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Arizona groundwater study
By Paul Dahlen, Eric J. Henry, M. Matsumura and Paul C. Johnson

Arizona has more than 9,000 UST facilities on file at the Arizona Department of Environmental Quality (ADEQ). Of these, about 4,300 have attained LUST status. The Arizona Legislature commissioned a study of LUST impacts: this comprehensive, statewide examination of the nature of LUST impacts to groundwater should lead to cost-effective and protective future management of LUST sites.

The two-year study involved the following:
- review of 417 ADEQ LUST sites and compilation of relevant data from 323 of those sites into an electronic database
- collection and analysis of more than 700 supplemental groundwater samples
- assessment of groundwater flow properties from 32 wells at 111 sites
- more detailed field characterization at six LUST sites representative of a range of conditions at Arizona LUST facilities
- empirical analysis of groundwater impacts at Arizona LUST sites, using the above-mentioned data sets, with emphasis on identifying relationships between site conditions (e.g., geology, depth-to-groundwater, etc.) and groundwater impacts
- collection of 300 groundwater-level measurements and resurveying of 175 monitoring wells to assess errors in standard practice and their impact on groundwater flow direction
- combined theoretical-spatial (GIS) analysis to identify LUST scenarios posing the greatest threats to the use of groundwater resources

The following provides a summary of the authors’ findings from this study.

**LUST site selection**
Lust files were not selected randomly for review. We selected them to ensure a representative range of hydrogeologic settings as well as a wide geographic representation across Arizona. Files known to contain MTBE data concentrations in groundwater were targeted, and for the analysis of remediation performance, a number of “closed” LUST site file reviews were emphasized.

The LUST site files reviewed were associated with releases reported in the 1978-2001 timeframe, the majority (97 percent) of which corresponded to releases reported prior to implementation of the 1998 UST upgrade requirements.

Therefore, overly broad conclusions should not be drawn from the observations presented. For example, because the results of this study are based predominantly on data from LUST sites having older (pre-1998 upgrade) UST installations, one might argue that the results are not directly applicable to newer (post-1998) tank installations and newer fuel formulations.

**LUST site setting and release scenario**
To place the results of the study in proper context, it is important to understand typical LUST site settings and release scenarios; for example:
- the majority of sites (84 percent) were located in areas where industrial/commercial and residential areas could be found within 1/4 mile of the site; the available information suggested that, on average, three other UST sites were located within a 1/4-mile distance
- the majority of the selected LUST sites were impacted by gasoline releases; the volumes of product released and the timing of the releases were generally unknown; all major components (tanks, lines, dispensers) of those UST systems (primarily pre-1998 systems) appeared to have been susceptible to failure

These typical LUST site settings place practical restrictions on accessible soil sampling and groundwater monitoring well locations. The close proximity to other UST/LUST sites complicates data interpretation. Unknown release dates, locations and volumes lead to a greater emphasis on the use of soil and groundwater sample analysis in the decision-making process.

**Hydrogeology**
Hydrogeological characteristics of LUST sites reviewed for this study are summarized as follows:
- the subsurface at most sites was composed of unconsolidated sediments, and the most prevalent qualitative geologic descriptors were “interbedded sands/silts/clays”, “mixed sands/silts/clays” and “mixed sands/gravels/cinders”
- quantitative subsurface characterization data (e.g., hydraulic conductivity) were available in very few site files
- the depth-to-groundwater was less than 50 ft at 50 percent of the sites with depth-to-water data, and was greater than 100 ft at only about 10 percent of the sites
- for sites with enough data to confidently determine dominant flow directions and horizontal hydraulic gradients (approximately 190), the gradients ranged from 0.0005 to 0.40 ft/ft; approximately 50 percent of the sites had gradients less than 0.006 ft/ft and 15 percent of the sites had gradients greater than 0.02 ft/ft
- for sites with sufficient data to determine apparent historical variations in flow direction (approximately 190), 75 percent had variations in flow direction in excess of 20 degrees, and 40 percent of the sites...
had variations in excess of 45 degrees (see related discussion of groundwater elevation determination errors).

The absence of quantitative aquifer characterization data precludes one from making confident estimates of groundwater velocity—a quantity of interest for many risk-based decision-making processes. The lack of quantitative information also necessitates reliance on the subjective qualitative descriptions of site hydrogeology, but there was little variation in the qualitative descriptions of the sites reviewed for this study. The apparent historical variations in flow directions suggest that non-traditional site assessment paradigms and conceptual models are needed for collecting and interpreting site assessment data. For example, the most commonly used LUST site conceptual model is the simplistic one in which groundwater flows horizontally in one direction, with dissolved contaminants also migrating only in that direction. Site investigation strategies will be based on this conceptual model (e.g., installing wells in a line along the assumed flow direction) and data will be interpreted in the context of this conceptual model. If the actual groundwater flow and contaminant migration are not adequately represented in the conceptual model, then this leads to poor characterization and erroneous conclusions.

**Characterization of typical LUST site assessment data**

A significant feature of this study relative to other state-specific LUST impact studies is the characterization of typical LUST site assessment data. Understanding the characteristics of the LUST site assessment data is critical to proper data interpretation and data use in decision-making. The following observations from the LUST site file review are of particular significance:

