New England Interstate Water Pollution Control Commission

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20 Years of LUST Busting The Changes, the Joys, the Frustrations...the Future?

Busting

by Patricia Ellis

uried fuel tanks had been leaking for years—probably for as long as they had been buried. Finally, in 1983, the CBS program 60 Minutes *aired* a story called "Check the Water," which brought national attention to the effects of leaking underground storage tanks. In 1984, Congress passed a new law, requiring the U.S. EPA to develop a regulatory program to prevent, detect, and clean up releases from UST systems to protect human health and the environment. On September 23, 1988, U.S. EPA issued comprehensive regulations (Federal Register, 1988) affecting owners and operators of UST systems throughout the United States.

The regulations went into effect on December 22, 1998, and tank owners were given ten years to meet some of the equipment compliance deadlines. The regulations incorporate three broad strategies:

- Identify and then correct faulty or leaking tanks
- Reduce the incidence of future releases by mandating minimum operating and performance standards
- Minimize hazards from releases by mandating a standard release investigation, response, and corrective action procedure

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The third area is meant to streamline and standardize the ways in which operators respond to suspected and confirmed releases from USTs. The two subparts of this section deal with release reporting, investigation and confirmation, and release response and corrective action.

Because of the large regulated universe of USTs at the beginning of the program (over two million tanks), EPA designed the program to be implemented by the states. Armed with the new federal regulations, the states were tasked to develop programs to manage the UST universe.

While I've only been with the UST program for 15 years, in honor of this anniversary, I would like to take this occasion to reflect on the life and times of the LUST side of the tanks program, starting with the advances in cleanup technologies.

20 Years of Technology Improvements

Early LUST cleanups consisted primarily of three methods. If contami-



L.U.S.T.Line

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nation was shallow, you could overexcavate and dispose of contaminated soils—"dig and dump," or "muck and truck." If groundwater was impacted, you could recover free product (normally by hand-bailing or mechanical skimming, or one- or two-pump groundwater pumping.

But pump-and-treat was the main way to clean up contaminant plumes. Pump-and-treat seemed like a "forever" type of corrective action, because you could pump, and pump, and pump, and the site still wouldn't clean up, because the petroleum contaminants sorbed to the soils and only slowly released to the groundwater. Whether or not you could manage to close a LUST project with pump-and-treat was highly dependent on the cleanup goals for the site. If you had to meet an MCL, you could be pumping forever.

Shortly after I joined the program, we began to see more and more ex-situ bioremediation of excavated soils. It seemed to be considerably cheaper than paying for disposal, but you needed sufficient space and time for the bugs to do the cleanup. In Delaware, we maintained a "Dirty Dirt List" to keep track of the soil piles. Keeping the covers on the piles intact was a nuisance, and letting the contractors and responsible parties know that a big mound of dirt next to the former tank pit was not really a bioremediation cell and probably wouldn't remediate very well that way, was a nuisance.

With a little guidance, however, ex-situ bioremediation was a reasonably inexpensive, effective technology. Of my biopiles, I had only one stolen, and one attempted escapee was chased for a day, apprehended, and returned to where it was supposed to be.

In-situ bioremediation of soils and groundwater came into vogue at about the same time. Unfortunately, in our experience, not everyone was good at designing and operating an in-situ bioremediation project, so some of these projects were not very successful.

Pump-and-treat with soil-vapor extraction (SVE). SVE. Air sparging, Air sparging with SVE. Biosparging. All were introduced into our toolbox to give us a few additional weapons for cleanups, and they are still commonly used. Various configurations of dual-phase/multiphase extraction have proven effective in tighter soils where some of the technologies that rely on the soil's ability to move fluids are ineffective, removing a combination of petroleum vapors, free-phase product, adsorbed product, and dissolved phase.

The U.S. EPA Office of Solid Waste and Environmental Remediation (OSWER) Directive on Monitored Natural Attenuation was issued in 1999, providing guidance on how to evaluate and monitor natural attenuation sites. It differed from some of the other guidance being issued at the time in that bioremediation was stressed-other processes, such as dispersion, diffusion, and dilution, or chemical or mechanical destruction were not included. A lot of sites were eliminated from consideration of this remediation option when, due to its resistance to biodegradation, large amounts of MtBE were found at the release site.

Various oxidation technologies are among the newer tools in our toolbox. They have the advantage of being relatively quick technologies, although not necessarily cheap, and they work reasonably well for the fuel oxygenates. They can help us meet the goals of faster cleanups.

What Chemicals Are We Looking At?

Life was simple in the early days most states looked at benzene, toluene, ethylbenzene, and xylene (BTEX), or even just BTX, and total petroleum hydrocarbons (TPH). Later, TPH was split into gasolinerange organics (GRO), diesel-range organics (DRO), and sometimes even high-range organics (HRO). Exceed the action levels and you're in the cleanup program.

With the advent of risk-based corrective action (RBCA) programs in the early 1990s, you needed some sort of toxicology data to be able to generate safe levels in soils and groundwater. One approach was to use groups of chemicals and choose a surrogate to represent the toxicology of the group (e.g., the method used by the TPH Criteria Working Group, 1997). Another method was to establish a list of chemicals of concern for each petroleum product and use available toxicology data for each chemical to generate acceptable concentrations. Some states kept the list short, and other states added long lists of analytes for required testing.

Around the time that the Santa Monica, California, wells were impacted with MtBE, tank programs began to realize that they needed to add another analyte to the list. A few states were already looking for MtBE at that point, but they were few and far between. In January 2000, 60 Minutes put the tank program in the spotlight again with a double-length segment devoted to MtBE. At least we had warning that the segment was going to air, because most states had to scramble to create fact sheets about the additive, field questions from the local print and news media, and respond to questions from residents questioning whether they had MtBE in their drinking water.

Two days after the 60 Minutes presentation, the EPA Office of Underground Storage Tanks (OUST) strongly urged the states to immediately begin monitoring and reporting MtBE and other fuel oxygenates at all LUST sites (U.S. EPA, 2000). Based on the New England Interstate Water Pollution Control Commission's survey on state experiences with MtBE being conducted at approximately that time (NEIWPCC, 2000), 42 states were looking for MtBE in groundwater, and 29 were looking for MtBE in soil samples. Only four or five states were looking for any of the other oxygenates "most of the time."

In another survey, based on responses from 27 states, over 91,000 LUST sites were closed prior to MtBE sampling/analytical requirements (Sakata and Martinson, 2001).

And what about the other oxygentate in gasoline?

"Many within the petroleum industry have suggested that it was overemphasis on benzene in the 1980s and early 1990s that caused them to neglect MtBE. It appears that we may not have learned from this oversight, and the pattern maybe repeating itself. Where there is now an emphasis on MtBE, in many places they are not looking for or evaluating the potential impact from the other fuel oxygenates."

GRAY AND BROWN, 2000

How Much Is Acceptable?

Now that more states are looking for the fuel oxygenates, one of the problems in dealing with them becomes "How much is acceptable?" There are no established maximum contaminant levels (MCLs), and little toxicological data are available for any of the fuel oxygenates, so deciding how

Now that more states are looking for the fuel oxygenates, one of the problems in dealing with them becomes "How much is acceptable?" There are no established maximum contaminant levels (MCLs), and little toxicological data are available for any of the fuel oxygenates, so deciding how to deal with them under a RBCA program can be a problem. Some states are waiting for EPA to establish an MCL, and others have tired of waiting and have established their own standards.

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Now that several reformulated gas (RFG) states have banned MtBE (including California, New York, and Connecticut) with the oxygenate mandate still in place, ethanol is becoming an emerging chemical of concern, with related issues of fate and transport, remediation technologies, analytical methods, and UST system compatibility.

As we look ahead to future changes in the composition of gasoline and other petroleum products, we must also look to the past, at various components of leaded gasoline, ethylene dibromide (EDB or 1,2-Dibromoethane), 1,2-Dichloroethane (EDC), and tetra-ethyl lead, which were not examined.

The RBCA Process

One of the greatest changes I've seen happen to the LUST program is the

development and application of the RBCA process, which involves evaluating all aspects of a site and determining how much of a release can safely be left in the ground, rather than remediating the site to a onesize-fits-all predetermined cleanup number. The program was developed in part to help us target our cleanup dollars to where environmental risk is highest.

For some states, where cleanup numbers were low or fixed for every site, this marked a significant change in the way of doing business. For others, where a more site-specific approach to setting cleanup goals was already being used, this represented less of a change.

I will admit, however, that the concept still gives many of us major heartburn when we see the cleanup numbers generated using the process. As we watch our soils and groundwater being left with "safe" levels of chemicals, particularly when you consider the small number of chemicals that we are actually looking for out of the huge number of chemicals in the products that are released, we can't help but wonder... (Ellis, 2003).

Quicker, Better Investigations

Another major change I've observed during my tenure with the LUST program is the development of many tools that allow us to do quicker, better investigations. When I started with the program 15 years ago, monitoring wells were the norm. If there was a release, the consultant sent in a workplan to install a few monitoring wells (usually no more wells than the absolute minimum needed to determine groundwater flow).

After a few weeks of waiting to get a driller and permits, the consultant would go out to the site and install three wells. After developing the wells and waiting a few weeks for the well to stabilize, groundwater samples would be collected. Then, after waiting a few more weeks for lab analyses, the consultant would write a report and send it in to the state.

Oops—with three wells, maybe you've got an upgradient well, and the other two are kind of cross-

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gradient/downgradient. That's not enough. So the consultant writes another workplan, proposes more wells, waits for approval, goes back to the field, puts in more wells, waits for the analytical. Good, we have a downgradient well this time, but we sure aren't at the end of the plume. Repeat the cycle.

With the advent of direct-push technologies, the consultant could propose a dozen holes, and get the samples collected in a day. The second round might then consist of monitoring well installations, this time in locations where they needed to be, where good data could be collected. Sometimes direct-push sampling was accompanied by a mobile lab that allowed decisions to be made in the field.

When the "diving plume" phenomenon became more common knowledge (see Weaver and Wilson, 2000), direct-push technologies could be used for three-dimensional plume characterization. Guidance documents were produced describing the benefits and process of expedited site assessments (U.S. EPA, 1997), involving direct-push sampling methods and a host of other technologies that could assist in more rapid and complete site characterization—smarter, better, faster, and often, even cheaper site assessments.

The 1998 Deadline...No More Leaking Tanks?

As the 1998 deadline for UST owners to close, upgrade, or replace their tanks approached, our workload increased drastically. Lots of people sputtered that the #!!%&##@ government was making them remove a perfectly good tank that wasn't leaking, but it was no surprise to us that a considerable number of those tanks had, in fact, been leaking—whether or not inventory and tank testing had ever given an indication of a release. The closer to the deadline these tanks were removed, or in many cases, after the deadline, the higher the chances were that the state was requiring MtBE analysis at the time of removal. Not only were a lot of tanks coming out of the ground, but they were triggering investigations for a chemical for which many states had not previously been looking and often had no experience in remediating.

We assumed that 1998-compliant tank systems wouldn't leak. They were state-of-the-art and had all the bells and whistles. You'd know it right away if any product dared to escape. We figured we'd get our backlog cleaned up, whittle down the last of the oldie-but-moldy sites, and work ourselves right out of a job. Bzzzzz! Wrong answer. Tank systems still leak somehow. We often just don't know how! Or the sophisticated leak-detection systems are just too much for some people—Darn things always buzzing, beeping, and alarming. Must not be working right! Turn them off!

In the future, as the number of releases declines, the backlog of old cleanups can be reduced. I, for one, hope that we don't pinch pennies when it comes to upgrading the requirements for new tank installations. If increasing spending a few hundred here and a thousand there on a new system will prevent a release that can cost from tens of thousands to millions to clean up, it's worth the price.

Somewhere along the line, it occurred to us that tanks often weren't the source of the problem. The lines, with all their joints and elbows could be a problem, sumps (or lack of sumps) could be a problem, and under the dispensers was a good place to look for, and find, contamination.

Then there are the miracle releases. If a tank system isn't tight, all of the chemicals should be escaping—not just the MtBE. Alas, the concept of vapor releases has emerged. And vapors don't just escape and waft off into the atmosphere, they can dissolve in soil moisture...and end up in the groundwater...and show up in monitoring wells...and nearby potable wells...and sometimes the not-so-nearby potable wells.

New Initiatives on the LUST Side

In October 2002, OUST rolled out its USTfields initiative to promote the cleanup of the approximately 200,000 abandoned tanks at brownfields with a series of pilot grants. The 2002 Brownfields law authorizes EPA to give grant money to states and communities so they can inventory, assess, and clean up petroleum-contaminated brownfields. (See *http:// www.epa.gov/swerust1/priorits.htm.*) This money complements the OUST USTfields initiative.

Another of the 2002 initiatives was a re-evaluation of UST system design. While this is a complianceside initiative, it will have impacts on the LUST side of the program down the road, identifying additional LUST sites as upgrades are made and, hopefully, decreasing the occurrence of future releases.

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"Accelerated Cleanup" was another of the initiatives rolled out in October 2002. This initiative was designed to address the backlog of 139,000 tank releases that still hadn't reached closure. It was designed to identify the holdups in the process. Are the investigations not getting underway? No RP? Recalcitrant RP? No money? Once an investigation is complete, is cleanup not getting started? Are the technologies applied at a site not successful, and if not, why not? Maybe the results of this initiative will allow us to work smarter.

Here are the figures from March 2004 (*http://www.epa.gov/swerust1/cat/ca_04_12.pdf*):

- 443,568 releases confirmed
- 408,834 cleanups initiated (92%)
- 311,125 cleanups completed (70%)
- 132,443 cleanups not yet completed (31%, with 50% of these

involving groundwater contamination)

Completed cleanups reported for 2003 met EPA's annual national cleanup goal of approximately 18,000 and reversed a three-year downward trend in the number of cleanups completed.

Wow! Five hundred twentythree of those confirmed releases are mine—0.1 percent! Four hundred forty-one of the cleanups completed are mine—0.1 percent. Eighty-two of the cleanups not completed are mine—0.06 percent. No wonder I'm tired! I don't think the answer lies in setting numerical quotas, though. Subliminal message—send money, lighten project load, stop leaks!

Setting numerical quotas for each state ignores many of the differences between state programs. Some states are required by law to remediate to MCLs—no MCL, no closure. In some states, all cleanups are paid for by the state cleanup fund, so you have less of a fight to get the cleanup initiated. In some states, each project officer may have as many as 300 LUST projects to handle, and it makes a considerable difference how those projects are funded, contracted, and so on, as to how that workload might compare with that of a LUST project officer in another state.

Try this calculation: take the number of days in the year, subtract weekends, holidays, vacation, and a few sick days and divide that by the average number of projects that an average project officer might have. That's how many days per year that you can average for each project (if you don't go to any training and don't attend and meetings and don't spend time on planning or program development). If you've got a few big LUST projects that suck up a bunch of your time, reduce the amount of time accordingly that you can devote to any of the lower-priority projects.

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A MESSAGE FROM CLIFF ROTHENSTEIN

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

As We Begin Our Third Decade, Strong Action and Creative Solutions Are Essential

This is a special year for those of us working in the underground storage tank program. In November we will celebrate the 20th anniversary of the program—and we have a lot to celebrate. Just this past year, we surpassed 300,000 cleanups, we continue to cut the number of new leaks—from a high of almost 67,000 releases in 1990 to about 10,000 last year—and we are beginning to make some real progress cleaning up abandoned petroleum brownfields sites. As former U.S. Senator David Durenberger said about our program, "With the right balance between technology, industry, federal, state, private, and public forces, you can get a lot done." We have struck the right balance, and we have gotten a lot done.

But as we celebrate 20 years of accomplishments, our work is not finished. We still have over 130,000 petroleum leaks not yet cleaned u,p and only six in ten gas stations are in full operational compliance. Far too often we hear stories about leak detection alarms that are turned off or equipment that is installed wrong, and we now have evidence about new or upgraded leaking tanks and pipes that should not be leaking. To make matters worse, we are facing these challenges at a time of tight budgets, highly stressed state cleanup funds, and growing concerns from citizens demanding faster cleanups.

These challenges call for strong action and creative solutions. Here's what I suggest:

■ Prevent releases in the first place. With cleanup budgets so tight, release prevention is critical. By integrating compliance and prevention into the design and execution of our cleanup funds we can create incentives for tank owners to prevent releases. By better educating tank operators and better training inspectors we can improve compliance. The good news is that we are close to launching a new Webbased training course for EPA and state inspectors. Once this is up and running, inspectors can take the training 24/7 at their own desks. As for tank operators, we just finished writing an easyto-use regulatory checklist patterned after EPA's



successful Environmental Results Program.

- Improve program integration. Fortunately, we just initiated a new partnership to share data with our colleagues in the drinking water program. Through this partnership we have learned that some states rank USTs as one of the top threats to their designated source water areas. This simple but important datasharing partnership will help us make the best use of our resources and increase public health protection.
- Develop new tools and technologies to streamline cleanups. This can be done through the use of multisite agreements, pump-and-treat optimization, and systematic project planning and real-time measurement—commonly known as "Triad." We also need better methods to detect vapor releases from tanks and cost-effective ways to make sure tanks are both liquid and vapor tight.

