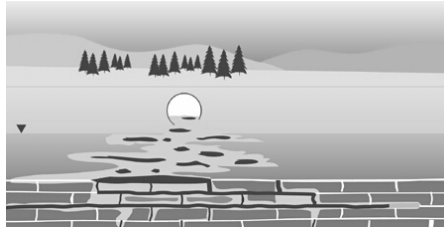


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## Welcome – Thanks for joining us. ITRC's Internet-based Training Program



### Strategies for Monitoring the Performance of DNAPL Source Zone Remedies



#### Technical and Regulatory Guidance

This training is co-sponsored by the EPA Office of  
Superfund Remediation and Technology Innovation

#### Presentation Overview:

The environmental problems associated with DNAPLs (dense, nonaqueous-phase liquids) are well known—extremely difficult to locate; small amounts contaminate large volumes; conventional groundwater extraction technologies do not work; and restoration of DNAPL sites to drinking water standards or maximum contaminant levels is considered unattainable. DNAPLs can be treated by implementing one of several or a combination of technologies. Despite the ever-increasing number of field applications of DNAPL removal technologies, many unanswered questions remain regarding the effectiveness of these technologies and how best to measure their performance with respect to site-specific remedial objectives.

This training addresses specific issues dealing with monitoring the performance of various DNAPL source zone remediation technologies. It is based on ITRC's *Strategies for Monitoring the Performance of DNAPL Source Zone Remedies* (DNAPLs-5, 2004). Performance is discussed in terms of effective and efficient progress toward the project goals. Elements of a robust performance monitoring program are described, including the need to establish appropriate performance goals and metrics well in advance. The applicability and limitations of various performance metrics, including the concept of mass flux, are discussed. Because of these limitations, a converging lines of evidence approach to performance assessment is stressed. While some issues pertaining to DNAPL fate and transport are covered in the document, participants are encouraged to review the material presented in the UK Environment Agency's *Illustrated Handbook of DNAPL Fate and Transport in the Subsurface* prior to taking the course.

ITRC (Interstate Technology and Regulatory Council) [www.itrcweb.org](http://www.itrcweb.org)

Training Co-Sponsored by: EPA Office of Superfund Remediation and Technology Innovation  
([www.clu-in.org](http://www.clu-in.org))

ITRC Course Moderator: Mary Yelken ([myelken@earthlink.net](mailto:myelken@earthlink.net))

## ITRC ([www.itrcweb.org](http://www.itrcweb.org)) – Shaping the Future of Regulatory Acceptance

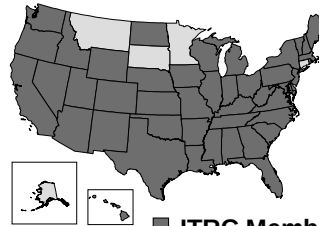


- ▶ Network
  - State regulators
  - Federal government
  - Industry
  - Consultants
  - Academia
  - Community stakeholders
- ▶ Documents
  - Technical and regulatory guidance documents
  - Technology overviews
  - Case studies
- ▶ Training
  - Internet-based
  - Classroom

Host Organization



ITRC State Members



■ ITRC Member State

Federal Partners



The Interstate Technology and Regulatory Council (ITRC) is a state-led coalition of regulators, industry experts, citizen stakeholders, academia and federal partners that work to achieve regulatory acceptance of environmental technologies and innovative approaches. ITRC consists of 45 states (and the District of Columbia) that work to break down barriers and reduce compliance costs, making it easier to use new technologies and helping states maximize resources. ITRC brings together a diverse mix of environmental experts and stakeholders from both the public and private sectors to broaden and deepen technical knowledge and advance the regulatory acceptance of environmental technologies. Together, we're building the environmental community's ability to expedite quality decision making while protecting human health and the environment. With our network approaching 7,500 people from all aspects of the environmental community, ITRC is a unique catalyst for dialogue between regulators and the regulated community.

For a state to be a member of ITRC their environmental agency must designate a State Point of Contact. To find out who your State POC is check out the "contacts" section at [www.itrcweb.org](http://www.itrcweb.org). Also, click on "membership" to learn how you can become a member of an ITRC Technical Team.

## ITRC Course Topics Planned for 2006



### Popular courses from 2005

- ▶ Alternative Landfill Covers
- ▶ Constructed Treatment Wetlands
- ▶ Environmental Management at Operational Outdoor Small Arms Ranges
- ▶ DNAPL Performance Assessment
- ▶ Mitigation Wetlands
- ▶ Perchlorate Overview
- ▶ Permeable Reactive Barriers: Lessons Learned and New Direction
- ▶ Radiation Site Cleanup
- ▶ Remediation Process Optimization
- ▶ Site Investigation and Remediation for Munitions Response Projects
- ▶ Triad Approach
- ▶ What's New With In Situ Chemical Oxidation

### New in 2006

- ▶ Characterization, Design, Construction and Monitoring of Bioreactor Landfills
- ▶ Direct-Push Wells for Long-term Monitoring
- ▶ Ending Post Closure Care at Landfills
- ▶ Planning and Promoting of Ecological Re-use of Remediated Sites
- ▶ Rads Real-time Data Collection
- ▶ Remediation Process Optimization Advanced Training
- ▶ More in development.....

Training dates/details at [www.itrcweb.org](http://www.itrcweb.org)

Training archives at <http://clu.in.org/live/archive.cfm>

More details and schedules are available from [www.itrcweb.org](http://www.itrcweb.org) under "Internet-based Training."

## Strategies for Monitoring the Performance of DNAPL Source Zone Remedies



### Logistical Reminders

- Phone line audience
  - ✓ Keep phone on mute
  - ✓ “\*6” to mute, “\*7” to un-mute to ask question during designated periods
  - ✓ Do NOT put call on hold
- Simulcast audience
  - ✓ Use  at the top of each slide to submit questions
- Course time = 2¼ hours

### Presentation Overview

- Performance overview
- Performance metrics
- Questions and answers
- Technology-specific tools
- Regulatory issues
- Stakeholder issues
- Links to additional resources
- Your feedback
- Questions and answers

No associated notes.

## Meet the ITRC Instructors



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### Instructor Biographies:

**Eric Hausamann** is an environmental engineer with the New York State Department of Environmental Conservation (NYSDEC). For the past 5 years, he has worked in the Division of Environmental Remediation advising staff on the selection and implementation of innovative technologies. Prior to working for NYSDEC, Mr. Hausamann worked in the hazardous waste remediation field as a consultant to industry. Eric received a B.S. in Mechanical Engineering from the University at Buffalo and a M.S. in Environmental Engineering from the SUNY College of Environmental Science and Forestry in Syracuse. He has been a member of the ITRC since 1998 and currently leads the DNAPLs Team. Under his leadership, the team has produced four documents on technical and regulatory issues relating to DNAPL site cleanup and continues to serve as a forum for the open exchange of fact and opinion on the topic of DNAPL source remediation.

**Dr. Konstantinos Kostarelos**, a professor at Polytechnic University, has been involved with NAPL research for over 10 years. Kostarelos started a new Subsurface Remediation Center at Polytech that has yielded outstanding results in recovering coal tar from soil. His research is not only focused on subsurface remediation, but NAPL detection technologies as well. For example, a recent development being studied is the use of partitioning interwell tracer testing for the detection and measurement of irregularly distributed NAPL-i.e., NAPL pools. Development of a field method for NAPL detection of is of great interest to Professor Kostarelos, and he is collaborating with Dr. Masoud Ghandehari (Polytechnic University) to develop a remote, real-time chemical sensor.

**Ryan Wymore**, CDM, has 8 years of experience in the field of environmental engineering, over 6 of which have been focused on innovative groundwater remediation technologies. Mr. Wymore currently specializes in enhanced bioremediation and monitored natural attenuation of chlorinated solvent-contaminated groundwater. He is leading the implementation of enhanced in situ bioremediation as the final CERCLA remedy for a TCE DNAPL residual source area in a deep, fractured basalt aquifer. He is also leading the evaluation of alternative technologies for several low-concentration VOC and nitrate-contaminated areas in a deep aquifer in the southwest US. Mr. Wymore recently documented one of the first reported cases of intrinsic aerobic microbial degradation of TCE-contaminated groundwater by indigenous bacteria in the world. Mr. Wymore has given over twenty-five presentations at various local, regional, national, and international symposia and meetings. Mr. Wymore is a registered Professional Engineer in the state of Idaho in the environmental discipline. He received his Bachelor of Science in Biological Systems Engineering from the University of Nebraska-Lincoln in December of 1997, and his Masters of Science in Civil/Environmental Engineering from the University of Idaho in May 2003. During his career he has worked for the Idaho National Engineering and Environmental Laboratory, North Wind Inc., and is currently at CDM.

## Performance Assessment Overview



**Presented by Eric Hausamann**  
**New York State Department of**  
**Environmental Conservation**

Today we'll be talking about strategies for assessing remedial performance at DNAPL sites, specifically the performance of in situ treatment technologies that target the DNAPL source.

Dr. Konstantinos Kostarelos will follow my overview with a discussion of the various types of performance metrics for DNAPL source zone treatment including a discussion of the pros and cons of concentration-based metrics, the pitfalls of estimating mass removal percentages, and techniques for measuring the impacts of treatment on the downgradient plume.

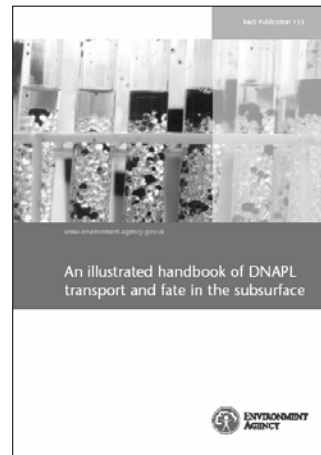
Mr. Ryan Wymore will then describe a number of source treatment technologies being used at DNAPL sites and the monitoring parameters specific to each technology.

The document we'll be discussing today is geared to those who have already made the decision to implement a DNAPL source treatment technology as opposed to a source containment approach.

## Course Pre-Requisite



- ▶ Possess a working knowledge of DNAPLs
- ▶ Review: “An illustrated handbook of DNAPL transport and fate in the subsurface”
- ▶ Other ITRC documents



Today's training assumes that you have a general working knowledge of DNAPLs and that you have reviewed and understand the material presented in the “Illustrated handbook of DNAPL transport and fate” published in the UK by the Environment Agency.

The ITRC DNAPLs Team has also produced four other documents on DNAPLs that you are encouraged to read. These and other recommended works are listed on the “Links to Additional Resources” page at the end of this presentation.

## What You Will Learn.....



- ▶ Appreciation for performance assessment
- ▶ Importance of a valid conceptual site model
- ▶ Value of converging lines-of-evidence approach
- ▶ Regulatory issues to consider when planning a performance assessment program
- ▶ Limitations of point measurements
- ▶ State-of-the-art techniques and tools for assessing performance

Today, you'll hopefully:

Gain an appreciation for performance assessment,

Understand the importance of building and utilizing a valid conceptual site model,

Discover the benefits of a converging lines-of-evidence approach to assessing performance vs. relying on a single metric,

Understand and appreciate some of the regulatory and stakeholder concerns about PA,

Learn about some of the practical limitations of point measurements like soil or groundwater concentration data, and

Hear a bit about some state-of-the-art techniques and approaches for measuring performance

## Major Take-Home Points



1. Performance goals and metrics should be established during design
2. MCLs are not a realistic short-term goal for a DNAPL source zone – alternate goals should be considered
3. Converging lines of evidence provide the most confidence in performance assessments

Major points of today's seminar:

Stress the importance of planning for performance assessment ahead of time.