- The majority of LUST site data were generated from conventional soil boring and groundwater monitoring well sampling activities.
- 10 or more soil borings were conducted at about 60 percent of the sites, and on average, four samples per boring were sent for laboratory analysis.
- 50 percent of sites had six or more groundwater monitoring wells installed; the majority of wells were constructed with 10- to 45-ft-long screened intervals; the spatial distribution of wells favored the source zone and cross-gradient areas; in this report, the LUST site “source zone” is the subsurface region where one finds petroleum liquid (e.g., gasoline) in the soil pores.
- For the 270 sites having groundwater monitoring wells, only about 70 percent had sufficient hydraulic data to confidently determine a dominant flow direction.
- For those sites with sufficient hydraulic data to confidently determine dominant flow directions (approximately 190), downgradient monitoring wells were not present at about 30 percent of the sites, and 60 percent of the sites had only one or two downgradient monitoring wells; only 16 percent of all wells (one of six) at these sites were classified as being hydraulically downgradient of the source zone; about 70 percent of the downgradient wells were located within 250 feet of the UST system, and about 90 percent were located within 500 feet.
- Typical measurement errors associated with groundwater elevation determination can be large enough to significantly affect the determination of groundwater flow direction at many Arizona LUST sites; in particular, data sets created with successive partial well surveys have the greatest potential to introduce errors; use of different groundwater-level sensors in the same sampling event can also introduce significant errors.
- Quantitative aquifer characterization data (i.e., hydraulic conductivity) were available for only about 10 percent of the sites having groundwater quality investigations, and the data indicated no clear correlation between qualitative geologic descriptions (i.e., “sands”, etc.) and measured quantitative properties.
- Limited chemical groundwater data were available for historically non-regulated fuel additives like MTBE, TBA and the alcohols (more data were available for MTBE concentrations in groundwater than for the alcohols).

Of significance are implications that these observations have with respect to the adequacy of assessment of dissolved plume impacts at LUST sites. For example, the selection of proper sampling locations, the determination of the extent of dissolved contamination and the use of these types of data for risk-based decision-making are difficult when the flow direction is uncertain, the groundwater velocity is unknown, and the extent of the more soluble fuel components is unknown.

**Impacts at gasoline-release sites**

Based on the data available for this study, the following was concluded concerning impacts at gasoline-release sites:

- Source zone sizes typically range from 1,000 to 10,000 ft² (50 percent of sites); only 14 percent of sites had source zones smaller than 1,000 ft², and 4 percent of sites had source zones larger than 100,000 ft².
- Free-product (liquid gasoline) was observed in one or more wells at about 50 percent of sites with groundwater quality data; free-product thicknesses measured in wells ranged up to 12.6 feet, but were typically less than 2 feet.
- Frequently detected chemicals-of-interest for this study included benzene, toluene, ethylbenzene, xylenes, trimethylbenzenes, naphthalene, MTBE and TBA—
these were typically found in the 100 to 10,000 μg/l range in source zone groundwater samples

- MTBE data were only available for two-thirds of the sites with groundwater quality data; MTBE was not detected at all sites, but its occurrence was relatively widespread across the state, including rural areas
- the alcohols (other than TBA) and fuel additives DIPA and ETBE were detected very infrequently in source zone groundwater
- given the spatial distribution of monitoring points (i.e., two or fewer downgradient wells at many sites, and limited data from downgradient distances in excess of 400 feet as discussed above) it is difficult to draw defensible global conclusions regarding the extent of downgradient chemical migration; the collective data from the file review process indicated that concentrations in groundwater as high as 1,000 μg/l extended as far as about 500 feet away from some UST systems, but the data also suggested that concentrations in groundwater in excess of 100 μg/l were rarely detected at distances greater than this (although it is important to note that there were very few wells at greater distances); the collective data also suggested similarity between the spatial extent of MTBE and benzene dissolved plumes
- data from the additional investigation/characterization of six sites contradict the last statement above; these data showed dissolved MTBE plumes that attenuated with distance more slowly than the associated dissolved benzene plumes
- a visual review of the data revealed no discernable increasing or decreasing trend in benzene or MTBE concentrations in groundwater at most sites

Of particular interest here is the discrepancy between the observations from the comprehensive analysis of the file review database and the results from the focused supplemental characterization at six LUST sites. This raises questions about the validity of conclusions drawn from large database analyses (especially as they are related to the spatial extent of groundwater impacts); it also suggests a need to examine the extent to which these types of analyses could be biased by typical LUST site monitoring well networks. This issue can likely be resolved only through additional detailed characterization at some sites, followed by comparison of those data with the results of the comprehensive database analysis.

**Relationship between LUST site characteristics and groundwater impacts**

The database was also used to investigate empirical relationships between LUST site characteristics and groundwater impacts. The following are of particular relevance to risk-based decision-making at LUST sites:

- there was no strong correlation between qualitative geology descriptors and groundwater impacts (similar impacts occurred for all qualitative geologic descriptors)
- there was no strong correlation between depth-to-groundwater and groundwater impacts (similar impacts occurred for all depths to groundwater)
- there was no strong correlation between the distance from deepest soil impacts to groundwater and groundwater impacts (similar impacts occurred for all distances between groundwater and deepest soil impact determined from chemical analysis data)
- source zone sizes tend to be about eight times larger at sites with free-product detections in wells; however, there was no strong correlation between measured free-product thickness and source zone size (sites with thicker free-product layers did not necessarily have larger source zones)
- there was no strong correlation between chemical concentrations in soil and groundwater impacts; in particular, groundwater impacts were often observed even when contaminant concentrations in soils were below detection levels; i.e., soil concentrations are not reliable measures or indicators of groundwater impacts at LUST sites
- quantitative subsurface flow properties cannot be reliably inferred from qualitative geology descriptors found in soil boring logs
- impacts to any of the roughly 19,000 domestic/municipal/utility wells are likely to be significant only under conditions where at least 10 LUST sites are within the water supply well’s capture zone and there is minimal biodegradation of the chemicals(s) of concern; a GIS analysis suggests that less than 6 percent of municipal/utility wells are currently in such settings
- impacts to any of the roughly 19,000 domestic wells in Arizona are likely only if the well is in close proximity to, and directly downgradient of one or more sites (i.e., 1,000 feet or less), and there is minimal biodegradation of the chemicals(s) of concern; a GIS analysis suggests that about 20 percent of domestic wells are within 1/2 mile of one or more UST sites, but the analysis is unable to determine the fraction located within 1,000 feet and also downgradient of UST sites; about 2.5 percent of domestic wells are within 1/2 mile of five or more UST sites

Current risk-based decisions are often predicated on three assumptions:

- groundwater impacts should be less as the depth-to-groundwater increases
- the extent of impacts should be less for sites described by finer-grained descriptors (e.g., silts/clays)
- the impacts are generally greater at sites with higher contaminant concentrations in soils
Observations from data analyses show these assumptions not to be universally true.