This November, when we pause to celebrate our program's 20th anniversary, we should take pride in the tremendous progress that we have made. By working together, we have successfully cleaned up more than two-thirds of all known leaks and prevented thousands of new leaks. As we begin the third decade of our program, we face even tougher challenges. But as before, by continuing to work together we will meet whatever the future brings. ■

OUST UPDATE

New Model Environmental Results Program Workbook for USTs Unveiled

The U.S. EPA Office of Underground Storage Tanks (OUST) has developed a Model Underground Storage Tank Environmental Results Program Workbooks to help state UST programs and state funds improve owner and operator compliance with UST regulations. States may need to modify the model workbook to reflect their own state laws. States may then request or require tank owners and operators to follow the final, state-specific environmental results program (ERP) workbook, which can help owners remain in or achieve compliance with UST requirements.

ERP is an innovative program that can improve the environmental performance of a large number of small sources within a state's regulatory system. Some states have successfully used ERP to improve environmental performance in other small business sectors, such as auto repair, dry cleaning, printing, and photo processing. ERP consists of three related components-inspection and performance measurements, self-certification, and compliance assistance—which work together to produce an integrated system that holds facility owners accountable for their environmental UST regulations.

The primary audience for the workbook is UST owners and operators who either volunteer or are required to use the workbook to determine whether or not their facilities comply with UST requirements. The 164-page workbook contains general information about ERP, instructions on how to use the workbook, regulatory requirements, best management practices, and compliance checklists for USTs and draft forms and worksheets in the appendices. The workbook is available only on the OUST Web site at www.epa.gov/oust/pubs/erp.htm (EPA-510-R-04-003, June 2004). For more information, contact Paul Miller (703) 603-7165.

EPA Report on Technologies to Remediate MtBE and Other Fuel Oxygenates

Over the past several years U.S. EPA has been documenting experience with technologies to remediate fuel oxygenates and has recently published Technologies for Treating MtBE and Other Fuel Oxygenates. The report is an overview of the treatment technologies used to remediate groundwater, soil, and drinking water contaminated with MtBE and other fuel oxygenates. It summarizes available cost and performance information for eight treatment technologies, provides examples of where they have been used, and contains additional sources of information. . The technologies range from exsitu drinking water treatment methods to in situ techniques.

The report was prepared by the Office of Superfund Remediation and Technology Innovation (OSRTI) and is available online at *http://www.clu*in.org/s.focus/c/pub/i/1073/. Much of the data in the report was derived from the MtBE Treatment Profiles database (http://clu-in.org/products */mtbe*), which provides project managers with examples of the use of technologies at specific sites. OUST and OSRTI are sending reference copies to regional and state LUST programs. EPA is not recommending the use of any specific product or service mentioned in the document. For more information, contact Linda Fiedler (703) 603-7194.

New Report on UST Dispenser Releases in South Carolina

U.S. EPA has produced a new report, *Frequency and Extent of Dispenser Releases at Underground Storage Tank Facilities in South Carolina*, which describes the results of information collected and analyzed from UST closure and assessment reports at sites in South Carolina. The report describes the background, purpose, methodology used, quality assurance and quality control procedures applied, results of the study, and conclusions. It includes supporting information in the appendices. EPA developed this report as part of its ongoing evaluation of UST systems and to contribute to the UST community's understanding of dispenser releases.

"This study reaffirms the threat posed by releases from dispensers," says OUST Director Cliff Rothenstein. "Nearly half of all facilities reviewed as part of this study had contamination under one or more dispensers, and nearly one quarter had contamination exceeding South Carolina's risk-based screening levels. With 256,000 facilities nationwide—only half of which have containment under their dispensers—the national implications are significant."

Rothenstein adds that while increased use of dispenser containment should help reduce the future risk posed by dispenser releases, vigilance on the part of inspectors, owners and operators, and service personnel is critical to minimize or at least contain future dispenser leaks.

Copies of the report (EPA-510-R-04-004, September 2004) are available through OUST's Web site at *www.epa.gov/pubs* or by calling NSCEP, OUST's publications warehouse at (800) 490-9198.

New Guide on Evaluating Alternative Cleanup Technologies at UST Sites

U.S. EPA has updated its manual, *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers,* for federal and state UST professionals. The one revised and two new chapters in the manual discuss monitored natural attenuation (Chapter 9), enhanced aerobic bioremediation (Chapter 12), and chemical oxidation (Chapter 13) at UST corrective action sites. The original manual was released in 1994 and then revised in May 1995.

A limited number of copies of the manual at no cost (EPA-510-R-04-002, May 2004) are available by calling NSCEP at (800) 490-9198. Copies can be downloaded at OUST's Web site at *www.epa.gov/pubs.* ■

Age-Dating Releases at LUST Sites: Part 1. Lead [Isotopic] Fingerprints

by Richard W. Hurst

"The significant problems we face cannot be solved at the same level of thinking we were at when we created them."

Albert Einstein

Sometimes we plan our research. Sometimes a course of research comes knocking at our door. My story begins circa 1989, when I began to receive calls, predominantly from attorneys, concerning my knowledge and/or ability to age-date releases of gasoline into the environment. I was recognized as a forensic geochemist, performing environmental isotope and geochemical research as a professor of geology/geochemistry at California State University, Los Angeles, and as a consultant for the petroleum industry and environmental firms.

Little did I know that those calls would lead me into a project that would envelop a substantial chunk of my research efforts over the next 15 years. The contribution has been well worth the time, both professionally and personally, having taken me full cycle from age-dating the oldest rocks in the world during my doctoral days to dating the youngest events, those associated with 20th-century releases of refined petroleum hydrocarbons.

LUSTing for an Answer

Given that the era of leaded gasoline in the U.S. has passed, analyses of samples for lead at LUST sites are performed less frequently. However, lead (Pb) and its four naturally occurring isotopes are persistent in the environment, as none are degraded by biogeochemical processes (Faure, 1986). As a result, lead isotope ratios (e.g., ²⁰⁶Pb/²⁰⁷Pb, ²⁰⁸Pb/²⁰⁶Pb) can provide valuable insights, serving as "fingerprints" of historic gasoline releases at LUST sites and offering answers to questions such as:

- What year did the gasoline release occur?
- How many releases occurred and did they commingle?
- What is the source (or sources) of the leaded or unleaded release?
- How should the liability for site remediation and cost recovery be apportioned among potentially responsible parties (PRPs)?

The ability to age-date a gasoline release is not trivial; many have tried. My contribution to this forensic effort has been to develop a model based on calibrated temporal variations or changes in the lead isotope ratios of leaded gasoline. Called the ALAS Model (Anthropogenic Lead Archaeo-Stratigraphy; Hurst et al., 2001; Hurst, 2002a, 2002b), since about 1993 it has been applied at about 100 LUST sites in the U.S. as a tool to assist regulatory agencies and PRPs (along with their representatives) answer the questions posed above.

In this first of a two-part series in LUSTLine, I will review lead isotopes, the details of the ALAS Model, and the age resolution possible. Given that many readers may be treading on unfamiliar turf, Part 1 provides the technical foundation needed. In Part 2, I will present representative applications of the ALAS Model at LUST sites via case studies that involved cost recovery and site remediation. In addition, the case studies will demonstrate how lead isotopes are used to: (a) differentiate natural from LUST-derived lead; and (b) model the relative contributions from commingled releases.

Used properly, with good sampling strategy and sampling protocols (i.e., a sound scientific approach), lead isotope ratios provide a viable means of: (a) estimating the year leaded gasoline was released into the environment (Kaplan, 2003; Schmidt, personal communication); and (b) fingerprinting sources of leaded/unleaded gasoline releases as well as their dissolved-phase constituents (e.g., BTEX, MtBE).

CSI Lead FAQs—What Clues Does Lead Leave Behind?

As stated above, the persistence of lead in the environment is well established, and hence, despite the fact that gasoline is no longer leaded, the lead from past gasoline releases remains adsorbed onto soil minerals as a record of that release long after the gasoline organic constituents have degraded.

From the perspective of anyone charged with the decision to close a site and/or assess liability, lead is gone from gasoline; however, from my perspective, lead from past releases is retained at LUST sites-in soils, free product, and groundwater; hence, it is important. Despite the clues left by lead, as with any CSI forensic investigation, representative samples should be collected for analysis prior to site remediation following appropriate sampling protocols. Let's examine some issues/questions that arise regarding sampling/analysis and their resolution.

Soil/groundwater lead concentrations do not exceed the regulatory threshold value, hence they are attributable solely to the natural background.

Many believe that if lead concentrations in a soil/groundwater are low, no anthropogenic lead is present. This cannot be resolved using concentration analyses alone, but by incorporating lead isotopes it is possible to fingerprint both natural and anthropogenic lead, even at low concentrations (e.g., tens of ppb), well below those of regulatory-mandated threshold values—this will be discussed in Part 2 in more detail.

Should I add a preservative to samples, and what about the potential for removing lead from particulates in groundwater when samples are acidified?

It is imperative that groundwater samples *never be acidified* because of

■ Isotopic Fingerprints *from page* 7

the potential to extract lead from suspended/colloidal particulates whose lead concentrations and isotope ratios reflect the characteristics of the aquifer material, not the contaminant! This will lead to artificially high dissolved lead concentrations that will be attributed, incorrectly, to a gasoline release (Hurst, 2000; Landmeyer et al., 2003).

Because any preservative may contain lead, no sample matrix should be preserved other than by chilling to preserve organics—lead does not degrade, hence it need not be preserved. Ask yourself, would we have a global lead pollution problem if lead degraded?

How is anthropogenic lead removed from soil without extracting background lead from the soil matrix (minerals)?

Sequential chemical extraction protocols have been developed to strip the anthropogenic lead component adsorbed on the surface of soil minerals without removing lead bonded in soil minerals (Hurst, 2000). This approach is very effective when it comes to deciphering the number of releases at LUST sites. At this time, I have collaborated with and trained researchers at MIT who perform the required extractions per my instructions following my evaluation of sitespecific conditions and client needs.

Can commingling of petroleum hydrocarbon plumes homogenize lead isotope ratios, compromising their utility?

On the contrary, commingling of plumes can be identified and modeled using lead isotope/concentration data from sequential chemical extractions in order to assess the relative contributions from each release.

ALAS Model: Historic U.S. Gasoline Lead Isotopic Temporal Variations

Ng and Patterson (1982) must be credited with identifying the rapid, temporal increases in ²⁰⁶Pb/²⁰⁷Pb ratios of the anthropogenic lead component of sediment in southern California and attributing the change to our increased reliance on Mississippi Valley Type (MVT) lead to produce alkyllead additives. Briefly, MVT lead ores have very high, or *radiogenic*, ²⁰⁶Pb/²⁰⁷Pb ratios (~1.3) relative to other ores whose ratios range from about 1.0 to 1.2. Furthermore, Ng and Patterson proposed, correctly, that the similarities between the ²⁰⁶Pb/²⁰⁷Pb ratios of the anthropogenic lead component in sediments and those of contemporaneous gasoline-derived aerosols from 1965 to 1975 indicated gasoline combustion, a major source of anthropogenic lead both locally and globally.

Their work, however, focused on global lead pollution, not the development of a chronometer to age-date gasoline releases. Realizing the need for improved accuracy in estimating the age of gasoline releases, my approach was to use the Ng-Patterson data as the prototype calibration curve and build upon it. The next leg of this journey was to:

- evaluate whether the temporal increases observed in gasoline lead isotopic ratios could be calibrated
- determine the age resolution of the hypothetical technique
- assess its geographic applicability

I started to acquire samples to calibrate what would eventually become the ALAS Model (e.g., archived leaded gasoline, free-product-impacted soils from documented releases). In short, this was a tedious task, but as a result of 10 to 12 years of work, the current ALAS Model calibration includes more than 125 free product/soil lead isotope analyses of documented gasoline releases throughout the U.S. (i.e., California, Illinois, Florida, New Jersey, Arizona, Massachusetts, Ohio, Washington, Texas, New York, Oregon, and Pennsylvania). The ALAS Model is shown in Figure 1. (At the scale of the figure, only about 35 of the 125 individual data points can be resolved.)

As I am my own toughest critic, I decided to further refine and evaluate the model. How? The ALAS Model remains the only gasoline agedating model for which historic data are available to, so to speak, model the model. First, using annual U.S. Bureau of Mines lead production figures (1920–1992), I calculated the contribution of lead from each state and foreign source relative to total U.S. lead production. Second, I integrated the results with published ore lead isotopic ratios for each source to calculate annual average ²⁰⁶Pb/²⁰⁷Pb ratios of U.S. industrial lead (Hurst, 2002b). These calculations and data acquisition required about 10 months.

What was the result? The correlation between the calculated ratios with those of ALAS Model calibration samples is statistically significant ($R^2 = 0.95$; Figure 1), indicating that the ALAS Model could, in fact, be modeled. It also suggested that major manufacturers of tetra-ethyl lead (TEL) (e.g., Ethyl and DuPont) purchased lead from the average U.S. lead market.

This result provided an answer to a valid question posed by detractors of the ALAS Model that alkylleads, *may*, on occasion, be manufactured entirely from a shipment of, let's say, Australian lead that has a very different lead isotopic signature. Furthermore, historical data acquired by Robert (1984) indicate that Ethyl and DuPont collaborated on TEL and other alkyllead production, hence they purchased lead from the same U.S. lead market.

Additional support came in the form of correlations between the ALAS Model and independent analyses of atmospheric aerosol lead isotope ratios (Figure 2), which are: (a) very significant when leaded gasoline combustion was a major source of lead in the atmosphere between 1962 and 1985 ($R^2 = 0.87$); and (b) poor, after 1985, as alkyllead concentrations in gasoline decreased from 1.1 to 0.1 gm/gal ($R^2 = 0.003$).

The significant correlation between the ALAS Model and aerosol lead isotope ratios was one of the first lines of evidence that the model had potential applicability throughout the U.S., rather than just California, where it was initially developed. But why should lead isotope ratios of the ALAS Model and aerosols from gasoline combustion be in such accord throughout the U.S.?

In 1933, the Ethyl Corporation capitalized on its virtual monopoly of TEL production and began marketing TEL throughout the U.S. (Robert, 1984). Despite the fact that there were numerous petroleum companies,



FIGURE 2. ALAS Model versus lead isotope ratios of atmospheric aerosols. Note the distinct similarity between the 206Pb/207Pb ratios of the ALAS Model and aerosols prior to 1985, when the dominant source of atmospheric lead was leaded gasoline combustion.



there was only one Ethyl Corporation from which gasoline refiners could purchase TEL, and Ethyl bought lead from the average U.S. lead market, which focused on MVT lead sources.

Economically, Ethyl realized that it made no sense to mine lead and either store it for long periods of time or transport it great distances. As realized by medieval alchemists, lead cannot be transformed into gold—in its heyday, about 1950 to 2000, lead commanded a maximum price of about 50 cents per pound. For this reason, Ethyl Corporation sited the majority of its TEL production facilities (Louisiana, South Carolina, Texas) proximal to sources of MVT ore (Robert, 1984).

Lastly, as observed in Figure 1, there are two ways lead isotope ratios are represented: as the "raw' $^{206}\text{Pb}/^{207}\text{Pb}$ ratio and as a "delta" notation, $\Delta^{206}\text{Pb}$, relative to a lead isotopic reference standard (i.e., like light-stable isotope ratios of carbon are reported). I will not discuss the details of reporting lead isotope results in the delta notation; suffice it to say it is used in litigation where small differences between isotopic ratios often confuse nontechnical folks who more clearly understand comparisons of numbers like +5.2 or – 3.7.

Why Does the ALAS Curve Look Like It Does?

Let's look deeper into the control imparted by the use of radiogenic MVT ores on the ALAS Model before versus after 1960. We will also get some sense of how rapidly lead went from the mine to the TEL market.

Prior to 1960, the ²⁰⁶Pb/²⁰⁷Pb ratios of gasoline lead fluctuated but remained low, about 1.15 to 1.175; observed fluctuations are dependent on sources of lead, and MVT lead contributed about 30 to 50 percent (average 42 percent) to annual domestic U.S. lead production prior to 1960. During the war years (World War II, Korean War), 1937 to 1954, lead was used, in part, for military/defense purposes.

In 1940, the proportion of less radiogenic foreign and domestic ore increased (25 to 50 percent of U.S. total lead production) while MVT sources declined (U.S. Bureau of Mines Yearbooks, 1939-1941). The result was immediate—an anomalously low 206Pb/207Pb ratio in 1940 (~ 1.155) relative to other years. Low 206Pb/207Pb ratios during the Korean War years also reflect a drop in domestic MVT ore production and/or its use by the military.

The post-1960 interval was initially marked by a decrease in ALAS Model 206 Pb/ 207 Pb ratios to about 1.15, followed by the steady, rapid increase to values of about 1.23 by 1990. The increased reliance on MVT lead, whose proportion of total U.S. lead increases systematically after about 1965 to greater than 85 percent by the 1980s, contributes to the dramatic increase in 206 Pb/ 207 Pb ratios observed in the ALAS Model during this time interval.