Stress that goals for the source zone need to be both measurable and achievable.

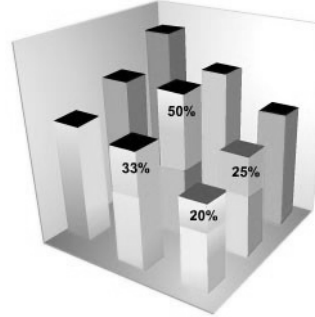
Advocate an approach to performance assessment that relies on multiple or converging lines of evidence. This involves looking at all the monitoring data and feedback from a remediation system in concert. DNAPL distribution in the subsurface is too complex and difficult to track using only one method to verify success.

## Performance Defined



### *Performance is a measure of:*

- ▶ Effectiveness
  - Have project goals been met?
  - Performance metrics
- ▶ Efficiency
  - Is system operating as designed?
  - Optimized in terms of time, energy, and cost



We consider performance to be “**effective and efficient progress toward remedial goals**”  
- Effective in the sense that the remedy meets or exceeds remediation goals; efficient in terms of minimizing the time and effort expended to attain those goals.

By monitoring various parameters or metrics, the technology's effectiveness and efficiency can be assessed. Decisions can then be made to either stop or continue operation, or transition to another remedial technology.

These two aspects of performance are introduced in Section 1.3 of the ITRC document.

## Why Measure Performance?



- ▶ Confirm remediation effectiveness
- ▶ Optimize system operation
- ▶ Monitor potential mobilization
- ▶ Couple to other technologies
- ▶ Determine achievement of contract milestones
- ▶ Refine conceptual site model
- ▶ Verify site closure decisions

Uses of performance monitoring data at DNAPL sites:

- to verify remediation effectiveness and be able to shut down your treatment system sooner rather than later.
- when optimizing system operation.
- to ensure that contaminants are not being mobilized beyond the treatment zone.
- to help decide when to transition to another remedial technology as part of a treatment train.

## Barriers to Robust Performance Assessment



- ▶ Technical challenges
  - Site complexity
  - Insufficient characterization
- ▶ Non-technical challenges
  - Budgetary constraints
  - Lack of standard tools and approaches
  - Vague or unspecific RAOs
  - Unsure what or where to measure

There are technical challenges to conducting a robust performance assessment having to do with site complexity or insufficient characterization.

An adequate PA program can be quite expensive.

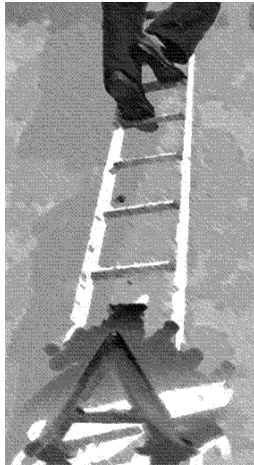
A lack of standard protocols or guidance on performance assessment strategies can make it difficult to interpret performance data and make comparisons

Where remedial action objectives are vague or not specified, it can be difficult to develop and apply the proper set of performance metrics.

Project managers are unsure about **what** matrix to measure, **where** it's most appropriate to measure, or **how** to design a performance monitoring program.

These challenges are addressed in the ITRC document and ongoing, applied research in the area of performance assessment

## Performance Goals Appropriate for Phased Cleanups



- ▶ Long-term
- ▶ **Intermediate-term**
  - Apply to source zones
  - Treatment train approach
- ▶ Short-term

*"Don't Expect to Achieve MCLs  
Within the Source Zone Any Time  
Soon" - Anonymous*

EPA recommends a phased approach for DNAPL source zone remediation and advocates the use of **intermediate performance goals**. Performance goals should consider the follow-on technology. Intermediate goals are useful in guiding the interim removal action in the DNAPL source zone. Each technology or unit process in the treatment train would have its own set of interim goals.

Performance goals should reflect the "phase-specific" nature of these efforts and the anticipated response of the source zone to treatment.

## Measuring Progress Based on Field Metrics



- ▶ Risk reduction is difficult to quantify directly
- ▶ We need measurable field metrics in order to gauge success

*"Given the unknowns in fully defining the human health and environmental effect of contaminants in ground water and soil, the dilemma is how to **define remediation technology performance** in a way that is both quantifiable and relevant to the goal of preventing adverse effects."*

National Research Council, 1997

The goal of a source zone remedy is to reduce the risk of exposure to chemicals through ingestion of groundwater, inhalation of vapors, etc. coming from the source. Exposure can be reduced either by: 1) containing the source or 2) depleting the source through treatment.

The concept of risk is controversial, partly because risk is difficult to measure directly. Regulators assess threats to public health and the environment on the basis of actual field measurements.

Risk reduction can be approximated by field-based metrics that represent risk: reduction in contaminant mass, concentration, toxicity, and/or mobility. ***The challenge at this point is to define performance in terms of quantifiable metrics that respond to treatment and change as progress is made.***

## Selecting Performance Metrics



- ▶ When to decide on measures of success
  - Define “success” up front during design
  - Involve entire project team
- ▶ Performance metrics are defined in terms of
  - Performance goals
  - Technology(ies) employed
  - Affected or targeted media
  - Location of potentially exposed populations
  - Expected response of geosystem to treatment

Agreeing on performance metrics and transition criteria up front can help avoid frustrations and delays down the road.

Section 3.3 of the document discusses the basis for selecting performance metrics for DNAPL source treatment projects. They are defined for a particular project in terms of:

The performance goals and objectives established for the project

The technology or series of technologies being used

The characteristics of the media within the DNAPL zone targeted for cleanup

The location of nearby homes or businesses who might be impacted, and finally

The expected response of the subsurface to treatment, which is often technology-dependent.

Section 5 of the document covers technology-specific monitoring parameters that could serve as appropriate metrics for assessing progress.

## Source Zone Treatment Technologies



- ▶ DNAPL recovery
- ▶ Soil vapor extraction / air sparging
- ▶ Thermally enhanced remediation
- ▶ Surfactant / cosolvent flushing
- ▶ Chemical oxidation
- ▶ Enhanced bioremediation

This slide lists some of the common technologies for treating DNAPL source zones. Our intent is not to advocate the use of one technology over another, but to provide examples of monitoring techniques and approaches used to gauge performance of various source zone remedies.

Conventional DNAPL treatment technologies include DNAPL recovery using in well pumping or bailing, soil vapor extraction for the vadose zone and air sparging for the saturated zone.

Innovative technologies include thermally enhanced remediation (steam, electrical), flushing technologies using surfactants or cosolvents, in situ chemical oxidation, and in situ bio.

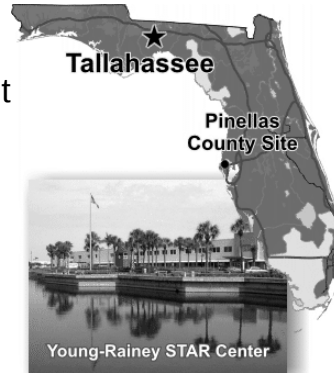
All of these technologies alter the subsurface conditions near DNAPL zone, in ways that can be measured. Understanding and measuring these physical changes with an appropriate monitoring program is key.

The next slide shows an example of a thermal remediation project and discusses the suite of metrics used to measure progress toward the remediation goals.

## Example: Young-Rainey STAR Center



- ▶ Performance-based contract
  - Soil and groundwater concent
  - Temperature
  - Hydraulic control
- ▶ Multiple lines of evidence
  - NAPL content in fluids
  - TPH monitoring
  - Temperature distribution
  - Interim samples



The Young-Rainey STAR Center is a former DOE facility located in Largo, Florida. The site consisted of two DNAPL source zones - Areas A and B. I'll talk about the Area A remediation which occurred in 2003.

The principal contaminants of concern (COCs) present in soil and groundwater are TCE and toluene. DOE selected an innovative combination of steam injection and electrical resistance heating and used an innovative, performance-based contract.

The primary remediation objective for Area A was **to remove NAPLs from the subsurface and attain concentration-based cleanup goals for soil and groundwater**. The metrics established by the DOE to assess performance were based on soil and groundwater concentration targets, temperature targets, and hydraulic control.

Progress of remediation was evaluated using several lines of evidence: NAPL content in extracted fluids, total petroleum hydrocarbon content in extracted water, temperature distribution, as well as interim soil and groundwater sampling. A more detailed description of this project, as well as several others, appears in Appendix B of the document.

## Survey of DNAPL Projects



| Method of Assessing Performance                      | Number of Sites |
|------------------------------------------------------|-----------------|
| Concentration reduction in specific monitoring wells | 63 (79%)        |
| Reduction in soil concentrations                     | 29 (36%)        |
| Achieve MCLs in monitoring wells                     | 11 (14%)        |
| Reduction in plume mass flux (or mass discharge)     | 18 (23%)        |
| Reduction in plume size                              | 20 (25%)        |
| Production of degradation by-products                | 22 (28%)        |
| Total mass removed                                   | 29 (36%)        |
| Mass remaining                                       | 14 (18%)        |
| Will not measure                                     | 0 (0%)          |
| <b>TOTAL NUMBER OF SITES</b>                         | <b>80</b>       |

This slide is based on a survey conducted by the Navy designed to collect information on DNAPL treatment projects to get an idea of the range of DNAPL sites out there and a sense of how successful they were. One of the questions dealt with the kinds of performance measures that were applied. This slide shows the breakdown of answers to this question.

## Converging Lines of Evidence



- ▶ There's no silver bullet
- ▶ Utilize indicators of progress
- ▶ Technology-specific parameters



*"No single metric by itself is likely to be adequate for assessing the performance and potential benefits of source depletion technologies; thus, conjunctive use of multiple metrics should be used to evaluate performance."*

EPA Expert Panel on DNAPL Remediation, 2003

There's no "silver bullet" solution to the PA problem. Every metric has limitations. By monitoring several metrics, a clearer picture of progress can emerge.

Dr. Kostarelos will now discuss the selection of appropriate performance metrics and some design considerations.

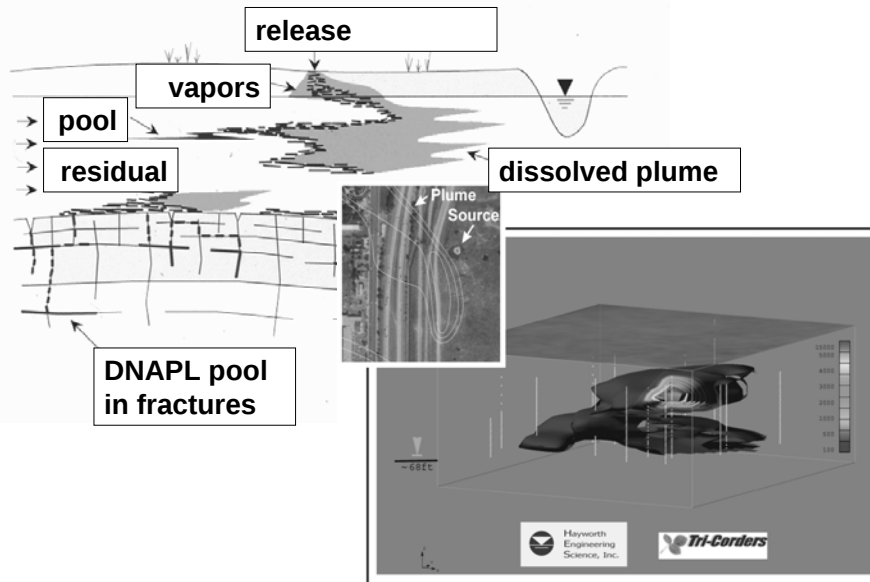
## Designing a Performance Monitoring Program for DNAPL Source Zones



**Presented by Dr. Konstantinos Kostarelos**  
**Polytechnic University**

Thank you, Eric. I am going to discuss the design of a Performance Monitoring program. If there are any questions about the material, please feel free to ask at the end of this section.