**Remediation performance**

Finally, this study investigated the performance of remediation technologies at Arizona LUST sites, with the intent of identifying relationships between technology performance and LUST setting. The data, however, were insufficient to draw defensible conclusions concerning the performance or cost-effectiveness of remediation technologies applied at Arizona LUST sites. This is in part a reflection of the ADEQ data requirements (closure can be granted based on only two monitoring events, and this is insufficient data from a technology evaluation viewpoint), as well as reflection of the limitations of data collected at many remediation sites (e.g., collecting groundwater samples during active remediation system operation). It is also a reflection of the history of LUST activities in Arizona: to date, much effort has been devoted to the initial characterization of LUST sites and less to remediation.

**Reference**


UTTU thanks Paul Dahlen, PaulDahlen@asu.edu, for his help on this article.

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**Remediation considerations**

*By Ralph J. Moran*

The following is an edited version of an article that originally appeared in *Ground Water Monitoring & Remediation*, Fall 2003. For a more thorough discussion of the ideas and the author’s disclaimer, please see the original article.

Those of us who make our living working on some aspect of environmental remediation projects can all point to many examples where current cleanup policy has worked as it is intended to work. We can all point to examples where an important risk was identified, where cooperation existed between responsible parties, regulatory oversight agencies, and other stakeholders, and where the implemented solution mitigated a risk in a timely and effective manner.

Unfortunately, it is perhaps just as easy for us to point to examples where the system has resulted in perverse outcomes—where obvious waste of public and private resources ensued; where there was a failure to identify, prioritize and mitigate important risks, where a property was not developed to its highest and best use (or perhaps at all), or where a site requiring cleanup sat idle while those involved bickered.

Surely, all of us would prefer to work under a system where examples of the former outnumber examples of the latter. Many factors contribute to the current system’s shortcomings, and stem, I believe, mostly from the following:

- a lack of clear, consistent methodological rigor in determining cleanup requirements, resulting in a near-chaotic aura of uncertainty surrounding the process
- a failure to fully analyze both targeted and countervailing risks
- a failure to consider these risks in the context of other risks we face as a society, and the ensuing lack of coordinated risk reduction policy
- inadequate concern for and measurement of what we, as a society, are actually getting in return for the resources expended on these cleanups
- regulatory agencies are simply too swamped with current cases to do much more than operate in a “putting out fires” mode; for them it is overwhelming to simply keep up with the current cases; plans or ideas to improve or overhaul the system fall deeper and deeper into the abyss of an ever-growing in-box
- the urgency to improve the system is muted by what I believe are common rationalizations, which follow

Rationalization #1: better safe than sorry.

Supreme Court Justice Stephen Breyer, in *Breaking the Vicious Circle: Toward Effective Risk Regulation* (1993), addresses this issue by asking rhetorically: “Since no regulatory agency is perfect, does it really matter if occasionally the nation spends a little too much money buying too much safety? After all, every scientific study
is filled with uncertainties that the final, specific numbers tend to hide. Why not err on the safe side?” His answer is that it does matter.

According to Justice Breyer: “...the resources to combat health risks are not limitless.” Breyer cites as an example a New York Times survey of experts predicting that total costs of certain categories of cleanups (abandoned Superfund sites, federally owned sites, private sites, UST cleanups, state required cleanups, abandoned mine sites) will be $300 to $700 billion. Additionally, he cites estimates for total Superfund cleanup costs as much as $1 trillion, and a Department of Energy estimate of its nuclear site cleanup costs to be $240 billion; together, these three categories add up to nearly $2 trillion. Monies the federal government spent annually, at the time of the estimates, to protect all aspects of the environment amounted to $100 to $120 billion. Whether it matters if we spend more money than actually needed is, according Breyer, clear: “...the money is not, or will not be, there to spend, at least not if we want to address more serious environmental or social problems...”

“Erring on the side of caution,” “better safe than sorry,” or the Precautionary Principle, as the larger concept is sometimes referred to, is a complex concept that no doubt has valid application to risk reduction. Unwise application of this concept, however, can create consequences that, in some cases, are greater than the risks targeted for reduction.

**Rationalization #2: a strict cleanup process acts as a deterrent to spills.** If a case can be made that any of these six rationalizations is legitimate, this one would probably stand the best chance, although I would still argue strongly against it as a valid defense of the current system. The simple fact is that the lack of clear, consistent, certain and reasonable cleanup regulation is a deterrent to spills/leaks/releases. It is also a deterrent to their cleanup.

The question, then, is this: if the current system acts as a deterrent to spills, is that sufficient reason to be unconcerned—or even less concerned—about fixing a broken system? Aren’t there better, more productive, effective, economical ways to promote prevention while having a reasonable cleanup system? I believe there are. From a regulatory perspective, enforcement should be the deterrent to sloppy, polluting practices. Punitive cleanup policy—which is just as likely to deter cleanup as it is to deter spills—should not.

**Rationalization #3: punish the polluter.** Although this category is closely related to #2, I believe it merits its own category. Part of the irony is that to “punish the polluter,” the polluter must first be brought into the cleanup system. Whether parties enter the system voluntarily (because they know it is the right thing to do), or they enter begrudgingly, the bottom line is that they are in the system. An argument can therefore be made that these are the good guys, who, by acting responsibly, are agreeing to play by the rules, although they may not always agree with the rules and may try to challenge them. Are these the people that should be subjected to a sometimes punishing system, or should punishment be reserved for those avoiding the system?

**Rationalization #4: it’s good for the economy, so why worry?** Regulations that may produce uncertain or non-justifiable environmental benefits should not be a great concern because society will benefit from all jobs produced by compliance activities. This notion that environmental cleanups benefit society in any way other than necessary protection from unacceptable risks to human health and the environment—or if you will, that we can over-remediate our way to economic health—is seriously flawed and not based on sound economic principles or practices.

