Figure 3: Site map of SEAR demonstration at U.S. Marine Corps Base Camp Lejeune. Well field consisted of six extraction wells (EX1-EX6), three surfactant injection wells (IN1-IN3), and two hydraulic control wells (HC1 and HC2). Building 25 is an operational dry cleaning facility.

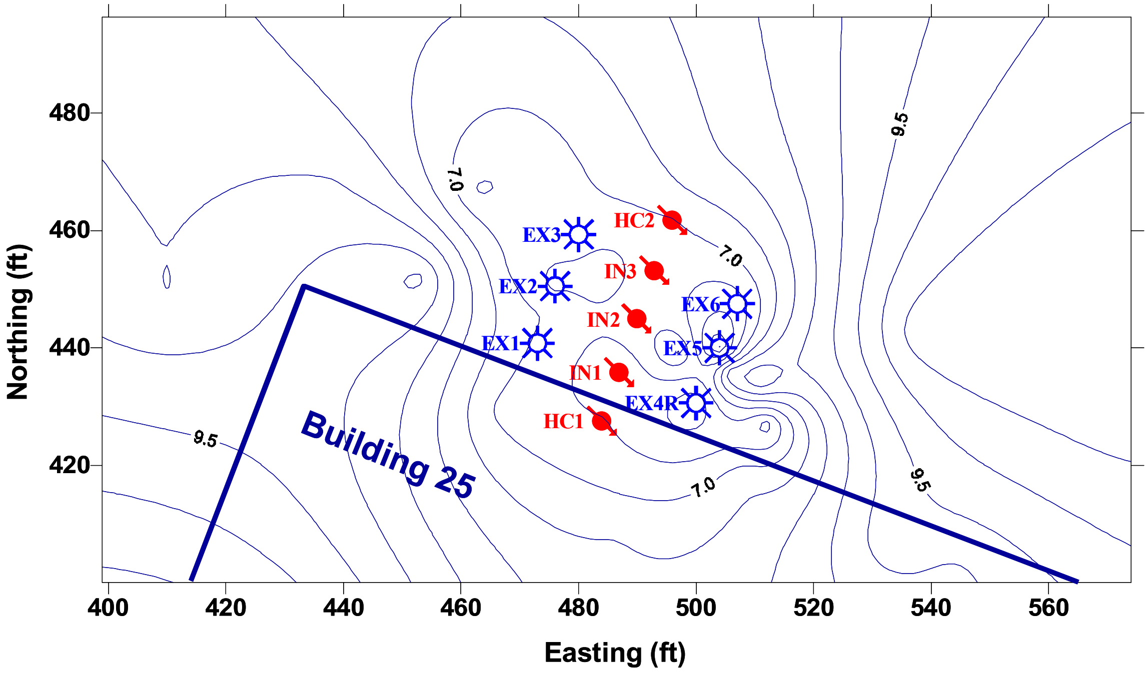
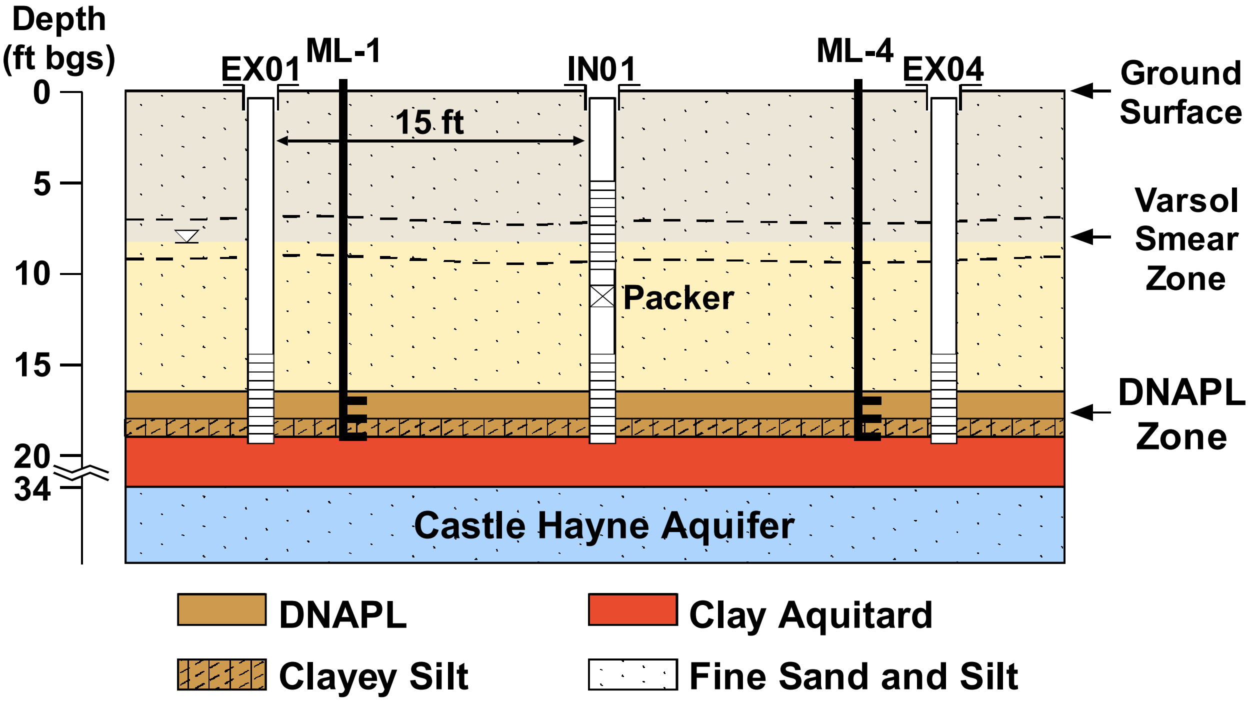