## Conceptual Site Model of DNAPL Source Zone



Developing a site conceptual model is an important part of the Performance Monitoring program. It is also important to a design of the Remediation program.

A lot of information is used to develop a conceptual site model. The information comes from several sources:

1. Historical records
2. Site investigations
3. Site sampling and analysis
4. Computer simulations
5. Experience

Performance monitoring results should continually be fed back into the conceptual site model - to make it less "conceptual" and more representative of real and dynamic source zone conditions.

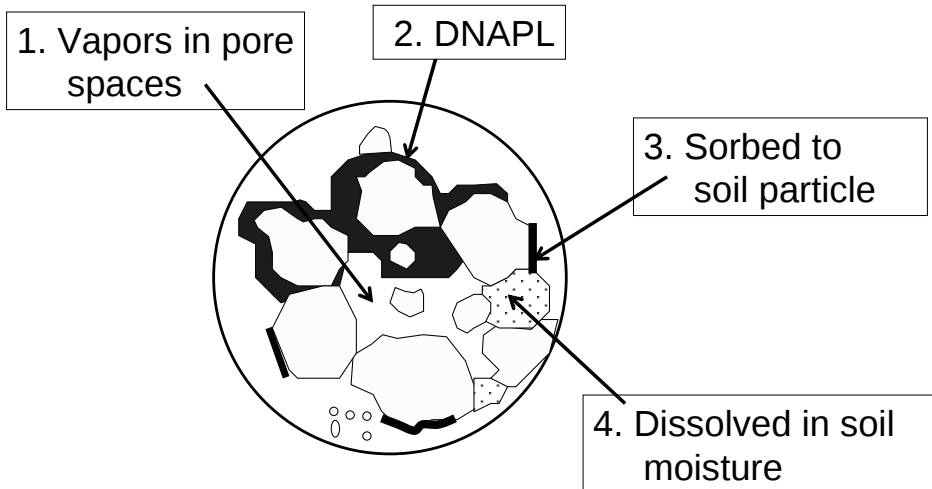
## Major Concepts

- ▶ Partitioning
- ▶ Saturation
- ▶ Retardation
- ▶ Rebound



Before discussing performance metrics, it is helpful to review a few major concepts. First, let's discuss partitioning of DNAPL in the subsurface.

## Partitioning of Contaminant

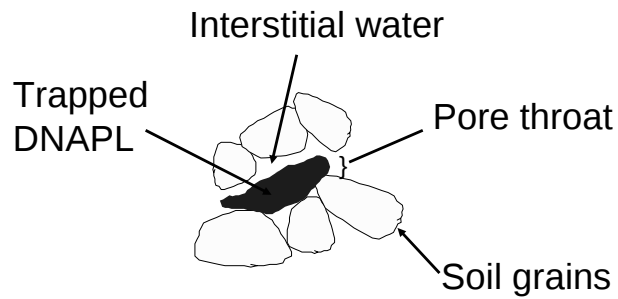


Source: Suthersan, 1996

When introduced in the subsurface environment, DNAPL can partition among several subsurface media:

1. The contaminant may evaporate and its vapor occupy some of the pore space.
2. The contaminant may remain, as DNAPL.
3. DNAPL may become sorbed onto soil surfaces.
4. The contaminant may dissolve into the soil moisture or groundwater.

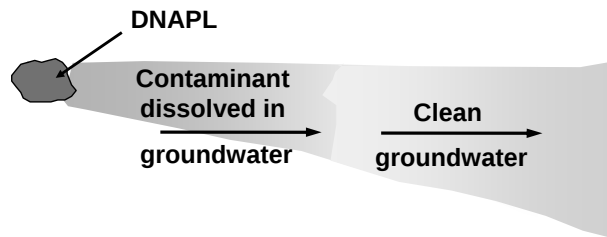
$$S_{\text{NAPL}} = V_{\text{NAPL}} / PV$$



Saturation ( $S_{\text{NAPL}}$ ) is a measure of the volume of NAPL ( $V_{\text{NAPL}}$ ) within the soil pore space expressed as a fraction of the total pore volume, PV. The saturation can vary from 0% (no NAPL) to 100% (fully saturated with NAPL). Keep in mind that the total saturation is always 100%, so if  $S_{\text{NAPL}}$  is < 100%, the saturation of other phases must be greater than 0%.

## Retardation

- ▶ A delay in the movement of a dissolved species
  - Sorption onto soil surfaces
  - Sorption onto organic matter
  - Partitioning into a non-aqueous phase

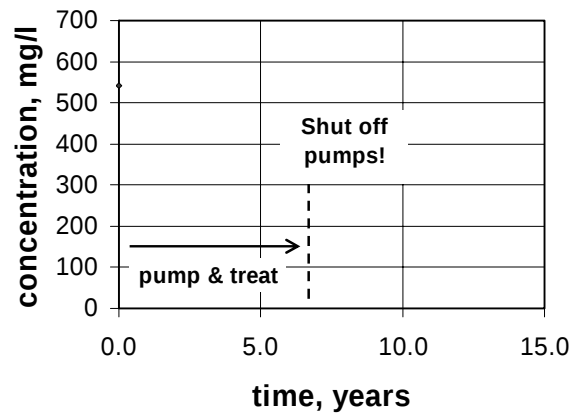


**Retardation** is a delay in the travel of the a solute when compared to the flow of solvent

The delay, or retardation, can be caused by such factors as sorption onto soil surfaces and organic matter, or partitioning into a non-aqueous phase.

## Rebound

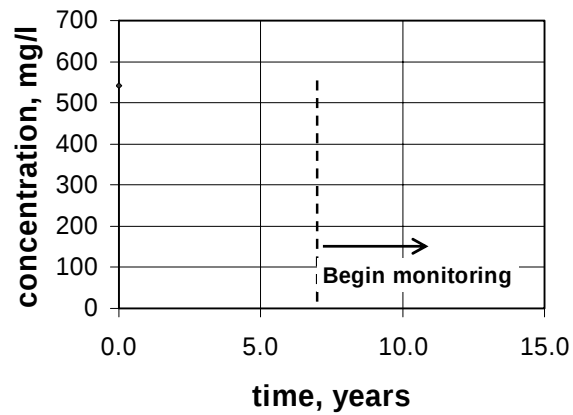
- Definition
- Causes
- Monitoring



**Rebound.** Sites were discovered with contaminated groundwater. Pump and treat was applied and had the effect of lowering the concentration of the contaminant. It was assumed that the remediation effort had succeeded. After several months, dissolved concentrations increased to original pre-treatment levels.

## Rebound

- Definition
- Causes
- Monitoring



One reason for rebound is non-equilibrium effects of the NAPL dissolution. Another reason may be the dilution effect of drawing clean groundwater that mixes with the contaminated zones.

Rebound can also occur in the vadose zone. e.g, when soil vapor concentrations decrease rapidly upon startup of SVE, stabilize, then rebound to near initial levels after the system is shut down.

Rebound is one reason long-term monitoring of DNAPL sites is important AFTER active remediation has been completed.

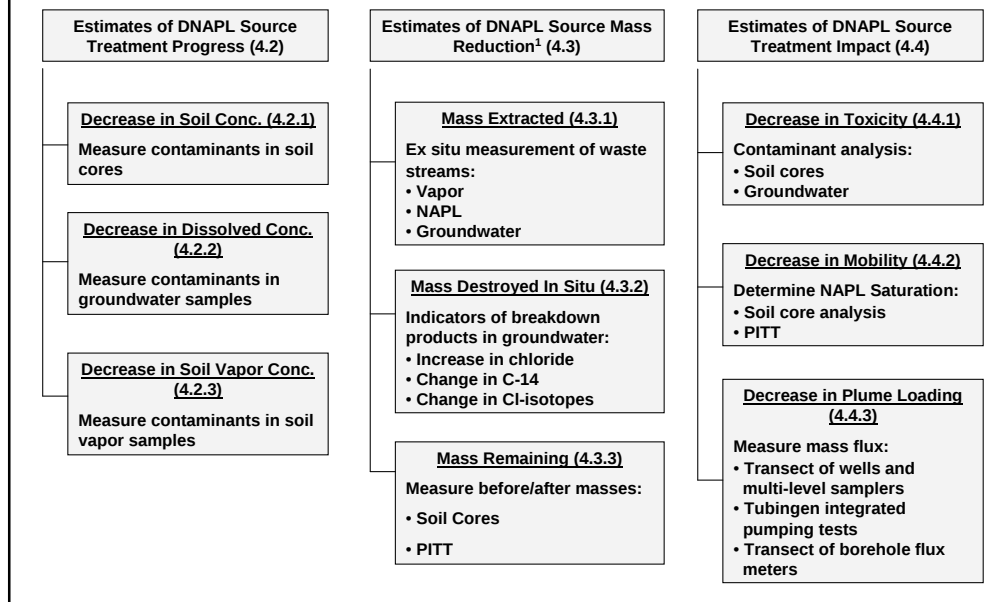
## Possible Changes Resulting from Remediation



- ▶ Redistribution of DNAPL
- ▶ Increased solubility
- ▶ Impact on microbes
- ▶ Subsurface alteration
- ▶ Preferential flow
- ▶ Precipitation/clogging
- ▶ Secondary water impact
- ▶ Gas generation

Performance assessment is most often determined by a metric that is compared before and after treatment. Must consider possible changes resulting from remediation when designing the performance assessment program.

## Categories of Performance Metrics



The performance metrics in the ITRC Performance Assessment document are grouped in to 3 categories.

We will discuss the benefits and disadvantages of the metric, realizing that the best approach is to use several of them in an intelligent and well-balanced manner – what has been called a “converging lines of evidence” approach.

## Estimating Source Treatment Progress



- ▶ **Decrease in Soil Concentration (4.2.1)**  
Measure contaminants in soil cores
  
- ▶ **Decrease in Dissolved Concentration (4.2.2)**  
Measure contaminants in groundwater samples
  
- ▶ **Decrease in Soil Vapor Concentration (4.2.3)**  
Measure contaminants in soil vapor samples

Methods used to estimate the progress of a DNAPL treatment:

There are three metrics: changes in soil concentration, dissolved concentration, and soil vapor concentration.

## Decrease in Soil Concentration



- ▶ Measuring soil concentration
- ▶ Low probability of detection

| Probability of detection | Number of random samples required where: |               |                 |
|--------------------------|------------------------------------------|---------------|-----------------|
|                          | $A_S/A_T=10$                             | $A_S/A_T=100$ | $A_S/A_T=1,000$ |
| 98%                      | 38                                       | 390           | 3,950           |
| 90%                      | 22                                       | 230           | 2,400           |
| 75%                      | 14                                       | 138           | 1,390           |
| 50%                      | 7                                        | 70            | 700             |
| 30%                      | 4                                        | 36            | 360             |

Measuring soil concentrations requires 1. collecting soil samples from discrete locations 2. analysis of the samples for contaminants 3. interpreting the data and statistically averaging the results for the areas between sampling points.

This approach has limitations. First, the selection of sampling points to locate DNAPL leads to a high likelihood of error.

Other limitation involved in using soil concentration as a performance metric are listed on the next slide.