Many more jobs have been lost through the lack of clear, consistent, and certain cleanup policy than have been or ever will be created by the current system. The real estate, lending, and construction industries (as well as the myriad businesses that support these industries) have all been affected by the stigma, cost and uncertainty associated with environmental cleanups. Remediation liabilities have either forced small businesses (which employ the bulk of workers in our society) out of business or have compelled them to endure severe cutbacks.

Sound economic principles tell us that for an endeavor to be worthwhile and beneficial to society’s economic health, the public must not only benefit from the additional employment, but more importantly, the public must obtain some lasting, on-going benefit. Milton and Rose Friedman (1990) point out: “If all we want are jobs, we can create any number—for example, have people dig holes and have them fill them up again. Our real objective is not just jobs but productive jobs—jobs that will mean more goods and services to consume.”

**Rationalization #5: the more strict the regulation, the better for the environment.** If “X” cleanup level is protective of human health and the environment, isn’t one-half of “X” even better? The short answer is no.

An unnecessarily strict cleanup policy results in fewer, more protracted cleanups and therefore diminished protection of human health and the environment. Fewer cleanups occur for two reasons:

- a significant number of entities, businesses or individuals faced with expensive and uncertain cleanup requirements choose, in some form or another, to walk away from their obligations
- sites and risks compete for resources; because there is not an infinite supply of societal resources avail-

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able to address environmental cleanups, decisions and actions at one site are inextricably connected to decisions and actions at future sites; the largest implication of this connection is that resources expended needlessly on one site are forever unavailable to be spent on the next, perhaps more deserving site.

Until this second concept is understood by responsible parties, policymakers, regulators and other stakeholders, the prospects for more reasonable remediation policy (and more, importantly, for risk reduction policy in general) are greatly reduced.

I strongly believe that few responsible parties would argue over or avoid processes or costs necessary to mitigate unacceptable risks to human health and the environment. “Right-sized” regulation will bring more parties to the table and will allow those already at the table to reduce risks posed by their sites more quickly and efficiently.

Rationalization #6: polluting businesses pay for cleanups, and no one else pays the consequences. Some perceive that compliance with cleanup regulations, whether it be “right-sized” regulation or over-regulation, is essentially free to society because it’s paid by business. Therefore, why bother ensuring that the degree of cleanup is necessary or reasonable?

While it can be easily shown that the public does pay for cleanups, either through taxes or through the higher costs of goods and services, let’s assume, for argument’s sake, that businesses pay the full direct costs of environment cleanup. Does this assumption turn this rationalization into valid reasoning?

While research on this topic has identified numerous societal consequences resulting from the unwise use of public or private resources, for the purposes of this paper, let’s focus on one, the consequence referred to as “redirected innovation” (Hammit 2002). In other words, what would we all be doing if we weren’t working on cleaning up sites that actually did not require additional work? First, we could do a better, quicker, and more thorough job of identifying and remediating the sites that actually pose significant and unacceptable risks to human health/the environment. What if we did so well in identifying true risks and prioritizing our time that fewer of us were needed to address these remediation projects?

Technology companies could redirect their resources to designing a new, faster, cheaper microprocessor, making us all more productive. Government entities with remediation liabilities could divert resources to provide additional services to their constituents. Oil companies, an industry I’m familiar with, could spend more of their resources developing the next cleaner-burning fuel, investigating methods for coaxing more oil and gas out of existing fields, developing methods to squeeze a few more gallons of usable fuel from a barrel of oil, or exploring alternative energy forms.

Consultants (engineers and geologists) could focus their efforts on
  • designing better, cheaper pollution control devices
  • designing more fuel-efficient and lower-emission vehicles
  • designing earthquake-resistant buildings
  • drawing up plans to develop a property that is vacant and stigmatized

Regulators could use these resources to focus on and address issues that pose greater threats to human health or the environment.

Conclusion

Our nation has made great strides over recent decades in focusing the public’s attention on the need for and the importance of environmental protection. These efforts have paid off in the form of demonstrable improvement of our environment.

Clearly, more remains to be done. For continued improvement to be made, however, we must ensure that government policy focuses the nation’s limited resources on effective and efficient intervention.

Environmental remediation projects and the policy that governs these cleanups are important components of our nation’s programs to protect human health and the environment from unacceptable risk. As such, it is important that we understand, investigate and attempt to improve, eliminate or minimize aspects of this policy, or influences to policy implementation, that contribute to less than optimal outcomes.

Enormous benefits will be gained by improving current remediation policy, and these benefits can be realized by society as a whole. Moreover, serious consequences to our society result from unwise use of our limited risk-reduction resources—consequences that need to be better understood and accounted for. This understanding can provide the impetus for improving remediation policy so that important risks can be identified and addressed quickly, efficiently and effectively.

Reference


UTTU thanks Ralph J. Moran, moranrj1@bp.com, for his help on this article.
Research on Fenton’s oxidation of MTBE

Fenton’s oxidation, a process that can use iron as a catalyst, produces •OH, the hydroxyl ion, that can transform organic compounds and mineralize them to CO₂ and H₂O. “Hydroxyl radicals have one unpaired electron and are strong, non-selective, highly reactive oxidants, only second to elemental fluorine in reactivity. Fenton’s oxidation produces •OH from Fenton’s reagent [Fe²⁺] and hydrogen peroxide, H₂O₂” (Bergendahl and Thies, 2004).

