature of the release.

Age-dating based on degrees of biodegradation (Christensen and Larsen, 1993) was inappropriate (the fresh-dispensed diesel fuel was erroneously estimated to be eight years old by this method). However, when the total sulfur content was measured in the NAPLs and modern dispensed samples using ASTM Method D-4294-03, and then compared to the historic trend for diesel fuel #2 sold in the northeastern U.S., as compiled from National Institute of Petroleum and Energy Research (NIPER) annual databases, the apparent NAPL ages became clear.

Figure 4 clearly demonstrates that most of the 25 NAPLs (M#) and all eight of the dispensed diesel fuels (D#) from the site contained less than 0.5 percent (<500 ppm) sulfur. This indicated that most of the NAPLs were consistent with low-sulfur diesel fuels produced after the 1993 regulation requiring <500 ppm sulfur. The few NAPLs containing more than 500 ppm total sulfur were likely from the area of the site where the former owner's USTs storing pre-1993 diesel fuels were located. These results demonstrated that the increase in NAPL thickness observed in 1997 was the result of recent releases of diesel fuel, and thus the responsibility of the new owner.

Defensible Evidence

Chemical fingerprinting of gasoline- and diesel-fuel-derived contamination at LUST sites can help resolve environmental forensic questions surrounding the source and/or age of contamination as a means of establishing the responsible party. Chemical fingerprinting can be combined with other environmental forensic investigation data (e.g., geology/hydrology, refining history, operational history, and regulatory history) to increase the defensibility of any conclusions. At the heart of chemical fingerprinting is our ability to tailor or modify analytical methods to provide sufficient chemical detail to identify and distinguish gasoline and diesel fuel derived from different sources at LUST sites. ■

Scott A. Stout, Ph.D., Allen D. Uhler, Ph.D., and Gregory S. Douglas, Ph.D. are senior consultants with NewFields Environmental Forensics Practice, LLC, a technology firm that specializes in environmental liability assessment management for industry and government. The authors have worked together for almost two decades in the realm of environmental chemistry, geochemistry, and environmental forensics. Together they have published more than 200 papers, periodicals, and book chapters in their respective fields of expertise. Contact Allen Uhler at auhler@newfields.com *for additional information.*

References

Beall, P.W., S.A. Stout, G.S. Douglas, A.D. Uhler. 2002. On the role of process forensics in the characterization of fugitive gasoline. *Environmental Claims Journal.* 14(4):487-506.

Bence, A.E., K.A. Kvenvolden, and M.C. Kennicutt II,1996, Organic geochemistry applied to environmental assessments of Prince William Sound, Alaska, after the *Exxon Valdez* oil spill—a review. Organic Geochemistry. 24(1): 7-42.

Christensen, L.B. and T.H. Larsen, 1993. Method for determining the age of diesel oil spills in the soil, *Ground Water Monitoring and Remediation,* Fall Issue, 142-149.

Douglas, G.S., W.A. Burns, A.E. Bence, D.S. Page, and P.D. Boehm, 2004, Optimizing detection limits for the analysis of petroleum hydrocarbons in complex environmental samples, *Environmental Science & Technology,* 38: 3958-3964.

Douglas, G.S. and A.D. Uhler, 1993, Optimizing EPA methods for petroleum-contaminated site assessments, *Environmental Testing Analysis,* 5: 46-53.

Gruse, W.A., 1967, *Motor Fuels. Performance and Testing,* New York: Reinhold Publishing Corporation

Kaplan, I.R, 2003, Age dating of environmental organic residue. *Environmental Forensics.* 4: 95-141.

Kaplan, I.R., Y. Galperin, S. Lu, and R. Lee, 1997, Forensic environmental geochemistry: differentiation of fuel-types, their sources and release time. *Organic Geochemistry* 27:289-317.

Stout, S.A., A.D. Uhler, K.J. McCarthy. 2004. Characterizing the source of fugitive middle distillate fuels A case study involving railroad diesel fuel, Mandan, North Dakota. *Environmental Claims Journal.* 16:157-172.

Stout, S.A., A.D. Uhler, K.J. McCarthy, S.D. Emsbo-Mattingly, 2002, Chemical fingerprinting of hydrocarbons, In: B.L. Murphy and R.D. Morrison, eds., *Introduction to Environmental Forensics.* Academic Press, Boston, pp.137-260.

Stout, S.A., A.D. Uhler, K.J. McCarthy, K.J. and S.D. Emsbo-Mattingly, 2001, The influences of refining on petroleum fingerprinting – Part 2. Gasoline blending practices, *Contaminated Soil, Sediment & Water,* November/December Issue: 42-44.

Stout, S.A., A.D. Uhler, K.J. McCarthy, T. Naymik, 1998, Environmental forensics. Unraveling site liability, *Environmental Science & Technology,* 32: 260 A-264 A.

Uhler, R.M., E.M. Healey, K.J. McCarthy, A.D. Uhler, A.D. and S.A. Stout, 2003, Molecular fingerprinting of gasoline by a modified EPA 8260 gas chromatography/mass spectrometry method, *International Journal of Environmental Analytical Chemistry* 83(1): 1-20.

U.S. Environmental Protection Agency (2000), Fuel standard feasibility. In: Heavy Duty Standards/Diesel Fuel, RIA EPA420-R-00-026, 122 p.

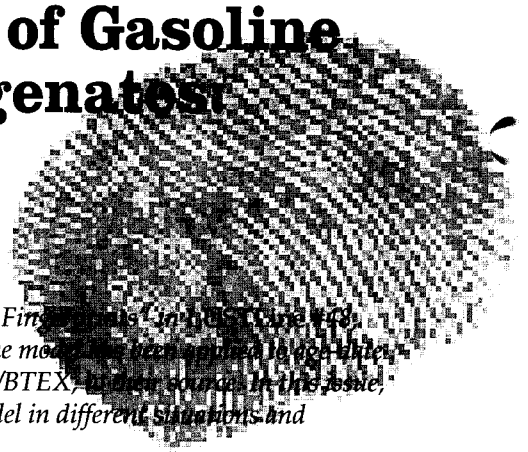
Missouri's PSTIF Takes the Paper Out of Paperwork

Missouri tank owners have a new time-saving option available for reducing paperwork and streamlining communications. The Petroleum Storage Tank Insurance Fund (PSTIF) has established a Web-based procedure for tank owners to send in their leak-detection records, line-tightness tests, and other documents concerning UST operations. Insured tank owners or operators who choose to do so can now conduct all business necessary to continue their participation in the Tank Fund via the Internet. Of course, the paper option is still available.

"As far as I know, we're the first state agency in the country to offer this option to tank owners," says Carol Eighmey, PSTIF Executive Director. "The option was announced in late December, and more than 30 tank owners signed up to use it during January."

Interested *LUSTline* readers can see how it works by viewing a seminar on the PSTIF's Web site, *http://www.pstif.org.* Tank Fund staff who respond to claims are expecting this new tool to give them quicker access to pertinent records about the UST system when a leak from an operating system is suspected or discovered. ■

A Model for Estimating the Age of Gasoline Releases and Tracing Fuel Oxygenates: Part II. Case Studies



by Richard W. Hurst

Assuming you've read "Age-Dating Releases at LUST Sites: Part I. Lead [Isotopic] Fin[illegible] you are now an expert in the ALAS Model and I'll now move on to explain how the mo[illegible] releases and correlate unleaded gasoline releases, including dissolved phase MtBE/BTEX [illegible] In this issue, I have selected some representative case studies involving the application of the ALAS Model in different situations and regions throughout the United States.

As a review of Part I in this two-part series: The development of the ALAS Model (Anthropogenic Lead ArchaeoStratigraphy) began circa 1989 and continues through today. The model utilizes calibrated, temporal changes in stable lead-isotope ratios (e.g., $^{206}Pb/^{207}Pb$) of leaded gasoline to estimate the year leaded gasoline (or refined middle distillates that have been cross-contaminated with alkylleads, e.g., TEL) was released into the environment. The precision of ALAS Model ages are as follows: ± 1 year for releases that occurred between ~ 1965 and 1982 and ± 2 years for 1982-1990 releases; the precision for releases prior to the 1960s is on the order of 10 years. For reference, the ALAS Model curve is shown in Figure 1.

Note: Although the initial development of the ALAS Model commenced in 1989, at which time it was called the LABILE Model (Los Angeles Borderland Industrial Lead), it was not immediately applied to estimating the year of gasoline releases. First applications of the model began some five years later, circa 1994, following further calibration and evaluation of the technique outside of the Los Angeles area. The case studies discussed in Part II were chosen because they are both representative applications of the ALAS Model and cover the time period from the model's inception through 2004.

Lead Fingerprinting in Action

The case studies I've selected will be used to exemplify the versatility of the ALAS Model and lead isotopes in "CSI"-type investigations involving:

- episodic leaded gasoline releases
- releases of leaded gasoline and unleaded gasoline
- identifying sources of fuel oxygenates, specifically MtBE, in groundwater (as a non-age-dating, fingerprinting-type approach)

The last point may initially appear enigmatic, but please bear with me; the fog will be lifted.

The specifics with regard to each case study represent a range of scenarios and conditions under which the ALAS Model was tested in various locations throughout the U.S. Each site is introduced via its scenario, followed by the lead isotope results, the ALAS Model ages, and an epilogue, if appropriate.

Example #1: A Southern California Gasoline Incursion (episodic releases)

Scenario

After the construction in Southern California of a subterranean parking structure in the early 1990s, following a month of heavy rainfall, free product began seeping out of the walls of the parking structure. Subsequent to emergency team responses, geotechnical investigations were conducted to identify potential source(s) of free product and remediate the problem by installing sump pumps to remove free product that continued to seep into the structure.

Potential responsible parties (PRPs) included two operating gasoline service stations located up hydrologic gradient and within 200 meters of the underground structure. As is the case with many service stations in operation for decades, there were records of minor releases; hence both were designated as PRPs (service stations 1 and 3). A third service station (service station 2), located significantly down hydrologic gradient, was identified, yet not suspected of having caused the release. All service stations dispensed unleaded fuel.

Standard gas chromatographic and light-stable isotope (carbon, hydrogen) analyses were performed on free product collected in monitoring wells and via sump pumps, BTEX-impacted groundwater, and dispensed unleaded gasolines. The results were not definitive with regard to the source of free product and its age, but potential liability was assigned to service station 3 based on the presence of lead-free product discovered in groundwater monitoring wells proximal to the station.

Lead Data

Lead-isotopic and concentration analyses were performed on selected free products, BTEX-impacted groundwater, and dispensed unleaded gasolines from all three service stations. The results are plotted on a lead-isotope discrimination diagram (Figure 2; $^{206}Pb/^{207}Pb$ versus $^{206}Pb/^{204}Pb$). Clustering of lead isotopic data on this discrimination plot indicates the source of lead in the samples defining the cluster is the same.

As observed in Figure 2, it is immediately apparent that the lead-isotope ratios of free product and BTEX-impacted groundwater differ markedly from those of the dispensed gasoline from the three service stations. Hence, these stations are not the source of the free product. Liability charges leveled against the operating service station owners were dismissed by the courts.

ALAS Model Ages

ALAS Model ages, derived from the lead-isotope ratios of the free product and BTEX-impacted groundwater

FIGURE 1. *ALAS Model Calibration Curve: 37 of ~125 calibration samples can be resolved at the scale of the figure; the line depicts the ALAS Model as calculated from U.S. Bureaus of Mines annual lead production figures and known lead isotope ratios of lead ores mined globally.*

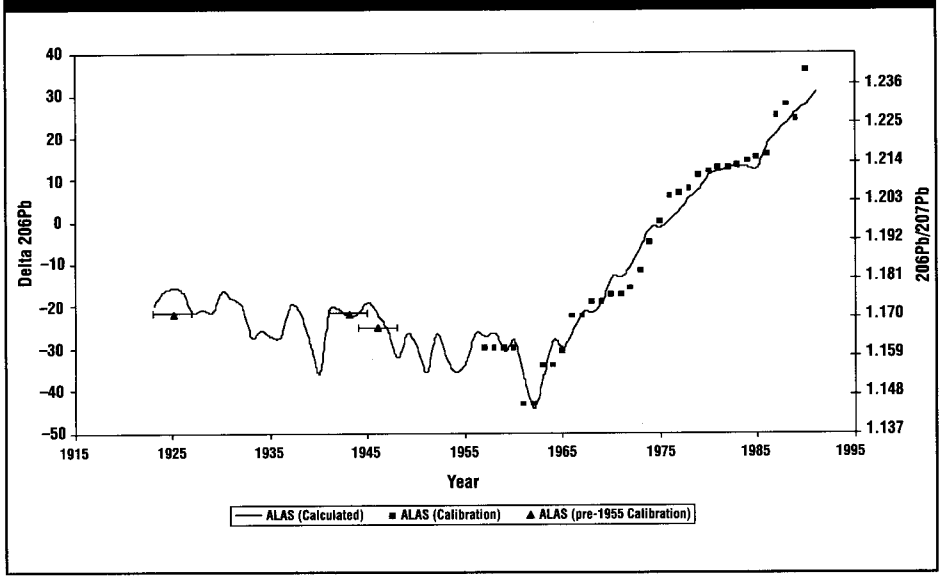
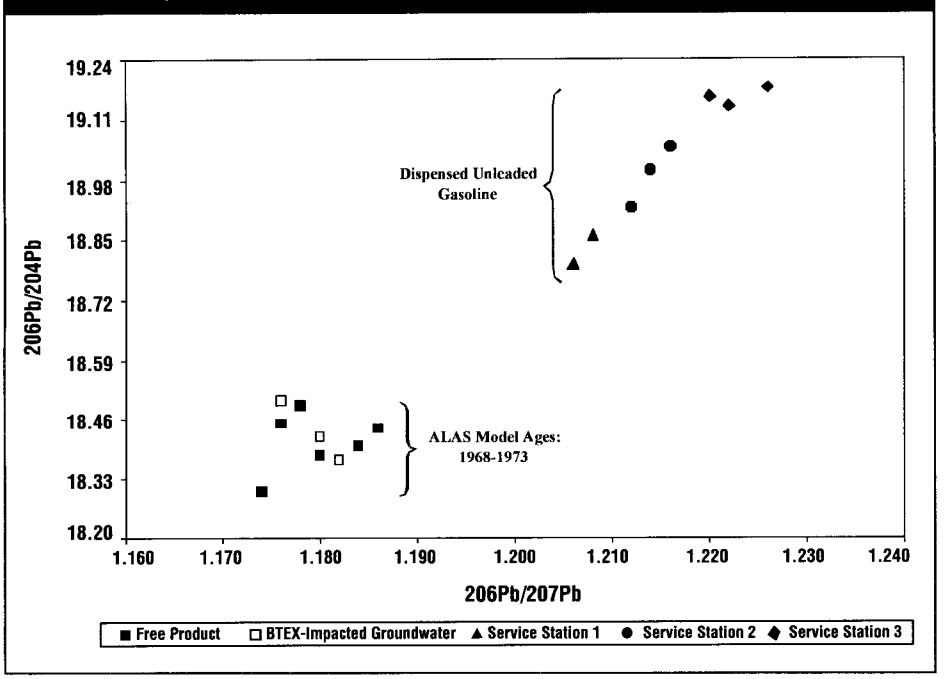


FIGURE 2. *California Case Study. Lead isotope discrimination plot depicting lead isotope ratios of free product seeping into an underground parking structure versus those of dispensed unleaded gasoline from 3 service stations—the lead data and ALAS Model ages released the service station operators from liability.*



yielded ages ranging from 1968 to 1973, suggesting a series of episodic releases during this time interval. The age data further exonerated the operating service stations, especially service station 3, whose owners remained the main focus throughout the investigation.

Epilogue

Following the submission of the ALAS Model ages to the courts, new evidence was introduced. The site of the underground parking structure had, in fact, been the site of a gasoline service station that operated from 1969 to 1975. In fact, Los Angeles County Fire Department records indicated emergency responses to gasoline releases of significant volume at the site from 1971 to 1975, ages that corroborated the results of the ALAS Model.

Example #2: Commingled Plumes in the Midwest (multiple episodic releases)

Scenario

This site in the Midwest involves a large (2-3 km), fairly stationary plume of free product in an industrial area. The free product or products appear to be "old," based on the presence of alkyllead (1-3 gm/gal). The question, again, centers on the age of the free product and the number of releases responsible for the plume. This is a forensic investigation in which lead isotopes were effectively integrated with high-resolution gas chromatography (i.e., in which peak heights/areas are provided for forensic work).

Lead Data

Lead isotope ratio (e.g., $^{206}Pb/^{207}Pb$) analyses of seven free product samples from the plume were correlated with high-resolution gas chromatographic analyses, specifically, methylcyclohexane – isooctane ratios (MCHx/Isooct; Figure 3) measured on split samples. Why use these organic constituents as a reference?

As we know, the refining of gasoline, like many other technologies, has evolved. Pre-1950s gasoline was refined less than its modern counterparts; lead was added to improve the octane rating. Circa 1950, catalytic reforming was introduced. This refining process produced higher proportions of octane-enhancing organic constituents in gasoline (e.g., isooctane, 2,2,4 trimethylpentane; BTEX compounds) relative to organics, such as MCHx, that did not enhance gasoline octane ratings. Hence, as catalytic reforming was more widely used, gasoline became more refined chemically, so the MCHx/isooctane ratio decreased, albeit not systematically, over time.