The minimum in 1962 is linked directly to a workers strike at the largest MVT lead mine in Missouri. What is so important here, as observed in 1940, is the "from mine to market" factor—in 1962, MVT ore production ceased for months but was replaced by less radiogenic lead from Idaho (U.S. Bureau of Mines Yearbook, 1962).

As observed in 1940 and again in 1962, the ALAS Model ²⁰⁶Pb/²⁰⁷Pb ratio decreases immediately (Figure 1). These observations indicate just how rapidly lead went from the mine

■ Isotopic Fingerprints from page 9

to TEL production and further support my contention that large quantities of lead from sources that were not representative of the average U.S. market did not occur because they would have been recorded in the ALAS Model.

How Precise and Accurate is the ALAS Model?

When applied properly, by defining a site-dependent sampling strategy, integrating lead-organic geochemical analyses of a statistically significant suite of samples, and quantifying commingling among multiple releases, ALAS Model ages have proven reliable and accurate—as long as you do the science.

The analytical uncertainty of the model is a function of the steepness (i.e., slope) of the ALAS Model calibration curve (Figure 1). Where the ALAS Model uncertainty is greater, between about 1965 and 1982, an analytical uncertainty of ± 1 year in the model age of a release is attainable. The model age uncertainty increases to ± 2 years for releases that occurred post-1982. For releases that occurred prior to the early 1960s, where the ALAS Model is much "flatter," the ALAS Model age resolution increases to ten-year intervals. Furthermore, the fluctuations observed in the ALAS Model curve prior to about 1970 can produce more than one unique ALAS Model age. (See Figure 1.)

ALAS Model ages throughout the U.S. have been quite accurate, typically agreeing to within two years (Figure 3) with the "suspected" age of a release. The "suspected" age of a release means my client provided a best estimate of the age of the release, based on inventory/Haz-Mat/fire department records. It is important to recognize that ALAS Model ages have always been determined independently with neither prior knowledge of the "suspected" age or year of a release at a particular site nor the *age*(*s*) *that would most benefit a client's* exposure in litigation involving hydrocarbon contamination at a site.

What Have We Learned So Far?

The ALAS Model is based on systematic increases observed in lead iso**FIGURE 3.** ALAS model ages versus the age of gasoline releases throughout the U.S. The excellent correlation between the model and suspected age of releases from actual site remediation demonstrates the utility and accuracy of the ALAS Model.



tope ratios of gasolines caused by shifts in sources of lead ores used by the U.S. lead industry, including manufacturers of alkylleads, to more radiogenic Mississippi Valley Type deposits. Acquisition of high-quality samples of known age and highprecision lead isotopic analyses over about 14 years has resulted in a calibration curve whose model age uncertainties range from \pm one to two years for gasoline releases that occurred between 1960 and 1990, a major era in the history of leaded gasoline usage.

Numerous site-specific investigations involving free-product releases throughout the U.S. 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. Part 2 of this series will provide the reader with selected representative applications of the model to site-specific investigations in which hydrocarbon remediation, cost recovery, and apportioning of liability were the predominant issue(s).

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A Primer on Lead Isotopes

There are four naturally occurring, stable isotopes of lead (Pb), three of which are radiogenic (i.e., their abundances increase over time due to the radioactive decay of uranium, U, or thorium, Th). The Pb isotopes produced (radioactive parent with half-life, t1/2, in billions of years or Ga; Faure, 1986) are: ²⁰⁸Pb (²³²Th, $t_{1/2} = 14.01$ Ga); ²⁰⁷Pb (²³⁵U, $t_{1/2} = 0.7038$ Ga); and ²⁰⁶Pb (²³⁸U, $t_{1/2} = 4.468$ Ga). The fourth Pb isotope, ²⁰⁴Pb, is not radiogenic, having no radioactive parent nuclide. By convention, either ²⁰⁴Pb or ²⁰⁶Pb is used as a reference isotope; analytical results are reported as Pb isotope ratios (e.g., ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁷Pb). Over earth history, Pb isotope ratios have increased by 30 to 100 percent or more (Stacey and Kramers, 1975).

References

- Doe, B.R., 1970, *Lead Isotopes*, Springer-Verlag, 137 pp. Faure, G.R., 1986, *Principles of Isotope Geology*, Wiley &
- Sons, 589 pp. Hurst, R.W., 2000, Applications of Anthropogenic Lead ArchaeoStratigraphy (ALAS Model) to hydrocarbon remediation, *Jounal: Environvironmental Forensics*, Vol. 1, pp. 11-23.
- Hurst, R.W., D. Barron, M. Washington, and S.A. Bowring, 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*, Vol. 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*, Vol. 9, pp. 1-7.
- Hurst, R.W., 2002b, Lead Isotopes as Age Sensitive, Genetic Markers in Hydrocarbons: 3. Leaded Gasoline, 1923-1990, *Environmental Geoscience*, Vol. 9, pp. 43-50.
- Hurst, R.W. and Schmidt, G.W., In press, Age Significance of nC17/Pr Ratios in Forensic Investigations of Refined Product and Crude Oil Releases, *Environmental Geoscience*,
- Kaplan, I.R., 2003, Age dating of organic environmental residues, *Journal: Environvironmental Forensics*, Vol. 4, pp. 95-141.
- Landmeyer, J.E., P.M. Bradley, and T.D.Bullen, 2003, Stable lead isotopes reveal a natural source of high lead concentrations to gasoline-contaminated groundwater, *Environmental Geology*, Vol. 45, pp. 12-22.
- Ng, A. and C.C. Patterson, 1982, Changes of lead and barium with time in California off-shore basin sediments, *Geochimica et Cosmochimica Acta*, Vol. 46, pp. 2307-2321.

Lead Isotopic Ratios in Ores

The major source of Pb for gasoline additives, sulfide ore (e.g., galena, PbS), contains ~865,000 ppm Pb but virtually no radioactive parent nuclides, U or Th. Hence, once a galena forms, its lead isotope ratios are "frozen in time"—they do not change. Ores used to produce alkylleads (TEL) include imported (i.e., Australia, Canada, Chile, Mexico) and domestic sources (i.e., ID, UT, CO, MO region; U.S. Bureau of Mines *Yearbooks*, 1956-1989).

The ²⁰⁶Pb/²⁰⁷Pb ratios of these ores are: ~1.0–1.1 (Australia, Canada, CO, ID); ~1.20 (Chile, Mexico, UT); and ~1.32 (MO; Doe, 1970). *The significance of the MO region ores, with regard to leaded gasoline, centers on the systematic, increased reliance of the U.S. lead industry, including Ethyl Corporation, on radiogenic MO region lead caused gasoline lead isotope ratios to increase systematically; calibration of this change would lead to the development of the ALAS Model* (Hurst, 2000, 2002a, 2002b).■

- Robert, J.C., 1984, Ethyl: A history of the corporation and the people who made it, University of Virginia Press, 448 pp.
- Rosman, K.J.R., W. Chisholm, C.F. Boutron, J.P.Candelone, and S.Hong, 1994, sotopic evidence to account for changes in the concentration of Greenland snow between 1960 and 1988, *Geochimica et Cosmochimica Acta*, Vol. 58, pp. 3265-3270.
- Shirahata, H., R.W. Elias, and C.C. Patterson, 1980, Chronological variations in concentrations and isotopic compositions of anthropogenic atmospheric lead in sediments of a remote alpine pond, *Geochimica et Cosmochimica Acta*, Vol. 44, pp. 149-162.
- Stacey, J.S. and J.D. Kramers, 1975, Approximation of terrestrial lead isotope evolution by a two-stage model, *Earth and Planetary Science Letter*, Vol. 26, pp. 207-221.
- Sturges, W.T. and L.A. Barrie, 1987, Lead 206/207 isotope ratios in the atmosphere of North America as tracers of US and Canadian emissions, *Nature*, Vol. 329, pp. 144-146.

U.S. Bureau of Mines, 1920-1989, Mineral Yearbook.

SNAPSHOTS FROM THE FIELD

Lightning Strike Causes Underground Storage Tank Explosion

On June 8, 2004. at about 4:00 in the afternoon. lightning struck an underground storage tank in Simpsonville. South Carolina. The resulting spark ignited vapors in the tank, resulting in a large explosion and complete destruction of the tank. The tank



was a 10,000-gallon fiberglass tank that had previously contained gasoline. It had been empty since August 2002 and met the standard for temporarily out-of-service. As the tank was owned by a large public utility, an in-depth analysis of the event was conducted. The owner determined that a -10,000 amp. (-10ka) lightning bolt struck the vent line. A 15' x 30' section of concrete and backfill was lifted approximately 10 feet into the air, accompanied by a loud boom and heavy, black smoke. One of the 18" x 18" steel access covers was blown approximately 125 feet into the air and landed 70 feet from the UST.

Photos by Dale W. Stoudemire



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

Asked Questions

How to Collect Reliable Soil-Gas Data for Risk-Based Applications—Specifically Vapor Intrusion Part 3 – Answers to Frequently

by Blayne Hartman

Since I wrote Parts 1 and 2 in July 2002 and October 2003 (LUSTLines #42 and #44), vapor intrusion has continued to be a "box-office blockbuster" throughout the environmental remediation community. I have provided vapor-intrusion training to no fewer than 12 states, several U.S. EPA regions, and the Department of Defense. Others, including U.S. EPA staff and the American Petroleum Institute (API), are providing training at conferences and to interested parties. Groups such as EPA's Office of Solid Waste and Emergency Response and the Office of Underground Storage Tanks, ITRC, and API have formed vapor-intrusion technical workgroups. Many states have written soil-gas policy/guidance, promulgated regulations (e.g., CT, LA), prepared draft documents (i.e., NJ, MI), or are presently contemplating preparing guidance (i.e., WA, AZ). Everyday, I receive phone and e-mail inquiries on a variety of topics, including soil-gas protocols, analytical methods, and sampling strategies. With all this interest, I figure it's time for Part 3 in this series: Answers to Frequently Asked Questions. The following questions are accompanied by answers, as I see them, that I hope will be helpful.

What is the primary reason that soilgas sampling for vapor intrusion differs from soil-gas sampling for typical site assessment?

The difference is in how low a concentration you have to measure. For site-assessment applications, we typically worry about contaminant concentrations above 1 µg/L. For vapor-intrusion applications, we measure down to levels as low as 1 µg/m3, fully 1,000 to 10,000 times lower. This means that we need to be much more careful in how we collect and analyze samples. Field and analytical techniques that are suitable for higher concentrations are often not suitable for these ultra-low concentrations. Small contaminant blanks from equipment, fingers, clothing, the working surface (e.g., the tailgate of your pick-up), even the ambient air can be enough to fail acceptable risk levels.

Why do you say that vapor units are the most common (and very significant) error in vapor-intrusion assessments?

In the vapor-intrusion world, labs and regulations employ a vast array of units, including most commonly ppmv, ppbv, $\mu g/L$, $\mu g/m3$, mg/m3, and %. It's enough to drive a geologist and risk assessor mad. Even the engineers are having trouble (although they will never admit it).

For water samples, a ppb is equivalent to an μ g/L. For vapor, a ppbv is not equivalent to a μ g/L.

Because the vast majority of us in this field (e.g., regulators, consultants, project managers) are used to dealing with groundwater, it is very easy to carry over this equivalency to vapor samples. Undoubtedly, this is the most common error that I see being made by practitioners in the vaporintrusion field. And it's huge! The reason? For benzene, one µg/L is equal to ~300 ppbv; for TCE, ~180 ppbv. So, we're talking greater than two orders of magnitude error if the units are inadvertently thought to be equivalent.

This confusion about units occurs most commonly in the follow-ing situations:

- When vapor-risk models, such as EPA's Johnson-Ettinger model spreadsheets, are used. If you inadvertently flip the units, you'll start off two orders of magnitude too high or too low. Compare the magnitude of this error to the sensitivity of some of the other common J-E model parameters from default values. Porosity: factor of 5; Qsoil: factor of 3; Ventilation rate: factor of 10. The point is this error is much greater than all of the others combined.
- Calculating soil-gas concentrations from groundwater data using Henry's constant. For benzene, the equilibrium soil-gas concentration with 10 μ g/L in the groundwater is ~2 μ g/L. If

you inadvertently write it as 2 ppbv, then you have erred by 300 times.

 Comparing on-site results in units of µg/L to off-site results reported in ppbv. If the off-site confirmation samples show hits at 100 ppbv and the on-site data were all below detection at a DL (detection level) of 1 µg/L, don't panic. The results agree.

What's an easy way out of unitconversion madness?

- Instruct your lab on what units and detection levels you want the data reported in.
- Go to *www.HandPmg.com* for a handy-dandy, easy-to-use unit conversion spreadsheet.

What are "vapor clouds" and why should we care about them?

Vapor clouds refer to situations where there is subsurface contamination of the soil vapor with little or no coincident soil or groundwater contamination, hence the term "cloud." They arise from leaking vapors, not from contaminated soil or groundwater. Common sources for vapor clouds are sites that contain surface sources of chlorinated solvents (e.g., vapor degreasers, dry cleaners, clarifiers), where the dense chlorinated vapors enter the vadose zone from above, or where vapors are leaking out of USTs. You should care about vapor clouds for a number of reasons. First, unlike groundwater, vapors can move in all directions, regardless of the groundwater gradient, and move quickly—approximately 25 feet/year by molecular diffusion alone. So, a vapor cloud from a dry-cleaning washer unit can move laterally underneath adjoining businesses in a strip mall within one year and represent an upward migration threat to nearby residences within a few years.

Vapors leaking from an UST can move downward through the vadose zone to the groundwater and represent a groundwater contamination threat. (See "The Downward Migration of Vapors," *LUSTLine* #29 and "The Great Escape from the UST," *LUSTLine* #30 for discussions of this pathway.)

When the J-E model underpredicts the measured risk, or indoor air results don't match with groundwater patterns, or when vertical profiles of the soil gas don't show increasing concentrations with depth, vapor clouds should be suspected and soil-gas data, not soil or groundwater data, must be collected to adequately assess the upward vapor risk pathway.

Finally, as pointed out by a reviewer of this article from the rainy south, while vapor sources can exist anywhere, vapor clouds are more likely to exist in areas with deeper groundwater and less rain. In areas with shallow groundwater and abundant rain, any leaking vapors are more likely to get scrubbed (partition) into the groundwater (similar to a "Mister Coffee").

Is it true that an equation written to allow passive soil-gas data to be converted to concentration units is now applicable for vapor-intrusion assessment?

Yes and no. It is true that an equation has been written by a firm providing passive soil-gas services. The analysis of passive soil-gas samplers gives the mass on the passive collector (e.g., micrograms [μ g] or some other form of relative units), not concentration. Concentration is mass/volume. So, to convert mass to concentration we must know the volume of vapor that comes into contact with the adsorbent during burial. There is no way to know this and no accurate way to measure this volume on a true passive sampler. Therefore passive soil-vapor data cannot be used for quantitative upward vapormigration assessment, despite what you might be hearing. One could pump a known volume of air through a passive collector, similar to the NIOSH methods or TO-17, but this is far different than simply burying a collector into the ground and is actually a form of active soil-gas surveys.

Why weren't you more bullish on flux chambers in your last article?

The primary purpose of the article was to describe the two common chamber methods (i.e., static and dynamic), how to use them, and the pros and cons of each. The article was written in response to numerous questions I was receiving from both the consulting and regulatory communities about the technique. But the overriding problem with the approach is whether chambers can be located properly. In many structures, the primary entry of soil gas into the structure is through discontinuities in the floor slab (e.g., cracks, holes, sumps), and these locations might be concealed by barriers such as floor coverings, walls, and stairs.

However, as I wrote in the article, I think flux chambers have their place when the right conditions exist. Examples of "right conditions" include slabs in good condition with limited pipes/utilities poking through, larger slabs (i.e., larger than a typical residence), and undeveloped lots in warmer climates or where estimates of a future stack effect due to the building can be made.

If you elect to use flux chambers, be sure that enough chamber measurements are collected to get a representative value over the footprint of the building (analogous to placing enough borings on a typical site) and that they are located near edges where the slab meets the footing, over any zones with more cracks, and over the center of the contamination, if known.

Assuming uniform subsurface contamination, five chambers might be appropriate (one on each side of the structure and one in the center). If the contamination is not directly below, then fewer chambers on the side of the contamination might be appropriate. In all cases, chambers should be deployed for long enough periods to enable temporal variations to be assessed, similar to indoor air measurements (8 to 24 hours depending on the conditions; 24 hours if large temperature differences exist between day and night).

Why do you recommend small purge-and-sample volumes for soil-gas samples?

Multiple reasons. I too often see soilgas data from large Summa canisters (3L to 6L) with tracer/leak compound detections. (By tracer/leak compound, I am referring to a compound such as butane or isopropanol, deliberately applied during sample collection, that acts as a tracer of leaks from the surface or leaks in the sampling system.) Also, successive duplicate samples (i.e., one collected after the other) show larger variations than duplicates collected with smaller volumes. Remember, the larger the volume collected, the greater the uncertainty as to the source of the sample. (See Figure 1.) That's a plain fact.