Bergendahl and Thies (2004) studied MTBE and Fenton’s oxidation in hopes of garnering information on

• “the effectiveness of Fenton’s oxidation of MTBE with Fe⁰ as the source of Fe²⁺ iron catalyst”
• determining effective operating conditions
• quantifying the process’ kinetic rate parameters

Fenton’s oxidation reaction can remove organics from water but “requires the continuous addition of dissolved Fe²⁺.” A solid form of iron, zero-valent iron, Fe⁰, would be preferable over Fe²⁺ because Fe⁰
• could be attached to or coated on larger stationary solids like sand filtration material
• mobilized in and attached to soil grains in contaminated aquifers

Fenton’s oxidation is attractive to some MTBE remediators because the oxidation can transform organic compounds. In the past, MTBE has been destroyed by the use of
• ultrasound/Fe²⁺/H₂O₂
• UV/H₂O₂ advanced oxidation

Advanced oxidation

The primary byproducts of advanced oxidation of MTBE include
• acetone
• tert-butyl formate (TBF)
• tert-butyl alcohol (TBA)
• methyl acetate
• 2-methoxy-2-methyl propionaldehyde
• formaldehyde

Given sufficient time and hydrogen peroxide, these byproducts are completely transformed to CO₂ and H₂O.” In the presence of H₂O₂, Fe⁰ is transformed into Fe²⁺ by

\[ K_{Fe^0} = \frac{[Fe^0]}{[Fe^{2+}][H_2O_2]} \]

Fe⁰ + H₂O₂ ➔ Fe²⁺ + 2OH⁻

Then Fe²⁺ can react with H₂O₂ in Fenton’s oxidation reactions:

\[ K_{Fe^{2+}} = 76 M^{-1}/s \]
\[ K_{Fe^{3+}} = 0.02 M^{-1}/s \]

Fe³⁺ + H₂O₂ ➔ Fe²⁺ + H⁺ + HO₂⁻

“While hydroxyl radicals [•OH], hydroperoxyl radicals (HO₂⁻) and organoradicals are produced during Fenton’s oxidation, the hydroxyl radicals are thought to be the strongest oxidants in this process. The hydroperoxyl and organoradicals may remain in the solution or be scavenged at rates slower than the hydroxyl radicals react.

In addition to reaction with organics, •OH may be scavenged by H₂O₂:
• OH + H₂O₂ ➔ HO₂⁻ + H₂O⁰

Experiments

Goals of the experiment (using Fenton’s oxidation, iron and MTBE) over a reaction time of 24 hours, were to find the
• optimum pH
• optimum H₂O₂

Researchers performed experiments at least three times and ran controls. Following a procedure outlined by the California MTBE Research Partnership, they prepared samples with a solid-phase micro-extraction (SPME) and used a gas chromatograph to test for MTBE and acetone. “The method detection limits were 1 mg/l for MTBE and acetone. The other possible byproducts of MTBE oxidation, TBF, TBA and others were not quantified, as the SPME/GC technique used was not able to resolve these other compounds” (Bergendahl and Thies, 2004).

In addition:
• TOC (total organic carbon) was measured with a Shimadzu total organic carbon analyzer
• H₂O₂ was determined with a Cobalt-UV spectrophotometric method

Results

Researchers found the following:
• reactions occurred over a wide pH range
• the greatest reduction in MTBE, 99 percent, occurred at a pH of 4.0
• at a pH of 7, MTBE was reduced by 96 percent
• the lowest reduction, 72 percent, occurred at a pH of 3.0
• all other experimental conditions showed an MTBE reduction of 93 to 95 percent

The researchers hypothesized that “in Fenton’s oxidation with Fe⁰, Fe²⁺ is continuously formed and available for reaction with H₂O₂, producing •OH, before it is
involved in precipitation reactions that are feasible in less acidic conditions” (Bergendahl and Thies, 2004). Experiments performed to the effective dose of H$_2$O$_2$ indicated that:

- at a H$_2$O$_2$:MTBE molar ratio of 44:1, MTBE was reduced by only 24 percent; acetone concentration increased to 160 μg/l
- at a molar ratio of 440:1, MTBE was reduced by greater than 99 percent; acetone concentration was 60 μg/l
- at a molar ratio of 220:1, acetone concentration significantly decreased
- the Fe$^{0}$: H$_2$O$_2$ molar ratio of 1.8:1 could degrade 1 mg of MTBE

Experimental data to measure TOC (total organic content), which is an indication of mineralization (large TOC reduction, more mineralization), indicated that:

- at a pH of 4.0 and H$_2$O$_2$:MTBE molar ratio of 220:1, TOC was reduced by about 84 percent
- at a pH of 7.0 and H$_2$O$_2$:MTBE molar ratio of 440:1, TOC was reduced by more than 98 percent
- at a pH of 4.0 and H$_2$O$_2$:MTBE molar ratio of 440:1, and also at a pH of 7.0 and H$_2$O$_2$:MTBE molar ratio of 220:1, TOC remained below detection limit

Conclusions

From these experiments, researchers were able to determine rates of reactions. Some rate constants are as follows:

- for reaction of H$_2$O$_2$ with Fe$^{0}$, 0.44/M/s for pH 7.0
- for reaction of H$_2$O$_2$ with Fe$^{0}$, 0.23/M/s for pH 4.0
- at a pH of 4.0, 37 percent of MTBE was converted to acetone
- MTBE degradation rate as affected by advanced oxidation, at a pH of 7.0, was 1.9 x 10$^8$/M/s; at a pH of 4.0, reaction rate was 4.4 x 10$^8$/M/s

The second-order rate constants determined from H$_2$O$_2$ degradation were:

- 0.44/M/s for pH 7.0
- 0.23/M/s for pH 4.0

Other findings:

- the concentration of Fe$^{2+}$ does not increase above 1.4 x 10$^{-5}$ M for pH 4.0, but reaches as high as 2.5 x 10$^{-5}$ for pH 7.0
- •OH concentrations are predicted to be up to 7.1 x 10$^{-11}$ M for pH 7.0, reaching a maximum at pH 4.0 of 3.8 x 10$^{-11}$

Given these results, researchers believe that Fenton’s oxidation of MTBE could be a reasonable alternative technology for treating MTBE-contaminated water.

Reference


UTTU thanks Dr. John Bergendahl, jberg@WPI.EDU, for his help on this article.