Figure 3 provides an excellent example of a hyperbolic mixing curve, indicative of two free products (or endmembers), each bearing their own distinctive Pb isotope – MCHx/isooctane signature, that has commingled. The chemical characteristics of the two endmembers are as follows:

Endmember 1: MCHx/Isooct ~ 0.1; $^{206}Pb/^{207}Pb$ ~ 1.17

Endmember 2: MCHx/Isooct ~ 16, $^{206}Pb/^{207}Pb$ ~ 1.135

■ *continued on page 8*

■ **Isotopic Fingerprints** *from page 7*

It is very important to note that the data points that plot between the two endmembers would yield fortuitous correlations and/or ALAS Model ages *if interpreted as individual data;* this is a common pitfall, overlooked by many consultants—each intermediate datum point is a mixture of the two endmembers and does not, in itself, represent the chemical characteristics of a separate release! So, what are the consequences with respect to the age of the releases?

ALAS Model Ages (and apportioning liability)

Endmember 1, with its exceptionally low $^{206}Pb/^{207}Pb$ ratio, ~ 1.135, yields an ALAS Model age of 1962, whereas the ALAS Model age of endmember 2 is 1967—both ages were totally consistent with known gasoline production and refining in the area that commenced in the mid-1950s and ended by the late 1960s. However, the property transferred ownership circa 1965, which leads to the question: Which owner bears more liability for site remediation?

The results depicted in Figure 3 indicate that the majority of the data points (5 of 7) plot closer to endmember 1 (e.g., $^{206}Pb/^{207}Pb$ ~ 1.17), whose ALAS Model age is 1967. The lead isotope data were used in conjunction with historical documents to apportion more liability for cleanup costs to the post-1965 owners of the property.

Example #3: Something Old, Something New in Florida (leaded + unleaded releases)

Scenario

Free product was not present at the Florida site; rather, evidence for gasoline releases was obtained by gas chromatographic analyses of BTEX-impacted sediment (~100 to ~7,000 ppm). The facility at the site operated from the mid-1950s through 1991, but liability fell solely to the last owner even though historical inventory records indicated that there had been transfer-line failures and repairs during the tenure of the first owner (mid-1950s to 1975). The issue centered on the presence/absence of an older on-site gasoline component. Could liability be shared?

TABLE 1 LEAD GEOCHEMICAL AND ALAS MODEL AGE RESULTS: BTEX-IMPACTED SOILS, FLORIDA

SAMPLE LOCATION	Concentrations (ppm) BTEX	PB	$^{206}PB/^{204}PB$	$^{206}PB/^{207}PB$	AGE (ALAS)
Dispenser Islands	2,000	0.2-0.5	19.08	1.222	1986-1990
Transfer Lines	100-300	4-8	18.43	1.158	1964-1966

Lead Data

Five BTEX-impacted soil samples were collected from locations in the vicinity of suspected sources of gasoline releases. Soil sampling locations included areas proximal to the last owner's dispenser islands and trenches proximal to transfer lines. Each soil underwent a series of five chemical extractions (Tessier et al., 1979; Hurst, 2000) using combinations of reagents to extract lead adsorbed onto the soil matrix in order to evaluate the possibility of commingling of multiple sources of lead (Hurst, 2000). The results are summarized in Table 1.

Both laboratory and field data indicate that water-soluble gasoline constituents carry the lead isotopic signature of the source of a leaded or unleaded gasoline release into groundwater, making the lead-isotopic system a viable method to identify the source as well as trace the fate and transport of MtBE/BTEX in groundwater systems.

ALAS Model Ages

The data indicate that at least two releases occurred. The younger ALAS Model ages, 1986 to 1990 (1988 ± 2), derived from soil samples proximal to the location of the last owner's dispenser islands, were most likely the result of an unleaded or low-lead gasoline, given the history of site operations. The older release, estimated to have occurred in 1965 ± 1, occurred within the operating period of the previous owner. Although not depicted in a figure herein, $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ ratios from the 25 sequential chemical extractions of the five soil samples exhibited a range that was uniformly distributed between the endmember lead isotope ratios, 1.158 to 1.222. As in the previous case study, significant commingling of lead from the two gasoline releases had occurred. The relatively uniform distribution of lead-isotope ratios between those of the two endmembers (e.g., dispenser island and transfer lines) suggested the two releases were of similar magnitude. With this information in hand, the parties involved settled out of court, sharing the cost of site remediation equitably.

Example #4: Non-Age-Dating Applications of Lead Isotopes—Tracing Unleaded Gasoline and Dissolved-Phase BTEX/MtBE

Scenarios

"Unleaded" gasoline spills from operating service stations (California, New Jersey, Washington) were suspected of impacting local groundwater resources with dissolved-phase BTEX and MtBE. Each service station owner denied responsibility. It was necessary for us to ascertain the source of the dissolved-phase gasoline constituents. Was a release of dispensed unleaded gasoline from a suspect service station the source of BTEX/MtBE?

As observed in the southern California case study and through laboratory gasoline/water exchange experiments (Hurst et al., 2001), water-soluble gasoline constituents, BTEX/MtBE, carry lead derived from their gasoline source into groundwater without changing (i.e., fractionating) the lead-isotopic signature of the source leaded or unleaded gasoline. Furthermore, while natural (unimpacted) groundwater lead concentrations are very low, typically <1 ppb, gasoline-derived lead that enters groundwater via "hitchhiking" on these water-soluble organic phases raises groundwater lead concentrations by orders of magnitude, which "swamps out" the natural lead.

FIGURE 3. *Midwestern U.S. Case Study. Lead isotope discrimination diagram identifying two distinct sources of leaded gasoline in a large, commingled plume. Note that lead isotopes can be used effectively with organic geochemical analyses to discern the number of sources, the age of each source, and apportion liability to operators.*

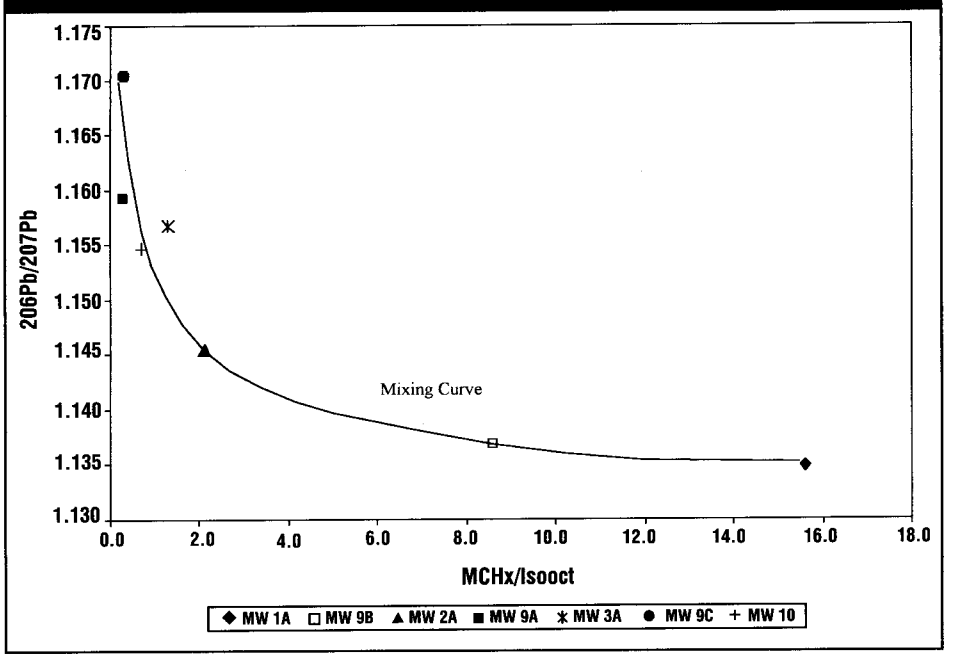
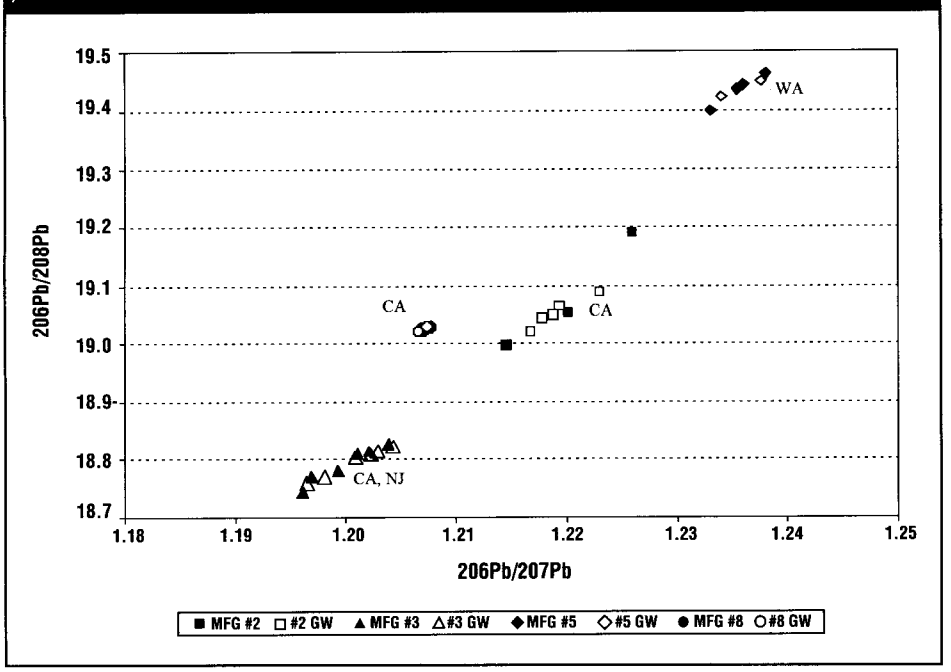


FIGURE 4. *Lead Isotope Ratios of Unleaded Gasoline and Dissolved Phase MtBE/BTEX. The strong similarity between lead isotope ratios of unleaded gasoline suspected of impacting groundwater and MtBE/BTEX-impacted groundwater demonstrates the application of lead isotopes to fingerprint such release.*



What this all means, isotopically speaking, is that measured lead-isotope ratios of gasoline-impacted groundwater bear the lead-isotopic ratios (the fingerprint) of the offending gasoline rather than those of natural lead in the area (Hurst et al., 2001; Hurst 2002a). With this determination we can now identify the source of the dissolved phase via comparative isotopic fingerprinting.

Lead Data

At each site, samples of dispensed unleaded gasolines (all grades) from the suspected source of free product and gasoline-impacted groundwater located downgradient were collected and analyzed. The results are plotted in Figure 4 on a lead-isotope discrimination diagram (sample designations are dispensed unleaded gasoline from different manufacturers).

Figure 4 shows that in each case the lead-isotopic ratios of gasoline-impacted groundwater containing dissolved-phase BTEX and MtBE form a well-defined cluster with those of unleaded gasoline dispensed by the service station suspected of being the source of the release. For example, unleaded gasoline dispensed by MFG #2 is isotopically indistinguishable from downgradient gasoline-impacted groundwater, #2 GW. The minimum lead concentration of gasoline-impacted groundwater at any site was ~ 10 ppb, with maxima ranging up to ~ 150 ppb. By comparison, at each site of concern, lead concentrations of unimpacted groundwater were significantly lower (0.08 to 0.95 ppb), indicating the predominance of gasoline-derived lead in groundwater.

The unleaded gasoline-groundwater data indicate that lead-isotopic ratios of water-soluble unleaded gasoline components, such as BTEX and MtBE, carry the isotopic signature of their source into groundwater. At each site, given the agreement between the lead isotope ratios of the dispensed unleaded gasolines and those of MtBE/BTEX-impacted groundwater, the current service station owner at the site was designated as the responsible party and required by the appropriate environmental agency to remediate the gasoline-impacted groundwater.

What Can We Learn from the Case Studies?

The results of the case studies presented here, as well as results from numerous investigations involving free product releases throughout the U.S. (see Part I), exemplify the utility and accuracy of the ALAS Model as a tool in forensic investigations in which estimates of the age and identification of sources of leaded-gasoline releases are an important issue.

Lead isotopes can also help us to discriminate among sources of dissolved-phase hydrocarbons (e.g., MtBE and BTEX) in groundwater.

■ *continued on page 23*

Making Sense of Subsurface Vapor Attenuation in Petroleum Hydrocarbon Sources

by Robin Davis

Many of us in the profession of managing petroleum leaks from underground storage systems have pondered the question of why there are so many contaminated sites due to leaks from these systems, including sites where buildings overlie the contamination, yet so few sites where vapor intrusion into overlying buildings is actually detected. Issues associated with the vapor-intrusion exposure pathway generated considerable interest with the advent of Risk-Based Corrective Action (RBCA) evaluations. These evaluations typically use the Johnson Ettinger model (J&E) (Johnson and Ettinger, 1991) to estimate concentrations of contaminants that may remain in place without causing human exposure to vapors due to vapor intrusion to indoor air.

The J&E model is an excellent screening tool; however, it often predicts results indicating that the vapor-intrusion pathway is complete when that pathway may be incomplete. This overprediction may be due to the fact that the model does not account for biodegradation and the resulting attenuation of petroleum vapors that takes place in the subsurface before those vapors reach an overlying receptor.

The U.S. EPA published draft guidance entitled "Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils" in November 2002 that advocates the use of the J&E model. Recognizing that the November 2002 guidance may be overly conservative at petroleum sites, the U.S. EPA formed a work group in early 2004 to study the behavior of petroleum products in subsurface soil. As a member of this group, I reviewed and compiled multidepth vapor data from numerous published references and public-domain documents to evaluate biodegradation of petroleum vapors in the subsurface. This paper presents the results of the compilation.

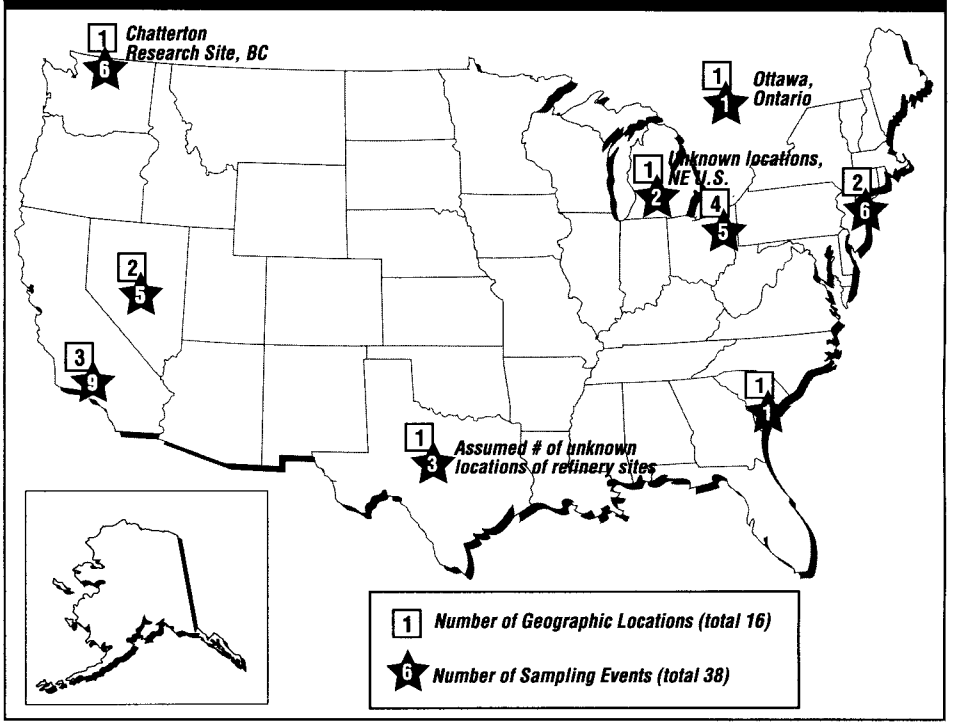
Data Compilation

The references I reviewed contained data for 38 vapor-sampling events. The events took place at 32 individual sample points from 16 separate geographic locations in the U.S. and Canada. Four of the sample points had multiple sample events over time. Thirteen of the sampling events included analysis of both benzene and total petroleum hydrocarbons (TPH). Benzene vapor concentrations were reported for 29 sampling events; TPH vapor concentrations were reported for 22 events. Figure 1 shows a map of the 16 geographic locations where 38 multi-depth vapor-sampling events took place.

Table 1 lists the 38 sample events where multidepth concentrations of vapor-phase benzene and/or TPH were measured and the attenuation factors calculated for each event. Attenuation factors were calculated for benzene and TPH for an individual event by dividing the vapor concentration collected from the shallowest location at a sample point by the vapor concentration collected from the deepest location at the same sample point.