So, if you are sampling near the surface, large extraction volumes will increase the potential that atmospheric air might be drawn down the outside of the probe body. If you are sampling under a slab, large extraction volumes will increase the potential that samples might be from a deeper depth or outside the slab. In addition, large purge-and-sample volumes can create vacuum conditions that cause contaminant partitioning from the soil into the soil gas.

All of these issues increase the potential that the collected soil-gas sample is not representative of in-situ soil vapor at the target depth. Finally, the larger the volume required, the larger and more complex the sample collection system required (e.g., vacuum pumps, larger sample containers).

What about when air labs tell me l need to collect 6L volumes to reach my required DL?

You shouldn't need to. Soil-gas DLs for VOCs of 0.2 to 0.5 ppbv (~ 1 μ g/m3 for most compounds) can be reached with only 300 cc of sample (as reported to me by a nationwide air lab) using method TO-15, and

■ continued on page 14

■ Vapor Intrusion *from page 13*

with volumes as small as 50 cc using methods 8260 SIM or 8021. Yes, larger canisters are useful in case repeated runs are required. But, for the TO-methods, one to three liters should be more than sufficient to enable re-runs, if necessary. For methods 8260 or 8021, 500 cc should be more than sufficient.

Is it true that the toxic organic (TO) methods are the only appropriate method for analyzing soil-gas samples?

No, but you may be hearing this from some of the labs that specialize in these analyses. The argument is that EPA methods such as 8260 and 8021 are soil and water methods that use liquid standards and hence are not appropriate for air samples. Further, according to the argument, soil-gas samples are air samples and, thus, should be analyzed by air methods that use gaseous standards. The key difference in the methods is not the type of standard but how the standard and sample are introduced into the analytical instrument. TOmethods use air concentrators. Methods 8260 and 8021 use direct injection or purge-and-trap injection systems.

For the majority of compounds of concern at vapor-intrusion sites (e.g., BTEX, chlorinated solvents), there is no significant difference caused by the injection methods. For some compounds (typically the more polar ones such as ketones and alcohols), methods 8021 and 8260 can give different values from the TO-methods by up to a factor of two to three if the



FIGURE 1. A basketball or a baseball? The 6L Summa canister has a volume about the size of a basketball, whereas the mini-can has an approximate volume of a baseball.

purge-and-trap injection method with liquid standards is used. In the cases where this might be an issue, either use the TO-methods or ask the laboratory to use vapor standards for 8260 or 8021.

The decision on what analytical method to use should be based primarily on the required detection level, project scope, and cost—in this order. See Table 1 to help you decide.

For example, if the compounds of concern at a site are only TCE, PCE, TCA, and DCE, then the GC-ECD is more than likely to reach the DLs required and it costs one-third what a TO-15 SIM would cost. And yes, the data will be legally defensible if the

Summary	y of Analytical Methods for	r VOCs i	n Soil-Gas Samples
METHOD	DETECTION LEVEL (µG/M3)	PRICE*	COMMENTS
8021 for MTBE/BTEX	10 to 20	\$75	False positives if high TPH
8260	100	\$ 100	Complete VOC list & naphthalene
8260 SIM	5 to 10	\$ 150	Subset of 5-10 compounds#
T014 or 15	1 to 5	\$ 250	Complete VOC list, no naph.
T015-SIM	0.01 to 0.05	\$ 325	Subset of 5-10 compounds#
GC-ECD	0.5 to 5	\$ 90	Chlorinated compounds only

* Listed price are estimated and will vary around the country.

You select the subset from the full VOC list.

lab follows the method QA/QC.

Why do you promote on-site analysis so heavily?

Mostly because on-site analysis allows you to use your brains in realtime. This is especially powerful for vapor-intrusion assessments because additional locations can be added, either spatially or vertically, based on the real-time data. It also allows mistakes (e.g., leaked gas breakthroughs, inconsistent numbers, hardware blanks) to be recognized on-site and verification or replicate samples to be collected as needed. Laboratorygrade instruments, including mass spectrometers, can be transported into the field, and they fulfill necessary analytical protocols.

Isn't your opinion biased, since you provide on-site services?

Yes, but not for this reason. The real reason for any bias is the power that real-time data and decision making bring to assessing this risk pathway—and I'm not the only one who feels this way. A growing number of federal and state regulatory agencies and consultants are hopping on this bandwagon. In fact, EPA has a realtime, instantaneous analyzer called the Trace Atmospheric Gas Analyzer (TAGA) that staff actively promote and use on vapor-intrusion sites. Also, EPA is a strong supporter and promoter of the Triad approach that includes on-site analyses (http://www.clu-in.org/triad/#usin).

(See "LUST Innovations, TRIAD, and Computer Imaging Move LUST Site Investigation into the 21st Century," *LUSTLine* #45.)

Why are you so worried about the hardware required by the TO-methods for soil-gas samples?

For a number of reasons, primarily:

- There are many connections and fittings, all with dead-volume and possibilities of leaks. (See Figure 2.)
- More hardware means more can break, have blanks, or not work properly.
- Few field technicians or fieldsampling companies have the experience of testing and using the hardware properly or fixing or repairing it if problems are recognized.
- Often, the connecting fitting/ tubing or flow chokes are reused between samples without being cleaned. Very recently, a lab provided me 30 canisters for a program with only two flow chokes (one to use plus a spare). What's wrong with this picture? If you're reusing flow chokes between samples, how do you know that they are not contaminated from the previous sample? At a minimum, a cleaning kit and instructions on how to clean the flow choke between samples should have been included.

Throw into this mix the bulkiness of the hardware (ever tried to put sixteen 6L canisters in your car?), and hopefully you can understand my concern.

I keep getting tracer/leak gas detections in my samples, and the regulators are not accepting the data. What am I doing wrong?

The problem probably stems from any one or all of the following scenarios:

- Collecting too large a volume of soil-gas sample (>1 liter) too close to the surface
- Not adequately sealing at the surface of the ground where the probe rod enters
- Leakage at the coupling inside the probe rod, if the post-run tubing method is being used



FIGURE 2. Comparison of a sampling train provided by a lab to fill canisters for off-site analysis vs. a syringe used for on-site analysis. The larger dead-volume and numerous connections of the sampling train increase the chances of equipment blanks and leaks.

- Using a permeable tubing to collect soil-gas samples
- Loose fittings on your sampling system train

What tubing do you recommend?

Rigid-wall, nylon tubing, 1/8" or 1/4" outer diameter. Believe it or not, Teflon, while inert, has a relatively high sorption for many compounds. The 1/8'' nylon tubing is easier to work with than the 1/4" tubing if soil-gas sampling is your only need. If permeability testing is desired, the 1/4" tubing is better. Stainless-steel tubing is fine for shallow sampling but is logistically more difficult to install as the sampling depth increases (>5'). Flexible tubing (e.g., rubber, plastic), such as the type available on rolls at the hardware stores, or tygon tubing should be avoided at all costs (too permeable).

What is an "alpha factor," and how do I use it when trying to scope a vaporintrusion project?

An alpha factor is a unitless empirical attenuation factor relating the indoor air concentration to either a subsurface soil-gas concentration (α_{se}) or to

a groundwater concentration (α_{gw}) as follows:

 $(\alpha_{sg}) = C_{indoor} / C_{soil gas}$ $(\alpha_{gw}) = C_{indoor} / (C_{water} * H)$

H is the compound's unitless Henry's law constant.

U.S. EPA and most oversight agencies have tabulated acceptable levels for compounds in breathing air for various risk levels (C_{indoor}). So, if you know the alpha factor that the oversight agency allows for soil gas or groundwater, you can calculate the required "fail level" and hence, detection level for the compound in either the soil gas or groundwater. Let's try one to see how it works:

From Table 2 of the EPA draft vaporintrusion guidance, the allowable air concentration for benzene at a 1 in a million risk level is $0.31 \mu g/m3$. For soil-gas samples collected at 5 feet below the structure, the default alpha factor from Figure 3a of the guidance for sandy soils is 0.002. What is the

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■ Vapor Intrusion *from page 15*

soil-gas "fail level" and what analytical method(s) could be used? Rearranging the first equation above:

 $C_{\text{soil gas}} = C_{\text{indoor}} / (\alpha_{\text{sg}}) = 0.31 / .002 = 155 \, \mu\text{g}/\text{m}3$

From Table 1 in this article, we see that all the methods can reach this detection level.

But, for sub-slab sampling, the EPA draft vapor-intrusion guidance uses a default alpha factor of 0.1. Now what is the soil-gas "fail level" and what methods suffice?

Answers:

Soil-gas "fail level" = 3.1 ug/m3 Analytical methods = 8260 SIM,

TO14, or TO15

What is the EPA vapor-intrusion "dead zone"?

Well, to be honest, it's my own term to describe the lack of direction in EPA's draft vapor-intrusion guidance on what sampling to do between 5 feet and the sub-slab (in review of this article an EPA representative called it the "No Predictive Modeling Zone"). This amounts to a $4 \frac{1}{2}$ gap in the vadose zone where there is no instruction. And yet, this is an important zone.

A number of key processes influencing the soil-gas concentrations are active in this zone, including bioattenuation, surface reaeration, barometric pumping, and infiltration of surface precipitation. Vertical profiles of soil gas adjacent to or under structures can be very informative and demonstrate that attenuation of the contaminant is occurring. Agencies should allow and encourage these data. The San Diego County Department of Environmental Health (DEH) is currently writing regulatory guidance and protocols for the "dead zone."

What is your opinion on sub-slab vs. near-slab sampling?

The default approach right now by some agencies is to collect sub-slab soil-gas samples and apply an alpha factor of 0.1 to 0.01. But sub-slab sampling has its share of problems.

Operationally, sub-slab sampling is easy to do. But for the responsible

party (RP), sub-slab sampling can definitely be a "Prozac moment." First, sub-slab sampling is much more intrusive than outside sampling and, more likely than not, will require access agreements and attorneys, especially if you are an RP with deep pockets. Second, the proper alpha factor to apply is not known, so the significance of detected values is not clear, and you may over exaggerate the risk. Third, sub-slab data alone give you no information on what is going on below in the vadose zone towards the source.

For these reasons, I typically recommend that clients refrain from sub-slab sampling at the start. Instead, I prefer to collect soil-gas data around the structure for an underlying source (e.g., groundwater contamination), or on the side of the structure towards the source for a lateral source (e.g., adjoining groundwater or soil contamination or a vapor cloud), in an attempt to demonstrate there is no potential risk. If oxygen levels are high, groundwater levels are not within two feet of the structure (e.g., basement, slab, crawlspace), and areas for air penetration exist around the slab (e.g., lawns and gardens), then chances are high that reaeration is occurring under the slab, and nearslab data will be representative of sub-slab, especially for residences with small slabs.

Remember also that contaminants in the vapor phase, like balls and groundwater, cannot run uphill and accumulate under a slab at higher concentrations than the source concentration. In other words, the very highest the sub-slab soil-gas concentration can be is the same as the soil-gas concentration at the source. So, assuming a groundwater source, if you measure the soil-gas concentration just above the groundwater, the sub-slab concentration can be no higher, even with preferential pathways. If the risk calculation passes using this measured value, you need not collect sub-slab samples.

Likewise, if you measure the soil gas midway between the source and structure, the soil-gas concentration will be approximately one-half the source concentration assuming a homogeneous vadose zone with no advection. So if measured values all around the structure at the middepth agree, and the risk calculation passes by more than a factor of two, sub-slab sampling is likely not necessary unless you have reason to suspect a preferential conduit.

If you must go sub-slab, try to stay in garages (if technically sound) to do so. And remember, collect enough samples to get a representative value under the slab. EPA recommends three sub-slab samples per domestic residence to characterize spatial variability, although I personally think one per side and one in the middle is better (total of five).

What's this I'm hearing about using radon gas as a natural tracer?

As mentioned previously, the difficulty with sub-slab soil-gas data is that the alpha factor is not really known and regulatory default values tend to be conservative, so use of them may overestimate the risk. Measurement of naturally occurring radon inside the structure and subslab can allow a site-specific alpha factor to be calculated that may be considerably less than the value allowed by the regulatory agency. That same alpha factor can then be used to estimate the indoor air concentration of the contaminant of concern, assuming that all vapors are entering the building at equal rates.

Keep in mind that like all the other tools being used for vaporintrusion assessment, radon has its limitations too. First, and perhaps foremost, you must have radon in high enough concentrations to be useful. Then there's a host of other questions: Are there any inside sources of radon (e.g., cement block, granite stone, and shower water)? How will the values vary with barometric pressure fluctuations? From season to season? And remember, indoor and sub-slab samples create access headaches. Nevertheless, if you are already collecting sub-slab samples, concurrent collection of radon data may prove useful, and it does not cost a great deal (<\$100 per sample).

Are hydrocarbons really bioattenuating in the shallow vadose zone, or is it propaganda by the oil companies in an attempt to minimize their vapor-intrusion problems? A vast number of studies have been performed that clearly demonstrate

the bioattenuation of hydrocarbon vapors in aerobic soils. Many, but not all of these studies, were performed by the oil industry (go to *www.API*. org to read published studies). In general, the studies show that when oxygen levels are 10 percent or greater and at least two feet of vadose zone exists between the contaminant source and the overlying structure, the hydrocarbons aren't likely to pose an unacceptable risk. (A published study by the New Jersey Department of Environmental Protection suggested oxygen levels as low as 6 percent are sufficient).

While there is a current effort to try and quantify the bioattenuation process and add a quantitative term to the existing models, it is more likely to expect that the bioattenuation rate will be extremely site dependent. The more accepted alternative is to document that this process is occurring by collecting vertical profiles of the soil gas for the hydrocarbons, oxygen, and carbon dioxide.

If shown to occur, some agencies are conservatively allowing a factor of 10 to 100 reduction in the alpha factor. EPA-OUST currently has a technical workgroup consisting of EPA and state regulators studying this issue with the intention of preparing guidelines or recommendations on assessing vapor intrusion at hydrocarbons sites.

To document that bioattenuation is occurring, I recommended that data be collected at a minimum of three locations vertically in the upper vadose zone to ensure that vertical variations are characterized adequately. If repeated data are desired, install vapor-monitoring wells (implants) for easy resampling.

What are the best current documents, including regulatory, on soil-gas collection for vapor intrusion?

• The most comprehensive regulatory document for the collection of soil-gas samples was written by California EPA (Department of Toxic Substance Control) in conjunction with the Regional Water Quality Control Board in January 2003.

http://www.dtsc.ca. gov/PolicyAnd-Procedures/SiteCleanup/SMBR_A DV_activesoilgasinvst.pdf

• The San Diego County DEH Site Assessment Manual has soil-gas collection guidelines for a variety of soil-gas applications, including upward vapor risk. These guidelines are not step-by-step protocols, but they present general issues that need to be considered and fulfilled. http://www.sdcounty.ca.gov/deh/ lwq/sam/vapor_risk_assessment_ 2000.html

• The API has written a soil-gas sampling document and has a number of papers on bioattenuation, J-E model, and other related topics.

http://www.api.org/bulletins

- EPA-ORD (Dr. Dominic DiGuilio) recently released a sub-slab soil-gas sampling standard operating procedure (SOP) that is available on the following Web site: (http://iavi.rti.org/resources. cfm?pageID=document).
- SOPs for vapor monitoring well/implants installation, subslab soil-gas sampling, deeper soil-gas sampling, and fluxchamber sampling are available on my Web site, as well as links to most of the above documents and Parts 1 and 2 of this series of *LUSTLine* articles. *www. HandPmg.com*

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20 Years *from page 5*

What Does The Future Hold?

I dream of leak-free tank systems, the end of operator error, gasoline in the tanks and cars and not in the environment (or better yet, vehicles propelled by something better for the environment), and...... ZZZZZZ. Actually, I'm too tired to dream. But for now, we're hanging in there, and we've got the program with the most "interesting" acronym. Go LUSTBusters!

