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Your Guide to Environmental Strategy Development and Innovative Remediation Technologies

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What's Inside:

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Special Focus On... TCA

THE TROUBLE WITH TCA

Understanding the Characteristics of Chlorinated Ethanes and 1,1,1-Trichloroethane

by Brant Smith, Ph.D., P.E., Senior Engineer & Laboratory Director, XDD

Chlorinated eth<u>e</u>nes and chlorinated eth<u>a</u>nes: what a difference a vowel can make. The treatment of chlorinated ethenes, such as trichloroethylene (TCE) or perchloroethylene (PCE), has become somewhat commonplace as such contaminants are known to be reactive with a wide variety of in-situ treatment technologies including in-situ chemical oxidation, in-situ chemical reduction and anaerobic bioremediation. However, the treatment of chlorinated ethanes is not as easy.

The key difference in treatment hinges on the fact that chlorinated ethenes have a double bond between the two carbon molecules and this second bond – the pi bond – is more accessible to transformation than the single bond – the sigma bond – which connects the carbon atoms in chlorinated ethanes.

Chlorinated ethanes have been used primarily as organic solvents in the role of cleaners and degreasers but they are also used as industrial intermediates, aerosols and even as anesthetics. Common with any cleaning solvent, chlorinated ethanes are usually found in the presence of the chemicals they were used to clean or co-solvents that were added to enhance specific properties. Compounds typically found with chlorinated ethanes include 1,4-dioxane, TCE, PCE, PCBs and various hydrocarbons similar to kerosene and diesel fuel.

1,1,1-Trichloroethane (**TCA**) is a common chlorinated ethane. It was introduced in the 1950's as a replacement for industrial cleaning solvents such as carbon tetrachloride, but it has also been used in paints, adhesives, and in aerosols. While the production of TCA for domestic use has been banned in the United States since 2002, TCA is now found at approximately 50 percent of all National Priorities List (NPL) sites identified by the EPA.

TCA is found at roughly 50% of all National Priorities List (NPL) sites.

As a contaminant, TCA is a hazard to both people and the environment. Current research indicates that it can adversely affect the circulatory and nervous systems as well as the liver. (There is no evidence to suggest that TCA is a carcinogen.) However, the primary impact of TCA may be to the environment. TCA can persist in the atmosphere for years and its atmospheric breakdown products can contribute to the depletion of the ozone layer.

The following characteristics are pertinent to understanding TCA's potential behavior in the environment:

- Water solubility (657 mg/L) is low when compared to TCE (1,312 mg/L) or other chloroethanes (5,060 mg/L for 1,1-dichloroethane), which means that if a significant amount of mass is present, it will likely be in a non-aqueous phase and water extraction technologies will only impact a small portion of the mass;

...continued on p. 2

INSIDE:
Find out how XDD recently tackled TCA at 2 tough sites!

Down N' Dirty With...

1,4-Dioxane

by Scott Crawford
*Senior Project Manager, **XDD***

This compound may have gone largely unnoticed up until a few years ago, but all that is changing. The USEPA considers 1,4-dioxane a "probable" human carcinogen. Since 90% of all 1,4-dioxane manufactured was used as a solvent stabilizing agent (particularly in 1,1,1-TCA), this compound has been lurking in the background for years – potentially above regulatory criteria – at many chlorinated solvent sites. While there is currently no USEPA MCL for 1,4-dioxane, EPA Regions and state agencies are adopting their own enforceable criteria (as high as 85 ppb in Michigan and as low as 3 ppb in California).

1,4-dioxane is highly soluble in groundwater, does not readily bind to soils, and readily leaches to groundwater. It is also resistant to naturally occurring biodegradation processes. Due to these properties, a 1,4-dioxane plume is often much larger (and further downgradient) than the associated solvent plume.

So if you have 1,4-dioxane at a site, what can you do to treat it? Presently, the majority of documented (and effective) strategies involve groundwater extraction and ex-situ treatment using Advanced Oxidation Processes (AOPs). These AOPs include use of ultraviolet light catalyzed hydrogen peroxide (UV/Ox), and ozone/hydrogen peroxide technologies (O_3/Ox), among others.