Most of the events included measurement of oxygen and carbon dioxide and a record of soil type. Benzene and TPH concentrations in the soil and groundwater and presence of free-phase product on groundwater were noted where available. Type of ground cover overlying contaminant sources was also tabulated, including presence or absence of pavement or buildings. This information is important because of a concern that pavement and buildings may block oxygen exchange between the atmosphere and the subsurface, potentially causing vapors to accumulate in the building or under the slab (Laubacher, et al., 1997; Hers, et al., 2000; Chuck Schmidt, personal communication, 2004).

FIGURE 1



Data Reduction and Results

The data indicate that biodegradation is a likely mechanism of petroleum vapor attenuation in the subsurface. The following sections describe the data collected and the nature of attenuation at the sampling events.

■ continued on page 12

TABLE 1

SAMPLE POINTS, CONSTITUENTS ANALYZED AND ATTENUATION FACTORS [1]

Site Name	Soil Type	CO_2[2]	O_2[3]	Adsorbed Benzene	Adsorbed TPH[4]	Dissolved Benzene	Dissolved TPH	Vapor Benzene AF[5]	Vapor TPH AF
Refinery VW-93	Sand and gravel with fine-to-medium sand	X	X					0.05	0.00001
Refinery VW-96	Sand and gravel, permeable, with clayey sand and gravel	X	X					0.0007	0.0002
Refinery VW-99	Sand and gravel	X	X					0.00004	0.0002
Akron, Ohio VMP-1	Sand, silty sand with clayey silt	X	X		X			0.002	0.001
Akron, Ohio VMP-2	Sand, silty sand with clayey silt	X	X		X			0.004	0.004
Columbiana, Ohio VMP-1	Silt and sandy silt	X	X		X			0.0004	0.01
Conneaut, Ohio VMP-1	Sand and silty sand	X	X		X			0.7	1.2
Kent, Ohio VMP-1	Clayey sand and gravelly sand	X	X		X			0.002	0.002
Paulsboro, New Jersey Site (Area) 1A	Sand, fine-medium-grained, minor silt and coarse sand	X	X			X		0.00001	
Paulsboro, New Jersey Site (Area) 2	Sand, fine-medium-grained, minor silt and coarse sand	X	X			X		0.00003	
Paulsboro, New Jersey Site D	Sand, fine-medium-grained, minor silt and coarse sand	X	X					0.5	
Port Hueneme, Calif. MP 7, Site 1, source area 7/98	Silts and sands	X	X						1.3
Port Hueneme, Calif. MP 7, Site 1, source area, 8/98	Silts and sands	X	X						0.6
Port Hueneme, Calif. MP 12, Site 1, source area, 7/98	Silts and sands	X	X						0.01
Port Hueneme, Calif. MP 12, Site 1, source area, 8/98	Silts and sands	X	X						1.3
Port Hueneme, Calif. VPo, Site 2, source area, 7/98	Silts and sands	X	X	X	X	X			0.00006
Handi Mart, Midvale, Utah	Sand, fine-to-coarse	X	X	X	X	X	X		0.02
Hal's, Green River, Utah, VW-3	Silt and clayey silt							0.01	0.02
Hal's, Green River, Utah, VW-5	Silt and clayey silt			X	X	X	X	0.0001	0.0004
Hal's, Green River, Utah, VW-10	Silt and clayey silt					X	X	0.00004	0.0002
Hal's, Green River, Utah, VW-11	Silt and clayey silt			X	X	X	X	0.003	0.004
Beaufort, South Carolina, NJ-VW2	Silt and fine-grained sand	X	X			X	X	0.02	0.0008
Coachella, Calif., COA-2	Sand (very permeable) with several thin interbeds of clayey silt	X	X					0.0001	
Coachella, Calif., COA-3	Sand (very permeable) with several thin interbeds of clayey silt	X	X					0.0001	
Huntington Beach, Calif., HB-3	Sand, coarse-grained	X	X					0.00008	
Huntington Beach, Calif., HB-5	Sand, coarse-grained	X	X	X	X			0.00009	
Chatterton, British Columbia, SG-BC, 9/2/97	Fill (dredged river sand)							0.0006	
Chatterton, British Columbia, SG-BC, 10/97	Fill (dredged river sand)		X					0.00002	
Chatterton, British Columbia, SG-BR, 5/97	Fill (dredged river sand)		X					0.001	
Chatterton, British Columbia, SG-BR, 6/24/97	Fill (dredged river sand)							0.00002	
Chatterton, British Columbia, S G-BR, 7/2/97	Fill (dredged river sand)							0.00001	
Chatterton, British Columbia, SG-BR, 12/1/97	Fill (dredged river sand)							0.002	
NE U.S. SVMP-1A	Sand, fine- to coarse-grained	X	X	X	X	X	X		0.01
NE U.S. Basement Location A	Sand, fine-to-coarse-grained	X	X						1.0
GP-01, Ottawa, Ontario	Clay	X	X		X				0.3
Stafford, New Jersey Building #73 and VP-9	Sand		X	X		X		0.001	
Stafford, New Jersey Building #63, VP-13	Sand		X	X		X		0.00008	
Stafford, New Jersey Building #14, VP-10	Sand					X		0.001	

NOTES

[1] X indicates constituent was analyzed at multiple depths
[2] CO_2 = Carbon dioxide
[3] O_2 = Oxygen
[4] Total petroleum hydrocarbons
[5] Vapor Attenuation Factor

TABLE 2 EVALUATION OF VAPOR ATTENUATION DATA FOR BENZENE AND TPH

Constituents	Number of Sample Events	Number of Sample Events with *Significant* Attenuation (<0.05)	% of Sample Events with *Significant* Attenuation (<0.05)	Number of Sample Events with *Insignificant* Attenuation (>0.1)	% of Sample Events with *Insignificant* Attenuation (>0.1)
Benzene	29	27	93%	2	7%
TPH	22	16	73%	6	27%

■ **Vapor Attenuation** *from page 10*

Sampling events exhibiting significant attenuation of benzene and TPH

Table 2 shows that 93 percent and 73 percent of the sampling events that analyzed for multidepth benzene and TPH vapors, respectively, exhibit vapor attenuation factors of 0.05 or less. Attenuation factors range from 0.05 to 0.00001. I consider these events to represent "significant attenuation" because the contaminant vapor concentrations decrease significantly upward from a contaminant source.

Events where significant attenuation was observed exhibited all of the following distinct characteristics:

- At least two feet of uncontaminated soil overlie the contaminant source.
- Hydrocarbon vapors decrease significantly away from the source.
- Oxygen is present in concentrations ranging from 5 to 10 percent.
- Oxygen depletion and carbon dioxide enrichment occur near the contaminant source, and gradual oxygen enrichment and carbon dioxide depletion take place with increasing upward vertical distance from the source.

Figures 2 and 3 show some typical sampling events where significant attenuation occurred in the presence of the distinct signature characteristics described above.

Sampling events exhibiting insignificant benzene attenuation

Insignificant attenuation is represented by the lack of upward-decreasing contaminant vapor concentrations and is associated with those sampling events exhibiting attenuation factors of 0.1 or greater. Attenuation factors range from 0.1 to 1.3. In every sampling event evaluated in this study where insignificant attenuation was observed, one or more of the following characteristics existed:

- No uncontaminated soil overlays the contaminant source.
- Little or no change in contaminant vapor concentrations takes place upward from the contaminant source.
- Oxygen concentrations are less than 5 to 10 percent.
- Oxygen depletion and carbon dioxide enrichment is constant.

Figures 4 and 5 show the characteristics of some representative events where no significant attenuation was observed. Of the 29 events where benzene was analyzed, only two (7%) exhibited little or no attenuation, with attenuation factors of 0.1 or more. Despite the low percentage of attenuation in these events, any route benzene could take through a complete exposure pathway warranted some serious discussion, because benzene is a known human carcinogen. Those two benzene sample events exhibit the following characteristics:

- **Paulsboro, New Jersey, Site D** (Figure 4): This event took place beneath a building where no clean soil overlies the contaminant source, as evidenced by constant high benzene vapor concentrations and constant oxygen depletion and carbon dioxide enrichment vertically upward through the soil column.
- **Conneaut, Ohio, VMP-1** (Figure 5): This event shows fairly constant contaminant concentrations and strong oxygen depletion and carbon dioxide enrichment, indicating that no clean soil overlies the source.

Sample events exhibiting insignificant TPH attenuation

TPH vapor attenuation was evaluated in the 22 events where TPH vapor was analyzed. Six events, or 27 percent of the TPH vapor sample events, exhibited insignificant attenuation. All of those events exhibited all of the signature characteristics of insignificant attenuation.

Evaluation of attenuation based on ground-surface cover

The type of ground-surface cover is known for 27 of the 29 events analyzed for benzene, and all 22 of the events where TPH was analyzed. Significant attenuation of benzene was observed at ten paved sites, ten unpaved sites, and beneath five buildings. Insignificant attenuation of benzene was observed at one paved site, no unpaved sites, and beneath one building.

Significant attenuation of TPH was observed at eight paved sites, eight unpaved sites, and none beneath a building. Insignificant attenuation of TPH was observed at five paved sites, no unpaved sites, and beneath one building.

These data do little to assist in making determinations about vapor attenuation and ground-surface cover. The Coachella data (Table 1), for example, exhibit significant attenuation under both paved and unpaved surface cover, and no build-up of vapors beneath the pavement. Similarly, the Chatterton data exhibited significant attenuation both under bare soil and beneath the building. The Stafford data collected beneath buildings #73, #63 and #14 all exhibited significant attenuation. These data serve to demonstrate that more information is needed at a

■ *continued on page 14*

FIGURE 2

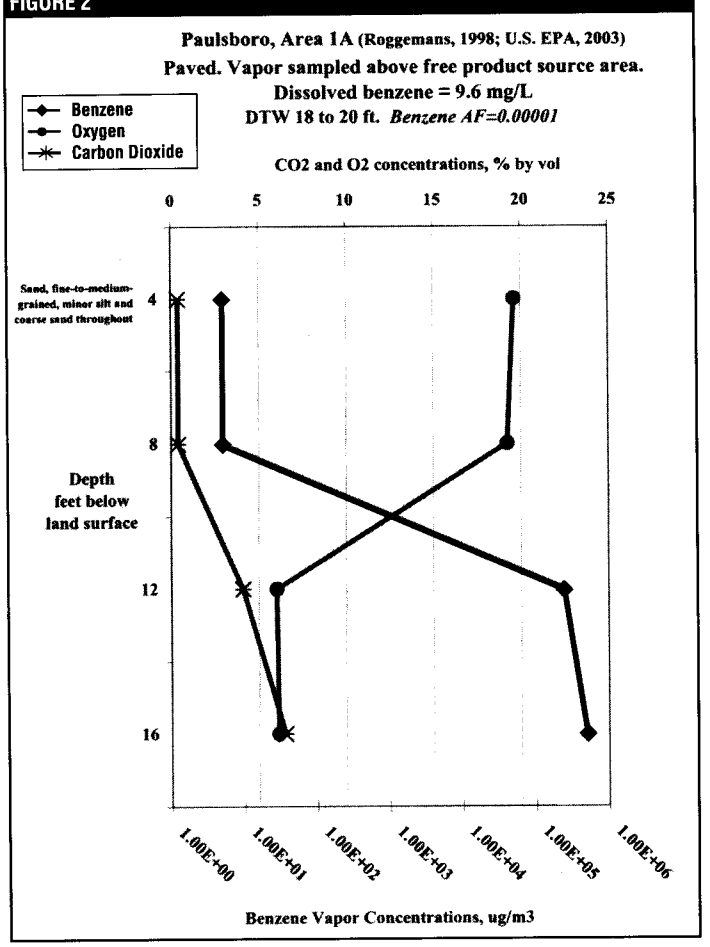


FIGURE 3

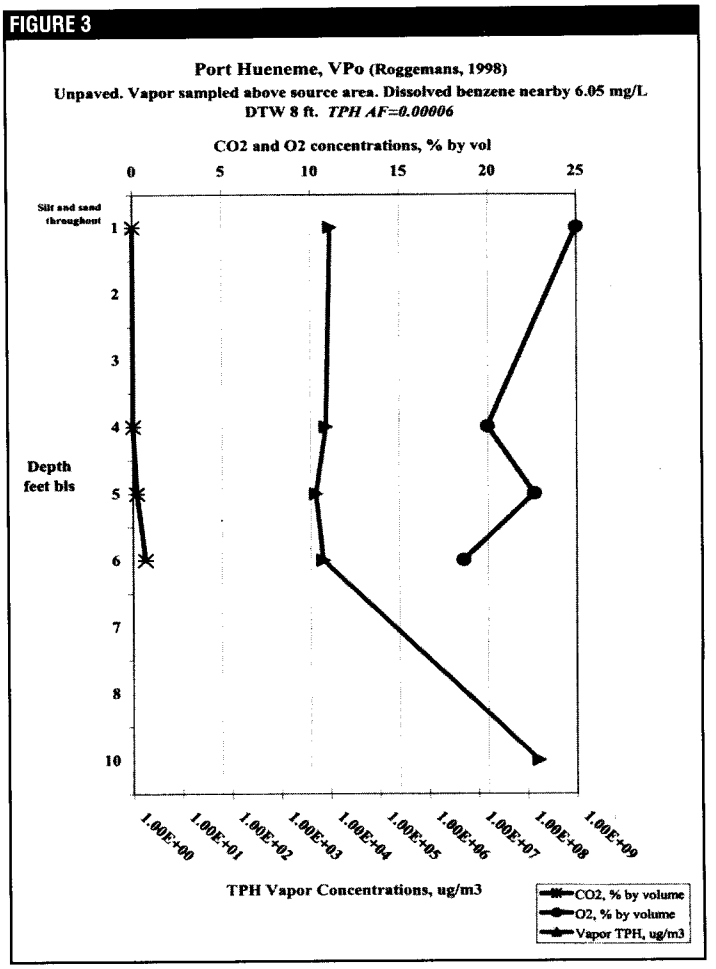


FIGURE 4

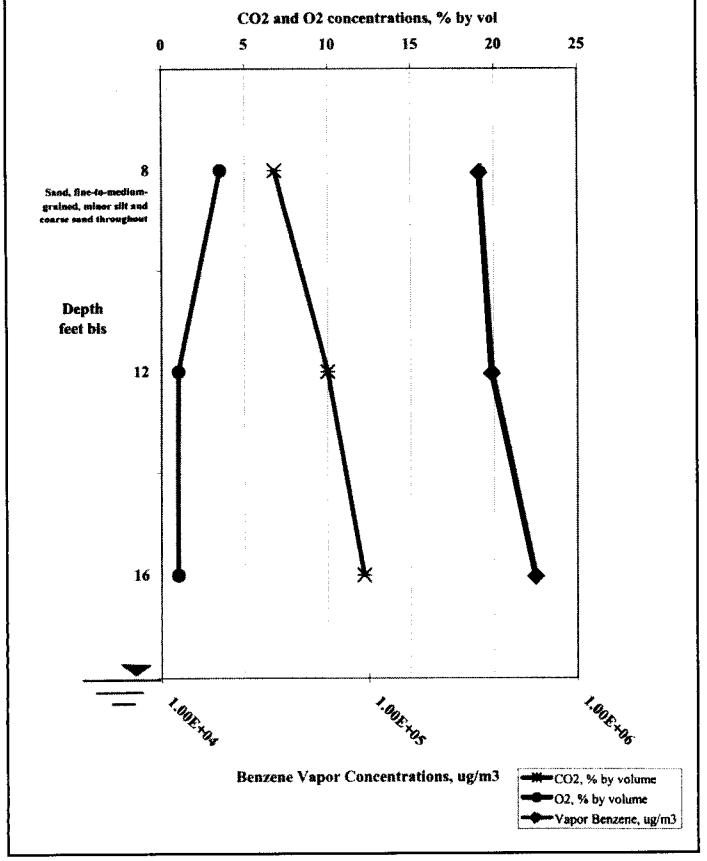
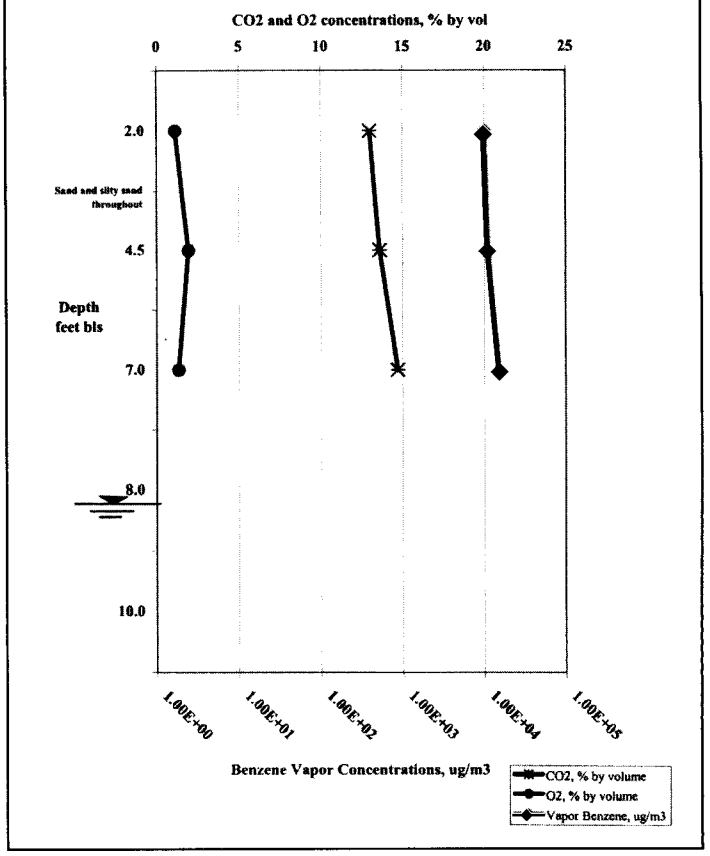


FIGURE 5



■ **Vapor Attenuation** *from page 12*

greater number of sites with various types of ground-surface cover.