Active biotreatment of PAHs

Researchers studied an aerobic biological treatment process that involved polyaromatic hydrocarbons. Their research objectives were to determine:

- overall loss of specific PAH
- volatilization losses
- effect of possible operating temperatures and microbial acclimation
- the relationship between volatile losses and solid-liquid and liquid-gas partition coefficients

Organic chemicals of concern (OCOC) are often degraded or “lost” in aerobic biological treatment processes by a number of processes, which can include the following:

- hydrolysis
- photolysis
- chemical complexation
- biodegradation
- volatilization
- sorption
- solubilization
- precipitation
- extraction or removal

“The predominant OCOC loss mechanism in an aerobic bioreactor will depend on factors that affect a particular mechanism. For example, the satisfactory microbial degradation of the OCOC, adequate nutrients, sufficient oxygen supply, acclimated organisms, a neutral pH, and adequate solids retention time are needed. Temperature also affects microbial activity and the relative rate of degradation” (Fairey and Loehr, 2003).

Other factors that affect OCOC loss include:

- Henry’s constant, K$^H$, of a chemical, “which affects relative escaping tendency of that compound from water and thus the possibility for volatilization”
- desorption of OCOC from the solid phase of soils and sediments, which is influenced by the organic sorption coefficient (K$^o$), the octanol water partition coefficient (K$^{ow}$), and carbon type (oily phase, soot, natural organic matter)
“Thus, the relative rates of the specific mechanisms will affect the fate of an OCOC in an aerobic biotreatment process. If an OCOC is readily soluble, has a large K_H value, and biodegradation is inhibited, volatilization is likely to predominate. In contrast, if biodegradation rate is faster than the volatilization rate, there should be little VOC (volatile organic compound) or SVOC (semi-volatile compound) volatilization.”

**Bioslurry study**
Researchers performed a batch treatability study using creosote-contaminated soil from northeast Texas. For each sample, pH was controlled, nutrients were provided and an acclimated seed was added to each flask to ensure adequate conditions for biodegradation. The study was performed at 20°C and 35°C. Experiments were carried out on three sets of 25 flasks each. The three sets varied in terms of how much Millipore water and nutrient stock solution was added, and when the flasks were sacrificed (day 33, day 64 and/or day 93) and analyzed. The setups included PUFs, polyurethane foam plugs, that were removed and analyzed for the volatile organic compounds. Thus, “Information about PAH volatile losses was obtained by analyzing the PAH that accumulated on the PUF during each of the three phases. Volatile losses did occur for the two- and three-ring PAH analyzed as well as for four-ring PAH, fluoranthene and pyrene. Of interest in this study was the total amount and fraction of a PAH that was volatilized (captured on the PUF) at a given temperature for each phase. This value was then normalized using the average initial mass of the compound in the slurry associated with that set of flasks (PAH mass on PUF/initial PAH mass in sample). This value was represented by the term \( V_{\text{frac}} \times V_{\text{max}} \). Values indicate the maximum fractional amount, expressed as a percentage of a specific PAH, likely to volatilize over the course of an aerobic bioslurry treatment process” (Fairey and Loehr, 2003).

**Conclusions**
Researchers concluded:

- high overall PAH losses occurred, particularly for the two- and three-ring PAH
- volatile PAH losses did occur in the aerobic bioslurry system; the maximum loss for naphthalene ranged from 9 to 17.8 percent; smaller amounts of the larger ringed PAHs volatilized
- volatilization became less important as microbial acclimation proceeded, “indicating that when an active acclimated microbial population is present in a well-mixed aerobic treatment process, microbial degradation of SVOC (in this case PAH) will be the primary loss mechanisms, not volatilization; under these conditions, the rate of SVOC degradation is faster than the rate of volatilization”
- PAH volatile losses were related to relevant partition coefficients that may affect losses; the researchers developed “several mechanistic predictive relationships for such losses” which “can be used as a guide, within the ranges of coefficients evaluated, to estimate the maximum SVOC losses that can be expected to occur in an aerobic bioslurry process”

**Life cycle assessments of fuels**
The U.S. EPA recently evaluated several different products using life cycle assessments (LCA) to determine the products’ merits in terms of “greenness” and quantities of bio-based material used in their production. Although the original paper evaluated the LCA of several products, this article will focus on a research study that is being conducted by the EPA to compare three fuels:

- gasoline with MTBE
- gasoline with ethanol
- a non-oxygenated reformulated gasoline

Using a mix of qualitative and quantitative generic data, this analysis evaluated the following impact category indicators:

- acidification (H⁺ mole equivalents)
- ecotoxicity (2,4-D equivalents)
- eutrophication (nitrogen equivalents)
- global warming (CO₂ equivalents)
- human health – cancer (benzene equivalents)
- human health – noncancer (toluene equivalents)
- human health – criteria (disability adjusted life-years, DALYs)
- ozone depletion (CFC-11 equivalents)
- photochemical smog (NOₓ equivalents)
- fossil fuel use (mega Joules surplus energy)
- water use (gallons)
- land use (acres)
- solid waste (pounds)

The analysis used a 3,200-pound passenger automobile driving 12,000 miles over a one-year period, which was 1999. “The functional unit (i.e., number of gallons of gasoline and additive) was calculated for each sys-
Trade-offs
The results of this study are still preliminary and are currently undergoing peer review. It is important to remember that the results are a consequence of the screening nature of the analysis, the data that were readily available, and the numerous assumptions made throughout the inventory and impact assessment efforts. In line with the screening level analysis, assessments of uncertainty were not attempted, so one cannot define the significance of the differences between the alternatives. Also, the results reflect the use of U.S. average data as a basis for the study. That is to say, site-specific conditions were not included at this screening level. It is anticipated that future efforts will be able to improve upon these findings, possibly uncover additional data, and allow for additional in-depth assessments where warranted. Given these cautions, the results from the inventory data and the resulting impact assessment illustrate that there are more similarities than dissimilarities between the alternatives. This is most likely due to the fact that for each system, blendstock gasoline makes up a large portion of the product. There are, however, notable differences brought to light by this analysis.