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References

- Ellis, Patricia, 2003. A Hot Dog by Any Other Name Could Be Your Drinking Water. *LUSTLine* Bulletin 44, July 2003, pgs. 1-6.
- Federal Regulations, 1988, 40 CFR 280 Underground Storage Tanks – Final Rule as of 9/13/88 http://www.epa.gov/swerust1/fedlaws/cfr.htm# 40cfr280.
- Gray A. and A. Brown, 2000, Fate, Transport And Remediation Of Tertiary Butyl Alcohol (TBA In Groundwater (Abstract) In Ground Water: Prevention, Detection, & Remediation Conference and Exposition. Special Focus: Natural Attenuation and Gasoline Oxygenates, November 14, 2000, Anaheim, California; P278
- NEIWPCC (New England Interstate Water Pollution Control Commission), 2000, Survey of State Experiences with MTBE Contamination at LUST Sites, June 2000.
- Sakata, Rachel, and Mike Martinson, 2001, *Update on* State MTBE Regulatory Standards & Guidelines: Drinking Water & LUST Cleanup. Presented at 13th Annual UST/LUST National Conference, March 20, 2001.
- TPH Criteria Working Group, 1997, Total Petroleum Hydrocarbon Criteria Working Group Series, Vol. 4: Development of Fraction Specific Reference Doses (RfDs) and Reference Concentrations (RfCs) for Total Petroleum Hydrocarbons (TPH). Amherst Scientific Publishers, Amherst, Massachusetts, 137 pp.
- U.S. EPA, 2000, Memorandum from Sammy Ng, OUST to Regional UST Program Managers and State UST/LUST Program Managers: Monitoring and Reporting of MTBE and Other Oxygenates at UST Release Sites, January 18, 2000.
- U.S. EPA, 1999, Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites, Directive Number 9200.4-17P. http://www.epa.gov/swerust1/directiv/d9200417.pd.f
- U.S. EPA, 1997. Expedited Site Assessment Tools For Underground Storage Tank Sites: A Guide for Regulators, (EPA 510-B-97-001), March 1997. http://www.epa.gov/swerust1/pubs/sam.htm.
- U.S. EPA, 1995, Use Of Risk-Based Decision-Making in UST Corrective Action Programs, OSWER Directive 9610.17 March 1, 1995. http://www.epa.gov/swerust1/ directiv/od961017.htm
- Weaver, James W., and John T. Wilson, 2000, Diving Plumes and Vertical Migration at Petroleum Hydrocarbon release Sites. *LUSTLine* Bulletin 36, November 2000, pps.12-15.

Vermont Vapor Stories The Evolution of Vapor-Release Assessment Techniques

by Andrew Shively

ince February 2002, the Vermont Department of Conservation's (DEC's) UST program has discovered situations that represent acute or chronic releases of vaporphase petroleum from UST systems. Since our initial investigations, we have grown increasingly concerned that underground petroleum vapor releases (UPVRs) have the potential to significantly impact human health and the environment. Our experience seems to support findings in New Hampshire and California. (see *LUSTLine* #46 and #47); however, the topic is still in its infancy, and more knowledge is needed to nurture a greater understanding of the potential impacts, investigative tools, and remedial solutions in UPVR scenarios

The LUSTLine #47 article titled "Tracking Troubling Vapor Releases in New Hampshire" discusses the relationship of UST system pressurization and vapor releases. The research conducted by the New Hampshire Department of Environmental Services (NHDES) provides a shot of adrenaline to our body of knowledge on the topic. The study documents the chronic and dynamic force of very low pressure within UST ullage systems, presents a remedial technology that can be used to control the ullage system pressure, and demonstrates the reduction of volatile organic compound (VOC) impact to groundwater. I would like to help reinforce our information base by providing a framework of specific elements and techniques that should be considered when determining if UPVRs are a suspected source of petroleum contamination at a facility.

In the beginning, it was hard to imagine how a little gas vapor from the in-tank monitor (ITM) probe riser could cause groundwater contamina-

tion. In fact, as late as 1998, few people in the business paid any attention to a little gas vapor under an USTsystem manhole. How many times did a seasoned UST inspector open an uncontained vent-riser manway and note moderate gasoline vapors? Plenty I'd say. Almost routinely. But the vapor concentrations were also routinely and quickly dissipated after the manway was allowed to remain open, and with no apparent liquid source, the potential threat of impact was dismissed. That was the paradigm we operated under until early 2002, when an incident occurred that expanded our awareness to include vapors as a possible source of petroleum compound impact to human health and the environment.

An Explosive Episode in Paradigm Progress

In late February 2002, I was notified that intermittent but significant gasoline vapors were inundating the indoor air space of a retail gasoline facility in northern Vermont. The UST owner contacted the DEC because he had recently discovered that the back room of his facility had been filling with gasoline vapors during evening deliveries. He had not been informed of this fact until the night staff started complaining to the manager.

The manager learned that over a period of a several months, every time gasoline was delivered, the uninsulated back room would reek of gasoline vapors. The night staff had temporarily solved the problem by venting the back room—a good idea, since that was where they took cigarette breaks during the cold (and I mean cold) winter nights. Since the vapors diminished after delivery and venting, little was said about the condition.

Upon my arrival, several initial steps had been taken to reduce the indoor air impact and diagnose the



cause. An air-purifying unit had been installed in the back room to reduce overall VOC concentrations inside the building. A soil-vapor extraction (SVE) vent leg and high-vacuum motor with carbon treatment had been installed adjacent to the building in the area where the electrical conduits from the tanks entered the back room—Area of Concern #1 (AOC #1)—and an initial UST system evaluation had been conducted by the consultant.

The initial evaluation revealed the following:

- An in-tank monitor (ITM) probe communication wire had been installed such that gasoline vapors could easily escape and accumulate in the subgrade manway of the probe riser.
- The electrical conduit junction box for the ITM communication wire and the UST interstitial sensor wire were not sealed, allowing vapors to migrate preferentially toward the building.
- The routine UST compliance inspection did not reveal any liquid release sources from the gasoline USTs.
- The UST and Air Pollution Control (APC) regulatory requirements were in compliance.
- No gasoline spills had been reported in the area of the facility, and no visual indications of small unreported spills were observed.

Based on the observed status of the UST features and lack of an observable or reported spill, a liquid release was concluded to be unlikely. The owner agreed to and arranged for a helium test to determine if any additional or less obvious vaporrelease sources existed. The only significant helium source identified was the previously mentioned ITM proberiser communication wire fitting. The



FIGURE 1. *ITM and interstice risers with electrical junction box, post repairs. Note UST system backfill.*

riser was contained in a 24" shallow manway with the UST system backfill exposed. (See Figure 1.)

As part of the emergency response, the SVE system was operated to reduce VOC impact to indoor air space. VOC influent concentrations measured during active SVE system operation declined from 200 to 300 parts per million (ppm), as measured by a photoionization detector (PID) at start-up, to 30 to 40 ppm within a few hours of operation. The SVE remained in operation until the helium test could be conducted and was shut down during testing.

Following testing and repairs to the ITM communication wire assembly and the junction box, a postrepair SVE start-up test measured no detectable influent VOCs by PID. Additional monitoring of the SVE system operation over the following week found no detectable influent VOC concentrations, and the emergency remedial equipment was dismantled and removed from the facility.

Groundwater monitoring conducted on the site indicted that no discernible additional impact of groundwater had occurred in the area of the SVE system, but a new previously unknown plume of methyl-*tert* butyl ether (MtBE) in groundwater was identified in another isolated area of the site (AOC #2). The common thread connecting AOCs #1 and #2 to the vapor release source location was electrical conduits for the ITM and interstice sensors for a diesel UST installed in a separate excavation from the gasoline USTs. The certainty of concluding that the new MtBE plume in groundwater was from the vapor release at the gasoline UST appears logical but not conclusive. What is certain, however, is that an underground petroleum vapor release can occur from an UST system, and it can cause significant human health impacts that require emergency corrective action. Furthermore, the force driving the emission of vapors appears related to delivery pressures.

LUST Sites Calling

Clearly, the scenario described above represents a potential human health impact-200 to 300 ppm VOC in indoor air is nothing to dismiss. The 1996 Threshold Limit Values (TLVs) for gasoline, as published by the American Conference of Governmental Industrial Hygenists (ACGIH), identify gasoline as a carcinogen and adopt a time-weighted average (TWA) exposure value of 300 ppm with a short-term exposure limit (STEL), or ceiling, of 500 ppm for airborne contaminants. At the time of the incident, the indoor air contaminant levels were taken very seriously, but the connection of a petroleum vapor release to a groundwater impact seemed less certain-at least until our next reported incident.

In October 2003, the DEC Sites Management Section (SMS) was notified of extremely high MtBE concentrations in groundwater downgradient of an active UST system at a location in Colchester, Vermont. The MtBE concentrations were the highest recorded in the four years of quarterly groundwater monitoring conducted at the site (See Table 1).

The site was monitored for a baseline of contamination concentra-

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MTBE Concentrations (ppb) in Groundwater, Colchester				
Date	MW-2	MW-3	MW-4	SS-2
5/18/1999	1	1	1,210	64
9/13/1999	420	260	900	160
12/21/1999	250	100	1,800	16
3/7/2000	160	100	2,100	12
5/31/2000	300	370	1,200	11
9/22/2000	213	1	264	66
3/29/2001	200	1,000	1,260	
6/18/2001	400	1,000	642	
9/17/2001	364	1,000	756	10
12/28/2001	84	500		
3/8/2002	1,200	240	2,300	28
6/3/2002	1,610	672	233	21
3/31/2003	192	1,080	1,520	10
9/11/2003	53,000	47,000	641	1,740
11/28/2003	33,000	64,000	4,400	130
3/18/2004	1,060	414		58
7/2/2004	191	198	5,720	29

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tions prior to a corrective action feasibility investigation (CAFI), and a pilot study of remedial options was scheduled for the fall of 2003. The groundwater analytical results took a drastic turn upward during the summer of 2003. Most unsettling was the fact that only MtBE seemed to be increasing, both significantly and suddenly. MtBE-contaminated groundwater was also infiltrating a storm sewer along the downgradient boundary of the site and discharging to a surface water feature (SS-2). (See Table 1.) Was this the lead edge of an upgradient plume? Was the source within the tank cavity? Was it a spill? Was it a UPVR impacting groundwater?

An inspection conducted at the facility during the summer of 2002 prior to the request for a CAFI had not found any signs of a liquid release or spill, let alone significant compliance deficiencies. APC records indicated the facility was in compliance with testing and inspection requirements. The operator maintained adequate documentation and operational release detection. The peak MtBE concentrations in groundwater suggested the source centered in the tank cavity. A PD test was suggested to determine if a potential vapor-phase release existed and, if so, to pinpoint the release location. The owner agreed to and arranged for a PD test with oversight by DEC, a contractor, and a consultant. The test was conducted in late October 2003.

Prior to the PD test, a routine inspection was conducted to establish a baseline of possible liquid release sources. The inspection resulted in the same conclusion drawn in 2002signs of a liquid release, unreported spills, or compliance deficiencies. During the test, several pressure-decay release sources were identified, including a misthreaded vent-riser cap and a compressed cap gasket. Other decay sources included loose fill risers at both gasoline USTs located on site. All of these potential vapor-release sources were repaired at the time of the test and the PD test ultimately passed.

Groundwater analytical results following testing and repair showed a marked decline in MtBE concentra-



FIGURE 2. VOC measurement by PID at suspected vapor release source.

tions, beginning with the monitoring location immediately downgradient (MW-2). Over time, it appeared that the MtBE plume migrated, as expected, along the groundwater gradient (MW-2 to MW-3) and was diluted with uncontaminated groundwater, thereby reducing overall groundwater concentrations (MW-3 to MW-4). Groundwater discharged from infiltration into the storm sewer (SS-2) also declined substantially following the October testing and repairs.

The SMS site manager considered the findings of the inspection and the reduction of groundwater concentrations over time to be indicative of a new release and requested additional investigation under a second \$10,000 release deductible. Currently, corrective action has been postponed for the site pending ongoing monitoring with declining VOC concentrations in groundwater (see Table 1) and declining discharge concentrations to surface water.

An Evolving Issue

The vapor-release issue and the second deductible came as a shock to the regulated entity, and, based on the findings of inspections, testing, and monitoring, a new "something" had clearly occurred. That "something" was clearly a contaminant from a petroleum storage system. Significantly, the results of testing and repairs appeared coincidental to the decline of MtBE concentrations in groundwater. I began to consider ways to bridge that gap between vapor-phase VOC emission concentrations and groundwater analytical concentrations.

The PID is an accepted portable device for direct-read measurement of VOC concentrations. We felt that collecting atmospheric and belowgrade, vapor-phase VOC concentrations would provide us with a useful set of data to determine the relative significance of detected vapor-phase VOC emissions from tank-top features and to help pinpoint the source of the emissions in an effort to make immediate repairs. The process would be to screen for atmospheric VOC concentrations before opening features, immediately upon accessing features, and during the incremental increase of UST ullage system pressure using pressure decay test methodology. (See Figure 2.)

The most obvious isolated subsurface areas of UST systems are the below-grade features contained in manways and sumps. Ancillary riser manways are generally uncontained (open bottom) and installed within the system backfill underlying the concrete pad. These types of features include vent-extractor risers, Stage I vapor-recovery poppets, in-tankmonitor risers, and unused risers. Vapor emission sources could exist at any uncontained feature connected to the UST ullage system, including Stage II and vent piping. For tank-top features, a competent concrete pad with tight manway covers acts as a cap, forcing emitting vapors to accumulate in the below-grade atmosphere of the capped manway. (See Figure 3.)

Below-grade access features allow for the accumulation and measurement of VOC emissions from tank-top features. The VOC emission data will assist in determining if a vapor release is occurring, the relative concentration of the vapor release, and the specific source point of emission. Other elements that impact the certainty of a vaporsource release determination include:

- Observed or documented information of UST system configuration
- Surface protection equipment features (i.e., contained or uncontained)
- Backfill material (i.e., compacted sand or peastone)
- Subsurface migration pathways (i.e., electrical conduits and back-fill pathways)
- Groundwater data (i.e., depth to groundwater and VOC concentrations)
- Testing results (i.e., pressure decay or helium)
- Repairs (e.g., tighten seals, replaced gaskets, additional pipe dope)

In June 2004 an exercise was conducted at another LUST site with active gasoline USTs to determine if a vapor release was occurring. The SMS site manager had been concerned that MtBE concentrations had been rising downgradient of the active UST systems. The site manager suspected the source could be from a vapor release because only MtBE was increasing-to the highest level ever recorded on-site. A pressure decay (PD) test was scheduled for mid June 2004. As part of the PD test, a vaporrelease screening was conducted with a PID before test set up, during pressurization of the common UST ullage system, and after repairs to source features.

Before the PD test setup, the atmosphere above each UST feature was screened with a PID to determine if fugitive VOC emissions were escaping the sealed manways or if ambient background VOC concentrations existed that could skew the values measured upon access to each feature. No VOCs were measured by PID during the atmospheric-assess-



FIGURE 3. Riser manway with 235 ppm measured at static ullage system pressure. Note condition of caps and backfill material at the base of the manway.

ment phase of the exercise. During test setup, all potential vapor emission sources in subgrade UST-feature manways were screened with a PID as the manway covers were removed.

The VOC concentrations measured represent VOC values that exist under chronic, standard operational system pressures. Based on the data presented in the *LUSTLine* #47 article, standard operational pressures of a Stage II-compliant UST systems remain greater than 0.0 inch water column (wc) and less than 1.0 inch wc. More importantly, this simple screening exercise is repeatable and does not require an induced increase of ullage system pressure.

From the setup screening exercise, three suspected VOC emission source locations were determined to exist—the ITM riser for the midgrade gasoline UST, the ITM riser for the premium-grade gasoline UST, and the vent riser for the premiumgrade gasoline UST. (See Figure 3.) Specific emission sources were pinpointed at each of these features, and the ongoing static VOC emission value was measured. The PD test began with the gradual increase of ullage system pressures to 5.0 inches wc positive pressure. (See Table 2.)

The VOC emission value exercise was then repeated at all potential emission sources. One additional emission source was identified at a system pressure of 5.0 inches wc. Based on the calculated rate of decay, the initial PD test was aborted at 5.0 inches wc, and repairs were made to the identified features with measurable VOC emissions. Repairs included:

- Tightening fittings of communication wires of electronic release detection equipment
- Removing and rethreading of riser features (riser bar caps) with additional (or any) pipe dope
- Replacing cap gaskets

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Table 2 Pressure-Decay Test VOC Emission Concentrations (in ppm)				
Initial	Mid ITM	Mid vent	Prem ITM	Prem vent
Static	79.5	ND	168	235
5.0" wc	146	83	<200	<300
Post repair				
Static	ND	ND	ND	ND
5.0" wc	ND	ND	>1.0	>1.0
10.0" wc	ND	ND	>1.0	>1.0

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One major advantage of conducting this type of pressure-decayassisted vapor-release assessment is that the VOC emission points can be itemized, the emission value can be measured, repairs can be made on the spot before proceeding, and a VOC emission reduction can be measured, real time. (See Table 2.) As a result of the above exercise, MtBE concentrations in groundwater immediately downgradient of the active UST system have begun to decline. (See Table 3.) Additional groundwater sampling is pending.

TABLE 3MtBE concentrations in
groundwater immediately
downgradient of an active UST system.
(Note the period of concentration reduction
following pressure-decay-assisted vapor-
phase assessment and source repair.)DateMW-10

Duto	
12/28/2001	950
3/25/2002	890
6/17/2003	510
11/18/2003	5200
7/9/2004	980

If MtBE concentrations in groundwater downgradient of the active UST system continue to decline as a result of the pressuredecay-assisted vapor-release assessment, the conclusion that a vapor release was occurring and that the source of the VOC emission was repaired, will lead us to a determination that a vapor-phase underground petroleum release had occurred.

The Evolution Continues....

The assessments presented include three examples of what I consider UPVRs. These are but three. Additional UPVR investigations are currently underway at ongoing groundwater monitoring sites and post-active remediation sites. The degree of certainty in determining that UPVRs exist varies considerably. The determination requires time-sensitive information from often different regulatory jurisdictions. LUST site monitoring data, spill data, APC data, and UST compliance data must all come together to provide a reasonable certainty that a release has occurred. These data must also lead to a high degree of certainty that the release can only be attributed to underground petroleum vapor-phase emissions from petroleum UST features.