Evaluation of attenuation based on soil type

All of the sample events took place in relatively permeable soil such as gravel, sand, and silt. The one exception was GP-01, Ottawa, Ontario, which took place in clayey soil (Table 1). This sample event exhibited insignificant attenuation of TPH, but TPH vapors were not measured throughout the entire soil column. Overall, the results of this analysis show that attenuation takes place in coarse soil types such as sand and gravel. These results, however, also indicate that there is not enough data to conclude anything about attenuation in fine-grained soil due to inconsistencies in multilevel sample collection.

Limitations and Uncertainties

The data compiled for this study show evidence that petroleum vapors are being biodegraded at many of the sampling points where clean soil overlies a contaminant source and where oxygen is present between 5 and 10 percent. Despite the relatively large data set analyzed in this study, there is still some uncertainty as to why some data do not exhibit subsurface vapor attenuation. The following information is needed to reduce these uncertainties:

- More data collected from a greater number of geographic locations because of regional variability in subsurface soil types
- Analysis of benzene, TPH, oxygen, and carbon dioxide from all sample points
- More sampling events per sample point to understand potential temporal variability of attenuation
- Consistency in data collection for multiple sampling events, including sampling at the same depths for each event
- A better understanding of the potential for vapors to accumulate beneath buildings to determine if replenishment of oxygen to the subsurface is impeded by overlying pavement and buildings and if building ventilation systems have an effect on vapor behavior in the subsurface

Moving Forward in Making Important Decisions

The findings of this study indicate that biodegradation of petroleum hydrocarbon vapors is a probable mechanism of attenuation in subsurface soils. These finding are consistent with other similar studies and show that the vapor intrusion pathway may not be complete at sites where at least two feet of uncontaminated soil overlies the contaminant source, and subsurface oxygen concentrations are 5 percent or greater. The results of this study show that bioattenuation factors can be evaluated at leaking UST sites and incorporated into the J&E model.

While evaluation of the vapor intrusion pathway is site-specific, and the question of why attenuation is not observed at some sites remains unanswered, some helpful strategies for managing sites where vapor intrusion may be a complete pathway include: the use of multidepth vapor sampling outside a building foundation to determine if the positive indicators of attenuation are present (Hartman, 2004; Hartman, 2005 personal communication); the use of more intrusive investigative techniques such as sub-slab soil vapor sampling if those indicators are not present or are inconclusive; and/or installing a vapor-extraction system.

Disclaimer

Any opinion expressed herein is that of the author and does not represent opinions of the State of Utah or the U.S. EPA.

Acknowledgements

I am grateful for the support provided by Joe Vescio, U.S. Environmental Protection Agency; John Menatti, Utah Department of Environmental Quality; Adam Harris, California State Water Resources Control Board; Dr. Paul Sanders, New Jersey Department of Environmental Protection; Dr. Chuck Schmidt; Dr. Blayne Hartman; and Dr. Todd Ririe. ■

Robin Davis is a Project Manager with the Utah Department of Environmental Quality, Leaking Underground Storage Tank program and member of EPA's petroleum hydrocarbon vapor intrusion workgroup. She specializes in fate and transport of petroleum hydrocarbons and data acquisition, reduction and analysis, most recently for the vapor intrusion exposure pathway. Robin can be reached at (801) 536-4177 or rvdavis@utah.gov.

References

American Society for Testing and Materials (ASTM). 1995. Standard guide for risk-based corrective action applied at petroleum release sites. E 1739-95.

Dupont, R. R., 2000, Final data summary report of in situ respiration test/bioventing system design evaluation, Utah State University, Division of Environmental Engineering.

Hartman, B., 2004, How to collect reliable soil-gas data for risk-based applications-Specifially Vapor Intrusion, Part 3-Answers to frequently asked questions. *LUSTLine* Bulletin 48, November 2004.

Hartman, B. 2005, personal communication

Hers, I., J. Atwater, L. Li, and R. Zapf-Gilje, 2000, Evaluation of vadose zone biodegradation of BTX vapours, *Journal of Contaminant Hydrology*, 46 (2000): 233-264.

Johnson, P.C. and R.A. Ettinger, 1991. Heuristic model for predicting the intrusion rate of contaminant vapors into buildings, *Environmental Science Technology* 25, 1445-1452.

Lahvis, M. A., A. L. Baehr, and R. J. Baker, 1999, Quantification of aerobic biodegradation and volatilization rates of gasoline hydrocarbons near the water table under natural attenuation conditions, *Water Resources Research*, 35, No. 3, 753-765.

Laubacher, R. C., P. Bartholomae, P. Velasco, and H. J. Reisinger, 1997, An evaluation of the vapor profile in the vadose zone above a gasoline plume, *Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water*, November.

Pearce, P., W. Parker, and P.Van Geel, 2002. Long term monitoring of hydrocarbon contamination using multi-level vapor phase piezometers, Environmental Forensics volume 3 p. 163:177.

Ririe, G. T., R. E. Sweeney, and S. J. Daugherty, 2002, A comparison of hydrocarbon vapor attenuation in the field with predictions from vapor diffusion models, *Soil and Sediment Contamination*, AEHS publishers, No. 11(4): 529-554.

Roggemans, S. 1998, Natural attenuation of hydrocarbon vapors in the vadose zone, thesis for Master of Science, Arizona State University.

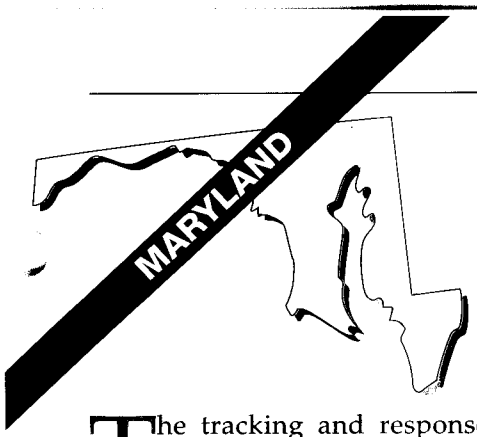
Roggemans, S., C.L. Bruce, P.C. Johnson, and R.L. Johnson, 2001, Vadose zone natural attenuation of hydrocarbon vapors: An empirical assessment of soil gas vertical profile data. *American Petroleum Institute*, December 2001, No. 15.

Sanders, P., I. Hers, M. Lewis, 2004, Investigation of vapor intrusion in homes over petroleum-contaminated groundwater in Stafford Township, New Jersey. Presented at the March 15, 2004 Vapor Intrusion Workshop, San Diego, California.

Schmidt, C.E., 2004, personal communication.

SECOR International, 2004, Soil vapor sampling report for Hal's Chevron, 138 W. Main St., Green River, Utah, March 5, 2004, prepared for the Utah Department of Environmental Quality, Leaking Underground Storage Tank Section.

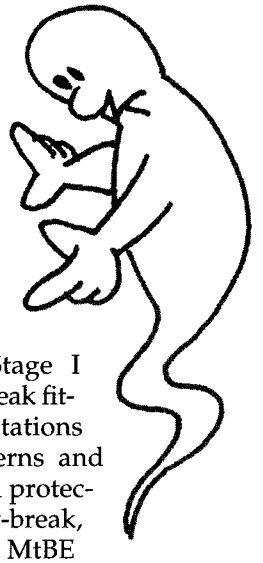
U.S. EPA, 2003, Indoor Air Vapor Intrusion database.



Maryland's MtBE Journey

As States Continue to Tackle the MtBE Problem on Their Own...

by Herbert Meade



The tracking and response to MtBE contaminations in Maryland has been an interesting journey for those of us at the Maryland Department of the Environment (MDE) Oil Control Program. This journey continues with the proposal of changes to Maryland's UST regulations that will increase the level of monitoring associated with gasoline storage tanks.

As background, over the past several years, MDE has seen an increase in groundwater cases that involve the gasoline additive MtBE. MtBE makes up to 11 to 15 percent by volume of the gasoline sold in Maryland as oxygenated gasoline, a.k.a. reformulated gasoline, used to meet the federal Clean Air Act requirement for reducing carbon monoxide and volatile organic compound emissions. In Maryland this type of gasoline is required to be sold in the most highly populated central portions of our state. However, MDE has found that all gasoline in Maryland contains some level of MtBE.

Tracking MtBE

Since 1998, MDE has separately tracked the number of known private wells impacted with MtBE across Maryland. These well impacts come to our attention through data collected from LUST site remediation activities, private homeowner sampling, or sometimes through routine evaluations by local health officials. Our data indicate that more than 600 private wells have been impacted with MtBE at 5 ppb or higher. Additional data show that approximately 20 public water supply wells have been impacted in the state.

Except for Anne Arundel County, the largest impacts tend to be across the top of the state in areas with fractured rock geology—Harford, Cecil, Carroll, Baltimore, and Frederick counties. The geology in these counties allows for the rapid transport and spread of MtBE in the groundwater. The MtBE impacts in Anne Arundel County, which has coastal plain geology, may have to do with the large number of shallow wells still in use.

Action Levels

In the early 1990s, Maryland established a 50 ppb action level for MtBE. The current state action level for MtBE is 20 ppb. This level is not an MCL but a level where a water treatment or alternative source should be secured. Our investigation level, at which we formally open a case for investigation activities, is 10 ppb.

The Sources?

MtBE by its nature is hydrophilic. In the early 1980s, MDE was seeing MtBE as the leading-edge component of groundwater gasoline contamination plumes. MtBE would be the precursor to other gasoline components, such as benzene and toluene. The sources of these early plumes were normally traced back to a liquid release from a gasoline UST system.

In the early 1990s, we noticed MtBE contamination from other sources, such as home heating oil tanks and underground diesel fuel tanks. We determined that MtBE had cross-contaminated into all petroleum products shipped in bulk. Today, approximately half of our groundwater MtBE cases can be traced back to a nongasoline source, such as a privately owned home heating oil tank. However, the largest numbers of impacted wells continue to be gasoline-UST related.

In the late 1990s, MDE observed an unusual occurrence at service stations in our state. We noticed MtBE levels in the groundwater around service stations that were in full compliance with state and federal regulations. All of these stations had complied with the storage system upgrade requirements and deadline of 1998. We attributed these contaminations to poor maintenance of overfill catchment basins, lack of sumps under dispensers, poor product handling by the public, and lack of containment around the Stage I vapor recovery dry break fitting. Even after the stations addressed our concerns and we mandated overfill protection at the Stage I dry-break, we saw the trend of MtBE impacts continue to climb.

Indeed, many UST regulators recognize that a good many compliant tanks are likely to be leaking, but below the leak detection threshold of 0.2 gallons per hour (which is equivalent to 1,752 gallons per year...and at 11 to 15 percent MtBE, this means that 193 to 263 gallons of MtBE per tank may be released into the environment)

In early 2000, MDE technical staff felt that a contributor to MtBE in the groundwater at these stations was the release of enriched MtBE vapors into the storage tank backfill. However, without the resources to conduct scientific studies, our concerns fell on deaf ears. The theory of MtBE vapor causing groundwater contamination has finally been substantiated by studies conducted in other states, such as California, New Hampshire, and Vermont.

At a lot of our sites we are seeing that underground gasoline storage systems that utilize Stage II vacuum-assist vapor recovery systems, which recover gasoline vapors from motor vehicles during fueling and return those vapors to the facility's storage system, are being continuously pressurized. These storage tanks were never designed as pressure vessels but as liquid-containing devices. The pressure is forcing MtBE-enriched gasoline vapors into the tank backfill area.

■ *continued on page 16*

■ **Maryland and MtBE** *from page 15*

Once out of the storage system, hydrophilic MtBE seeks soil moisture, attaches to the soil water droplets, and ultimately contaminates the groundwater. By the nature of service station construction, soils surrounding the storage tanks do not vent into the atmosphere. The vapors are retained subsurface by the concrete caps over the tank field and the asphalt over the majority, if not all, of the service station lot. MDE has found MtBE as the only contaminant in water under UST backfill at levels as high as 900,000 ppb.

What is MDE doing?

MDE has taken several steps to address the MtBE problem. First, we formally investigate any detection of MtBE at or over 10 ppb. We have a policy agreement with the local county health departments to share all case data for detections over 10 ppb. Historically, we have been able to find a point source for levels over 10 ppb. However, our ability to properly staff such investigations is becoming strained. Levels below 10 ppb are becoming very common across the state and may be attributed to contaminated stormwater runoff, poor petroleum handling, and groundwater recharge.

In August 2004, in response to citizen concerns, Governor Ehrlich asked MDE to write technical regulations that will require early detection and better containment of MtBE within underground gasoline storage systems in "high-risk groundwater use areas." These high-risk groundwater-use areas were defined by MDE in direct response to the MtBE issue in Maryland. All UST construction, containment, and leak detection regulations to date have focused on liquid releases, not vapor. We met with the regulated community, heard citizen concerns, and published our proposed regulations in December 2004. A legislative committee, under emergency conditions, approved these regulations on January 26, 2005.

Emergency Regulations

The emergency regulations focus on all existing and new underground gasoline storage systems in "high-risk groundwater-use areas" of Maryland:

Requirements for New Gasoline UST Systems within the High-Risk Areas

- Install double-walled piping and containment sumps with interstitial monitoring (statewide).
- Install four monitoring pipes in the tank field with connected soil-vapor extraction (SVE) piping.
- Use state-of the art leak detection, including detection for vapor releases, by performing a helium test yearly.
- Sample site water supply well yearly.
- Use of one of the following methods for improved control, detection, and prevention of releases:
  a. three or more monitoring wells and sample yearly
  b. a pressure-control device that maintains the UST's < negative pressure
  c. an SVE system on the tank field
  d. an alternative method approved by the MDE.
- Submit a Corrective Action Plan to MDE if "levels of concern" are detected at any time.

Requirements for Existing Gasoline UST Systems

- Test for vapor leaks by performing a helium test yearly, and test UST catchment basins and containment sumps yearly.
- Install three or more groundwater-monitoring wells.
- Sample site supply well and monitoring wells twice a year.
- Install one of the following:
  a. an SVE system on the tank field
  b. a tank-pressure-control device
  c. an alternative method approved by the MDE.
- Submit a Corrective Action Plan to MDE if "levels of concern" are detected at any time.

Other MDE Actions

- Working with industry to develop new programs to educate the public on petroleum-product handling and home heating oil storage.
- Developing a third-party inspection program that will require the detailed inspection of motor-fuel UST systems across the state. MDE's staffing levels do not allow for frequent inspections. We are averaging three to five years in our current cycle. We hope that this inspection program will note deficiencies in UST operations and ensure that those problems are corrected before releases occur. Our target for implementation is July 2006.
- Continuing to require the remediation of MtBE and other petroleum-contaminated sites across the state. MtBE can be cleaned up; however, the plumes of contamination tend to be larger than petroleum plumes without MtBE, and MtBE resists natural biodegradation. So MtBE cleanups take longer and are more costly.

Unfinished Business

Even with the measures mentioned, the ability of our state to respond to groundwater contamination is lacking in many ways. Our current needs include:

- Improved state laboratory support to analyze samples and turn reports around in a timely manner
- Funding for alternative water supplies or point-of-use filtration systems, where appropriate
- Adequate staff to investigate and oversee groundwater contamination cases.
- Increased oversight of heating oil tanks that should be required to have tightness testing and system upgrades
- A review of Stage II vapor recovery technology
- A review of the use of MtBE as an oxygenate and the overall need for oxygenates in our nation's gasoline supply
- A requirement for VOC sampling before property transfer and occupancy

Actions by Our Elected Officials/MtBE Ban

We suspect that there will be several MtBE-related bills introduced in the Maryland General Assembly this year. These bills may range from resolutions to Congress asking for help to the outright ban on MtBE.

It is simple to say, "Let's just ban MtBE." However, such an action must be carefully considered. If MtBE is banned and the RFG requirement is still in place, then an MtBE ban is the equivalent of mandating ethanol. Both chemicals have environmental and health concerns that need to be weighed, not to mention supply, transport, and market concerns. MDE has not taken a position on the MtBE-versus-ethanol discussion.

Are We in Crisis?

From a public perception standpoint, and if MtBE is in your well water, the answer is yes. Health studies, which are admittedly old, do not show adverse health effects from MtBE at levels that we normally see in impacted drinking water wells. However, we find that any degree of impact is unacceptable to the public involved. We feel that our new technical regulations and increased oversight can prevent and provide early detection of petroleum releases. ■

Herbert Meade is the Administrator of the Oil Control Program, Maryland Department of the Environment. He can be reached at hmeade@mde.state.md.us.