What about in-situ technologies? Various in-situ remedial options have been studied – such as enhanced biodegradation processes (including co-metabolic processes), air sparging, and pump and treat – but due to 1,4-dioxane's properties, many of these technologies yield only partial success. However, there have been several recent advances in in-situ chemical oxidation (ISCO) technologies that have proven effective for 1,4- dioxane – and, fortunately, for 1,1,1-TCA as well (*see article at right*). In **XDD**'s experience, hydrogen peroxide (applied in-situ under the proper conditions) is effective for 1,4-dioxane and 1,1,1-TCA. **XDD** has also applied alkaline activated sodium persulfate in bench testing, field pilot, and full-scale applications at a number of sites. This

...continued on page 4

The Trouble With TCA, *continued from page 1*

- TCA is denser than water (specific gravity of 1.34) meaning that if present in pure liquid phase it will sink to the bottom of aquifers (i.e., DNAPL);
- TCA has a partitioning coefficient of log K_{ow} of 2.33 (same as TCE) indicating that it would prefer to partition onto organic matter rather than stay in water, making it more difficult to treat; and,
- The potential for biodegradation varies depending upon the conditions, but the data seem to suggest a very low likelihood of reactivity under aerobic conditions and slow rates of reaction under highly reductive/anaerobic conditions. Further, when TCA is biotically reduced, it breaks down into products such as 1,1-dichloroethane and chloroethane. Natural abiotic reduction (e.g., reactions with reduced metals in the environment) can also form additional products including 1,1-dichloroethene and vinyl chloride.

When these characteristics are added up, TCA is a potential DNAPL that faces significant remedial challenges, and if left untreated, it could form additional compounds that are potentially more problematic.

For more information on remedial issues related to TCA & other chlorinated solvents, contact Brant at ***smith@xdd-llc.com***.

Remedial Solutions

XDD KO's TCA IN 2 SEPARATE BOUTS

Recent Field Results Reveal 99-Percent Reduction With ISCO

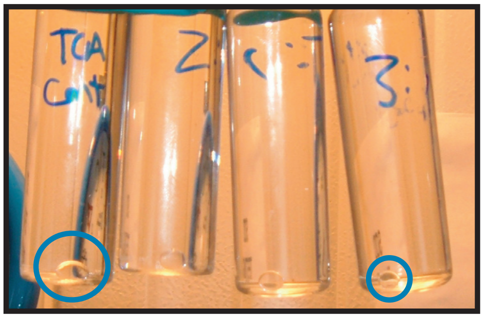
by Brant Smith, Ph.D., P.E., Senior Engineer & Laboratory Director, XDD

XDD has recently had great success in treating 1,1,1-trichloroethane (**TCA**) with a pair of in-situ chemical oxidation (ISCO) technologies. Catalyzed hydrogen peroxide (**CHP** or Fenton's reagent) and alkaline activated persulfate (**AP**) have both been applied by **XDD** on the bench and in the field at sites with TCA contamination with successful results.

XDD has applied CHP at a site with significant DNAPL phase TCA. The results have shown an average reduction in TCA groundwater concentrations greater than 80 percent after each application. The reduction in TCA in the DNAPL and soil phases has been significant enough – **up to 99 percent reduction** – that much of the targeted areas have surpassed their remedial goals. Results from the field application of AP at another TCA site have shown reductions in TCA groundwater concentrations as high as 98 percent.

Bench scale tests for both technologies reveal that each was capable of completely degrading TCA DNAPL if sufficient contact was made between the oxidant and contaminant.

These results are very encouraging as CHP and AP are ISCO technologies with different characteristics, which in turn will allow **XDD** to consider and select the most appropriate technology for any particular site. As a basic example, AP typically has a greater subsurface persistence and does not result in the evolution of the same quantities of gas and heat that are associated with CHP. This will tend to favor the selection of AP at sites with contamination under buildings or that have a limited injection rate which necessitates a longer injection period.



"I COULDA BEEN A CONTENDA!" shouts TCA, but to no avail, as alkaline activated persulfate pounds it into submission. The above photo shows the progressive destruction of TCA DNAPL (inside the blue circles) in an AP system.

Got TCA concerns? Then get in touch with Brant directly at ***smith@xdd-llc.com***.

A Closer Look At…

O&M OPTIMIZATION

by Mike Marley, L.E.P., President, XDD

Over the hundreds of sites for which I have reviewed, designed or optimized remedial systems over the past 30 years, I have observed that sites within the operations and maintenance (**O&M**) phase receive the least attention from both site owners and their consultants.

I have always considered this neglect strange since for many sites the O&M phase can represent a significant project cost. If you only have one or two sites, this article may raise some questions for you; but for those with many sites, hopefully this article will either instill confidence in the program you have or possibly spark some thought that may lead you to improve your current program – ***and lower your O&M costs***.