The timeliness of information from these four data sources has a big impact on the degree of certainty. Sometimes routine replacement of caps or general maintenance events can eliminate vapor sources. These events could be UST-compliance related or APC-compliance related. Collecting the UST and APC compliance data and establishing a chronology of events enables a comparison of MtBE concentrations in groundwater over time.

The groundwater monitoring results maintained as part of ongoing, pre- or post-remedial LUST sites may indicate erratic MtBE spikes, while the traditional benzene, toluene, ethylbenzene and xylenes (BTEX) concentrations decline. Sometimes these continued MtBE fluctuations drive remedial decisions long after BTEX standards have been meet. Conducting a pressure-decayassisted vapor-release assessment allows us to detect VOC emissions values to pinpoint source locations,



Photos by Charles Harp.

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

prioritize repairs, and confirm source-elimination results. The results of this effort provide a point in time in the chronology of LUST-site data, APC data, and UST data. If known VOC emissions are eliminated and a substantial reduction of MtBE concentrations in groundwater results, the certainty of concluding a UPVR existed has increased validity.

The current analysis of UPVR assessment results and recommended repairs indicate a correlation with groundwater MtBE concentration reductions. Ongoing maintenance of tank-top features can result in a reduction of chronic VOC emissions at tank-top features and a reduction of MtBE concentrations in groundwater. But as I stated in the opening paragraphs, the topic is still in its infancy, and more knowledge is needed to nurture a greater understanding of the potential impacts, investigative tools, and remedial solutions in UPVR scenarios.

I hope the framework of specific elements and techniques presented reinforces our information base when determining if UPVRs are a suspected source of petroleum contamination at a facility. Each small step taken to further understand the topic will promote greater certainty that UPVRs are a threat to human health and the environment and lead to a greater degree of pollution prevention and resource conservation.

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Honey, We Shrunk the Leaks Thoughts on Those Small-Time Vapor Releases

by Bruce Bauman

Trom recent articles and conference presentations there would appear to be-at least in several states—a heightened interest in the potential effects of subsurface releases of gasoline vapors from UST systems. The last couple of issues of LUSTLine have included several interesting articles that address the general topic of "small gasoline releases," which might be simply defined as UST system releases that are below the stated minimum release-detection rates identified in the federal regulations (i.e., 0.1 - 0.2 gph).

It can be considered a testament to the success of the state and federal UST programs that while we used to focus on releases of hundreds or thousands of gallons of gasoline, the debate has now moved to examining the effects of comparatively tiny releases. While it will always be our goal to minimize the frequency and amount of all UST releases, it will be very important at this time for all of us to better understand the prevalence and significance of these kinds of small releases. We need to put them in the context of our overall goals for UST management. We need to determine if existing regulations provide a sufficient framework for adequately addressing concerns with this potential groundwater pathway, or if new approaches might be required.

Can We Put Vapor Releases Into Perspective?

LUSTLine #46 provided a summary of the California "Field-Based Research" study, the first study to suggest that small vapor releases might be occurring in UST systems, especially those with vacuum-assist Stage 2 vapor recovery. That article also summarized a sophisticated and sensitive release-detection technology that can be used to identify certain types of releases that are much smaller than 0.2 gph.

LUSTLine #47 had a discussion of some detailed, site-specific field evaluations of vapor releases being conducted by the New Hampshire Department of Environmental Services (NH DEP). NHDES is also in the process of amending its UST regulations, including emphasizing the reduction potential problems from vapor releases. Presentations on this topic have been made at recent national conferences.

These articles appear to reflect a perception that is gaining increasing acceptance—that while we have been successful in greatly reducing the likelihood of liquid releases from USTs (and very importantly, greatly reducing the mass of the release), vapor releases into the tank pit might also contribute to groundwater impacts in some situations. Clearly, there are a number of case studies that would suggest this mechanism is real.



What is not clear, however, is how prevalent vapor release problems might be. For example: What percentage of existing USTs might have vapor releases? What is the nature of those releases (e.g., the mass of vapor expelled, the composition of the vapor, reformulated gasolines versus conventional gasolines)? What are the potential groundwater quality impacts of those types of releases under different environmental conditions (e.g., type of backfill and native soils, depth to groundwater)?

While there are interesting observations regarding vapor releases in a handful of sites in a few states, I'm not certain that we are currently able to routinely differentiate groundwater impacts that are caused only by vapors (versus impacts that may be caused by a combination of other known potential "small release" sources that may occur from various parts of the UST system) from operation and maintenance practices, or even consumer-related releases.

Will the Real Source Please...

I think most LUST investigators would agree that it is frequently very difficult to determine the specific

■ Small-Time Vapor Releases from page 23

source or sources of gasoline that have triggered the need for corrective action at a site. As all the "causes of leaks" studies show, there are multiple potential sources from various components of UST systems. Those studies also indicate that sometimes, small releases of gasoline (e.g., weeps, drips, overfills) may occur at dispensers, in sumps, or other locations. It's also known that there can be routine, small (or less frequently, relatively large) surface releases from consumers filling their vehicles or gas cans.

Individually and collectively, those small releases may elude the capability of the release detection technologies routinely employed to meet regulatory requirements. We need to keep in mind that all of these other potential sources cannot be ignored in any holistic assessment of how small releases might impact groundwater quality. But, as our time/space continuum does not allow a discussion of the broad topic of all the types of small releases here, we'll mainly focus on vapor releases.

While some of the current vapor studies may be able to make some initial estimates regarding the concentrations of vapors that might be released from various parts of an UST system, it is more difficult to get a handle on the mass of vapor discharged from the tank and how those discharges might vary over time. It is even more difficult to estimate how much of that vapor (and which vapor components) might actually get transferred to the water table.

Wanted Soon: More Data

It can be expected that biodegradation would play a very significant role in potential attenuation of vapors during vadose zone transport or at the water table. For example, a 2002 lab study documented the cometabolic biodegradation of MtBE and pentane vapors—pentane is found in high concentrations in gasoline vapors (Dupasquier et al., 2002).

In one of the most informative research articles published on this topic of small releases, Swiss researchers (Pasteris et al, 2002) found that while gasoline vapors (specifically, MtBE) from a small NAPL release in a lysimeter would migrate to a shallow water table (< 2 m from their emplaced source), less than 1 percent of the mass of the MtBE ended up in the water. This was sufficient to cause a high concentration of MtBE at the water table (over 3 ppm) but represented a very small mass. Most MtBE was volatilized, and some was biodegraded. No petroleum hydrocarbon compounds were detected in

While it will always be our goal to minimize the frequency and amount of all UST releases, it will be very important at this time for all of us to better understand the prevalence and significance of these kinds of small releases.

groundwater in that study, primarily because of biodegradation.

A follow-up study (Dakhel et al., 2003), using different hydrological conditions and a gasoline with both MtBE and ethanol, showed much more MtBE transport to the water table, perhaps because of reduced biodegradation owing to the presence of ethanol and reduced volatile losses. While these two studies are very helpful in identifying key processes regarding small releases, they have their limitations, and further lab and fieldwork will be required to fill out our knowledge base.

To better understand the potential water quality effects of vapor releases, it would be very useful if we had good data from a number of UST sites that would indicate how much of the vapor that may escape actually ends up at the water table, versus how much is volatilized to the atmosphere or biodegraded. Clearly, that will be affected by a number of sitespecific properties, such as the "size," intensity, and duration of the vapor releases, the type of backfill and native soils, the type of paving over the UST, the depth to groundwater, and possibly factors like the presence or absence of previous releases at that site.

Given our limited knowledge of the nature of groundwater quality

impacts from vapor releases, proper care should be exercised in estimating how vapors may have contributed to groundwater contamination at any existing UST facility. For example, in a recent incident in Maryland, a number of private drinking water wells around a UST facility were found to have MtBE. (See related article on page 34.) Because the tanks at that facility tested tight, and because an extensive evaluation of possible sources indicated there may have been some sources of vapor losses, there have been some presumptions that vapor problems are the primary source.

From my limited understanding of that specific site, at this point in time I'm a little skeptical that vapor releases have been the only source of the groundwater problems. I would not discount that they may have contributed to some fraction of the overall groundwater impacts, but it is far from clear that they are the sole source of contamination.

The Work at Hand

Concerns about vapor and other small releases have prompted the Maryland Department of Environment to begin accelerated development of new UST regulations. Hopefully those regulations will not be rushed. We need to take the time to allow our current, limited understanding of small releases to be expanded sufficiently to ensure that cost-effective, flexible approaches to this complex problem can be crafted.

We should also learn a good bit more about the characteristics of the soluble plumes that can be created from small releases and how they may differ from plumes created by large NAPL releases. Modeling research by the American Petroleum Institute and others suggests that the contaminant mass flux (see LUSTLine #46, "Flux Redux," or Einarson and Mackay, 2002)) associated with plumes from small releases will be much less likely to impact offsite drinking water wells than plumes from larger releases (even though both may have similar concentrations of dissolved components in the source area).

As the authors of the various *LUSTLine* articles on this topic have indicated, there is still a lot of work to

be done before we can truly obtain a sufficient understanding of what's going on and when environmental problems might arise from vapor or other small releases. To recap, we all probably agree that vapors can and do escape from UST systems and that, in some cases, those vapors can impact groundwater quality near the tank field. There also is likely consensus that vapors of the more soluble and less biodegradable gasoline constituents would present a greater likelihood of contributing to elevated concentrations in groundwater.

We have learned a good bit in the last few years, and that knowledge clearly indicates that this issue is worthy of more investigation. But before effective solutions can be developed and implemented, we have a lot of questions to answer, including:

- Can we reliably detect very small releases?
- How many existing UST sites have similar problems with vapor releases?
- What are "typical" vapor-release rates for the existing population of UST systems?
- Is there a de minimis rate of subsurface release of gasoline from

an UST system that could be considered highly unlikely to result in any significant or long-lasting degradation of groundwater quality?

- What do we know about the characteristics of plumes caused by small releases that might influence the kind of corrective action required?
- What routine UST maintenance and groundwater monitoring practices would be the most helpful in preventing problems or minimizing problems, should they arise, and might such approaches provide an equivalent level of environmental protection as new release detection/ prevention technologies?

What Is "Vapor-Tight"?

In his remarks at a recent technical conference, U.S. EPA Office of Underground Storage Tank Director Cliff Rothenstein stated that regarding vapor releases, "We need to get to the bottom of this. We need to find out the source of the problem and... make sure systems are both liquidand vapor-tight." This is an admirable performance goal for UST systems, but the key issue will be to

Information from API on Small Vapor Releases

The American Petroleum Institute and its Soil/Groundwater Technical Task Force have been actively investigating various topics associated with small releases for several years, and they have ongoing projects that will also help us better understand and manage this issue. Visit *www.api.org/groundwater* to obtain more information or download some of the following reports:

- Simulation of Transport of Methyl Tert-Butyl Ether (MTBE) to Groundwater from Small-Volume Releases of Gasoline in the Vadose Zone, Bulletin No. 10, http://api-ep.api.org/filelibrary/bulletin10.pdf, June 2000
- Evaluation of Small-Volume Releases of Ethanol-Blended Gasoline at UST Sites, Bulletin No. 19, http://api-ec.api.org//filelibrary/19_Bull.pdf, October 2003
- Evaluation of Potential Vapor Transport to Indoor Air Associated With Small-Volume Releases of Oxygenated Gasoline in the Vadose Zone, Bulletin No. 21, December 2004
- Maximum Potential Impacts of Tertiary Butyl Alcohol (TBA) on Groundwater From Small-Volume Releases of Ethanol-Blended Gasoline in the Vadose Zone, Bulletin No. 22, December 2004
- Maximum Potential Impacts of Tertiary Butyl Alcohol (TBA) on Groundwater From Small-Volume Releases of MTBE-Blended Gasoline in the Vadose Zone (in progress)

determine an acceptable definition of "vapor tight."

A closely related question was addressed in *LUSTLine* #47 ("The Limits of Leak Detection"), where author Marcel Moreau noted the ability of certain technologies to detect "phenomenally" small releases. He wondered if there was a practical environmental benefit, asking "Can leak detection be carried too far?" That is a question that must also be asked about vapor releases. Is there some threshold level of vapor release that might be regarded as unlikely to cause groundwater problems?

It will take some concerted effort by all parties, probably over the next year or two, to get a sufficiently comprehensive understanding about the nature and potential impacts of small releases/vapor releases. Then we must development management options that will provide efficient and cost-effective approaches that are commensurate with the level of health and environmental protection we wish to achieve. I would expect that like other aspects of the UST program, individual states will tailor their response to the nature of the problem as it is characterized in their state. We've made a very good start toward figuring out this problem, and I'm confident that it won't be too long before we will have come up with a handful of good solutions.

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References

- Dakhel, N.; G. Pasteris, D. Werner, and P. Hohener, 2003, Small-volume releases of gasoline in the vadose zone: impact of the additives MTBE and ethanol on groundwater quality, *Environmental & Science Technology*, 37(10); 2127-2133.
- Dupasquier, D., S. Revah, and R. Uria. 2002, Biofiltration of methyl tert-butyl ether vapors by cometabolism with pentane: modeling and experimental approach, *Environmental & Science Technology*, 36 (2); 247-253.
- Einarson, M.D., and D.M. Mackay, 2001, Estimating future impacts of groundwater contamination on water supply wells, *Environmental & Science Technology*, 35 (3), pp. 66 A-73 A
- Pasteris, G., D. Werner, K. Kaufmann, and P. Hohener, 2002, Vapor phase transport and biodegradation of volatile fuel compounds in the unsaturated zone: a large scale lysimeter experiment, *Environmental & Science Technology*, 36 (1), 30-39.

Spill Buckets: Mistaken Expectations?

by Dale W. Stoudemire

"Spill prevention equipment that will prevent the release of product to the environment when the transfer hose is detached from the fill pipe (e.g., a spill catchment basin)." This is the extent of federal guidance for spill prevention equipment that most of us who regulate underground storage tanks were given—many state statutes also reflect this guidance. The concept of a spill catchment basin or

bucket is simple, and several designs on the market fit the concept exactly, so you might think this was the only guidance we needed. Well, surprise, it has become increasingly apparent that we had the mistaken expectation that these buckets would continue to function with little cost or maintenance for the life of the tank system.

Hints of a Problem

In South Carolina, our first hints of a problem showed up as we investigated a possible subsequent release at a site already undergoing cleanup. Monitoring reports showed unexplained increases in contaminant levels, but tank and piping tightness tests indicated that the systems were tight. In the absence of compelling evidence, we initially attributed these increases to errors in the baseline contaminant estimations.

After several quarters of problems, we began to look for other possible sources for the contamination. In one instance, we found that a seal in a spill bucket had moved out of position, allowing product to leak out every time fuel was leaked from the hose into the spill bucket. This displaced gasket was our first discovery of what threatens to become a large and costly situation.

As our inspectors began to see more spill buckets that had various problems, beginning in mid-2003 our program began to focus on spillbucket integrity during routine inspections. If the condition of a bucket appeared suspicious, the inspector would pour a small amount of water into the bucket and observe the level for several minutes. If the water level dropped, we assumed the water was leaking from the bucket into the environment. If the leak was later found to be the result of a leaking drain that fed back into the tank, the bucket was not counted as leaking.

Questions have been asked about this protocol. This "test" was not designed as part of a controlled study. The inspectors were not attempting to measure the performance of the population of spill buckets. Rather, they were deciding whether a situation encountered at an inspection needed further investigation.

The question of disposal of the test water has also been raised. We do not pour water into every bucket that we inspect. The inspector only tests a bucket if he or she is reasonably certain that it has a problem. Disposal of the water has not been an issue, because almost every bucket tested

with water turned out to be leaking, and the water drained out through the existing hole. Considering that the holes in the buckets have already been releasing pure petroleum, the small amount of water is not considered a significant problem.

During this same time period, we also began to find buckets with severe problems that had developed since the last annual inspection. We began to see more displaced gaskets and large cracks or splits in the buckets, usually in the flexible bellows. In response to these findings, I decided to examine the data for trends.

The Study

Even though the data were collected for routine inspections and not as a part of a controlled test, examining it provided useful information. Our database tracks the inspections and any violations that we encounter. We conduct about 4,000 inspections annually, so a direct examination of each inspection was not practical. I looked at the results of 12 months of inspections in a selected region—a total of 910 tanks at 337 locations.

Since the records for each of these inspections contained informa-



A spill bucket with a large horizontal split in the plastic bellows. The brown spot below the tip of the screwdriver is the soil beneath the bucket.

tion on any leaking spill buckets that were encountered, it became a simple matter of counting the number of tanks with leaking spill buckets and dividing by the total number of tanks with spill buckets to get a percentage.

What I Found

Of the 910 tanks in the sample, 76, or 8.4 percent, had leaking spill buckets. Assuming this population was representative for the state, I applied the 8.4 percent to the entire population of tanks in the state and arrived at the conclusion that an estimated 1,032 spill buckets are currently leaking statewide. This means that there are 1,032 potential releases that will have to be reported and investigated. Some of these investigations will undoubtedly result in the discovery of contamination requiring remediation. Since it appears likely that this problem will worsen over time as the buckets age and continue to degrade, I anticipate we will discover more of these leaks in the future.