NEW HAMPSHIRE

USGS Study Looks at MtBE Occurrence in Rockingham County, New Hampshire

by Gary Lynn

The U.S. Geological Survey, in cooperation with the state Department of Environmental Services Waste Management Division, completed a cooperative study on the occurrence of MtBE in randomly sampled private and public water supply wells in Rockingham County, New Hampshire. The full study was published in the January 2005 edition of *Environmental Science and Technology* and can be accessed at *http://nh.water.usgs.gov/Publications/2005/es049549e.pdf.*

The occurrence of MtBE in Rockingham County was studied because of the county's high risk for MtBE contamination of water supplies due to its heavy dependence on groundwater for water supplies (94% of residents) and participation in the reformulated gasoline program. The major findings of the report are as follows.

- The frequency of MtBE detections in public water supplies in New Hampshire continues to increase both statewide (12.7% in 2000 to 15.1% in 2002) and in Rockingham County (20.3% to 23.1% in the same time period), based on a 0.5 µg/L detection limit.
- MtBE was frequently detected in both public (40%) and private (21%) water supplies above a 0.2 µg/L detection limit.
- MtBE detections correlated well with the degree of urbanization.
- Public water supply wells located further from underground storage tanks had statistically significantly lower levels of MtBE than wells located closer to tanks.
- MtBE concentrations were higher in relatively deep bedrock wells with low water yields.

In New Hampshire, the percentage of public water supplies with MtBE detections continues to increase. All of the MtBE detections in the study's randomly sampled private wells were below the state's drinking water standard of 13 µg/L; however, 4 of the 120 public water supply wells exceeded the MtBE standard.

The detection of higher concentrations of MtBE in deep bedrock wells was an unexpected finding. There are a number of potential explanations; one of the most plausible explanations is that the deeper wells are in tighter bedrock formations with lower yield. For this reason, they are less likely to significantly dilute water in fractures containing MtBE.

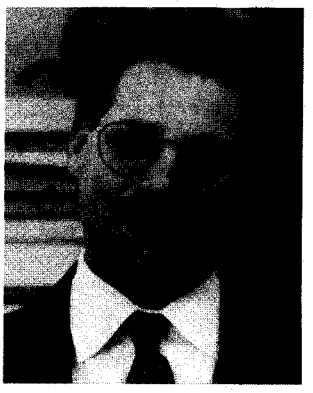
The private well detections did not correlate well with distance from underground storage tanks. These data suggest that there are significant sources of MtBE contamination unrelated to tank-system releases. Based on my personal communications with the study's primary author, Joseph Ayotte, the public water supply MtBE contamination detections correlated better with UST installations than known LUST sites. This unpublished finding establishes that a stronger statistical relationship exists for UST installations versus LUST sites, but does not establish a causal relationship. A potential explanation could be that the UST installations are more commonly associated with high urban densities or other factors that also correlate with MtBE water supply detections.

Another plausible explanation, however, is that UST sites pose a potentially more significant threat to public water supplies than known LUST sites because, (a) existing leak-detection technologies do not detect vapor and small liquid releases from sumps/spill buckets at active installations, (b) UST installations are more numerous than LUST sites, and (c) LUST sites are being actively remediated, while undiscovered releases at active UST installations are not. DES believes that the Rockingham County data tend to confirm the need for our stepped up inspection and leak prevention efforts. ■

Gary Lynn is the Petroleum Remediation Section Manager at the State of New Hampshire Department of Environmental Services. He can be reached at glynn@des.state.nh.us.

A MESSAGE FROM CLIFF ROTHENSTEIN

Director, U.S. EPA Office of Underground Storage Tanks



We're Here To Protect America's Environment

I've been the national tank program director for almost five years, and in my tenure, I've seen outside forces that are significantly impacting our work and how we do it. I think the start of a new year is a good time to reflect on the forces that are changing our program, how we've adapted to meet those changes, and our ultimate job.

The Forces Changing Our Program

Over its 20-plus-year history, the national tank program has been evolving, and it will continue to evolve over the next decade. But during the last five years, I've noted certain factors that are significantly impacting the program.

- **Resources are continuing to tighten.** Both state and federal budgets have gotten tighter over the years. And state tank cleanup funds have come under increased financial pressures. In fact, approximately one-third of the funds have claims exceeding their fund balances and several have experienced fund diversions, leaving less money for tank cleanups.

- **Remaining sites to be cleaned up are more complex.** In the earlier years of the program, cleanups were easier and completed more quickly. We're now seeing that one-half to two-thirds of the remaining sites require groundwater remediation or include technical difficulties because of complicated geology, such as fractured bedrock. These circumstances make cleanups more costly and take longer to complete, compared with soil-only contaminated sites.

- **MtBE is being discovered at two-thirds of all leaking UST sites.** These discoveries result in longer and more costly cleanups. Cleaning up MtBE can double the cost of an average petroleum cleanup—and this increases the demands on limited cleanup dollars. Because MtBE plumes are typically larger than other contamination plumes, cleanup can take as much as one and one-half to three times longer than sites without MtBE. And some states are reopening closed sites and reevaluating for MtBE, diverting resources away from sites not yet cleaned up.

How We've Adapted

In spite of these significant changes, EPA and our tank partners have adapted and developed tools and techniques to help us continue our progress in preventing, detecting, and cleaning up petroleum releases.

We have:

- **Identified opportunities to reuse abandoned gas stations.** Rosalia, Washington, citizens are enjoying a new community visitor center, located at a site that was previously an old, abandoned gas station and an eyesore in their rural community. This reuse scenario is a great example of what stakeholders can accomplish when they partner in order to accomplish a common goal.

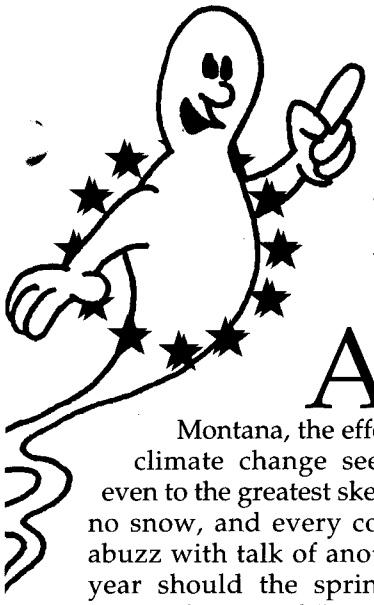
- **Developed ways to improve compliance.** Improved compliance will translate into fewer releases of gasoline products to the environment. To improve compliance, we've developed tools—such as the Environmental Results Program, previously applied to small business sectors like dry cleaners—for use in the tank program.

- **Worked to reduce the cleanup backlog.** Over the last few years, states and U.S. EPA have focused on reducing the cleanup backlog. Now, at less than 130,000 cleanups, the backlog has decreased to its lowest level since 1992.

- **Focused on preventing new leaks.** If we prevent leaks, we'll have fewer cleanups. And as a result of our focus on prevention and compliance, we've seen confirmed releases drop significantly—approximately 35 percent over the last year.

Our Ultimate Job

With the day-to-day crunch of work—be it looking for reuse opportunities, conducting inspections, assessing sites, or cleaning up sites—it's imperative that we remember our ultimate purpose. Our bottom-line job, day after day, is to protect the environment and human health from underground storage tank releases and keep America's land and water clean and safe for all citizens and future generations. ■



The Second European Conference on MtBE: A View from the U.S. Continental Divide

by Jeff Kuhn

As I write this article in Helena, Montana, the effects of global climate change seem tangible, even to the greatest skeptic. There is no snow, and every coffee shop is abuzz with talk of another bad fire year should the spring rains fail again. The annual "Race to the Sky" dogsled race has been cancelled, and our local ski resort has become "the Rock," as we affectionately call it in the spring when the weather warms and the slopes turn to brown rock and bare soil. Only trouble is, it's January. And when it should be 20 degrees below 0 outside, it's 45 above. I find the "tropical" weather very unsettling. It reminds me of other times, other changes.

For example, 1979, the year MtBE was first introduced into the United States—Jimmy Carter was president, U.S. citizens were being held hostage at the embassy in Teheran, and I was an exchange student living in central Germany. It was cold war Europe—détente complete with "Checkpoint Charlie" in Berlin, Russian soldiers garrisoned in most East German cities, and a hated wall that rifted east from west separating many German families.

The New Europe

Twenty-five years later, I found myself back in Europe attending the Second European Conference on MtBE in Barcelona, Spain. Being there was delightful and unsettling—like spring weather in Montana in January. There were obvious cultural changes in Europe since my student days; others I could not quite put my finger on—changes that could only be sensed, like an all-too-early shift in the seasons. Europe was not the same place I remembered. The fall of the Berlin Wall in 1989 signaled the end of the cold war. "Checkpoint Charlie" is now in a museum in Berlin. Since that time the population shift from east to west has deeply affected the fabric of German culture and society and changed the face of Europe as well.

More recently, terrorism touched European soil with the Madrid train bombings, allegedly in retaliation for Spain's support of the U.S. in the war on terror. With this backdrop in mind I was not so sure how Americans would be received at a scientific conference on MtBE in Spain. Our arrival in Barcelona also happened to coincide with the U.S. election results—the headline on Spain's morning paper *La Prada* announced the relection of President Bush.

But in contrast to the political tensions that I expected to encounter, Barcelona was warm and welcoming. Students crowded the streets at night. The cafés were packed. It reminded me more of post-Olympic Game celebrations—the Olympics were held here in 1992. Maybe the party had never stopped. But one thing was sure—the warmth of Barcelona was no illusion.

And the Conference?

The Second European Conference on MtBE was held in a medieval monastery now used by the Institut d'Estudis Catalans—the Institute of Catalonian Studies—a university dedicated to the preservation of the Catalonian language and culture. As one of six Americans who attended the meeting, I was very happy to recognize a number of European colleagues from previous international meetings held in the U.S., and truly appreciated the warm greeting that our group received.

The two-day conference focused on the use of oxygenates in Europe and the successes of various remediation technologies in Europe and the U.S. The meeting provided a platform for researchers, regulatory officials, public agencies, and consultants to present scientific studies, discuss the extent of MtBE contamination in Europe and other countries, compare various remediation alternatives being used, and review innovative treatment technologies implemented in a variety of different pilot projects.

"Where Are the Regulators?"

While the meeting was well attended by academic representatives from many European countries, U.S. participants noted the absence of regulatory representatives. Our inquiries as to their absence led to responses indicating that regulatory representatives did not typically attend such technical meetings. They said regulators often worked independently of the scientific community and had little contact with actual remediation projects.

I was curious how an approach so different from that taken in America was status quo in so many European countries. The most common answer to our question seemed to indicate that stronger divisions exist in Europe between government officials, corporations, and academia. These divisions, in turn, translated to a lack of communication in sharing advances in technologies at a number of different levels.

Differences between languages and cultural identities were much less of an obstacle than I originally anticipated—European society is well adjusted to these challenges and even more so in scientific meetings, where all presentations and discussions occur in English.

Participants and Topics

The scientific organizing committee for the conference included the following individuals: Damia Barceló, IIQAB-CSIC, Barcelona, Spain (chair); Erik Arvin, Technical University of Denmark, Denmark; Peter Werner, Dresden University of Technology, Germany; Thomas Track, DECHEMA, Frankfurt, Germany; Juergen Büsing, European Commission, DG Research, Brussels, Belgium; and Mira Petrovic, IIQAB-

■ *continued on page 20*

■ European MtBE Conference
from page 19

CSIC, Barcelona, Spain (scientific secretary).

The conference included speakers and attendees from Germany, Switzerland, Spain, France, Denmark, Belgium, Lithuania, England, Scotland, the Netherlands, Sweden, Austria, the Czech Republic, and, of course, the U.S. Speakers gave talks in five general subject areas:

- Occurrence fate and behavior of MtBE and other fuel oxygenates in soil-water systems
- Analysis of MtBE in water and soil matrices
- Biotic and abiotic degradation of MtBE
- In-situ and ex-situ treatment of MtBE-contaminated soil and water
- Risk assessment and legal aspects of MtBE contamination

Specific presentations focused on a number of different studies involving MtBE contamination. There were several very interesting presentations involving the Leuna MtBE site located near Halle in the former East Germany. Leuna was the site of a large chemical manufacturing plant that was repeatedly bombed during World War II. The plant later served as a major refining location and produced MtBE for use at service stations in East Germany.

The massive MtBE plume present at the site has been the focus of ongoing research under the European project entitled "METLEN." Martin Bittens (UFZ Germany), who presented an overview of the Leuna site at the National UST/LUST Conference in 2004, was also present at the meeting and coauthored a number of papers presented at the meeting. Other talks focused on the European "WATCH" (Water Catchment Areas: Tools for management and control of hazardous compounds) Program. Talks from the U.S. contingent focused on MtBE remediation projects in New York, New Hamsphire, Montana, and Kansas.

Issues Raised

A Danish colleague, Dr. Erik Arvin (Technical University of Denmark), and I were invited to chair a roundtable session to conclude the meeting and summarize significant issues, problems, and solutions discussed during the session. We prepared a short list of questions for the participants and focused conversation from the audience on each question. Many interesting points were raised, including:

- Concern over the reopening of closed sites in the Netherlands and Denmark, where no previous characterization for MtBE or other oxygenates has occurred. How should this be done and what has been the experience of the U.S.?
- Debate over whether European tank systems are sufficiently designed to prevent MtBE releases.
- Concern from German representatives that Germany and other European Union countries are beginning to increase their use of MtBE and expect that they will see concentrations increase in groundwater.
- Concern from the World Health Organization (WHO) about establishing standards for MtBE and other recalcitrant compounds for European countries in view of other more pressing world needs.
- Debate over whether country-by-country standards are appropriate or whether a broader standard adopted by the European Union would adequately address the needs of each country.
- Discussion about how to disseminate technical information and data on the use of innovative technologies.
- Acknowledgement from most countries that they did not know the extent of groundwater contamination from MtBE, since testing for MtBE has not been required.
- A desire for a greater degree of collaboration on groundwater-contaminant issues between Europe and the U.S.

Catching Up

Many of the arguments discussed during our roundtable discussion were reminiscent of the many debates that occurred in the U.S. as EPA's Blue Ribbon Panel gathered scientific data and public input during its series of meetings in the late 1990s. The wide range of opinions expressed by the European countries was quite similar to those expressed by our states in the early days of the MtBE debate.

At the conclusion of the roundtable, it appeared that most participants were willing to admit that groundwater testing must be completed by each country to determine whether MtBE and other oxygenates should be recognized as compounds of concern in Europe. A hopeful sign, but still an indication that although academic research efforts at sites such as Leuna are quite advanced, European regulatory policy may be lagging 10 years behind the U.S. in the field of oxygenates.

Damia Bacelo from the Institut d'Estudis Catalans, Barcelona, Spain, concluded the meeting with closing comments, thanking all participants, especially the U.S. contingent, whose participation and presentations helped make the conference a great success.

Tearing Down Walls

So what did we take home from Barcelona other than wonderful cuisine and a severe case of jet lag? The end of the cold war has created a huge need for technology transfer in Eastern Europe, especially in the area of contaminant research. European scientists and academic researchers are hungry for U.S. remediation technology, and especially the results of pilot-project research efforts involving innovative technologies. They also want to take advantage of the advances we have made in the development of groundwater-modeling software and learn from our collective research experience—much of which we readily share with the world via the Internet.

As I finish this article, snow is falling again in Helena. Yet, I'm not entirely convinced it's still winter rather than a brief intermission from global climate change. I wonder how

■ *continued on page 31*

Wander LUST

by Patricia Ellis

A roving column by reporter Patricia Ellis, a hydrologist with the Delaware Department of Natural Resources and Environmental Control, Tank Management Branch. Pat served as a member of U.S. EPA's Blue Ribbon Panel on MtBE. She welcomes your comments and suggestions and can be reached at *Patricia.Ellis@state.de.us*.

We Can Do This the Easy Way Or....

A Stream-of-Consciousness Diatribe on LUST Stuff That Can Really Get on Your Nerves

Do you ever feel that there's a little black cloud just following you around, waiting to rain on you every chance it gets? Well, there are certainly days that I do. I guess if life were easy, it wouldn't be very interesting. I'd like to tell you about one of my little black clouds. It's a project that has taken up a considerable amount of my time for about the past two years. Actually, it's taken up a lot more of my time than it should have, because of the actions—or lack of actions—of one of my responsible parties. I've avoided names to protect both the innocent and the guilty.

It all started with a phone call late one Friday afternoon, just before a holiday weekend. (Most problem phone calls come in late on a Friday afternoon, when there are usually only a few people left in the office.) "My water tasted funny," says the caller, "so I had it analyzed, and it has one part per million MtBE and one part per million benzene. What are you going to do about it?"

Of course, the site couldn't have been any farther from the office and still remain in the state. I scramble for the carbon-filter vendor and plead with him to get filters installed ASAP. I'll worry about a purchase order later, when there's someone around to authorize it. Next, I arrange with the lab for glassware and mobilize to sample the nearby wells starting Monday.