## Decrease in Soil Concentration

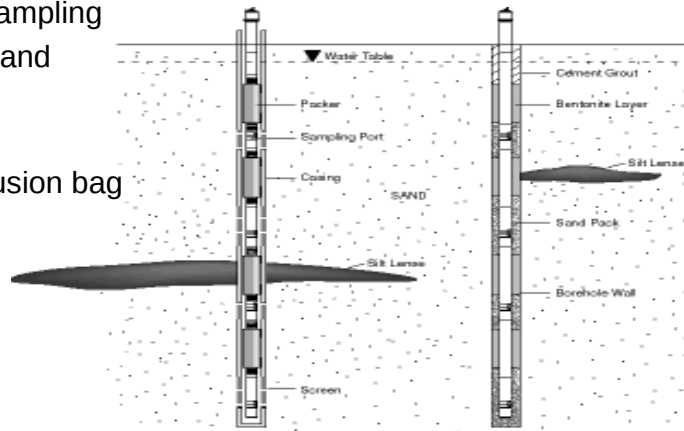


- ▶ Other limitations
  - Losses due to evaporation
  - Mixing of sample within the vertical profile
  - Identifying concentration changes due to DNAPL movement, rather than remediation
  - Size of sample required to identify DNAPL

Other limitations (discussed in more detail in Section 4.2.1 of the PA document) include loss of DNAPL volume due to evaporation. If soil is mixed within the vertical profile, interpreting the results will lead to error. If the DNAPL moves, the change in soil concentration will be misunderstood. Finally, the size of the sample **required** to determine the presence of DNAPL could be larger than the size collected and lead to a misinterpretation of the results.

## Decrease in Dissolved Concentration

- ▶ Applicability and use
- ▶ Multi-level sampling
- ▶ Well design and installation
- ▶ Purging
- ▶ Passive diffusion bag samplers
- ▶ Limitations



This slide discusses measuring dissolved concentration to assess progress. Several topics regarding measurement of dissolved concentration to assess DNAPL treatment progress are discussed in the PA document, such as:

- applicability and use
- multilevel sampling
- well design and installation
- purging
- passive diffusion bag samplers, and finally
- limitations

## Decrease in Dissolved Concentration



- ▶ Applicability and use
- ▶ Limitations
  - Rate-limited process
  - Groundwater dilution
  - Rebound effect



Groundwater quality is often used to assess the performance of many DNAPL remediation projects. Conventional groundwater monitoring techniques are well-known and can be found in the literature.

One problem is highly variable groundwater levels. Another important factor is the effect of DNAPL dissolution rate, solubility limits, groundwater flow rates.

A final consideration regarding rebound effect is that any DNAPL remaining will dissolve into groundwater, and likely return groundwater concentrations to original levels.

## Decrease in Soil Vapor Concentration



- ▶ Applicability and use
  - Volatile and some semi-volatile DNAPLs
  - SVE remediation
- ▶ Limitations
  - Soil gas flow rates variations
  - Variations in concentrations
  - Volatilization rates of DNAPL constituents

DNAPLs that are volatile can be detected in soil vapor extracted from the vadose zone. The concentration of DNAPL constituents can also be measured during an SVE remediation process to determine the total DNAPL recovered from the subsurface.

Difficulties using the soil vapor concentration as a performance metric is that a continuous measure of both soil gas flow rate and contaminant concentration in the soil gas are needed to accurately determine the mass recovered. Because different DNAPL constituents may have different volatilization rates, the estimate of DNAPL mass recovered can be further complicated.

## Source Mass Reduction

### Mass Extracted (4.3.1)

Ex situ measurement of waste streams:

- ▶ • Vapor
- NAPL
- Groundwater

### Mass Destroyed In Situ (4.3.2)

Indicators of breakdown products in groundwater:

- ▶ • Increase in chloride concentration
- Change in C-14
- Change in Cl-isotopes

### Mass Remaining (4.3.3)

Measure before/after masses:

- ▶ • Soil Cores
- PITT

The second category of performance metrics are those to estimate the DNAPL mass reduction. There are three approaches: measurement of the mass extracted, measuring the mass destroyed in-situ, and measuring the mass remaining.

## Mass Extracted

- ▶ Measuring concentration in extracted fluids:
  - Vapor phase
  - DNAPL phase
  - Groundwater phase

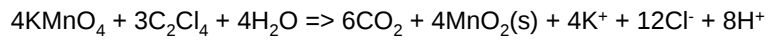


$$\text{Mass}_{\text{Extract}} = \text{Conc}_{\text{Fluid}} \times \text{Flow rate}$$

Determining the fraction of DNAPL mass reduction is a difficult calculation to make because of the difficulties measuring contaminant mass. The mass of DNAPL brought to the surface can be determined fairly easily. Calculating DNAPL mass remaining in the subsurface is not easy.

- ▶ Measuring breakdown products in groundwater
  - Increase in chloride concentrations
  - Changes in stable carbon isotope ratios
  - Changes in isotopes of chlorine

Example: The stoichiometric reactions of potassium permanganate ( $\text{KMnO}_4$ ) with perchloroethylene (PCE), thereby generating chloride ions



Mass reduction can be estimated for those remediation techniques that destroy the DNAPL *in-situ* by determining the concentrations of indicators.

Isotopes of carbon have been used as an indicator of the oxidation of chlorinated ethenes. A chlorinated solvent mixture undergoing oxidation becomes enriched in C13 over time. The C12/C13 ratio can be monitored to gauge the effectiveness of oxidation process.

Using chloride isotopes as indicator parameters of mass destroyed has been suggested recently, and the concept is similar to that for carbon isotopes. The approach has not yet been developed, though.

## Mass Remaining



- ▶ Estimating mass before and after remediation
  - Soil cores
  - Partitioning Interwell Tracer Testing (PITT)



Soil samples analyzed in order to quantify the contaminant mass. There are a number of techniques to collect soil samples for chemical analysis from the DNAPL source area and each technique has its benefits and limitations. Contaminant mass remaining is typically calculated by measuring contaminant concentration and multiplying by the volume and density of the media. Potential problems with quantifying contaminant mass using soil concentration data include all of difficulties discussed earlier when attempting to quantify average contaminant concentrations.

## Partitioning Interwell Tracer Testing



- ▶ Applicability and use
  - Conservative and partitioning tracers injected
  - Provides estimate of the average DNAPL saturation across the swept pore volume
- ▶ Limitations
  - Heterogeneities result in poor sweep efficiency
  - Requires unique skill set

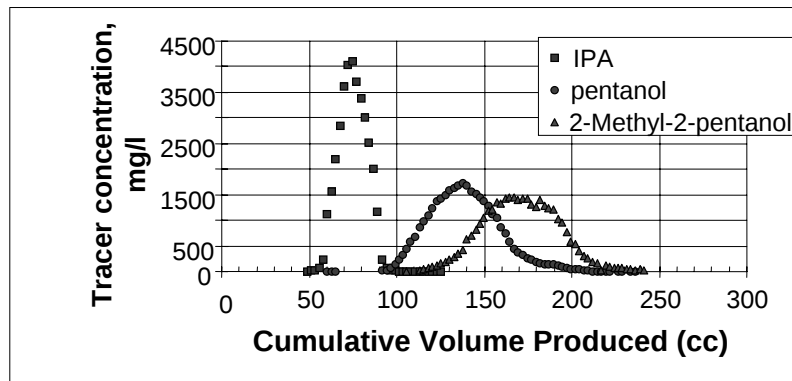
A PITT consists of injecting a suite of conservative and partitioning tracers into one or more wells and the subsequent production of the tracers from one or more nearby extraction wells. After the tracer is injected, potable water or air is injected to drive the tracers across the zone of interest. The conservative tracers pass unhindered through the DNAPL zone, while transport of the partitioning tracers is retarded by interaction with the DNAPL. The tracer responses at monitoring and extraction wells are used to estimate the average DNAPL saturation, the swept pore volume, and the total volume of DNAPL in the subsurface.

Limitations. PITT is a relatively new and innovative technology. Differences in media permeability can have a dramatic effect on the sweep efficiency of the tracers.

Because the tracer will preferentially move through the most permeable zones, less tracer will go through the low permeable regions. The flow rate of the tracer moving through the low permeable zones may be 10 or even 100 times lower than through the more permeable layers.

DNAPL mass located in the lower permeability zones may not be detected using the PITT due to low "sweep efficiency". Methods to improve sweep efficiency exist such as using **viscosifiers** and **foam**.

## PITT Tracer Response



|                 |               |                    |
|-----------------|---------------|--------------------|
| Tracer results: | IPA, 2M2P     | $S_{or} = 17.37\%$ |
|                 | IPA, Pentanol | $S_{or} = 17.54\%$ |
| Mass balance:   | Gravimetric   | $S_{or} = 17.5\%$  |

This slide shows laboratory data as an example of the PITT theory. The conservative tracer, IPA, is compared to the two partitioning tracers, 2-methyl-2-pentanol and pentanol, and the DNAPL saturation was determined to be 17.4 and 17.5%, respectively. The **method of moments** is used to compute these results. These results are compared to the gravimetric measurement of 17.5% saturation. The conservative tracer was used to measure the swept pore volume of about 75 ml.

The experimental and theoretical basis for the use of partitioning tracers is presented in detail in Jin (1995), Jin *et al.* (1995), and Dwarakanath (1997). The execution of a PITT requires the completion of a series of tasks that include **tracer selection, design simulations, implementation, and analyses**.

## Source Treatment Impact



### Decrease in Toxicity (4.4.1)

- ▶ Contaminant analysis:
  - soil cores
  - groundwater

### Decrease in Mobility (4.4.2)

- ▶ Determine NAPL Saturation:
  - soil core analysis
  - PITT

### Decrease in Plume Loading (4.4.3)

- ▶ Measure mass flux:
  - Transect of wells and multi-level samplers
  - Tubingen integrated pumping tests
  - Transect of borehole flux meters

The final category of performance metrics are those used to estimate the impact of DNAPL source treatment. Three groups in this category are decrease in toxicity, decrease in mobility, and decrease in plume loading.

## Decrease in Toxicity

---

- ▶ Removal of target compounds leaves less toxic residual
- ▶ Measurement
  - Soil cores
  - Groundwater
- ▶ Limitations

An indirect measure of performance is the impact of DNAPL treatment. The first metric that we will discuss is the decrease in toxicity. This is especially applicable for sites containing mixtures where the removal of certain target compounds from the mixture to reduce the overall toxicity or mobility may be a more appropriate measure of success. Toxicity is not easily measured. In addition, there can be questions about verifying long-term stability of the observed toxicity reduction effect. This requires long-term testing or sufficient fundamental understanding to predict long-term effects with certainty.

## Decrease in Mobility

---

- ▶ Mobility reduction via source depletion
- ▶ Measured indirectly
  - Soil cores
  - PITT
- ▶ Limitations

Mitigating the further spread of the source by **decreasing DNAPL mobility** is another often cited objective of DNAPL source remediation. The goal in such a case is to deplete the source sufficiently to reduce DNAPL to a residual saturation level, or to a point of relative stability (EPA, 2004). It should be noted that reaching residual saturation does not always equate to reaching a point of immobility. Immobilized DNAPL held in place by a balance of dynamic forces can be upset by changes in groundwater flow, tidal effects, earth pressure, and ground vibration. Mobility changes can be measured by direct observation of product levels in wells but is most often measured indirectly by assessing DNAPL saturation from soil cores or a PITT.