What I Learned

Once I identified the problem, I searched for possible causes. The answer was surprising—spill buckets

are not designed to last for the life of the tank system. Many spill buckets are made from high-density polyethelene (HDPE) or have HDPE components. As we have learned from experience with flexible piping, HDPE can degrade from long-term contact with petroleum.

According to a representative for a major manufacturer, many spill buckets installed for the 1998 upgrade requirement are approaching the end of their useful lives. In defense of the manufacturers, I must say that I was never told the spill buckets were designed to last; I only assumed it. The representatives I spoke with have been very forthcoming about the performance of their products. The mistake was not in the claims for the performance of the buckets. Rather, it was in my assumptions about them. Unfortunately, I suspect that many tank owners and regulators share my assumptions.

What to Do

There are several things that tank owners can do to lengthen the life of their spill buckets:

- Check spill buckets after every delivery to ensure that spilled fuel is removed immediately. As many of us have seen, spill buckets are not always thoroughly cleaned after catching small petroleum spills. In addition, the buckets often contain sand, dirt, or debris. According to the manufacturers, this material, if left in the bucket, will significantly shorten the life of the bucket. Water and debris of any kind should be removed from the bucket weekly.
- Replace cracked or broken spill-bucket lids immediately.
- Check clamps and seals regularly, and tighten, adjust, or replace as needed. Although I have not yet discovered the exact cause for it, exposure to fuel seems to cause the seal on some models to become displaced. Regular inspection and maintenance should detect this problem early and help prevent any possible releases.
- Be prepared to replace spill buckets periodically, and budget accordingly. If buckets



A spill bucket with a vertical split. The screwdriver is touching the soil beneath the bucket.

A completely deteriorated spill bucket. More than half of the bottom is missing. The lid was in place, so it is not clear how the leaves got into the bucket.

installed in 1998 are nearing the end of their useful lives, then a six-year replacement cycle might be a workable planning guide. I learned that, in South Carolina, the cost of replacing a spill bucket is around \$1,500. On a four-tank installation, the owner will need to plan on budgeting about \$6,000 for replacement. On a six-year replacement cycle, at an average cost of \$1,000 per year, spill-bucket maintenance could cost more than some owners spend annually on release detection.

All of these suggestions are for the short term. A long-term solution is for tank owners to insist on spillbucket designs that correct these problems. They should use their buying power to encourage manufacturers to select more durable plastics or corrosion-resistant metals that will last for a more reasonable period of time. Current designs could also be modified so an easy and less expensive replacement cycle could be implemented.

Pay Attention

Many tank owners and regulators have assumed that spill buckets are relatively maintenance free and will last for the life of the tank system. It turns out that this assumption was wrong. Spill buckets appear to have a much shorter life span than some other tank-system components, so regular maintenance is required to extend bucket life, and owners should plan for regular replacement. As regulators, we must emphasize the condition and functionality of the spill bucket, not just verify that one has been installed. ■

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Should Remote-Earth Testing of Galvanic Cathodic Protection Systems Be Required?

by Kevin Henderson

esting of underground storage tank UST cathodic protection (CP) systems has historically been one of the more problematic aspects of UST regulation. Industry standards provide a great deal of latitude with respect to exactly how CP testing is to be conducted. In addition, very little is prescribed relating to adequate documentation of such testing. Therefore, it can be difficult for regulators to evaluate whether or not testing and the resultant documentation is sufficient to indicate compliance with UST rules and regulations. More importantly, the adequacy of the CP system to effectively mitigate the potential for a corrosion failure of the UST system may be in question.

In an effort to improve this situation, the Mississippi Department of Environmental Quality (MDEQ) developed a guidance document titled "Guidelines for the Evaluation of Underground Storage Tank Systems" Protection Cathodic (MDEQ, 2002). This guidance document is intended to foster a more uniform approach for not only how CP testing is conducted but also what criteria are necessary in order to "pass" the test. In addition, specific forms must be completed that provide documentation on exactly how the test was conducted so it can be reproduced and a means for effectively evaluating the methodology/ results of the test.

One requirement of the MDEQ policy that is relatively unfamiliar to many practitioners is the testing of galvanic CP systems with the reference cell placed far away from the tanks being tested. Measuring CP with the reference cell placed some distance away from the tanks is commonly referred to as "remote" or "remote-earth" potential. In this article, I'll discuss remote-earth testingwhat it is, its significance, and why you should consider incorporating this practice when evaluating galvanic CP systems. Although remote-earth testing is applicable to all galvanic CP



systems, this discussion will be limited to the testing of sti-P3 tanks. To help the reader better understand the seemingly mystical science of cathodic protection, I'll also discuss factors that influence CP testing.

Reference Cell Placement

While it is important to realize that many factors must be considered when testing the structure-to-soil potential of a cathodically protected tank, reference cell placement is of critical importance. The basic idea is that the reference cell must be placed where it can "see" the tank. The concept is analogous to a flashlight beam—if the reference cell is placed directly over the tank, the portion of the tank that lies within the imagined flashlight beam is the area of the average potential (voltage) measurement.

The commonly accepted best practice is to place the reference cell in the soil directly over the centerline of the tank being tested and as far away from any anodes as is practical (Moreau, 1999). Measurement of the cathodic protection with the reference cell placed directly above the tank is referred to as the "close," or more commonly, "local" potential.

While it is desirable to provide dedicated access ports or test sta-

tions, practical considerations usually dictate that the reference cell is placed wherever soil access is available above the tank. This means that the reference cell is usually placed within the submersible-pump manway or some other existing opening through the pavement.

It is critically important that the reference cell be placed in the soil and never on top of the concrete or asphalt when measuring the tank potential (NACE, 2001). If there is no access to the soil, holes must be drilled through the pavement in order to conduct a valid test. Testing with the reference cell placed on the pavement will usually introduce significant errors.

Unfortunately, the commonly accepted best practice is not always followed by CP testers, and the reference cell is more typically placed practically anywhere that will yield the desired result (a "pass" or a "fail," depending on the objectives of the person conducting the test). Given this "anything goes" scenario, reference cell placement has ranged from the soil over the tank to the flower bed across the parking lot to the drainage ditch behind the store building and everywhere in between.

Local Reference Cell Placement

When obtaining the local potential, only a relatively small portion of the top of the tank is measured. Therefore, it has become common practice to place the reference cell at three points along the top of the tank (each end and the middle) in an effort to measure as much of the tank as possible (Moreau, 1999). Because local measurements look at specific areas of the tank, an area that is not receiving adequate cathodic protection may be identified. However, since only the top portion of the tank is measured, local potentials tell you nothing about the degree of cathodic protection along the bottom half of the tank.

Portions of the tank other than the top may be evaluated by conducting potential profiling, which involves the drilling of holes in close proximity to the tank so that the reference cell may be placed at various depths, allowing measurement of the potential from ground level to below the bottom of the tank (NACE, 2002). Unfortunately, it is not usually practical to perform potential profiling since drilling is required and few tank facilities have such an arrangement of test holes installed.

Permanent reference cells buried at the time the tank is installed may allow you to measure the tank potential at locations other than the top of the tank. However, in order to interpret the test results properly, it is critical that the exact depth and orientation of the permanent reference cell relative to the tank is carefully documented. Although a number of sti-P3 tanks were installed with permanent reference cells (PP4 test stations), the exact burial location of the reference cell was often not adequately documented.

Îf the location of the reference cell is not known with a high degree of certainty, such potential measurements are of little value, since the cell could have been buried in close proximity to one of the tank anodes. If the reference cell is in close proximity to an anode, the structure-to-soil potential measurement is likely to be higher (more negative) than it really should be because the measurement will be influenced by the voltage gradient of the active anode, (See the "raised-earth" discussion below.) Although only the top of the tank is usually tested, conventional wisdom is that it is reasonable to assume that the top portion of the tank would be the most difficult to protect with sti-P3 tanks since this area is farthest away from the anodes. While this is a logical assumption, it may be prudent to keep in mind that most corrosion failures seem to occur along the bottom of the tank. One of the reasons that the factory-installed anodes are attached near the bottom of sti-P3 tanks is to help protect the more susceptible tank bottom.

While it is important to realize that many factors must be considered when testing the structure-to-soil potential of a cathodically protected tank, reference cell placement is of critical importance. The basic idea is that the reference cell must be placed where it can "see" the tank.

Determining "True" Local Potential

Factors that complicate our ability to obtain accurate ("true") local potentials must be considered when evaluating the significance of such measurements. Local potentials may be subject to interference or "shielding" from various sources at a typical tank facility (Peabody, 2001). Shielding prevents or otherwise interferes with the current reaching the reference cell as it normally would if there were no interference. In the absence of other readily apparent explanations, shielding is commonly cited as the reason for substandard CP readings when the reference cell is placed locally (STI, 2001a).

Given that there may be numerous "foreign" metallic structures present (e.g. the submersible pump head, metallic product piping, electrical conduits, tank risers), it seems reasonable that these structures could interfere with obtaining local potentials. However, there are differing opinions regarding the validity of the concept of reference-cell shielding caused by electrically isolated tank appurtenances. Accordingly, caution should be exercised whenever shielding is cited as the cause of substandard cathodic protection readings. Further testing or evaluation may be necessary by a person qualified as a "corrosion expert" to better determine the "true" cathodic protection status of the tank.

In addition to shielding, local potentials may also be influenced by the effect of "raised earth," a term used to describe the voltage gradient that is present in the soil near an active anode (NACE, 2001). If there are active anodes in proximity to the reference cell, the potential measured on the protected structure will appear to be higher (more negative) than it actually is. The potential will appear erroneously high (more negative), since the measurement includes the voltage drop induced by the voltage gradient of the active anode. Because of the raised-earth effect it is possible for the tank to appear well protected when it may, in fact, not be protected at all.

While not typically a significant concern on well-coated tanks that have only factory-attached zinc anodes, raised earth can have a substantial effect on those tanks that have had magnesium anodes retrofitted or buried nearby. It is not uncommon to have magnesium anodes buried within the submersibleturbine manway in an effort to protect metallic piping. In these cases, the reference cell must not be placed within the submersible turbine manway.

If the structure-to-soil potential of the tank is measured at the submersible-pump manway, the observed potential will be higher (more negative) than it really is since it will include the voltage drop caused by the current output of the magnesium anode. Depending on the soil resistivity and the amount of current produced by the anodes, it may not be possible to place the reference cell locally such that the observed potential is not influenced by the voltage gradient of an active anode.

Other metallic structures commonly found in the tank environment described above that can have an influence on the observed potential include the galvanized skirts present on most manways. Although the

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voltage drop produced by these skirts is not as pronounced as with magnesium anodes, the zinc coating of the galvanized skirt may also cause the observed tank potential to be higher (more negative) than it actually is. The magnitude of the error that will be caused by this



voltage drop depends largely on the proximity of the reference cell to the skirt and the condition of the galvanized metal. Figure 1 is a field example of a series of measurements made within the submersible-turbinepump manway of a sti-P3 tank. The tank in this example has substandard CP that continuity testing indicates is caused by a short between the tank and the fill riser.

The manway in this example is filled nearly to grade with sand backfill, a common practice when containment sumps are not present. The manway is a typical 2' x 2' steel manway with a 10 inch galvanized steel skirt. A potential measurement of -730 mV was observed with the reference cell placed at grade level in the soil within the manway. Grade level in this example placed the tip of the reference cell approximately 35" from the top of the tank and 6 " up inside the metallic skirt (measurement point P-1). The soil was then excavated approximately 7" placing the tip of the reference cell 1" below the bottom of the manway skirt and a potential of -658 mV was obtained (P-2).

If the "true" potential of this tank is -658 mV (the remote potential of this tank was -656 mV), the galvanized skirt of the manway has apparently caused the tank potential to be 72 mV higher (more negative) than it actually is.

As can also be seen from the data in Figure 1, soil resistivity may also influence the observed potential. If you assume the "true" potential of the tank as it would normally be measured is –658 mV, it can be seen that the voltage difference between measurement points P-2 and P-7 is 103 mV. It is likely that this difference is caused by the voltage drop present in the soil column between the tank and the reference cell. Although the amount of error caused by this voltage drop is normally disregarded because the –850 mV criterion is considered to compensate for this error (Peabody, 2001), it is something to keep in mind when evaluating test data.

Another problem sometimes presented by soil resistivity characteristics can be seen in cases where a layer of very high-resistivity soil is present above the tank. Consider the case where a tank is buried in sand backfill, but the top of the excavation is filled to grade with pea gravel. In this situation, it would be very difficult to measure adequate CP with the refer-

ence cell placed on top of the backfill, typically as it would be when obtaining the local potential. The tank would appear to be completely unprotected when it could actually be very well protected along the most susceptible (bottom) portion of the tank.

Contact resistance between the reference cell and the tank backfill, material is another factor that sometimes makes it difficult to obtain accurate local potentials. Although contact resistance is normally compensated for by the use of voltmeters with very high (10 megohm or greater) input resistance, it can be troublesome when the backfill material is very dry or is of crushed stone/pea gravel composition. Water is usually added to the soil at the point of contact with the reference cell in an effort to minimize contact resistance. Additionally, petroleumcontaminated or frozen soils can cause a high contact r esistance and should be avoided whenever testing CP (Moreau, 1996).

Local Variability

A rather large degree of variability is seemingly inherent in local potentials even when there are no apparent reasons for it. It is not uncommon to



observe a substantial variation in the potential just by moving the reference cell around a few inches this way or that. Figure 2 depicts the test data obtained by a MDEQ inspector and illustrates very clearly the variability that can be seen when attempting to measure the local potential. The variation within the 2' x 2' manway near the center of the tank (where the automatic tank gauge probe is installed) shows a variation of 159 mV in the potential, depending on where the reference cell is placed within the manway. The same variability can be seen within the manway of the submersible-turbine pump, although here it is only 42 mV. All of these measurements were made with the tip of the reference cell placed below the bottom of the manway skirts in order to remove any influence they may have.

Are these differences in the tank potential real, or is this just an artifact of measurement difficulties inherent in the environment above the tank? Are the readings being shielded by metallic tank appurtenances in the congested above-tank environment? Is there an anode buried somewhere within or near the manways that is affecting the readings? Should the test for this tank be declared a "fail" since the potential at test point "E" is -819 mV? Given that the reasons for this variability are not well understood, can the remote-earth potential help us decide what the most logical answers to these questions should be?

Remote Earth

Another way to measure the structure-to-soil potential is to place the reference cell some distance away (or remote) from the tank. By doing this, the factors discussed above that can make obtaining local potentials problematic may be mitigated. The structure-to-soil potential that is measured at remote earth can be thought of as representing the average potential of the entire tank shell. Remote earth is achieved when the structure-to-soil potential of a buried metallic structure remains constant, irrespective of how far away or in what direction the reference cell is placed.

It is generally accepted that the reference cell must be at least 25–30 feet away from a sti-P3 tank in order

to achieve a remote-earth condition (STI, 2000). Under normal conditions, this distance is sufficient to place the reference cell outside the area of influence generated by the voltage gradient of an active anode. Since a volume of soil has a finite resistance (STI, 2000), the potential will remain essentially the same no matter how far away or in what direction the reference cell is placed once remote earth has been achieved.

Placing the reference cell remotely accomplishes several things, including:

- Minimizing the raised-earth effect voltage gradients of active anodes may impart on the observed potential.
- Minimizing the "shielding" effect tank-top appurtenances may have on the observed potential.
- Mitigating the error imparted by high-contact resistance between the reference cell and the tank backfill materials.
- Providing the average potential over the entire tank, the only practical way to "see" the bottom of the tank.
- All things being equal, making the test results generally more reproducible than those obtained with the reference cell placed locally. This is because it is usually not known exactly where the reference cell was placed to obtain the local potential and, as long as remote earth has been established, it does not matter where the reference cell is placed to obtain the remote potential.

Determining "True" Remote Earth

An important aspect of remote placement is the need to establish that a "true" remote-earth condition has been achieved. In the simplest scenario, remote earth is established by placing the reference cell in the soil a certain distance away from the protected structure and measuring the potential. The reference cell is then moved out away from the protected structure an additional ten feet, and the potential is again measured. This process is repeated until there is no appreciable difference between two potential measurements. When there is no difference between the two potentials, it can be assumed that remote earth has been achieved.

Factors that can complicate the establishment of true remote earth must also be considered when attempting to measure the remote potential. For example:

- The reference cell should not be placed in proximity to any other cathodically protected structures, such as natural gas pipelines.
- Chain-link fencing, commonly found at UST facilities, is galvanized, and the reference cell must not be placed near it since the raised earth produced by the zinc in the galvanized coating can influence the observed potential.
- Since any buried metallic structures (e.g., water lines, electrical conduits, other utilities) can influence the remote potential, the reference cell must also not be placed over these structures (Peabody, 2001).
- It is better if any buried metallic structures are not between the reference cell and the protected structure, although this is generally not a significant factor.