ARRGH!! About a week later lab results show that seven more wells are contaminated. How can these people not taste or smell this stuff? So now we need to install more filters and expand the sampling radius even farther.

Eventually, 16 contaminated wells are identified. By now I decide I'd better get a contractor to handle the routine well sampling and filter change-outs, because it's costing me two or three full days per month to handle the sampling. Why are the big sites never anywhere near the office? This one is a two-hour or longer drive each way. (I know, that's no big deal to Big Sky readers.) But, the wells are temporarily under control, even if it means changing out filters every month or two.

Sorting Out the RP(s)

A search of the database shows three nearby operating gas stations. Why is it never just one? Two of the sites have been leakers before. One of the sites had a line break back in the mid 1980s that dumped more than 3,000 gallons of gasoline overnight. Ten years of investigation and remediation later, it got its closure letter. Amazingly, during the entire time that it was an active LUST site, the consultant included MtBE as an analyte—and it was absolutely nondetect the entire time.

About the time that the closure letter was issued, the tanks were removed, and a new property owner installed a new double-walled system. The owner was not very happy with DNREC back when he installed his tanks; he was required to install a double-walled system because he was in a wellhead protection area. At least double-walled tanks should have a decreased chance of leaking, so maybe this one is not the source of well contamination.

The second station had also been a LUST site. At the time that tanks were removed in the mid-1990s and before a new system was installed in the same hole, a moderate amount of overexcavation was done to remove highly contaminated soil. Unfortunately, the limit of reach of the excavation equipment and the water table were both reached at about 20 feet, so a little residual contamination was left in the ground—4,800 ppm BTEX and 2,100 ppm TPH. A few wells were installed at the site, with 12 ppm BTEX being the hottest groundwater sample collected in a year of monitoring in the downgradient-most well.

A quick Bioscreen-modeling run

■ *continued on page 22*

■ **WanderLust** *from page 21*

said the contamination shouldn't go more than about 300 feet. Probably a few assumptions in the model were wrong—like the default grain size. Recent well installations have documented the presence of a few great coarse sand and gravel layers that might help speed things on their way downgradient.

The 12 ppm BTEX as a starting number for the model might not have been a good assumption either, since the plume was not very thoroughly defined. This was coupled with assumptions of first-order decay rates. And, at the time of the earlier project, MtBE was not a required analyte. Well, as it turns out, not just the MtBE has traveled 1,200 feet, but also the benzene.

The consultant for the earlier LUST project also stated that the surrounding area was all served by a public water supply—except that he missed the 200-or-so trailers hidden in the trees directly downgradient of the station. They don't show up on a search of the well permit database because they predate 1968, when the permitting process first began.

I had better feelings about the chances that the third station was not a source. It is about three years old, has double-walled tanks, double-walled pipes, a bells-and-whistles leak-detection system, and an operator with an excellent compliance record in the state and in surrounding states. There actually was another former LUST in the area, but the tanks hadn't been used since 1974, so I doubted that it could have contributed to the MtBE contamination in the wells.

Armed with my consultant, a Geoprobe, and umpteen individual well permits (Geoprobe investigations require well permits for each individual property, signed by the property owner), we set out to finger the guilty party. The investigation narrowed it down to two of the possible sources. Of course, one of them is pretty much directly downgradient of the other. Both have had releases, but have both contributed to the current well contamination? Both RPs were sent notices to begin hydrogeologic investigations to determine the nature and extent of their releases.

Obstruction!

So far, one of the RPs has been very responsive. During several phases of well installation, using multilevel cluster wells to define the plume vertically as well as horizontally, a plume of groundwater contamination has been identified between the station and the impacted wells, and a work plan for remediation is getting its final touches prior to submission to DNREC.

As for the second RP, it's been a totally different story. When DNREC initially conducted its investigation, this RP refused us access for Geoprobe sampling, so we sampled immediately downgradient from his property, and came up with elevated MtBE in the groundwater. That's when he got the letter requiring an investigation.

It was hard to hide my satisfaction when some of the samples came up somewhat smelly, and really hard to keep from gloating when I could smell product as they were drilling from about 30 feet away, and the auger was bringing up dark gray sand instead of light brown sand. At least I didn't jump up and down and sing "I told you so!"

When he didn't respond by the deadline, he got a phone call. He claimed he couldn't possibly have a leak because the #@%##* state made him install a double-walled tank system, and he had no plans to investigate. When he still wouldn't respond, he received a Notice of Violation. Still no investigation.

In the meantime, more impacts were identified in a second cluster of homes with domestic wells located much closer to our problem station. Rather than issuing a Secretary's Order with a penalty, we issued a Notice of Intent to take over the investigation and cost-recover all expenses plus overhead. Finally, he scheduled a meeting with us.

After two hours of discussion and a few threats to walk out of the meeting, our recalcitrant RP still had no answer as to whether or when he would conduct the investigation. A few weeks later, a somewhat wimpy investigation work plan arrived. The plan was short on the required multilevel sampling on the downgradient side of the property, which had been required because of the locations and known depths of some of the impacted wells in the neighborhood nearest the station.

The plan had more than adequate coverage in the upgradient direction, because the RP was intent on showing that his contamination (including the MtBE) had come from the upgradient tanks that were last used in 1974. Rather than reject the plan entirely, we approved it with the condition that additional sampling be conducted at specified deeper intervals on the downgradient side.

Rather than giving the required five days notice prior to fieldwork, the consultant snuck a fax into my office at about 4:55 one afternoon informing me that the investigation work would be conducted the next day. I guess he hadn't counted on my getting the fax in time to show up at the site, but I did make it down there by about 10 a.m.

It was hard to hide my satisfaction when some of the samples came up somewhat smelly, and really hard to keep from gloating when I could smell product as they were drilling from about 30 feet away, and the auger was bringing up dark gray sand instead of light brown sand. At least I didn't jump up and down and sing "I told you so!"

Watch Out for the...Oops

I should mention that the RP had been warned that since he insisted on sticking to the perimeter of his property for drilling, so as not to put any holes in his beautiful asphalt, there was the potential for encountering underground utilities on all four property boundaries.

"Miss Utility" had marked the utilities. On the day of the sampling, the consultant had stepped about two feet off one of the spray-painted markings. Using a 4-inch (in diameter) hand auger, he drilled for about four or five feet to make sure the location was clear. Then, the drill rig was put in place. It had an 8-inch auger. The holes were drilled. The extra diameter was just BIG enough to cut through 275 phone lines out of a bundle of 300.

The phone company trucks showed up about six hours after the

hole was drilled, and when I left the site, they were setting up tents for a long repair session. I'm sure that someone eventually got a hefty bill for that repair. When I'm drilling, I like to avoid the utility mark-outs by at least five feet, but that would have put the hole in the pavement instead of in the grass.

Marching Orders

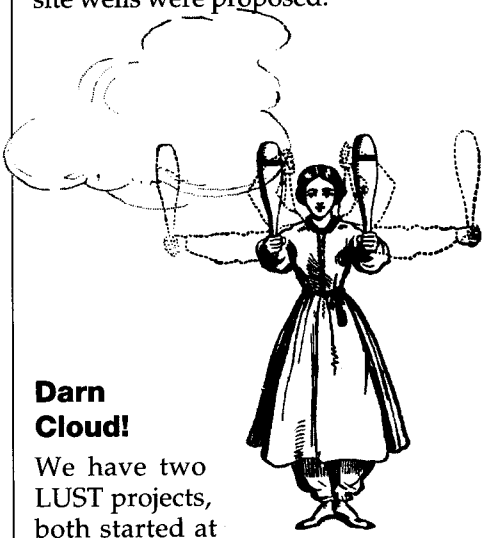
Of course, the sampling report didn't make the 90-day deadline, and it came with absolutely no conclusions or recommendations, even though the first round of samples from the temporary wells showed 380 ppm MtBE at the top of the water table at 20 feet, and 16 ppm MtBE at 40 feet, on the downgradient property boundary.

The next letter to the RP from DNREC provided a detailed set of marching orders with an equally long list of deadlines for getting additional tasks completed, such as installing permanent onsite wells, doing offsite plume delineation, and their taking over the sampling and filter maintenance for wells in the second impacted neighborhood.

One thing we learned from the temporary wells on the site is that there is still a diverging groundwater flow pattern, just as there had been previously when the station was a LUST site. One component of groundwater flow is toward the first station and the first neighborhood of impacted wells. The other component of flow is toward the second neighborhood of impacted wells.

Unfortunately, a six-lane highway runs between the two stations. Between overhead and underground utilities and the highway, it is extremely difficult to find any locations where holes can be drilled between the two stations that would show whether the plume of the "recalcitrant RP" has crossed the highway. Of course, any plume crossing the highway is doing it on a diagonal, so without multiple sampling points on both sides of the highway, it is hard to determine whether the two plumes may be merging in the vicinity of the first station.

Sixteen months after the original letter went out requiring the RP to "determine the full extent of contamination, both laterally and vertically, a workplan was just submitted. It includes several permanent monitoring wells, all onsite, and nothing more. Even though the first round of samples from the temporary wells showed elevated MtBE on the downgradient property boundary, no offsite wells were proposed.



Darn Cloud!

We have two LUST projects, both started at the same time. One of the sites has identified a 1,200-foot long plume and will have a corrective action plan in any day now. The RP at other site is doing everything the hard way—kicking, screaming, protesting, foot-dragging. He has only just figured out that he has had some sort of a release, probably coming from the vicinity of the tank field. In the meantime, another neighborhood's domestic wells have been impacted since the first request to do an investigation.

At the same time, DNREC has been working toward extending a public water line into the first neighborhood. Sixteen wells were impacted, and about 30 homes will be connected to the water line. Some residents aren't very happy about having a water bill in the future. Four people in the neighborhood have been opposed to the water line solution, and of course, it is through one of their properties that we need an easement to extend the line! After five months of negotiations, we have our signed easements and can complete the engineering work needed to bid out the installation.

No end in sight any time soon for this project. Unfortunately, I have two other projects that are about the same scale, one with 25 well impacts and one with 21 impacts, so far, and I am also the project officer for about 70 more LUST projects. ■

■ Isotopic Fingerprints *from page 9*

Both laboratory and field data indicate that water-soluble gasoline constituents carry the lead isotopic signature of the source of a leaded or unleaded gasoline release into groundwater, making the lead-isotopic system a viable method to identify the source as well as trace the fate and transport of MtBE/BTEX in groundwater systems.

Are Other Fuel Releases Datable via the ALAS Model?

Although developed to estimate the age of leaded gasoline releases, the ALAS Model has been successfully applied to age-dating releases of jet-A, diesel, kerosene, motor oil, and heating oil. The condition under which the ALAS Model can be applied to middle/heavy petroleum distillate releases includes situations where fuels are suspected of accidentally acquiring small, yet significant quantities of alkylleads during refining. The condition is recognized when lead in a middle/heavy petroleum distillate exceeds normal concentrations (< few hundred ppb lead). As with unleaded gasoline, lead-isotopic ratios may be used to correlate environmental releases of these products to their source. ■

Richard W. Hurst, Ph.D., is the President of Hurst & Associates, Inc. and has been a Professor of Geology/Geochemistry since 1978 at California State University, Los Angeles. He can be reached at (805) 492-7764 or Alasrwh@aol.com. *Check out his Web site at* www.hurstforensics.com.

References

Hurst, R.W., 2000, Applications of Anthropogenic Lead ArchaeoStratigraphy (ALAS Model) to Hydrocarbon Remediation, *Journal of Environmental Forensics* 1, pp. 11-23.

Hurst, R.W., Barron, D. Washington, M. and Bowring, S.A., 2001, Lead Isotopes as Age Sensitive, Genetic Markers in Hydrocarbons: 1. Co-Partitioning of Lead with MTBE into Water and Implications for MTBE-Source Correlations, *Environmental Geoscience* 8, pp. 242-250.

Hurst, R.W., 2002a, Lead Isotopes as Age Sensitive, Genetic Markers in Hydrocarbons: 2. Kerogens, Crude Oils, and Unleaded Gasoline, *Environmental Geoscience* 9, pp. 1-7.

Hurst, R.W., 2002b, Lead Isotopes as Age Sensitive, Genetic Markers in Hydrocarbons: 3. Leaded Gasoline, 1923-1990, *Environmental Geoscience* 9, pp. 43-50.

Hurst, R.W., 2005, ALAS, A Model for Estimating the Age of Gasoline Releases and Tracing Fuel Oxygenates (e.g. MtBE): Part I. Model Development, *LUSTLine* #48, p. 7.

Tanks Down East

by W. David McCaskill

David McCaskill is an Environmental Engineer with the Maine Department of Environmental Protection (DEP). "Tanks Down East" is a regular feature of LUSTLine. *David can be reached at* David.Mccaskill@maine.gov.
As always, we welcome your comments.

Small Spills Count... THE SPILL DRILL

As with most of Northern New England, Maine has been blessed with abundant water and rocks. Do we have rocks! We've got our famous rock-bound, wave-lashed coast. We've got our springtime crop of rocks popping up in farmers' fields after the winter frost, ready to be transformed into sturdy stone walls. And we've got fractured bedrock with water-filled cracks covered by precious little soil to absorb petroleum-product spills. This generally thin covering of glacially derived soils all too often fails to provide much of a barrier to petroleum contamination that seems to be inevitably attracted to private water wells. More than 50 percent of Mainers receive their drinking water from private wells drilled into fractured bedrock. Because petroleum use and groundwater use often occur in close proximity (think corner store, basement oil tank, lawnmower, and backyard water well), private water wells often serve as unwitting monitoring wells.

In New England, small petroleum spills count, whether they are from underground tank overfills at the corner mom-and-pop convenience store, careless home heating oil deliveries, or a homeowner sloshing gasoline between the gas can and the lawnmower in the backyard. In this edition of "Tanks Downeast" I'm going to discuss some of the strategies that Maine has included in its quiver of groundwater protection tools to target these "little" spills.

Spillage During Deliveries at UST Facilities

According to about two-and-a-half years of Maine DEP's spill records, underground tank overfills make up 40 percent of spills over 10 gallons. Once a tank is overfilled, the spill bucket is the only thing between the driver and a flood of gasoline across the pavement! To understand why this can happen and why it shouldn't happen (in case you haven't come to that realization), let's quickly brush up on the basics of a gravity fuel delivery at a gas station.

Dropping Fuel at a Gas Station

Before anything else happens, the driver should gauge the tank to make sure that the amount of fuel in the truck will fit into the target UST. To begin the delivery, the driver clamps one end of the delivery hose to the tank fill pipe and the other end to the fuel outlet on the bottom of the tank truck. A valve is opened at the truck and because of gravity, fuel flows through the hose. If all goes according to plan, once a compartment on the tank truck is empty, the valve underneath the tank truck is closed, the hose is disconnected from the truck's fuel outlet, and "walked" back to the UST by methodically lifting the hose from the tank truck end to the underground tank end to drain the residual fuel in the hose into the underground tank.

Once a tank is overfilled, the spill bucket is the only thing between the driver and a flood of gasoline across the pavement!

If the overfill prevention device was ignored or bypassed, and if it turns out the UST didn't have enough space to hold all the fuel in the truck compartment, the driver will have about 20 feet of a 4-inch hose that is full of product—about 14 gallons to dispose of. Hmm, how do you cram 14 gallons of fuel into a 3- to 5-gallon spill bucket? Well, you don't.

So it occurred to us that our overfill prevention efforts were not working. (See *LUSTline* #31, "If Only Overfill Prevention Worked," if you want to understand why it doesn't work). We continued to have spills because drivers were trying to squeeze too much product into an UST. We needed to be sure that spill buckets were large enough to hold the contents of a typical delivery hose when overfill prevention equipment failed.

15-Gallon Spill Buckets

Beginning in March 2004, DEP upgraded its UST rules, adding a requirement (among others) that all new UST installations and all replacement spill buckets must have at least a 15-gallon capacity. If, in the case of a replacement, a 15-gallon spill bucket does not fit, then the largest capacity that will fit must be installed.

During testimony on this rule, one oil company representative suggested that the larger spill buckets will encourage delivery drivers to spill more into the spill buckets and therefore increase the maintenance cost for removing and disposing of the gasoline and water mixture. Now maybe we're naïve, but we don't believe that tanker drivers go around surreptitiously filling spill buckets with fuel with a malicious gleam in their eye.

The simple truth is that spill buckets get filled with fuel because drivers have nowhere else to put the fuel. For example, when a driver arrives at a gas station whose owner has ordered too much fuel, he is faced with a knotty decision: Does he refuse to deliver after driving from Searsport to Stonington? Or does he fill the tank, hoping that a cus-

tomer will have arrived and pumped enough gas into her SUV to subtract the difference?

While it may be true that large-capacity spill buckets will increase tank owner maintenance costs, it seems equally true that small-capacity spill buckets increase our cleanup costs. This makes a pretty strong argument to us to (a) have the larger-capacity spill buckets and (b) get all stakeholders involved in figuring out how to avoid having spill buckets full of fuel in the first place. To encourage stakeholder involvement, DEP has decided that training of the delivery drivers by their employers will have to take place!