## Decrease in Plume Loading



- ▶ Goals of source treatment might include
  - Reduce contaminant migration
  - Reduce plume longevity
  - Reduce life-cycle costs
  - Speed transition to more passive technologies
- ▶ Mass flux or mass discharge rate is a direct measure of progress

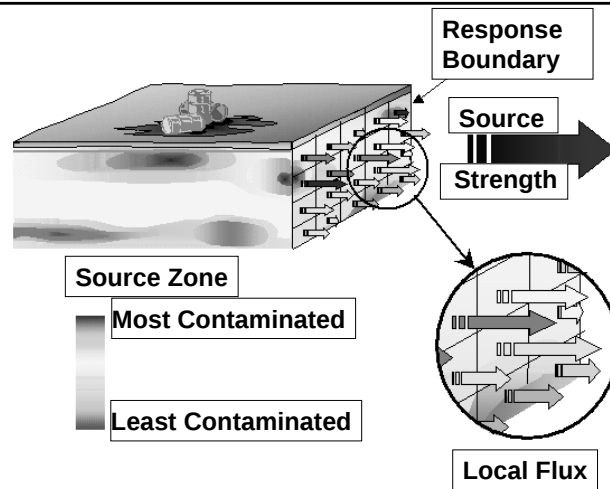


The goals of removing mass from a source zone include reducing the risks of:

1. contaminant migration by either the dissolved or vapor phase,
2. reducing plume longevity,
3. reducing overall remediation costs,
4. accelerating the natural attenuation of any remaining mass, and
5. speeding the transition to more passive technologies.

Mass flux is often the most meaningful metric in assessing progress towards these goals.

## Concept of Mass Flux



Source: Wood, 2004

Using plume load as a measure of success, shutdown of the remedial system could be considered when the mass release rate from the source to the groundwater (mass flux) falls below the assimilative capacity or “natural attenuation capacity” of the aquifer. Natural attenuation capacity can be defined for groundwater systems as a measure of its ability to lower contaminant concentrations along aquifer flowpaths. The natural attenuation capacity of groundwater systems depends upon hydrologic (dispersion and advection) and biological (biodegradation rates) factors and can be assessed using quantitative models (USGS, 2003). Mass flux is defined here as the “rate at which solute mass in the groundwater plume crosses a spatial plane oriented at a right angle to the direction of groundwater flow” (Rao *et al.*, 2003). Figure 4-2 illustrates the complexity of mass flux in a heterogeneous subsurface, and the value of mass flux as a metric in source remediation.

## Measuring Mass Flux



- ▶ Methods
  - Continuous groundwater extraction
  - Integrated pump tests
  - Multi-level sampling
  - Borehole flux meters
- ▶ Limitations

Mass flux can be measured along one or more planes oriented perpendicular to the flow direction. Measurements near the source zone will provide an estimate of source strength. Most of the methods discussed below also allow mass flux measurements down-gradient, providing valuable data on the rates of attenuation and plume responses to source treatment. There are four methods available to estimate mass flux:

1. Analyze samples recovered during continuous groundwater extraction;
2. Measure contaminant concentrations and groundwater velocity during short-term pump tests ("integrated pump tests");
3. Measure contaminant concentrations at multiple locations across a transect, using multi-level samplers to generate geostatistical average concentrations, and;
4. Measure contaminant concentrations and groundwater velocities at multiple locations and depths using passive borehole flux meters.

Each of these methods is described briefly in the ITRC PA document.

These approaches to mass flux estimation are relatively new, particularly the passive flux meters and integrated pump tests. Development and testing are ongoing, and there is little experience to use as guidance at this point. Later on, Ryan Wymore will describe a mass flux-based performance study that was conducted at Hill AFB which showed considerable promise.

## Question and Answers



Intermediate goals?

Performance  
metrics?

Cost considerations?



Converging  
lines of  
evidence?

[www.itrcweb.org](http://www.itrcweb.org)

No associated notes.

## Technology-Specific Performance Monitoring



**Presented by Ryan Wymore**  
**CDM**

The information in this section is intended as “suggested monitoring requirements” for planning purposes – actual monitoring will vary depending on site-specific conditions and the technology being deployed.

## Section Overview

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- ▶ Review of key definitions
- ▶ Technology-specific monitoring tools
  - Conventional DNAPL remediation technologies
  - Thermal technologies
  - Surfactant/cosolvent flushing
  - Chemical oxidation
  - Enhanced in situ bioremediation

In this section we will provide an overview of conventional, in situ thermal, surfactant and co-solvent flushing, in situ chemical oxidation, and enhanced bioremediation DNAPL remediation technologies. We will also cover technology-specific performance and system efficiency monitoring tools.

A brief overview will be provided for each technology, followed by a description of the technology-specific monitoring tools.

For each technology, we will emphasize aspects of performance monitoring

## Key Definitions



- ▶ Remedial effectiveness
  - The ability of the system to achieve remediation goals
- ▶ System efficiency
  - Optimization of time, energy, and costs toward the achievement of remediation effectiveness using a specific technology.

There are two types of performance monitoring: remedial effectiveness and system efficiency monitoring.

The ultimate goal of remedial effectiveness monitoring is to compare before and after states of various performance metrics.

System efficiency monitoring is intended to optimize the remedial process

The frequency of both types of monitoring depends on the remedial technology applied.

## Conventional Remedies



- ▶ DNAPL recovery
  - Pumping DNAPL from wells
- ▶ Soil vapor extraction
  - Using a vacuum to remove volatile contaminants from the vadose zone
- ▶ Air sparging
  - Injecting air below the water table
- ▶ Key monitoring parameters
  - Mass of contaminant removed

Conventional remedial technologies include DNAPL recovery using in well pumping or bailing.

Soil vapor extraction relies on creating a subsurface vacuum and “pulling” volatile contaminants to wells screened in the vadose zone above the water table. The effectiveness is heavily dependent on the heterogeneity and permeability of the soil as well as the volatility of the contaminants.

Air sparging involves the injection of air into the saturated zone below the water table. This technology relies on stripping of volatile contaminants and creating conditions favorable for aerobic biodegradation. High soil heterogeneity, low permeability, and low volatility compounds can also adversely effect the effectiveness of air sparging for remediation.

The key performance assessment monitoring parameter for these conventional technologies is contaminant mass removed.

## Monitoring for Thermally Enhanced Remediation



- ▶ Steam enhanced extraction
- ▶ Electrical resistance heating
- ▶ Thermal conduction
- ▶ Key monitoring parameters
  - Temperature
  - Vapor concentration
  - Dissolved concentration
  - Soil concentration

Thermal technologies accelerate DNAPL remediation by using heat to force contaminant phase change from liquid to vapor. Heat is generated either by: injected steam, electricity flowing between electrodes or heat conduction between thermal wells.

SEE relies on creating steam at the surface and injecting it into the subsurface treatment area, and physically moving the contaminants with a steam front to extraction wells. SEE is effected by soil heterogeneity and can be less effective in low permeability silts and clays. SEE can achieve subsurface temperatures well above the boiling point of water (100°C).

ERH uses electricity from a municipal power line and and inputs it into the subsurface via electrodes. ERH relies on the flow of electricity between electrodes to resistively heat the subsurface to the boiling point of contaminants and water.

Conductive heating or insitu thermal destruction (ISTD) uses electricity and inputs it into the subsurface using heater or thermal wells. Heat flows through the soil from the thermal wells primarily by thermal conduction.

In terms of performance assessment, similar remedial effectiveness and system efficiency monitoring parameters are used for each of these technologies. These include subsurface temperature, vapor and mass recovered, soil concentrations, groundwater concentrations, vacuum, pressure, and power consumption. Concentrations of dissolved phase contaminants are also monitored on the periphery and below the treatment volume to ensure that contaminants are not migrating outside of the remediation area.

## Electrical Resistance Heating (ERH) at Paducah, KY DOE Facility



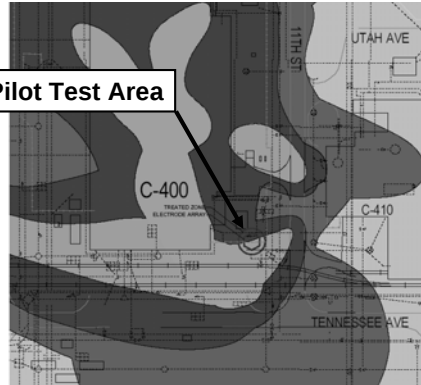
- >100 mg/l
- 10-100 mg/l
- 1-10 mg/l
- Dissolved TCE

**TCE Release:**  
1,000,000 lb?

**Performance Metrics:**

- ▶ Subsurface temperature
- ▶ Soil concentration
- ▶ Dissolved concentration

ERH Pilot Test Area



800  
ft

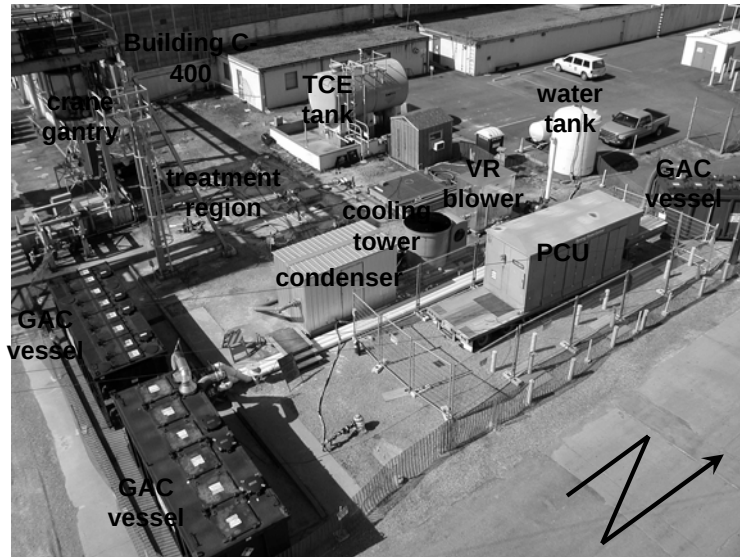
Case study of an ERH pilot test conducted at the US DOE Paducah Gaseous Diffusion plant in 2003 for the remediation of TCE DNAPL.

Groundwater encountered approximately 50 ft bgs. Silt-sand overlying soils extend to approximately 56 ft bgs, and the Regional Gravel Aquifer (RGA) extends from about 56 to about 100 ft bgs. TCE is present as residual DNAPL throughout the unsaturated and saturated zones. DNAPL is also believed to be present as pools in some areas. An estimated mass of near 1,000,000 lbs of TCE were released to the subsurface at this site.

The treatment area was near the suspected source of TCE (an aboveground storage tank) and associated piping near Building C-400, within an identified "source area" that covers approximately 200,000 square ft. Six electrodes were installed in an area of approximately 30 ft in diameter and VOCs were removed by vapor extraction and carbon absorption. Treatment continued for 175 days of active heating. The estimated heated treatment area was 43 ft in diameter.

The overall objective for the project was to demonstrate the implementability and cost effectiveness of the ERH technology for treating the unsaturated and saturated zones. The performance criteria established for soil was 75% mass removal in the vadose zone. The goal established for groundwater was reducing average TCE concentrations to below 1% of aqueous solubility.