While vehicle operation dominated many of the impact categories in this analysis, corn growing was often responsible for differences within categories. Corn growing appears to exhibit both advantages and disadvantages in moving to an ethanol system. Using a biobased feedstock in the ethanol system reduces the amount of fossil fuels needed and correspondingly reduces the global warming effects. At the same time, releases from corn growing contribute to multiple impact categories. Additionally, corn growing requires acreage and water for irrigation, although the question remains as to whether additional land will need to be converted into agricultural use for growing corn in the future. In general, if the impacts of corn growing (and ethanol production) could be reduced, the negative impacts of the ethanol system would essentially be similar to the other alternatives with benefits still existing in global warming, human health - noncancer, ozone depletion, and fossil fuel use. Note that research is underway to use fewer pesticides (e.g., Bt corn) and fewer nutrients (e.g., obtain nutrients from air as in legumes), and to use biowaste as a feed (e.g., breakdown cellulose) for ethanol production.

Unlike the production of ethanol from corn, the MTBE system does not produce similarly distinctive outcomes. Although the occurrence of MTBE in drinking water supplies has become a national concern, and the main reason for conducting this study, the study did not point to any significant impacts due to local releases of MTBE at refueling stations. Even though MTBE spills may result in localized effects, the amount of MTBE that was estimated to be leaking from transportation and storage facilities in the life cycle inventory is small in relation to the large amount of material that is being moved and released from these gasoline systems.

What LCA can do
According to Curran (2003), “These results are an interesting first step in approximating the inputs and outputs associated with the three systems. While it is apparent that the activity of growing corn sets the ethanol system apart, quantification of water use in the petroleum-based systems, runoff of agrochemicals from corn fields into waterways, and impacts from transportation is needed to better understand the potential impact of selecting one of these additives.”

LCA demonstrates how complex the factors of “green” can be. “Information generated by LCAs can be used as a basis for supporting purchasing decisions by highlighting the difference in environmental impacts among choices. LCA does not, however, make the decision, although at times the best choice may be obvious. Other factors need to be included in the final decision-making process, including the consequences of diverting the use of land from growing crops for food to growing crops for fuel, or dedicating additional acreage to crop production. The full implementation of any LCA depends entirely on the values that the decision-maker holds, and the values, such as local impacts versus regional or global concerns, that are made when choosing among alternatives” (Curran, 2003).
See also “Ethanol fuel from corn faulted as ‘unsustainable subsidized food burning’,” an analysis by a Cornell scientist,” http://www.news.cornell.edu/releases/Aug01/corn-basedethanol.hrs.html

References


UTTU thanks Ms. Curran, Curran.Maryann@epa.mail.epa.gov, for her help on this article.

Can tanks be too old to upgrade?
By Jim O’Day

I have never been keen on the idea of “rebuilding” used, shop-fabricated tanks. In the Midwest, this has become a popular method for compliance with state AST regulations. New bottoms, doubled bottoms, interior linings, vent openings and structural supports seem to be the most common items installed. Barrel stretching or making two tanks from one are also being done. There is no consensus in the regulatory community regarding acceptability of the type of work or of methods employed.

Field repair of tanks is reasonable in some situations, but often not a sound choice. At issue are the tank’s prior service use, age, type of original construction methods and materials used. I recently declined to replace bottoms on several vertical, shop-built tanks, a decision I seem to be making frequently these days. We receive requests to do this work more often today than in the past, and we routinely turn down the work because of the tank’s age or condition. The work that is done by others does not often meet any API repair standards.

My position is that the majority of these tanks being worked on are just too old; they are at the end of their service life. Many contractors doing this work today do not share my views on this; granted, I am somewhat biased because my company manufactures new tanks. We are required to build to specified standards, using specified materials, attachments and construction methods. Old tanks built just 20 years ago (shop-built) are different from today’s tanks because the standards back then were different. The product today is superior to those made 20 years ago.

The tanks I declined to repair had manufacturer’s markings that dated the tanks to fabrication during the 1940s; no other markings or data were available. These tanks would have been manufactured during the time of the new steel shortage, which is a materials quality concern. Compared to today’s standards, the materials used then were questionable, as were construction methods. These particular tanks had shell materials 30 percent thinner than required under today’s standards and although the steel strength was unknown, it was assumed to be no greater than today’s steel. Re-building these tanks to meet any industry standards was not economically feasible. Even so, many companies “re-build” and “upgrade” these tanks to “new” standards.

As regulatory attention is being focused toward the future upgrading of existing aboveground tanks, it is important to be realistic when determining whether a tank is too old or too lacking in integrity to rehabilitate. For a tank with a pedigree, certified material, recognized construction methods and today’s minimum design criteria, a good case can be made for upgrading. The reality is that this tank is most likely a site-built terminal tank, not a 15,000-gallon bulk storage tank.

Industry standards address and guide field repairs made to aboveground tanks. If followed, these standards produce an acceptable result. The catch is that if one were to follow these standards, the field upgrade would cost more than a new replacement tank. These economic issues go away quickly, however, as the tank sizes increase above 50,000 gallons. Smaller, new tanks do not cost that much compared to the cost of rebuilding. If one follows API 653, it would not make economic sense to rebuild smaller tanks—but a 50,000-gallon tank costs enough to change that. Labeled or Listed tanks are, however, stronger candidates for rebuilding.

Manufacturers today spend thousands of dollars testing the construction processes and performance of tank designs. It seems careless to consider tanks without a pedigree as candidates for continued service merely because of a facelift. Even so, regulators who consider the rebuilding of old underground tanks a sin routinely give their blessing to this activity.