An O&M optimization program should consist of a simple systematic process that will allow you to easily evaluate and analyze sites to determine potential cost savings across a number of key categories. The core of the program should utilize a database to store key site data, which then will enable you or **XDD** to analyze the potential results and savings that can be derived from changes in the site management process. *(See chart below.)*

Examples of key categories which can be analyzed as part of your optimization program include:

Site Grouping/Packaging

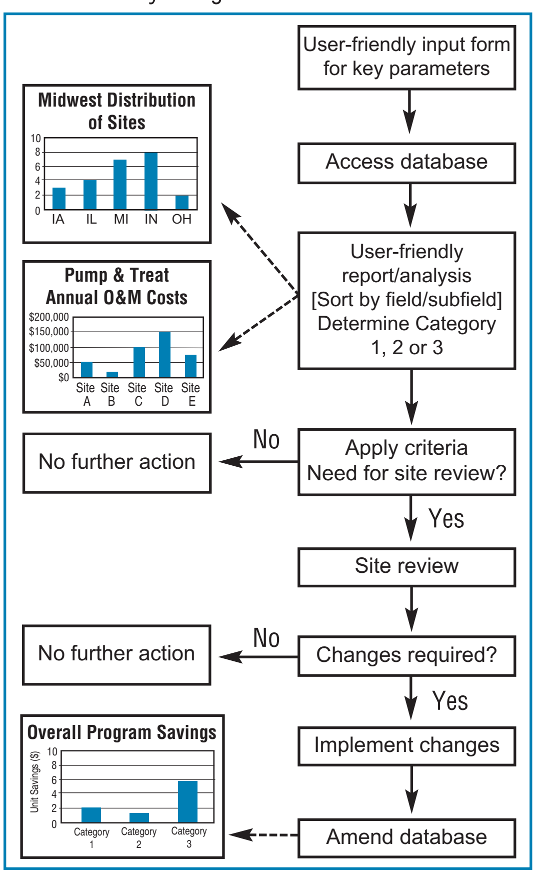
- Understand efficiencies that can be achieved by streamlining O&M activities across several sites. Key parameters in this category may include geographic location of sites (and the response time for unscheduled events), necessary field operator skills and agency sampling requirements.

Monitoring/Sampling Optimization

- Evaluate site monitoring and sampling needs, such as frequency, data management and permit requirements. Additional parameters to consider include the number of wells/samples needed, analysis requirements (field kits vs. labs), and opportunities for waste minimization (*e.g.*, on-site treatment).

Remedy Evaluation/ Optimization

- Review current and alternative remedial technologies and their associated parameters to determine annual and projected life-cycle costs. Some questions to consider include: Is there a potential for risk-based closure or reclassification? How reliable is the remedial system and can its efficiency be increased? What would the payback analysis look like if there was a remedy change?



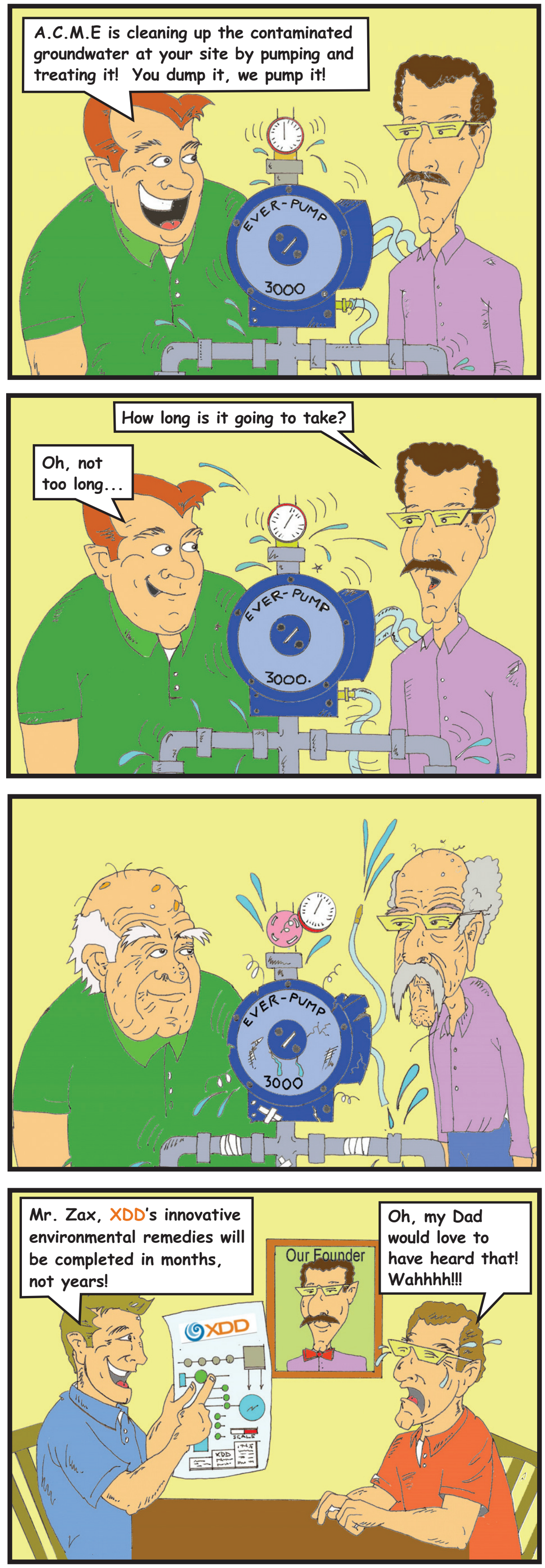
Above: A flowchart illustrating a database process used when evaluating a client's operations & maintenance (O&M) activities.