## Paducah ERH Project Layout

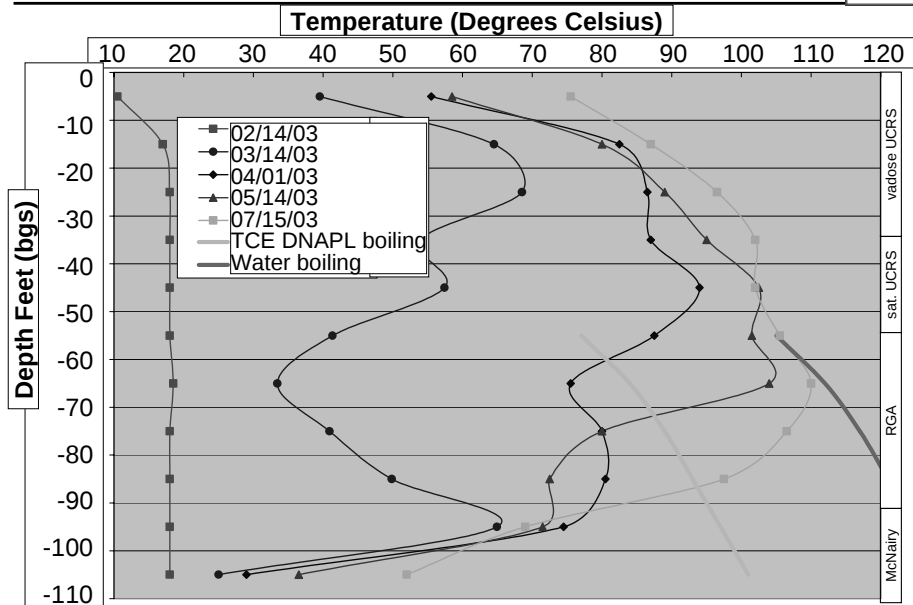


This is a picture of the pilot test area. The ERH equipment includes a power control unit (PCU), electrodes, steam condenser, water cooling tower, vacuum blower and in this case granular activated carbon (GAC) for vapor treatment. Subsurface temperature at every 5-foot interval and pressure (using piezometers) were monitored in the treatment region throughout the pilot test operations.

The following metrics were also used to evaluate the system efficiency:

- Uniform temperature gradients throughout the test cell;
- TCE removal rates as a function of operational time and energy consumption;
- Constructability of the SPH system in the C-400 Building area;
- Construction and operation costs as a function of TCE mass removed or destroyed;
- No negative effects of the SPH system on adjacent utilities and facilities.

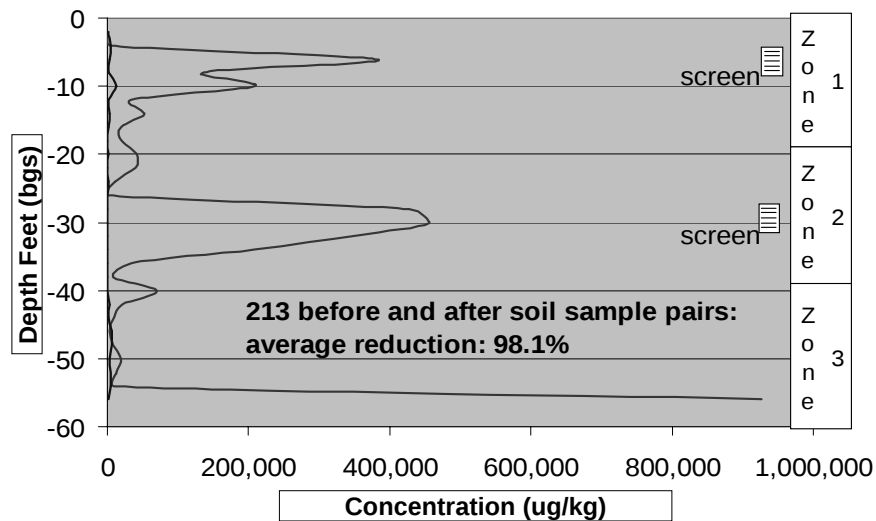
## Paducah ERH Pilot Test: Temperature Versus Depth



This slide shows an example of system efficiency monitoring for the Paducah ERH pilot test. The graph shows the increase in subsurface temperature over time at depth. The boiling point of TCE in the presence of water is depressed from 87°C to about 73°C. Each colored line represents a date during the pilot test. The green line represents the boiling point of TCE at depth and the blue line represents the boiling point of water at depth. As you can see the boiling points of both TCE and water increases with depth due to the subsurface pressure.

Subsurface temperatures reached the boiling point of the TCE following about six weeks of operations.

## 57 Paducah ERH Pilot Test: Soil Concentrations

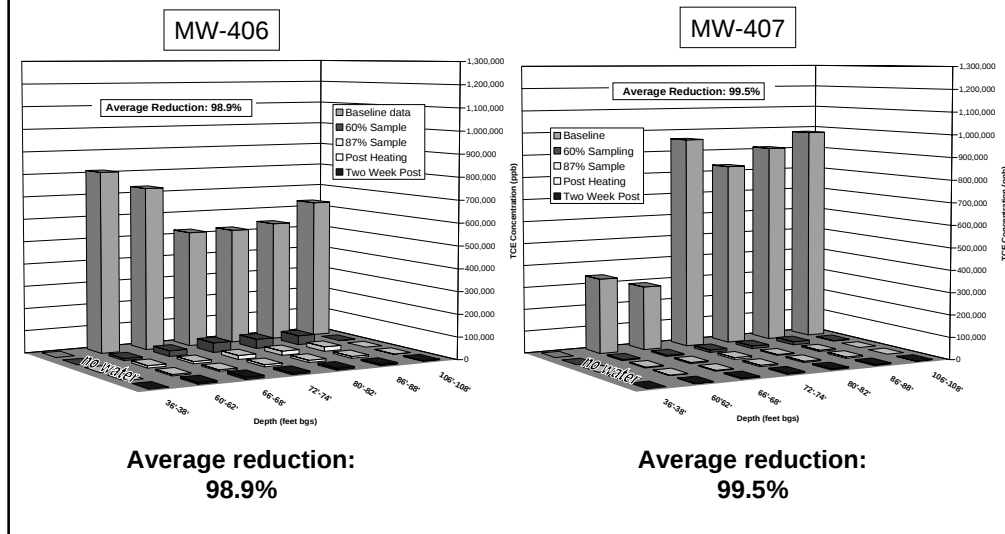


This slide shows an example of using soil concentrations as a performance metric to assess effectiveness. The graph shows the average TCE concentrations in soil before (red line) and after (blue line) the pilot test.

The method for measuring the soil was an average of nine pre and post pilot test soil cores sampled at every 2-foot interval. The pre soil samples were taken during the drilling of the electrodes and temperature monitoring points.

Based on the average soil concentrations, remediation performance exceeded the goal of 75% mass removal. The average soil concentrations decreased by 98%, from an average of approximately 125 mg/kg before treatment to 2.5 mg/kg after treatment. As might be expected, the variability was very large. Averages from the nine pre-test cores (generally 28 samples each, over a total depth of 56 ft) varied from 1.3 mg/kg to 464 mg/kg. Averages of the post-test soil cores varied from 0.1 mg/kg to 6.5 mg/kg.

## Paducah ERH Pilot Test: Groundwater Concentrations



This slide shows an example of using groundwater concentrations as a performance metric to assess effectiveness. The response boundary for groundwater concentrations was two multilevel monitoring wells located inside the remediation area that were sampled at six depth intervals. Groundwater was also monitored at two locations that were outside of the pilot test area.

The average groundwater concentrations from the two multilevel wells within the treatment zone did reach the target criteria of 11 mg/L TCE, with an average reduction of approximately 99%. Similar results were observed at all six depths sampled, with initial concentrations ranging from 500 to 1,000 mg/L TCE in most samples, and final levels from 1 to 10 mg/L.

It is worth noting that the groundwater goals for this pilot test are far above MCLs, but they were realistic given the technology being implemented and the location of the pilot test in a DNAPL source zone.

Also, other sites at which thermal remediation technologies have been applied are discussed in the Appendix.

## Monitoring for Surfactant/Cosolvent Flushing



- ▶ Technology description
- ▶ Key monitoring parameters
  - Contaminant analysis
  - Groundwater quality
  - Injection/extraction flow rate
  - NAPL saturation
  - Visual changes in extracted fluids

Surfactants are compounds that alter the properties of organic-water interfaces. They can solubilize and/or mobilize zones containing DNAPL.

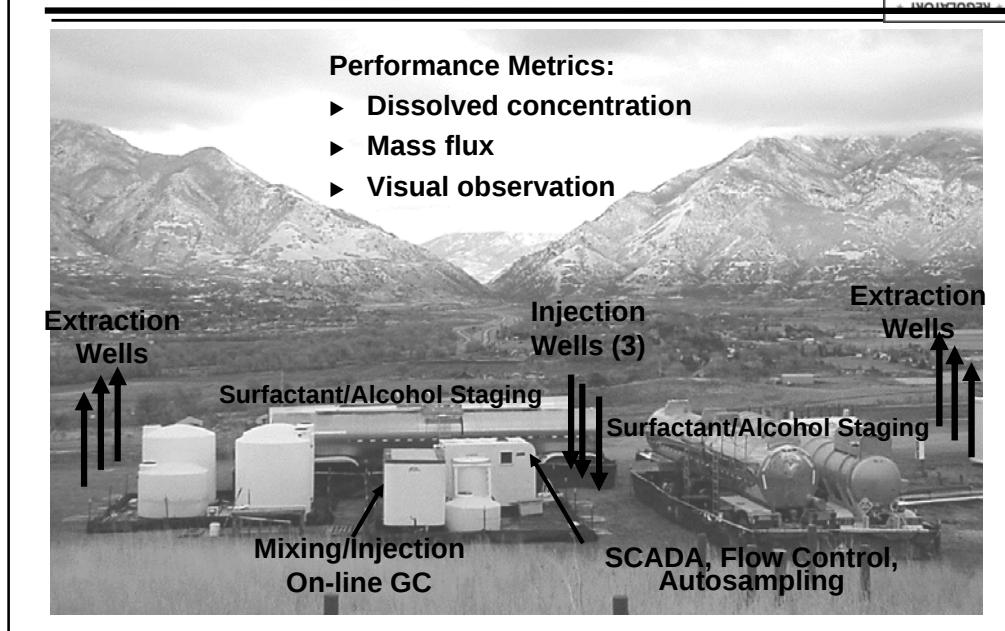
Cosolvents are similar to surfactants in that they alter the properties of solution interfaces. Examples include alcohols such as methanol, ethanol, and isopropanol.

Surfactant/cosolvent flushing is a DNAPL-removal technology that involves the injection and subsequent extraction of chemicals to solubilize and/or mobilize DNAPLs. Technology described further in a recent ITRC DNAPLs team document. The link for this document is provided at the end of the training.

Key performance monitoring parameters for this technology include measuring contaminant concentrations in extracted fluids, monitoring groundwater quality, measuring the injection/extraction flowrates, and lastly looking for visual changes in extracted fluids.

An example of a surfactant flushing application is presented in the next few slides.

## Hill Air Force Base OU2 Surfactant/Cosolvent Flushing Project



This slide shows a picture of the layout of a surfactant/cosolvent flushing demonstration project at Hill AFB OU-2. Contamination at the site is primarily TCE DNAPL in the source zone and a large chlorinated solvent plume extending several hundreds of feet downgradient.