My friend, who is in the tire retreading business, and I joke about all the truck-tire garbage on the road. He tells me that the retreading technology is better than ever, but the tough part is determining when the tire core is just too old or lacks the integrity to be rebuilt. When a retread tire fails, the tread is typically okay, but the original tire to which the new tread was applied generally comes apart. We should take a lesson here and apply the same logic when it comes to rebuilding tanks.
Reference

UTTU thanks John Hartmann, publisher of Petroleum Equipment & Technology Magazine Archive (http://www.pe-t.com), for allowing us to reprint this article. More than 800 articles appear on his Web site, and new articles are being posted regularly to the site. John Hartmann & Associates may be reached at Jhartmann@pe-t.com or 847-382-4010.

Research notes

Containment of groundwater contamination plumes: minimizing drawdown by aligning capture wells parallel to regional flow

Researchers investigated “the parallel capture well orientation and determined the advantages and disadvantages of the system with respect to plume containment.” Using complex potential theory and other methods to delineate capture zones, Christ and Goltz (2004) investigated “the geometry of the capture zone curve for wells aligned parallel to flow along the center of the plume and developed a simple graphical method that can be used to determine the engineered parameter values:

• well flow rate, Q
• number of wells, N
• distance between wells, D
to obtain a given capture.” The authors add that “This method will aid groundwater remediation site managers in design and evaluation of plume containment systems.”

Extraction wells that are oriented co-linearly, parallel to regional flow, will

• capture a larger area of the aquifer without an increase in well flow rate
• achieve the same center and ultimate CZW (capture zone width) as the perpendicular configuration (this occurs when wells are oriented conventionally, perpendicular to regional flow)
• offer more flexibility during attempts to minimize drawdown through well placement

Christ and Goltz (2004) contend: “If we allow an extraction well to be located in an uncontaminated region of the aquifer, downgradient from the contaminant plume, we can further reduce drawdown (up to 19 percent in one example). We find the proposed parallel configuration has a lower drawdown and higher removal efficiency than the perpendicular configuration, particularly for plumes that have their widest point near to or upgradient of the plume center.”

The influence of substrate and electron acceptor availability on bioactive zone dynamics in porous media

Investigators examined “the influence of dissolved oxygen (DO) and substrate availability on the formation and dynamics of “bioactive zones” in a water-saturated porous medium... The location and size of these bioactive zones are controlled by both physicochemical (e.g., subsurface heterogeneity, environmental conditions, the nature and concentrations of substrates, electron acceptors, and nutrients) and microbiological (e.g., the dynamics and physiological status of the microbial community) factors. Because many of these factors are in a state of flux in the subsurface environment, and because the subsurface environment is generally heterogeneous, the formation of bioactive zones is expected to be a temporally and spatially variable process.”

Investigators used two approaches. For the first, they monitored “the spatial and temporal variability of DO and aqueous substrate (salicylate and naphthalene) concentrations during miscible-displacement experiments.” For the second, they monitored microbial activity using “multiple fiber optics emplaced in the porous medium to detect luminescence produced by Pseudomonas putida RB1353, a bioluminescent reporter organism that produces light when salicylate (an intermediate of naphthalene degradation) is present.” Results of the study indicated that “the location and size of bioactive zones in porous media are influenced by substrate and DO availability. Luminescent reporter organisms do provide real-time in-situ monitoring of microbial activity in porous media and can provide insight concerning how microbial populations respond to changes in local environmental conditions.”

Information sources

U.S. EPA publications and information
Reports available to view or download at http://clu-in.org/techpubs.htm include:

• CalEPA Evaluation Report: Hapsite GCMS, an instrument that measures volatile organic compounds in water, soil and soil gas
• Enhanced Access Penetration System (EAPS), which describes a direct push system developed to drill through refusal points
• Technologies for Treating MTBE and Other Fuel Oxygenates, EPA 542-R-04-009
• Technology News and Trends, which contains articles on in-situ chemical oxidation in fractured bedrock

Other CLU-IN documents include:
• CLU-IN Contaminant Focus Update, and its new search area, MTBE, at http://clu-in.org/contaminantfocus/
• National Institute for Environmental Health Studies (NIEHS)/Biosensors for Environmental Monitoring, an Internet seminar, available at http://clu-in.org/studio

Other documents and Web sites
• Brownfields and Land Revitalization Technology Support Center Internet site, http://www.brownfieldstsc.org
• Cleanup News (EPA 300-N-04-002), http://www.epa.gov/compliance/resources/newsletters/cleanup/cleanupnews.html
• ESTCP Cost and Performance Report: Natural Pressure-Driven Passive Bioventing (CU-9715), produced by DoD Environmental Security Technology Certification Program (ESTCP), available to view or download at http://www.estcp.org/documents/techdocs/CU-9715.pdf
• Fingerprint Analysis of Contaminant Data: A Forensic Tool for Evaluating Environmental Contamination (EPA 600-S-04-054), http://www.epa.gov/tio/tsp/issue.htm

• Making the Case for Ecological Enhancements (ECO-1), http://www.itrcweb.org/ECO-1.pdf

Books
Quantitative Geology and Geostatistics is available from Kluwer Academic Publishers; e-mail kluwer@wkap.com for more information.

UTTU obtained many of these sites from TechDirect (http://clu-in.com/techdrct), Ground Water Monitoring & Remediation (http://www.ngwa.org), and other publications. We thank the editors and writers for allowing us to reprint this material.

Corrections to UTTU, Volume 18, No. 4, 2004
In the article "Limitations of TPH analysis," shown on pages 2-4, please note these corrections:

• Page 2, middle column, lines 1 through 5 should read: ...thousands of hydrocarbons (non-polar molecules composed exclusively of carbon and hydrogen atoms) and minor nonhydrocarbons (polar molecules containing nitrogen, sulfur, or oxygen in their structure, called NSOs or hetero-atoms) make up crude oil...

• Page 2, middle column, bulleted line 25 should be deleted

• Page 3, last bulleted line in left column should read: ...about 6 mg/l for Bunker C (HEAVY fuel oil)

• Page 3, right column, second paragraph: first two bullets should be deleted (The correct text appears in bullets 3 and 4.)

UTTU regrets these errors and again thanks Dawn Zemo and Gary Foote for their help on this article.