Want to talk more about O&M and program optimization? Contact Mike at ***marley@xdd-llc.com***.

PLANET XDD

by R.W. Kane, Jr.

"As Time Goes By…"



1,4-Dioxane*, continued from page 2*

technology is also proving to be highly effective for both 1,4-dioxane and 1,1,1-TCA (and has the advantage of being more stable in the subsurface, allowing for longer reaction time in-situ). ISCO methods have a distinct advantage over the ex-situ AOP processes in that ISCO typically results in significantly lower capital costs and shorter remediation (and associated O&M) timeframes.

Want to find out more about 1,4-dioxane issues or in-situ remedial technologies? Drop Scott a line at ***crawford@xdd-llc.com***.

EPRI RELEASES ISCO GUIDANCE FOR MGP SITES

The Palo Alto, CA-based **Electric Power Research Institute (EPRI)** has recently published a report on **XDD**'s evaluation of in-situ chemical oxidation (ISCO) technology for former manufactured gas plant (MGP) sites. The report, entitled "*In Situ* Chemical Oxidation of MGP Residuals: Field Demonstration Report," details the results of **XDD**'s two-year study to determine the technical feasibility, economics and limitations of ISCO for MGP residuals (TPH, PAHs and BTEX). The report provides guidance to managers in understanding the site conditions for which ISCO may be a cost-effective remedial alternative, the criteria for determining the most applicable ISCO technology, and the site-specific cleanup objectives that ISCO may achieve at MGP sites.

To purchase a copy of the report from EPRI (Product ID: 1015411), visit ***http://my.epri.com*** or call **(800) 313-3774**. For additional information on the study or MGP treatment options, please contact **XDD**'s Jaydeep Parikh, one of the study's principal researchers, at *parikh@xdd-llc.com*.

Hot Topics!

Resources for the latest environmental remediation issues

Goodbye, Bioscreen. Hello, Bioscreen-AT. The Michigan DEQ suspended the use of Bioscreen in its risk-based site closure evaluations because of apparent errors in the underlying Domenico solution to the groundwater transport equations. The DEQ proposes Bioscreen-AT as an alternate model, which can be downloaded at *www.sspa.com/software/BIOSCREEN.htm*.

EPA Innovative Technology Evaluation Report: XDD In-Situ Chemical Oxidation Process Using Potassium Permanganate (EPA 540-R-07-0005, 2006). **XDD**'s in-depth evaluation of an ISCO process was performed under the EPA SITE Program and demonstrated the efficacy and limitations of using potassium permanganate in highly stratified glacial till for the treatment of chlorinated solvents. To view the complete report, go to: *http://www.epa.gov/nrmrl/pubs/540r07005/540r07005.pdf*.

Design and Performance Evaluation of Air Sparging Trench for the Treatment of VOCs and Arsenic. Air sparging trenches are being constructed throughout the U.S. without proper consideration for long-term operational issues. This recent presentation delivered by **XDD** addresses several key issues, including the effect of air flow, biomass growth, and mineral precipitation on the conductivity and performance of the trench. View the presentation at: *http://www.xdd-llc.com/images/XDD_AirSpargingTrench.pdf.*

INSIDE THIS ISSUE: Sensitively understanding and then mercilessly destroying TCA!

PLUS: You can't possibly expect to get any work done until you've read the latest installment of... XDD PLANET

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