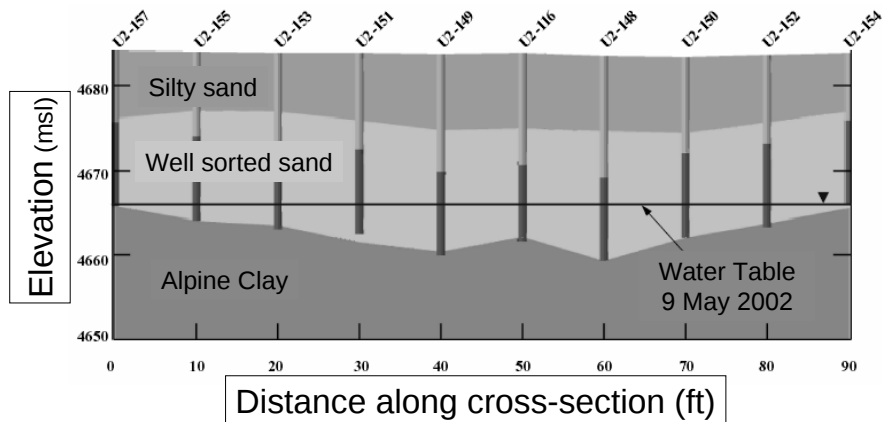
Three lines of evidence were used to measure progress: groundwater concentrations, mass flux, and visual observation of extracted fluids.

## Hill AFB OU2: Flux-Based Performance Study



### ► Two flux measurement approaches

- Passive flux meters
- Integrated pumping



One of the metrics applied was contaminant mass flux. This site is distinct in that there's a geologic "saddle" immediately downgradient of the source that forms a natural spillway for contaminated groundwater to pass through.

Two mass flux techniques were employed to compare their results: passive flux meters (PFM) and integrated pumping.

June 2002 – first flux measurement (pre-treatment)

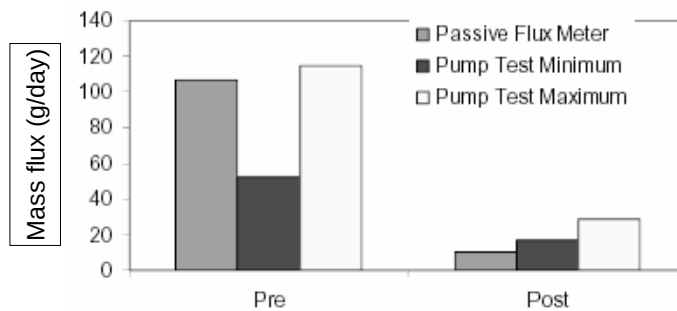
July 2002 – surfactant/alcohol flood

June 2003 – second flux measurement (post-treatment)

## Hill AFB OU2: Results of Mass Flux Measurements



Pre and Post-Source Removal Total Mass Flux of TCE and *cis* 1,2-DCE



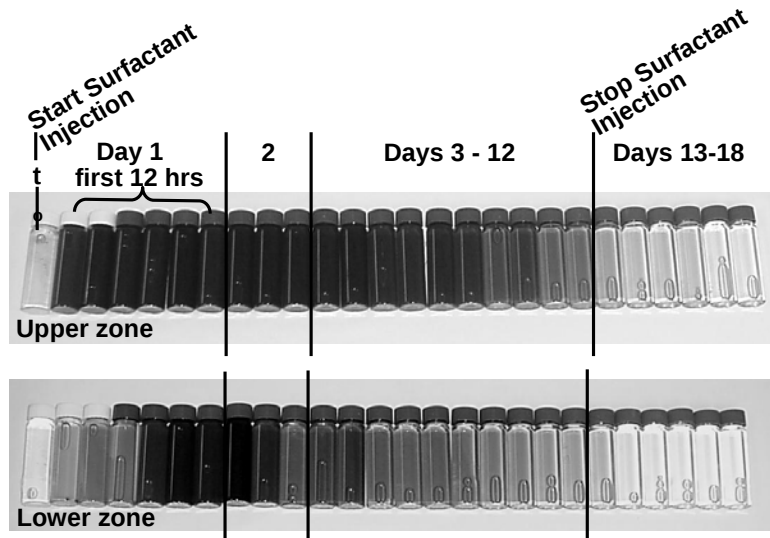
Source: Hatfield, 2003

The results of the flux-based performance field study at Hill AFB OU-2 are presented here. The graphs shows general agreement between the two flux measurement techniques used to assess the reduction in the rate of mass discharge (or flux) and presumably the impact on the downgradient plume.

- Based on passive flux meters - 90% reduction in flux
- Based on integral pumping - 67-75% reduction

Not shown on the graph is the raw dissolved concentration data used to calculate mass flux. Just looking at the concentration data separately without factoring in the localized flow rate, there was an 88% reduction in average dissolved concentration (i.e., pre and post-treatment).

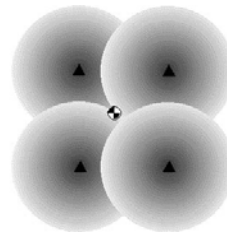
## Hill AFB OU2: Extracted Fluid Visual Changes



This shows an example of visual changes in extracted fluid, which can be used qualitatively to assess the performance of this technology. Note the very dark colors progressing to light, indicating the approach to a limiting return on investment for continuing the flushing operation.

## Monitoring for In Situ Chemical Oxidation (ISCO)

- ▶ Technology description
  - Hydrogen peroxide
  - Permanganate
  - Ozone
- ▶ Key monitoring parameters
  - Contaminant analysis
  - Water quality parameters
  - Injection rate
  - Oxidant persistence



This technology involves injection of oxidants and other amendments directly into a source zone. The injected oxidants create free radicals that react with the contaminant, breaking chemical bonds and producing innocuous substances such as carbon dioxide, water, and chloride (for chlorinated solvents). Oxidants are normally injected and not extracted, however, sometimes a recirculation system is used.

Examples of common oxidants include permanganate, hydrogen peroxide, and ozone.

A primary design concern is the proper oxidant concentration and dose. The concentration and dose are determined by the oxidant demand and reaction kinetics. Other variables include the horizontal and vertical spacing of injections, which are largely determined by the site geology.

Key monitoring parameters include contaminant analysis in soil and groundwater, water quality parameters (pH, chloride), rate of injection (or extraction if recirculated), and oxidant concentration to assess persistence and distribution

## Performance Monitoring Considerations for ISCO



- ▶ Oxidation is a destructive technology
- ▶ Allow sufficient time to evaluate conditions after the site reaches equilibrium
- ▶ All oxidant must be consumed before post-treatment conditions are assessed
- ▶ Post-treatment rebound (increase) in dissolved contaminants can be observed due to desorption and NAPL dissolution

See <http://www.itrcweb.org/isco-1.pdf>

This slide lists some general performance assessment considerations for this technology:

1. Oxidation is a destructive technology

No ability to measure/track extracted contaminant mass

Documentation of treatment effectiveness requires before and after contaminant delineation

Sampling and analysis of all phases (especially soils) is required to characterize contaminant mass destruction

2. Allow sufficient time to evaluate conditions after the site reaches a new, post-treatment equilibrium

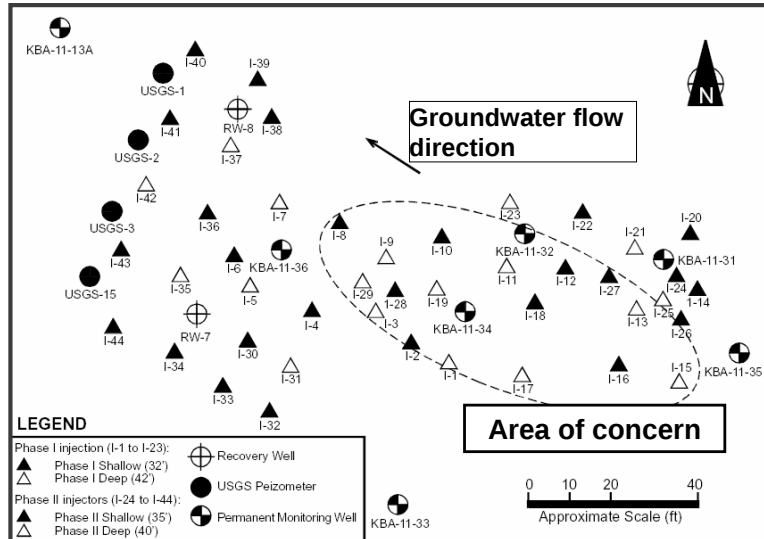
3. All oxidant must be consumed before post-treatment conditions are assessed

4. Post-treatment rebound (increase) in dissolved contaminants can be observed due to desorption and NAPL dissolution

Refer to the ITRC document on In Situ Chemical Oxidation, which is available as a link in the additional resources section

## Chemical Oxidation Using Fenton's Reagent at NSB Kings Bay, Site 11

### ► Performance metric: dissolved concentration

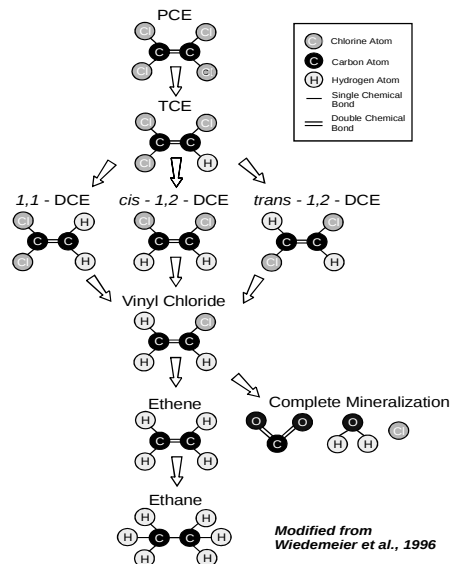


Case study of a chemical oxidation project employing Fenton's Reagent, in which changes in groundwater concentration were used as the means to assess performance. Site 11 is an old county landfill located on the Naval Submarine Base in Kings Bay, Georgia. Total chlorinated aliphatic compounds (CACs) were detected at concentrations of more than 9,000 micrograms per liter ( $\mu\text{g/L}$ ) in the groundwater within the landfill source area. A pump and treat system was installed to address the contaminant plume.

In 1998, the Navy decided to attack the source area using Fenton's Reagent. The cleanup goal for the RCRA corrective action was established by the state at  $100 \mu\text{g/L}$  for total CACs. Site performance monitoring included daily groundwater monitoring and off gas analysis. Parameters measured in the field included pH, peroxide, chloride, iron, alkalinity, carbon dioxide, and headspace analysis. After two injections and 13 months of monitoring to address rebound, total CAC levels dropped to below  $60 \mu\text{g/L}$  and indicated an average reduction of 94% across the site. As a result, the state of Georgia allowed the Navy to shut down the pump and treat system to allow natural attenuation to complete the restoration.

## Monitoring for Enhanced Bioremediation

- Technology description
- Key monitoring parameters
  - Groundwater quality
  - Stable-C isotopes
  - Microbial characterization
  - See Table 5-4 in the PA document



This technology involves injection of electron donor into a source area to stimulate ARD. This process is well understood and is described elsewhere in ITRC, EPA, and other documents (links provided at the end of the training.)

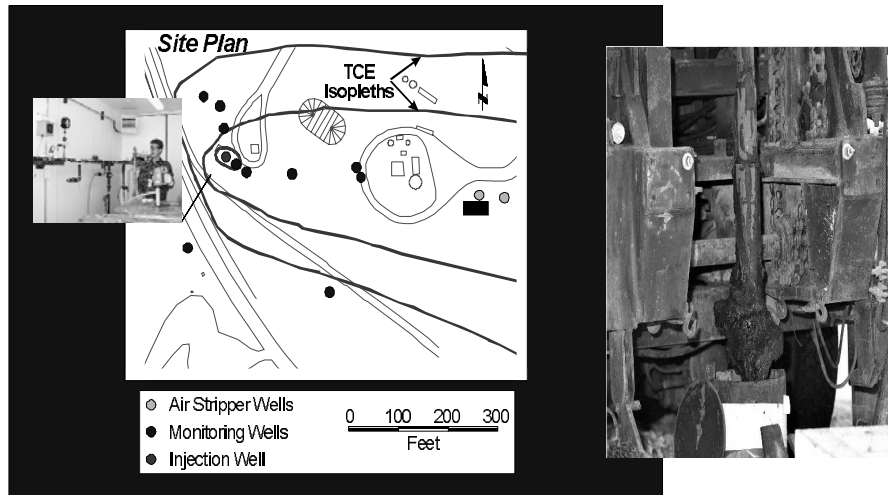
The reductive dechlorination pathway is shown here. It involves the sequential replacement of Cl atoms with H atoms, until ethene is produced, which is an innocuous byproduct. The process occurs most efficiently under methanogenic (strongly reducing) conditions. This implies that an adequate and well-distributed supply of electron donor is required.