Given that there is usually limited access to soil at locations that are remote from the tank, and there are other buried structures to contend with, it is often necessary to move the reference cell to several different locations around the facility and at varying distances away from the tank before it can be comfortably established that remote earth has been achieved. Only when the potential is essentially the same at two or more locations that are remote from the tank can it be assumed that remote earth has been achieved.

Remote vs. Local

Placing the reference cell remotely measures the average potential of the entire tank. Placing the reference cell locally measures the average potential of a small area on the top of the tank. Although local measurements can give you information about a specific area of the tank, it is sometimes problematic to be sure that the local measurement is representative,

■ continued on page 32

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■ **Remote-Earth Testing** *from page 31*

and it may be difficult to reproduce the test results. With remote measurements, it is normally easier to mitigate environmental influences and to reproduce the test results. The ability of a person to reproduce the results that someone else obtained during a previous test is a very important and desirable aspect of CP testing.

Remote measurements do not tell you anything about a specific area of the tank, and it is possible to have an area of the tank that is not protected and still have a "passing" remote potential. Similarly, local potentials (measured at the top of the tank) do not tell you anything about the lower portion of the tank, and it is possible to have an area of the tank that is not protected and still have a "passing" local potential.

Referring back to Figure 2, can the remote-earth potential help us decide which potential best represents the "true" local potential? Considering that the remote potential of the tank in Figure 2 is 972 mV and all of the local measurements (except test point "E") are well above -900 mV, it would seem reasonable to conclude that the -819 mV potential observed at point "E" is not representative and should probably be disregarded. The remote potential can sometimes help you decide what is the most representative local potential in those cases where it is not clearly evident.

MDEQ Testing Requirements

In the State of Mississippi, the reference cell must be placed both locally and remotely when conducting a test of a galvanic CP system. In order for the test to "pass," both the local and the remote potential must be -850mV or higher (more negative). The test result is declared a "fail" if both the local and the remote are lower (more positive) than -850 mV. If one of the potentials is -850 mV or higher but the other is not, the test is considered to be "inconclusive." (See Table 1.) With inconclusive results, the CP system must be modified/ repaired or evaluated by a "corrosion expert," who may evaluate the data or conduct further testing in order to declare either a pass or fail of the test.

TABLE 1 "Making the Call"			
LOCAL POTENTIAL	REMOTE POTENTIAL	TEST RESULT	
–850 mV or higher	–850 mV or higher	Pass	
lower than –850 mV	lower than –850 mV	Fail	
–850 mV or higher	lower than –850 mV	Inconclusive	
lower than –850 mV	–850 mV or higher	Inconclusive	

was conducted.

The results of the testing

revealed that 83 percent of the tanks

fully passed the evaluation. Of the

tanks that did not pass the evaluation, 12 percent failed and 5 percent

were inconclusive. (See Figure 3.)

This means that in only 5 percent of

the cases was there any discrepancy

between the local and the remote

potential with respect to the pass/fail

status of the tanks. Of the tanks that

were inconclusive, 53 percent passed

When obtaining the local potential, the reference cell can be placed anywhere along the centerline of the tank but not directly over the ends. Since the remote potential is also required, it was decided that only one local measurement of the potential directly over the tank would be required. Ideally, if only one local potential is measured, it should be obtained from the center of the tank. If the anodes located at both ends of the tank are functioning, the center of the tank should have the lowest

potential, since this is the area of the tank that would be the farthest away from the anodes.

With only one local measurement, it is possible that the anodes could be completely depleted on one end of the tank and this condition would not be recognized. While possible, it

seems reasonable that such a condition would usually be recognized when the MDEQ testing guidelines are followed, since the remote potential would likely be too low and the test result would be inconclusive.

MDEQ Findings

From July 2002 through March 2004, MDEQ inspectors measured the CP on 1,037 sti-P3 tanks as part of routine compliance inspections. Structure-to-soil potential measurements were obtained both locally and remotely on all of the tanks that were included in the data set for this study. The tanks measured ranged in size from 500 to 20,000 gallons and were installed from 1985 through 2002. No attempt was made to identify tanks that had been retrofitted with supplemental anodes at the time the testing

ve the lowest ¹ the remote but failed the local and
Figure 3 MDEQ Test Results
1037 TANKS TESTED
83% (858) Passed
12% (122) Failed
5% (57) Inconclusive

47 percent failed the remote while passing the local.

The MDEQ testing data indicate that the remote potential is just as likely to indicate a "fail" as it is a "pass" when there is a discrepancy between the local and the remote potentials of sti-P3 tanks. In only 3 percent of the cases where there is a discrepancy between the local and the remote does the remote indicate that the tank is protected when the local does not.

In comparing the local to the remote potential (without considering the pass/fail status), the local was essentially the same as the remote for 15 percent of the tanks. (See Figure 4.) The local was found to be higher (more negative) than the remote 42 percent of the time. While there are a number of factors that could cause

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this difference, the voltage gradient caused by active anodes in the soil near the tank (raised earth) is one possible explanation. The local potential was found to be lower (more positive) than the remote potential on the remaining 43 percent of the tanks. In the absence of other readily apparent reasons, shielding of the reference cell in the congested above-tank environment is the most logical explanation for this difference.

When a difference is measured between the local and the remote

suring sti-P3 tanks and that difference is +/-80 mV.

At the End of the Day

Although this discussion has been limited to sti-P3 tanks, remoteearth testing is equally applicable to most galvanic (sacrificial anode) CP systems. Of the 1,037 tanks tested by MDEQ,

the average local potential was –964 mV and the average remote potential was –962 mV. While it sometimes seems that the only thing certain with CP is that there are no certainties, the data would suggest that the remote potential is a valuable tool. Given the inherent advantages of measuring remote potentials (see Table 2), it would seem prudent to incorporate remote-earth testing when evaluating galvanic CP systems.

In addition to Mississippi, the states of Georgia, Kentucky, North

TABLE 2 Advantages of Local/Remote Reference Cell Placement		
	LOCAL	REMOTE EARTH
Ease of obtaining (soil access)	Х	Х
Reproducibility (between different testers)		Х
Variability (no change if reference cell moved)		Х
Shielding (from tank appurtenances)		Х
Shielding (from other metallic structures)	Х	
Raised earth (voltage gradient of anodes)		Х
Contact resistance (between cell & soil)		Х
Measures specific area of tank	Х	
Measures entire tank		Х
Overall cathodic protection status of tank		Х

potentials, how much is it? In the cases where the local was higher (more negative) than the remote, the average difference between the two was 80 mV. In cases where the local potential was lower (more positive) than the remote potential, the average difference was 79 mV. The remote is just as likely to be lower (more positive) as it is higher (more negative) than the local is when mea-

Carolina, and South Carolina also have policies that require testing of galvanic CP systems remotely. There are several other states that are in the process of adopting similar CP testing requirements. The Steel Tank Institute describes the use of remote earth testing for sti-P3 tanks (STI, 2001a). NACE International also recognizes that remote-earth placement of the reference cell can be an acceptable alternative and is useful when determining the significance of voltage drops (NACE, 2001).

While the data would suggest that the remote-earth potential by itself on a well-coated tank could be reliable, we will continue to require that both the remote and the local potentials be measured. We believe that each has its own distinct advantages/disadvantages. The remote measurement tells you the overall condition of the tank while the local helps to identify specific areas of the tank that may not be protected. Both measurement techniques should be utilized in conjunction with each other in order to evaluate galvanic cathodic protection systems in the best manner possible.

Kevin S. Henderson, P.G., is Compliance and Enforcement Manager for the Underground Storage Tank Branch, Mississippi Department of Environmental Quality. He can be reached at Kevin_Henderson@deq.state.ms.us.

To Learn About CP Basics: Check out LUSTLine #23, "Rust Thou Art and to Rust Thou Shalt Return," and LUSTLine #25, "Is This Tank Cathodically Protected?"

References

- MDEQ, 2002, Guidelines for the evaluation of underground storage tank cathodic protection systems, Mississippi Department of Environmental Quality, Jackson, MS.
- Moreau, Marcel, 1995, Testing cathodic protection systems, *LUSTLine* Bulletin #25.
- Moreau, Marcel, 1999, Combating CP-test heartburn, *LUSTLine* Bulletin #32.
- NACE, 2001, TM0101-2001, Standard test method, measurement techniques related to criteria for cathodic protection on underground or submerged metallic tank systems", NACE International, Houston, TX.
- NACE, 2002, RP0285-2002, Standard Recommended Practice, Corrosion control of underground atorage rank aystems by xathodic protection", NACE International, Houston, TX.
- Peabody, A.W., 2001, Peabody's xontrol of pipeline corrosion, NACE International, Houston, TX
- STI, 2000, Consideration of extraneous voltage cComponents in tank-to-soil potentials obtained for cathodic protection monitoring of sti-P3 Tanks", Steel Tank Institute, Lake Zurich, IL.
- STI, 2001a, *TankTalk Newsletter*, Vol. 16, Number 2, Ask the expert CP tests for sti-P3 Ttanks, Steel Tank Institute, Lake Zurich, IL.
- STI, 2001b, Recommended practice for the addition of supplemental anodes to sti-P3 USTs", Steel Tank Institute, Lake Zurich, IL.

MtBE Problems Set the Stage for New UST Regs in Maryland

ver the last several years, the Maryland the Department of the Environment (MDE) has seen an increase of groundwater cases that involve MtBE. Since 1998 MDE has found that close to 600 private wells have been impacted with MtBE at 5 ppb or higher across the state. Public well impact data show similar locational trends. The largest impacts appear to be across the top of the state in areas with fractured-rock geology. These areas include Harford, Cecil, Carroll, Baltimore, and Frederick Counties.

Early on, MDE technical staff felt that a contributor to the MtBE problem at these stations was the enriched MtBE vapors being released into the storage tank backfill from systems that utilize Stage II vacuum-assist vapor recovery under continuous pressure.

In response to these events, the governor has ordered MDE to write emergency technical regulations that will require early detection and better containment of MtBE in UST systems in the state's High Risk Groundwater Use Areas. All UST construction, containment, and leak detections regulations, to date, have focused on liquid releases, not vapor. The revised regulations are in the review process and are expected to be promulgated in January. Further details can be found on MDE's Web site at: *www.mde. state.md.us.* We'll provide up-to-date details in the next issue of *LUSTLine.*



The NEW LUSTLine Index—the long and action-packed story of USTs and LUSTs—is ONLY available online.

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

The Brownfields Beat

Oakland, California USTfields Pilot Wins Phoenix Award

The winners of the 2004 Phoenix Awards were announced on July 22, and the City of Oakland/Habitat for Humanity housing project was a Community Impact Award winner. This is one of only three such community awards nationwide. In all, 14 brownfields projects were honored for meeting the environmental challenge of transforming abandoned brownfields into productive new uses. In Oakland, an old petroleum-contaminated gas station was cleaned up, and four new single-family homes housing 13 people were built on the site. The project was the recipient of a 2000 USTfields Pilot grant. Phoenix Award winners were formally recognized at the Brownfields Conference in September.

New Federal ATF Building to Stand on Old LUST Site in DC

An old LUST site undergoing remediation in the northeast section of the District of Columbia is slated to become the new national headquarters of the federal Bureau of Alcohol, Tobacco, Firearms, and Explosives (ATF). Five USTs were removed from the site in 1991, and the presence of petroleum hydrocarbons and other contaminants was discovered over much of the area. A remediation system is in place, and the DC UST program is working with the U.S. Government Services Agency to clean up and prepare the site for construction. The building planned for the site will house approximately 1,100 ATF personnel and is expected to open in 2005. ■

Shell Oil U.S./Motiva to Phase Out MtBE in Gasoline

hell Oil Products U.S. and Motiva Enterprises, LLC are working toward substantially reducing and ultimately phasing out the use of MtBE in the gasoline the companies manufacture and sell in the United States. Shell Oil Products U.S. no longer manufactures or blends MtBE into gasoline produced at its four West Coast refineries, and Motiva has decided to cease blending MtBE into products it manufactures at two terminals in Louisiana. Combined, these two terminals distribute more than 430 million gallons of gasoline per year. Also, in response to Connecticut and New York MtBE bans, Motiva constructed and operates an ethanol import and blending facility at its terminal in Sewaren, New Jersey.

The companies are looking for other markets where they might be able to phase out the use of MtBE in their gasoline, consistent with federal fuel requirements, state legislation and regulation, market conditions, and the gasoline distribution system in that part of the country. The companies are responding to legislators and regulators who are asking that they remove MtBE from gasoline. To date, more than 20 states have or are considering a ban of MtBE. The companies say a complete phaseout will only occur if there is a change in current regulatory requirements.





ASTM Microbiology Work Group Seeks Data on FRP Deterioration

I was delighted to read Mr. Roggelin's *LUSTLine* #47 article, "Pipes and Sumps—As I See Them," on the biodeterioration of non-metallic piping. The phenomena that Mr. Roggelin discusses are not limited to piping. Unfortunately, most industry stakeholders with direct knowledge of failed fiber reinforced plastic (FRP) UST features are restrained from sharing that knowledge in open forums like *LUSTLine*. Mr. Roggelin was able to write a pithy article shedding much-needed light on this underdiscussed problem. My hat is off to him for a job well done.

I also encourage industry stakeholders with photos and other specific data about FRP biodeterioration to share it, either in *LUSTLine* or at ASTM Subcommittee D.02.14 Fuel Microbiology Working Group meetings. We can't solve industry problems or develop best practices for problem prevention as long as the affected folks pretend that denial is an effective prevention tool. The next ASTM D.02 meeting will be on December 5–9, 2004, in Tampa, Florida. Guests are always welcome at these meetings. People can get meeting details at ASTM's Web site: *www.ASTM.org*. Once at the Web site, click on "Meetings," "List of ASTM Future Meetings", and "Next 12 Months," then scroll down to "D02 Petroleum Products." ■

Frederick J. Passman, Ph.D. Chair, ASTM D.02.14 Fuel Microbiology Working Group

New Jersey Initiates an Enhanced Statewide UST Compliance Inspection Program

n August, New Jersey Department of Environmental Protection (NJDEP) Commissioner Bradley Campbell announced the start of a new, enhanced statewide UST compliance inspection program. NJDEP is establishing a group of 18 state and county inspectors to conduct compliance inspections at each UST facility once every three years. In past years, state UST inspections were conducted on the basis of complaints or referrals. "Millions of New Jersey residents get their drinking water from aquifers that are vulnerable to pollution from leaking tanks. New Jersey was long overdue for a more effective leakprevention program for underground tanks, but this has changed with the state making new funding available," said Campbell. In 2003, New Jersey voters overwhelmingly approved a public referendum to provide NJDEP a stable funding source for its UST inspection program. The complete news release can be seen at http://www.nj.gov/dep/newsrel/2004/04 0096.htm.

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FAQs from the NWGLDE

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

Guess What? With this issue of *LUSTLine* we are launching a new section called "FAQs from the NWGLDE" by the National Work Group on Leak Detection Evaluation, an independent work group comprised of 10 members—eight representing various states and two from the U.S. EPA. The Work Group plans to publish the answers to frequent questions they receive from regulators and people in the industry on leak detection. If you have questions for the group, please contact them at *questions@nwglde.org* . (Please note: the views expressed in this column represent those of the work group and do not necessarily represent those of any implementing agency.)

FYI, the mission of the NWGLDE is to:

- 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

Can ELLDs Be Used as a Line-Tightness Test Method?

Q. Companies such as Veeder-Root and INCON are marketing their electronic line leak detectors (ELLDs) to the regulated community as Line-Tightness Test Methods, in addition to meeting the line leak-detector criteria. Under the specs for each ELLD, the 11th edition, 2004, List Of Leak

Detection Evaluations For Storage Tank Systems shows that a 0.1gph test is possible, but does not specify its equivalence to a line-tightness test. However, the NWGLDE listing for Line-Tightness Test Methods does not list any ELLDs as being acceptable as a Line-Tightness Test Method (pg. 13, 11th edition of the List). So, my questions are: (1) Are there any ELLDs that can do a linetightness test? (2) If so, where can I find that list?

You are right, ELLDs are not listed by the NWGLDE under Line-Tightness Test Methods. However, many, but not all, of them were thirdparty tested at the 0.1gph leak rate under the same range of environmental and pipeline configuration conditions that are used to test systems that conduct monthly monitoring and line-tightness tests. The performance of the ELLD during third-party testing is documented on the NWGLDE List data sheet for the equipment.

If the ELLD has sufficient performance characteristics, it can be used to satisfy the monthly monitoring test or annual line-test requirements. The leak rate of 0.1gph is an equivalent leak rate at a lesser pressure, since the ELLD does not typically test the piping at one and one-half times the operating pressure. (See USEPA Standard Test Procedures for Evaluating Leak Detection Methods: Pipeline Leak Detection Systems, September 1990.) The decision to accept or deny use of this method remains with the implementing agency.

You can identify ELLDs that have an acceptable third-party result at a 0.1gph leak rate by looking at the method summary page for Automatic Electronic Line Leak Detectors at *http://www.nwglde.org/methods/automatic_electronic_lld.html*. ■

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