As to the issue of spill bucket replacement—which is frequently necessary as metal or plastic buckets rust or degrade—contractors were concerned that there would be no room between tank risers to allow for the installation of larger spill buckets. To that end, we have developed a spreadsheet of the dimensions of various makes and models of 10- and 15-gallon spill buckets to aid contractors in selecting a replacement (*http://www.maine.gov/dep/rwm/ust/ pdf/spillbucketdimensions.pdf*). To date, very few problems have been encountered.

Spillage During Deliveries at Home Heating Oil Tanks

Maine has over 415,000 fuel-oil customers, and Maine heating-oil dealers deliver more than 350 million gallons of fuel oil to these customers each year. On average, Maine DEP responds to one heating-oil spill a day at single-family residences. Over the last seven years, we have spent about $300,000 on public and industry outreach in the form of pamphlets, paid television ads, and newspaper ads. Is that too much? Is it too little? In that same time frame we have spent around $9.6 million in cleanup! You compare the numbers and decide.

Our latest outreach effort is a 20-minute training video, *Working Together for Spill Prevention*, directed at fuel-oil delivery drivers and oil-heat technicians. (See sidebar on page 26.) The video covers everything from proper delivery techniques to how to spill-proof basement heating oil tank installations.

Most times, everything works just fine. However, sometimes homeowners move the tank to another area in the basement, but leave the old, now unattached, fill pipe in the exterior wall of the house unbeknownst to the delivery driver!

Dropping Fuel at Home

So, let's go over the anatomy of a residential fuel-oil delivery. Because of the small quantities (100 to 200 gallons) delivered, the fuel-oil delivery operation is very different from the gas station delivery. It resembles the typical automobile-fueling operation, except that the fuel-oil nozzle usually clamps firmly to the fill pipe.

The driver connects a nozzle attached to a long hose coiled on the delivery truck to a fill pipe sticking out of the basement wall and opens a valve on the nozzle that allows the fuel oil to flow. Because the nozzle-to-fill-pipe connection is airtight, as fuel flows into the tank, the air inside the tank is vented out through a separate vent pipe.

Inside the tank, where the vent pipe connects to the tank top, there is a short tube, called a vent whistle, that extends into the tank. As air passes through this whistle tube on its way out the vent, a whistling sound is created. The vent pipe should be located close to the fill pipe so the delivery person can hear the whistling sound.

As the tank fills and the oil level reaches the bottom end of the whistle tube, air exits exclusively through the vent and the whistling sound stops. When the delivery driver doesn't hear the whistle, it's time to shut the nozzle valve.

The whistle is, in a sense, a reverse overfill alarm! The driver then carefully unhooks the nozzle of the hose from the fill pipe and coils the hose back on the reel on the truck. Because the hose has a valve on the end of it, the hose remains full of product between customers, and there is no need to drain it.

So what can go wrong? Most times, everything works just fine. However, sometimes homeowners move the tank to another area in the basement, but leave the old, now unattached, fill pipe in the exterior wall of the house *unbeknownst* to the delivery driver! In this scenerio, the driver's first clue is that no whistle is whistling, but not all tanks have the required whistle—or one that works. I've been told that even without a whistle, the old pros can listen to the sound emitting from the vent and tell when the tank is almost full. But for those without such talented ears, the biggest tip-off to trouble is when 300 gallons have been pumped into the "phantom" 275-gallon tank!

Other problem scenarios involve situations where tanks: (a) are overpressurized and bursting when the vent is blocked, (b) have insufficient capacity, or (c) are overfilled with product (without a whistle, how can you tell when a tank is full?)

Those are delivery-related spills, not to be confused with spills due to "acts of nature"—used in the broad sense. For example, snow and ice can fall from a roof and strike the fuel-outlet fitting and filter (located on the bottom the tank), thus releasing all or some of the contents of the 275-gallon tank. This scenario is restricted to tanks installed outside, but basement tanks can suffer a similar fate—but with dogs and kids substituted for the snow and ice! (See *LUSTLine* #33, "Those Tanks in America's Backyards and Basements.")

Spills During Yard Equipment Filling

In 2003, Maine passed a law to require that all gas cans sold in the state be "spill-proof" as defined by the California Air Resources Board (CARB). The purpose of this rule was to reduce: (a) the amount of volatile organic compounds (VOC) being released into the air due to spills during fuel transfers, (b) volatilization resulting from leaving the cap off the spout while the can is not in use, and (c) vapor diffusion through the walls of the plastic cans. These VOCs contribute to ground-level ozone, and the gas can rule was a component of a suite of regulations adopted by Maine and other New England states to prevent regional ozone problems. An obvious secondary benefit of these rules is that they help prevent small gasoline spills that could impact homeowner drinking water wells.

■ *continued on page 26*

■ **The Spill Drill** *from page 25*

Dropping Fuel into a Lawnmower

To prevent overfills while yard equipment is being filled, the spout of the gas can is designed to automatically shut off flow when the "target" container (e.g., your lawnmower's tank) is full. The spout seals itself off automatically when it's removed from the target tank so you never have to remember to put the cap back on. Finally, the area around the spout is designed to seal with the target container, reducing the release of fuel vapors but allowing air to vent into the gas can through an opening in the spout so gas can flow (sort of like a balance Stage II vapor-recovery system).

There have been problems encountered in some of the designs that have forced CARB to review their specifications. Soon after the Maine rule went into effect, yours truly ran out to purchase what turned out to be (in my opinion) a less-than-perfectly-designed can. The problem with the can I bought is that to dispense fuel the nozzle must be positioned almost vertically into the fill on the lawnmower, then the gas can spout is opened by pressing the can down onto the target container's fill opening. Cans with a round flange around the spout to push against encourage proper use. Those with a tab (like the one I bought) instead of the flange let you cheat by filling at an angle and splashing gas on the side of the lawnmower's fill allowing vapors to escape and increasing the likelihood of a spill.

Education and Outreach

But the best of tools (or regulations) will only take us so far toward success. We have to get people on board so they will comply with the rules rather than resist them. Wth respect to deliveries at UST facilities, the oil industry agreed during a public hearing on the rule to work with DEP to develop some training.

Recognizing that getting drivers into a state-sponsored training class is not likely to happen, but that these folks do get training from their employers on various matters, DEP is planning a "Stop the Spill" seminar/panel discussion this summer for the employers. During this training we will cover topics ranging from-how to train both the home heating oil delivery driver and the homeowner (tank upkeep and maintenanace) to what the transport driver needs to know about overfill devices and spill buckets. Weighty matters for sure.

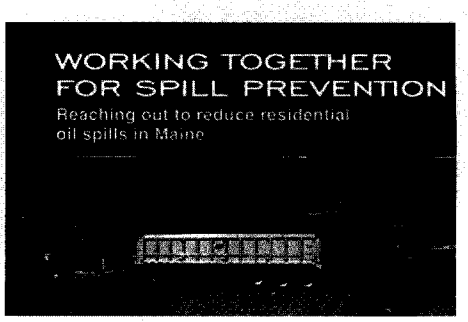
This training will probably be built around our home heating oil delivery video and the still-timely U.S. EPA video, *Keeping It Clean: Making Safe and Spill-Free Motor-Fuel Deliveries*. On the home front, we have already sent out 250 copies of our home heating oil delivery video to all the members of the oil industry trade groups in our state.

Homeowner education is always problematic. However the DEP has a weekly newspaper column entitled "In Our Backyard" that appears in many weekly papers throughout the state. We have used this as a vehicle to reach out to the homeowner on various environmental issues including heating oil tank safety and gasoline handling.

Keep on Chipping

The task of reducing the threat posed by transferring fuel at every level, from 10,000-gallon transport trucks to 3-gallon gas cans, is a difficult one because of the frequency of these kinds of events, the huge number of tanks involved, and the large number of people who carry out the transfers. But in New England, we have to continue to chip away at the problem because small spills count. ■

New Training Video for Fuel Oil Delivery Drivers and Oil Heat Technicians Available from Maine DEP



The Maine Department of Environmental Protection has developed a 20-minute training video, entitled *Working Together for Spill Prevention,* directed at fuel oil delivery drivers and oil heat technicians The video instructs the truck drivers of oil delivery companies on the fine, and rather detailed, art of making a home heating oil delivery and also instructs oil-burner technicians (the people who install, service, and repair furnaces and boilers) on how to spot problems with oil tanks and oil line installations when they are making service calls.

Using one of Maine DEP's crack oil spill responders, Tom Varney, the talents of part-time actor/DEP employee, Robert Demkowicz, and the technical assistance and collaboration of a local oil company, the video details all steps the driver should take to assure a spill-free delivery for both indoor and outdoor tanks.

These steps include checking the label on the fill pipe with the customer number on the delivery ticket, "walking" the delivery path first—without the hose—to assure it is free of obstacles, checking the fill and vent pipe, setting the meter, pulling the hose and attaching it to the fill pipe of the tank, listening for the whistle, stopping the flow when the whistle stops, and recoiling the hose with the nozzle pointing up so no oil drips out.

The finished video was delivered to various oil dealers throughout the state, primarily by the Maine Oil Dealers Association (MODA), a state industry trade group that represents oil dealers and gas station (convenience store) owners. To request a copy of the video or DVD, contact David McCaskill at Maine DEP at (207) 287-7056. ■

Tank-nically Speaking

by Marcel Moreau

*Marcel Moreau is a nationally recognized petroleum storage specialist whose column, **Tank-nically Speaking**, is a regular feature of* LUSTLine. *As always, we welcome your comments and questions. If there are technical issues that you would like to have Marcel discuss, let him know at* **marcel.moreau@juno.com**

Maine – The Way Sumps Should Be

What's Wrong with This Picture?

As I sat in a darkened conference room listening to the groans and snickers of an audience of UST regulators and industry folk viewing a series of decidedly ugly looking tank-top and dispenser sump pictures, I was thinking that the sumps I typically saw in Maine were much better looking than the ones I was seeing in this presentation. It wasn't until some time later that it occurred to me to ask, "Why?" Why is it that containment sumps in Maine are, generally speaking, substantially cleaner, drier, more functional and (presumably) more effective in performing their intended functions?

There was a time, some 20 years ago, when I too used to obtain similar reactions from audiences upon showing them slides of primitive "do-it-yourself" UST installations in Maine. But I would be hard-pressed to find such pictures in Maine today.

Okay, it's true that Maine's tank program is two decades old. Indeed, I would be seriously depressed if, after all this time, the situation in Maine's UST world had not improved. But the federal tank program is only a few years younger than Maine's, and a number of states have tank programs that are as old or older than Maine's.

Why Is Sump Appearance Important?

After all, unlike rest rooms, nobody is grossed out by a gas station because it has dirty sumps. Sump appearance is important because a really dirty sump is generally an indication of the presence of liquid. Typically, the liquid is mostly water (though some amount of product together with the water is not uncommon), and if water is getting in, then product can likely get out.

Also, if water is getting in to a sump, then chances are (a) alarms are going off and being ignored or (b) sensors are being "adjusted" to ensure that these "nuisance" alarms don't happen. Thus, while sump appearance is not the real issue, it is frequently an indication that a sump is not tight, which in turn compromises the ability of a sump to contain a release and/or the effectiveness of the leak warning mechanism.

What Accounts for the Difference in Sump Appearance?

Why do sumps in some states look like slimy swamp scenes from a B-grade *Creature from the Black Lagoon* movie, while sumps in Maine would be quite at home in a movie nominated for an Oscar? Brands of equipment used? The brands are generally the same, so I don't believe this is a factor. Climate? In other parts of the United States, the amount of precipitation may be greater, water tables may be higher, the compaction and weight-bearing properties of the soils may be different, but none of these factors seems very persuasive to me in explaining the difference.

Is the sample of Maine sumps that I have viewed representative of the population? I think so. My observations are based primarily on a study of the conditions of tank-top and dispenser sumps conducted on behalf of the Maine Department of Environmental Protection in 2002-2003 *(http://www.maine.gov/dep/rwm/ust/pdf/sumpstudyreport.pdf.)* Facilities included in the study were randomly selected and geographically dispersed across the state. A total of some 125 dispenser sumps and 87 tank top sumps were inspected.

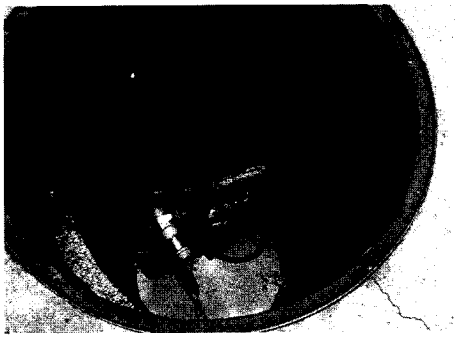


Photo courtesy of Ernest Rogglin

Waterlogged tank-top sump with disabled sump sensor.

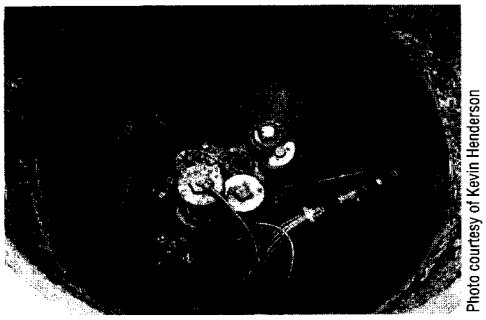


Photo courtesy of Kevin Henderson

A caved-in, waterlogged tank-top sump.

Ninety percent of the dispenser sumps and 85 percent of the tank-top sumps were found to be completely free of product. Where product was observed, it was typically no more than a puddle in a small area of the sump bottom. Seventy-seven percent of dispenser sumps and 43 percent of tank-top sumps were found to be completely free of water. Where water was observed, it was again usually no more than a puddle. The general condition of the sumps was also remarkably better than what was shown in the presentation referenced above.

What's Right with the Maine Picture?

So, what does account for this difference? Based on my knowledge and

■ *continued on page 28*

■ **Maine Sumps** *from page 27*

experience (and not any rigid scientific analysis) I would cite the following factors:

■ Workmanship

Proper installation, sealing, and backfilling of sumps are very important to long-term performance. Maine instituted the first state-level UST-installer certification program in the nation in 1986. I believe this program has significantly improved the quality of UST system installations in the state.

What distinguishes Maine's certification program from most others is effective enforcement. Maine established a volunteer board to oversee the installer certification program. The board is empowered to draft and sign consent agreements with certified installers who are found to be in violation of state regulations. Improperly installed sumps and sumps in no condition to act as secondary containment represent violations for which an installer can be held accountable and be required to fix.

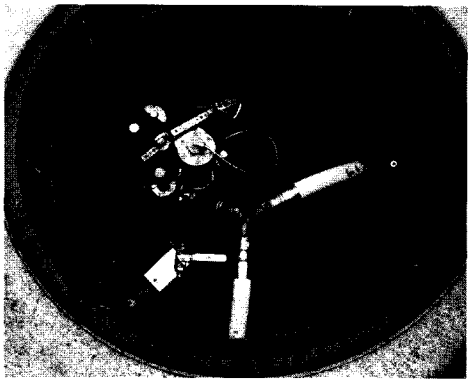
The board meets monthly and nearly always has several enforcement cases on its agenda. Sometimes the cases involve paper violations for failure to obtain required education credits, but often enough they are infractions of installation standards, manufacturers requirements, or industry practices. Typically, these infractions result in a requirement to redo the work properly, significant fines, certification suspensions, and, in a few severe cases, revocations of certification.

Because storage system installation is still very much a business where low bidders get the lion's share of the work, the temptation to cut corners is always very strong. Knowledge that cutting these corners can lead to significant financial and career consequences helps keep the players in Maine in line.

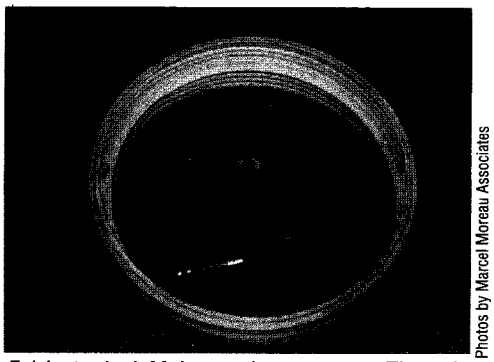
■ Requirement to Report Evidence of a Leak

Maine regulations define any amount of liquid (water or product) in a sump as "evidence of a leak," which must be reported to the state. Both owner/operators and certified installers are required to independently report the discovery of such evidence of a leak to the state. I don't believe for a moment that this requirement results in every incident of liquid in a sump being reported to the state, but it does provide a substantial incentive for installers and owners to remove this "evidence of a leak" when it is discovered to stay out of regulatory trouble. This requirement also provides owners/operators with an incentive to fix sumps where water intrusion is a perennial problem.

Liquid, especially product remaining in sumps for extended periods, has been frequently cited as a cause for failure of certain piping and containment systems. To my knowledge, Maine has yet to experience a failure of a piping system attributed to exposure to petroleum product.



Tank-top sump at an Environmental Leader facility in Maine. Believe it or not, this sump was six years old at the time the picture was taken.



Fairly typical Maine tank-top sump. There is some staining, most likely due to water intrusion, but the sump is now dry. This picture was taken during a random, unannounced inspection.