As with ISCO, the biodegradation reactions occur in the aqueous phase. Because of this, remedial effectiveness monitoring is almost exclusively changes in groundwater concentrations. Key groundwater parameters are presented in Table 5-4. Some examples include contaminants and daughter products and redox-sensitive parameters. Other more innovative monitoring tools include measuring changes in stable-C isotopes and characterization of the microbial community.

ISB has been shown to be effective for remediation of dissolved phase plumes. However, it has also recently been shown to be effective in DNAPL source areas because it enhances the bioavailability of contaminants.

## Enhanced Bioremediation at Test Area North

► Performance metric: dissolved concentration



Now we will examine an enhanced source area bioremediation project, which used changes in groundwater concentration as the primary means to assess performance. This case study is presented in the Appendix.

Industrial wastewater (including solvents), low-level radioactive wastes, and sanitary sewage were injected in the Snake River Plain Aquifer from the late 1950s to 1972 at the Test Area North (TAN) facility of the INEEL.

TCE plume is nearly 3 km long

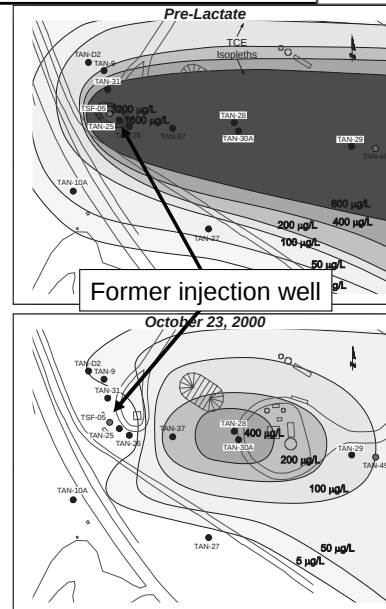
Residual source area is about 30 m in diameter

Contaminated aquifer is about 60-120 m deep

Aquifer is comprised of fractured basalt

## Test Area North EISB: Groundwater Concentration Changes

- ▶ Groundwater monitoring is conducted from 17 locations
- ▶ Pre-lactate injection concentrations were >3 mg/L in the former injection well
- ▶ Concentrations have been reduced to below detection in several wells by continued lactate injections

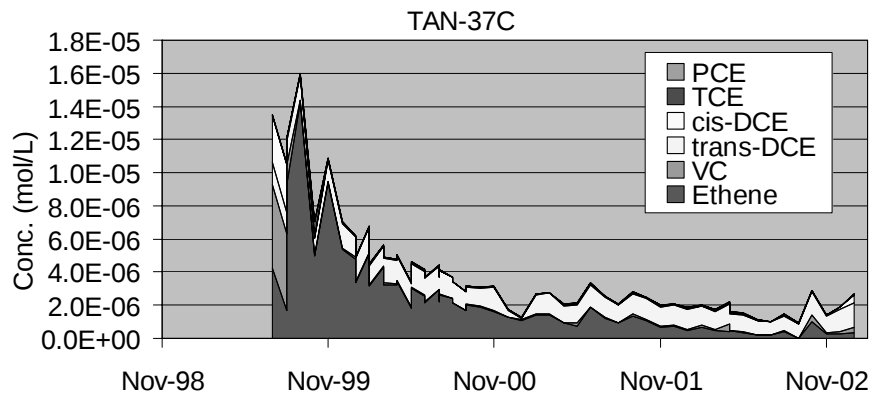


This slide shows an example of using groundwater concentrations as a performance metric to assess effectiveness for enhanced bioremediation. The remedial action goals at this site are based on MCL's. This is a plan view of the TAN site showing pre-lactate TCE contours and contours after 21 months of lactate injections.

Cover points on the slide.

It should be noted that continued operations are required because of the presence of the residual source near the injection well. A long-term cessation in lactate injections would result in eventual rebound of TCE concentrations in groundwater, an example of what Dr. Kostarelos discussed earlier.

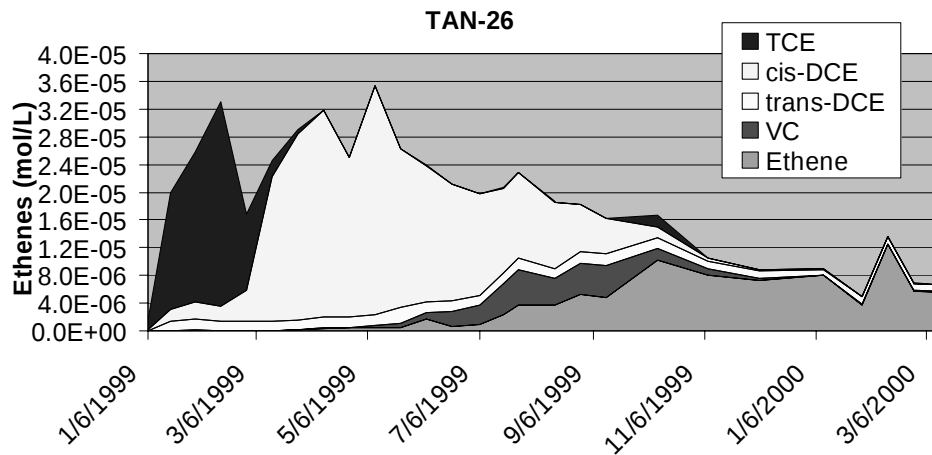
## Test Area North EISB: Long-Term Dechlorination



- Dark blue data series represents ethene
- Significant ethene concentrations at this well indicate complete dechlorination is occurring

This slide shows another example of using groundwater concentrations as a performance metric to assess effectiveness for enhanced bioremediation. In this case, this chart shows TCE and its degradation products DCE, VC, and ethene. Note that significant ethene production has been observed in this well. This monitoring location received significant concentrations of electron donor.

## Test Area North EISB: Enhanced Mass Transfer from Source Area



An important result from the TAN bioremediation project was the observation of enhanced mass transfer from the residual source. This chart shows chlorinated ethene concentrations from a TAN monitoring well.

Note the near 21-fold increase in TCE concentration from January to March 1999. This increase coincided with arrival of high concentrations of lactate at this well. These observations suggested that the TCE migration was caused by the lactate. Another important point is that the degradation of the TCE to c-DCE suggests that this TCE was bioavailable

By the next injection (2<sup>nd</sup> peak), the TCE was all degraded to **c-DCE** by the time it arrived at this well.

The enhanced mass transfer caused by bioremediation has been documented in several laboratory studies and is being observed in an increasing number of pilot and field-scale applications. In fact, the ITRC has formed a new team called Bioremediation of DNAPLs to further investigate this topic.

## Regulatory and Stakeholder Concerns

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**Presented by Eric Hausamann**  
**New York State Department of**  
**Environmental Conservation**

No associated notes.

## Health & Safety Issues



- ▶ Sampling hot media
- ▶ Handling chemical oxidants
- ▶ Vapor monitoring
- ▶ Electrical hazards
- ▶ Sampling extracted fluids
- ▶ Direct contact
- ▶ Shipping issues



The Health and Safety of site workers and the surrounding community is a major concern of regulators and stakeholders at every remediation project. H&S measures associated with typical remedial activities include worker personal protection such as respirator use when handling contaminated soil or perimeter air monitoring while an off-gas treatment system is operating. These are typically addressed in the HASP.

There seem to be very few H&S issues associated specifically with performance monitoring. Normal precautions that one should take while sampling or working around remedial system equipment apply to performance monitoring.

Two hazards that should be highlighted are groundwater monitoring within the targeted treatment zone during in situ thermal treatment or in situ chemical oxidation treatment. Some other concerns are listed as well.

## Regulatory Concerns



► Drilling in source zones

- Soil borings
- Monitoring wells



- Specialized sampling methods
- Statistical evaluation of data
- Regulations and permits
- Alternate goals for source zones

This slide presents some concerns expressed by regulators:

Drilling in source zones – some of the techniques for evaluating remedial progress discussed today may involve collecting samples from the source zone

Specialized sampling methods – regulators may be unfamiliar with specialized methods recommended for sampling hot media or indicator parameters

Statistical evaluation of data – many regulators are skeptical of any data that has been subjected to statistical manipulation

Regulations and permits – regulations or permits issued in some states may specify the performance verification methodology to be used to measure success and

Alternate goals for source zones – finally, the idea of alternate goals for the source zone or intermediate performance objectives may not be acceptable to some regulators

## Stakeholder Issues



- ▶ Stakeholders have a right to be involved in defining project outcomes
- ▶ Adequate characterization of source zone is expected
- ▶ Vapor intrusion concerns are real
- ▶ Newer assessment approaches and technologies need to be “sold” to non-technical audience
- ▶ On-going communication between the project team and stakeholders is key

Stakeholders include members of the community, such as residents and citizens groups, and native American groups, with particular interest in the project.

This slide highlights some of the concerns expressed by the public stakeholder representative on our team:

## In Summary...



1. Performance goals and metrics should be established during design
2. MCLs are not a realistic short-term goal for a DNAPL source zone – alternate goals should be considered
3. Converging lines of evidence provide the most confidence in performance assessments

And that concludes today's seminar. Again, we'd like to stress the importance of planning for performance assessment ahead of time and working to establish specific, measurable performance goals and metrics prior to treatment.

Also, goals for the source zone should be achievable as well as measurable. For phased approaches at DNAPL sites, alternate goals, besides drinking water standards or MCLs, should be considered for the saturated zone within the source area.

We have described an approach to performance assessment that relies on converging lines of evidence. This involves looking at all the performance data and feedback from the system to gauge success, not just basing decisions on a single metric.

You may download a free copy of ITRC documents at [www.itrcweb.org](http://www.itrcweb.org)

## Thank You for Participating



- ▶ **Links to additional resources**
- ▶ **2nd question and answer session**



Links to additional resources:

<http://www.clu-in.org/conf/itrc/dnaplpa/resource.cfm>

Your feedback is important – please fill out the form at:

<http://www.clu-in.org/conf/itrc/dnaplpa>

The benefits that ITRC offers to state regulators and technology developers, vendors, and consultants include:

Helping regulators build their knowledge base and raise their confidence about new environmental technologies

Helping regulators save time and money when evaluating environmental technologies

Guiding technology developers in the collection of performance data to satisfy the requirements of multiple states

Helping technology vendors avoid the time and expense of conducting duplicative and costly demonstrations

Providing a reliable network among members of the environmental community to focus on innovative environmental technologies

How you can get involved with ITRC:

Join an ITRC Team – with just 10% of your time you can have a positive impact on the regulatory process and acceptance of innovative technologies and approaches

Sponsor ITRC's technical team and other activities

Be an official state member by appointing a POC (State Point of Contact) to the State Engagement Team

Use ITRC products and attend training courses

Submit proposals for new technical teams and projects