Photos by Marcel Moreau Associates

■ Annual Inspections

Maine regulations require annual inspection of leak-detection equipment by third-party certified installers or inspectors. As a result, most sumps are inspected at least once a year, and any liquid found (whether or not reported as "evidence of a leak") is likely removed to save the storage system owner as well as the installer potential regulatory aggravation resulting from a state inspector discovering "evidence of a leak" that has not been reported. I believe this annual mopping up of sumps contributes to their relatively clean appearance, even after they have been installed for quite a number of years.

■ Environmental Leader Program

Maine's Environmental Leader Program provides recognition to owners of UST systems who successfully pass a regulatory compliance inspection, where every "i" must be dotted and every "t" crossed. While only a small percentage of Maine's facilities participate in this program, those that do invariably have such good-looking sumps that I expect the sump manufacturers would be delighted to feature them in their sales literature.

While not responsible for the overall good condition of Maine's sump population because of the small number of facilities participating in this program, I believe these sumps demonstrate that when someone bothers to make the effort, sumps can be maintained in pristine condition.

Is Maine Alone?

I cite Maine in this article because it is the state with which I am most familiar, not because I believe Maine is unique. Pat Rounds, President and CEO of the Petroleum Marketers Mutual Insurance Company in Iowa, also believes that sumps covered by his insurance program are in better condition than most. Inspectors working for the Iowa insurance program inspect each sump at each facility each year. Facilities with improperly maintained sumps are required to correct the deficiency or lose their insurance coverage.

According to Pat, "if proper installation, repair, maintenance, and operation of tank systems isn't expected by someone who can enforce that expectation, then as an industry we will get exactly what is expected...which, by the way, isn't a good-looking, dry sump."

■ *continued on page 31*

FAQs from the NWGLDE

...All you ever wanted to know about leak detection, but were afraid to ask.

What's All the Fuss about Equivalency?

This installment of the National Work Group on Leak Detection Evaluations' (NWGLDE's) FAQs focuses on continuing questions about automatic line-leak detectors and line-tightness tests. Please note: the views expressed in this column represent those of the work group and not necessarily those of any implementing agency.

Q. Some of the automatic electronic line-leak-detector listings in the List of Leak Detection Systems (the List) talk about "equivalent leak rates." What does that mean?

A. "Equivalent leak rates" are explained and demonstrated in *Standard Test Procedures for Evaluating Leak Detection Methods: Pipeline Leak Detection Methods*, EPA/530/UST-90/010, September, 1990. This protocol is one of a series of test procedures that cover most of the methods commonly used for UST system leak detection. According to the protocol, "Since leak rate varies as a function of pressure, the leak-detection test can be conducted at different pressures provided that the determinable leak rate at the specified test pressure is equivalent to or more stringent than the one mandated in the regulation."

For example, the automatic line-leak-detection hourly performance standard requires that a leak of 3 gal/h or larger at 10 psi must be detected within one hour with a probability of detection (P_D) of 95 percent and a probability of false alarm (P_{FA}) of 5 percent. Using Table 1.1 on page 4 of the protocol, the equivalent leak rate for an evaluation of an automatic line-leak detector at 20 psi would be 4.25 gal/h. This could also be calculated using the formula in Section 4.2 of the protocol.

Using this process correctly means that the third-party evaluator establishes a known equivalent leak rate at a known pressure, such as 4.25 gal/h at 20 psi, and performs the evaluation. If the evaluation results show that the equipment is capable of finding the equivalent leak rate with a P_D of 95 percent and a P_{FA} of 5 percent, then the protocol says that this equipment will be able to detect the hourly performance standard leak of 3 gal/h leak at 10 psi.

Another example is the annual line-test performance standard, which requires that a leak of 0.1 gal/h be detected at 1.5 times the operating pressure (which we will assume to be 45 psi). The measured equivalent leak rate would be 0.07 gal/h at 20 psi as shown in Table 1.1 of the protocol. If the results of the evaluation show that the equipment can find a leak this size 95 percent of the time with a false alarm rate of no more than 5 percent, then the protocol says that this equipment will detect the annual line-test performance standard leak rate.

Whether or not a third-party test used equivalent leak rates may be a crucial issue for implementing agencies as they determine if a specific piece of equipment satisfies the regulatory performance requirement for hourly, monthly, or annual release detection. Implementing agencies can often determine whether or not the evaluation used equivalent leak rates by reviewing the "Overview of Evaluation Method" section of the final report of a given third-party evaluation. Statements in the report that talk about "rates equivalent to 3 gal/h at 10 psi, 0.20 gal/h at 30 psi, and 0.10 gal/h at 45 psi" validate that the testing used equivalent leak rates. Another place to look is in the summary of the testing procedure where similar wording can be found.

Only recently did the work group begin to use the "equivalent leak rate" terminology in its list. We are at present reviewing the reports for previously listed line-leak detectors to make sure the language for each listing is appropriate. We anticipate the review will be complete by this summer. In the interim, each regulator should be able to make an accurate determination by referring to the third-party evaluation document discussed above.

About NWGLDE

NWGLDE is an independent work group comprising 10 members, including (8) state and (2) U.S. EPA members. This column provides answers to frequently asked questions (FAQs) NWGLDE receives from regulators and people in the industry on leak detection. If you have questions for the group, please contact them at *questions@nwglde.org*.

NWGLDE's mission:

- Review leak detection system third-party evaluations to determine if each evaluation was performed in accordance with an acceptable leak detection test method protocol and ensure that the leak detection system meets EPA and/or other applicable regulatory performance standards
- Review only draft and final leak detection test method protocols submitted to the work group by a peer review committee to ensure they meet equivalency standards stated in the U.S. EPA standard test procedures
- Make the results of such reviews available to interested parties ■

Field Notes

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

Coming Soon from the Folks at PEI

PEI is currently involved with four projects that should be of interest to LUSTLine *readers. All of the following projects are scheduled for completion within the first eight months of 2005 and include recommended practices, checklists, and training videos offered over the Internet.*

PEI/RP100

PEI's *Recommended Practices for the Installation of Underground Liquid Storage Systems* (PEI/ RP100-2000) is being revised and updated for the fifth time. The document has been widely accepted over the 18 years it has been in existence, with over 75,000 copies distributed worldwide. It is referenced in the federal UST rules and in the latest (2003) edition of the National Fire Protection Association's *Flammable and Combustible Liquids Code* (NFPA 30). The document is also required reading for the International Code Council's UST certification program. Of the 110 proposals PEI received to revise RP100, over half came from state and federal UST regulators.

Checklist for UST Owners/Operators

The same committee responsible for writing PEI/RP100 is also in the midst of preparing a checklist of proper and routine maintenance procedures that tank owners/operators, regulators, and service companies can use to minimize the risk of releases from UST systems. The checklist will also include recommended inspection frequency. Recognizing that properly installed UST systems are often not maintained properly once the contractor leaves the job site, the PEI Board of Directors assigned this task to the Tank Installation Committee.

The checklist is designed so the owner/operator of the facility can easily inspect three specific areas of the UST system to ensure the UST components are functioning properly: (a) under the dispenser (i.e., sumps, piping, product and vapor shear valves, flex connectors); (b) around the tank itself (i.e., corrosion protection, monitoring wells, vents, spill- and sump-containment manholes, sump sensors, flex connectors, overfill prevention devices); and (c) leak detection (i.e., automatic tank gauges, interstitial monitoring, inventory control, automatic line-leak detection).

The checklist will be made available to all PEI members and their customers free of charge in May 2005. The checklist will not be copyrighted and photocopying will be permitted. State and local UST regulators are encouraged to use it as well. Check with any PEI member for a copy or visit *www.pei.org.* to download a PDF file.

PEI/RP500

A draft of a new recommended practice on fuel-dispensing equipment inspection and maintenance (PEI/ RP500) is available for public input and comment through April 7, 2005. The purpose of the document is to provide a basic reference that consolidates published and unpublished information from equipment manufacturers, installers, and end users concerning the proper inspection and maintenance of motor vehicle fuel-dispensing equipment. The recommended practice is intended to minimize the possibility of fuel-dispensing-equipment failure, reduce fire hazards, promote fueling safety, and minimize environmental hazards. Equipment covered includes all above-grade, liquid- and vapor-handling components, from the base of the dispenser to the nozzle spout. Go to *www.pei.org* if you wish to receive a copy of the draft document. All *LUSTLine* readers are encouraged to submit comments.

Owner/Operator Training on the Internet

The fourth project, approved by the PEI Board of Directors January 6, 2005, involves the development of a complement of convenient, cost-effective, and relevant training opportunities to facility owners and operators in the petroleum marketing industry using distance learning via the Internet. PEI members involved in the petroleum marketing and UST system industries will benefit from the training, because each person/company taking the course will better understand how to use the equipment manufactured, distributed, installed, and serviced by PEI members. The topics will include:

- The ABCs of ATGs: Tanks
- The ABCs of ATGs: Tanks and Piping
- Double-Walled Piping and Associated Leak Detection
- Single-walled Piping and Associated Leak Detection
- Spill Containment and Overfill Prevention

The ATG courses will be available in April 2005. The others will be available in summer 2005. We previewed the first course at the LUST/UST Annual Conference in Seattle. Although pricing has not yet been determined, we envision that discounts will be offered to PEI members and endorsing organizations, including state UST agencies. Remember to check *www.pei.org* for the latest updates. We invite you to take a course or two. We think you will be impressed with the material and presentation and find it worth recommending to tank owners. ■

■ **Maine Sumps** *from page 28*

The Secret to Clean Sumps

So the common thread linking clean sumps in Maine, Iowa, and other places somewhere out there, I believe, is frequent inspection and effective enforcement of standards. After all, tank owners are only human—they will rise (or sink) to the level of our expectations (to borrow a phrase from Pat Rounds).

That said, many states are hobbled in their inspection efforts by a lack of inspectors, and many states' enforcement mechanisms are too labor-intensive to be effective in pursuing what are perceived as housekeeping-type violations. In addition, federal rules, which serve as a model for most state rules, do not describe specific maintenance requirements for UST systems.

Sumps merely serve as a very visible barometer of a storage system owner's overall maintenance efforts. If the pictures that prompted this essay are more representative of the status of the nation's sumps than the pictures of Maine sumps in my files, we have a long way to go before a satisfactory level of UST maintenance is achieved.

P.S.

Okay, I admit it, this essay is my decidedly unscientific (and undoubtedly biased) view of what may be responsible for the quality of installation and maintenance practices for UST-piping sumps in Maine. My intent is not to toot anyone's horn or gore anyone's ox but to stimulate discussion. ■

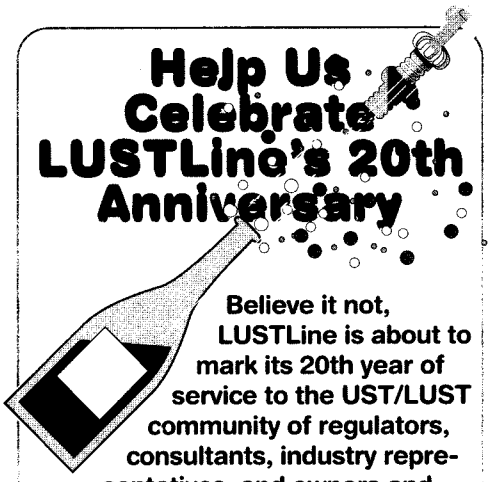
■ **European MtBE Conference** *from page 20*

changes in Europe will shape the future of those countries and whether they can learn from the environmental mistakes we have made in the U.S.—or if they will knowingly repeat some of them, such as our decision to protect air quality without carefully examining potential impacts to groundwater quality. For now, I'm optimistic and look forward to future discussions on oxygenates with my European colleagues.

And while I'm hopeful for a return to more normal winter conditions in Montana, I don't want to go back in time to Cold War Europe. In Montana, the Continental Divide will always separate weather systems between east and west along the Rocky Mountains. But the divide that separated Eastern Europe from Western Europe is gone and in its place is a new and relatively uncharted world for science and technology to grow. I hope the new Europe embraces the opportunity and tears down many of the other walls that exist between researchers, regulators, and industry—walls that represent obstacles to future advancement. ■

Jeff Kuhn is a hydrogeologist and manages the Montana DEQ Petroleum Release Section. Information regarding the 2nd European Conference on MTBE can be found at conference website: http://www.iiqab.csic.es/mtbe/. *The 3rd European Conference on MTBE will be held in Copenhagen, Denmark in 2005.*

Help Us Celebrate LUSTLine's 20th Anniversary



Believe it not, LUSTLine is about to mark its 20th year of service to the UST/LUST community of regulators, consultants, industry representatives, and owners and operators—our first issue hit the streets in August 1985. Over the years we have had the privilege of providing you with articles written by a host of contributors who have helped us keep you informed about the many-faceted issues associated with UST systems. So now it would be really special if you, our readers, would help us celebrate this auspicious anniversary by sending us your anecdotal short (paragraph or two) and (hopefully) sweet "nothings" that we can use to spice up our summer issue—which will also be our 50th issue. We realize that we could be opening up the ever problematic can of worms, opening ourselves up to attack from all sides. But, hey, we're adults now, we can deal with it.

If you wish to join in the "roast," just write to Ellen Frye at lustline@neiwpcc.org. Please get you comments to us by May 1, 2005. Tanks.

L.U.S.T.LINE Subscription Form

Name _____

Company/Agency _____

Mailing Address _____

_____

E-mail Address _____

❑ **One-year subscription.** $18.00.

❑ **Federal, state, or local government.** Exempt from fee. (For home delivery, include request on agency letterhead.)

Please enclose a check or money order (drawn on a U.S. bank) made payable to NEIWPCC.

Send to: **New England Interstate Water Pollution Control Commission**
Boott Mills South, 100 Foot of John Street, Lowell, MA 01852-1124
Phone: (978) 323-7929 ■ Fax: (978) 323-7919 ■ **lustline@neiwpcc.org** ■ **www.neiwpcc.org**

The Phoenix Awards: Know a Good Candidate?

June 30, 2005 is the deadline for getting Phoenix Awards applications to the Phoenix Awards Institute, Inc. The Phoenix Awards were created in 1997 to recognize individuals, groups, companies, organizations, or government bodies that are working together to solve the critical environmental problems of transforming old, contaminated areas into productive new uses. The awards are presented each year at the U.S. National Brownfields Conference held at a different city each fall. One winner will be selected from each of the 10 U.S. EPA Regions, and one project from outside the United States, as an international winner.

The brownfield redevelopment projects are broadly defined under this award program to include properties impacted by all types of contamination, and remediated under a variety of regulatory programs (e.g., Superfund, Resource Conservation and Recovery Act, brownfields, and voluntary cleanup programs). Projects that emphasize public policy initiatives associated with governmental programs are encouraged to apply. These initiatives may include abandoned petroleum sites without viable responsible parties (petroleum brownfields).

Applications may be submitted by an individual involved in the project or by a third party, with the primary project coordinator (e.g., property owner, environmental engineering firm, or project developer) or the entire project team listed as the applicant. To be considered, the brownfield redevelopment project must have been completed by the date the application is submitted. Projects are deemed "complete" if the end-use enterprise is presently conducting business at the site. Past Phoenix Award winners are not eligible for the same project in subsequent years. However, all previous non-winning applications will be considered in the following year's review process.

Criteria

Successful applications must demonstrate measurable results and/or impact on environmental improvement and long-term community economic benefits and emphasize five topics: (a) magnitude of the problems and project, (b) use of innovative techniques, (c) cooperative efforts of multiple parties to undertake the project, including financing solutions, (d) positive impact on the environmental (e.g., green buildings, greenways, energy use), and (e) the project's general and long-term economic impacts on the community. An independent panel of state, regional, and federal government leaders, along with environmental, business, and academic professionals will select the winners. ■

For more information contact Denise Chamberlain by e-mail at dchamberlain@arcadis-us.com, or by phone at (717) 761-0554

Citing Too Many Abandoned Gas Stations, Detroit Places Moratorium on New Stations

Detroit Mayor Kwame Kilpatrick placed a two-year hold on applications for new locations for service stations. "Too many stations have been abandoned. Many that remain have become eyesores in our neighborhoods," said the mayor. Amru Meah, director of Buildings and Safety Engineering, which oversees licensing and inspection of service stations, believes the moratorium is necessary for the city to bring existing stations into compliance. "Underground storage tanks are dangerous," said Sarah Lile, Director of Environmental Affairs. "Across the city we're still digging out tanks that were buried decades ago." The mayor's press release was issued on October 6, 2004, and can be seen in full at *http://www.ci.detroit.mi.us/mayor/releases/2004%20Releases/Moratorium%20on%20New%20Gas%20Stations.htm.*

L.U.S.T.LINE INDEX

August 1985/Bulletin #1 - November 2004/Bulletin #48

The LUSTLine Index—is ONLY available online.

To download the LUSTLine Index, go to www.neiwpcc.org/lustline.htm, and then click on LUSTLine Index.

L.U.S.T.LINE

New England Interstate Water Pollution Control Commission
Boott Mills South
100 Foot of John Street
Lowell, MA 01852-1124

Non-Profit Org.
U.S. Postage
PAID
Wilmington, MA
Permit No.
200