Figure 4: Generalized geosystem cross-section of DNAPL zone at Site 88, Building 25, MCB Camp Lejeune.

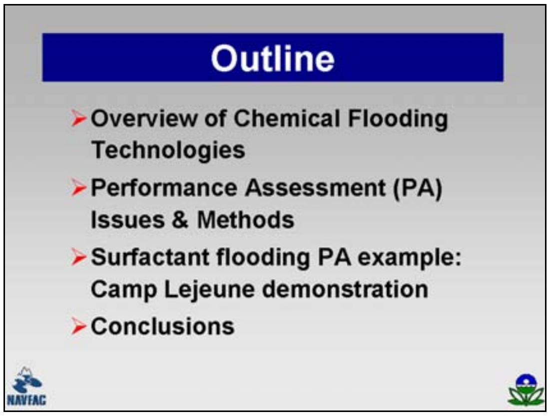


8. PRESENTATION VISUALS ~ *presented by Leland Vane and S. Laura Yeh*

Site-specific Validation of Surfactant/Co-solvent Flushing

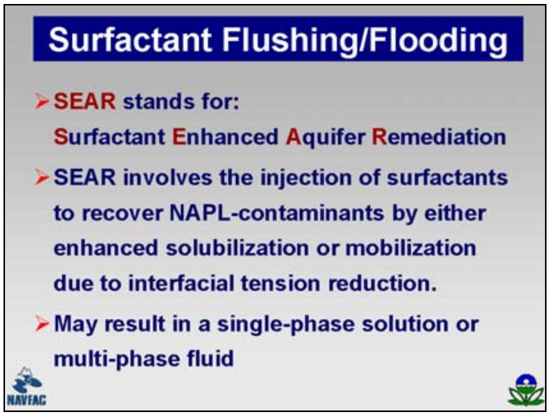
Leland M. Vane, Ph.D.
U.S. Environmental Protection Agency
&
S. Laura Yeh
U.S. Navy

2001 NATO/CCMS Pilot Study Meeting
Validation of *in situ* Remediation Performance



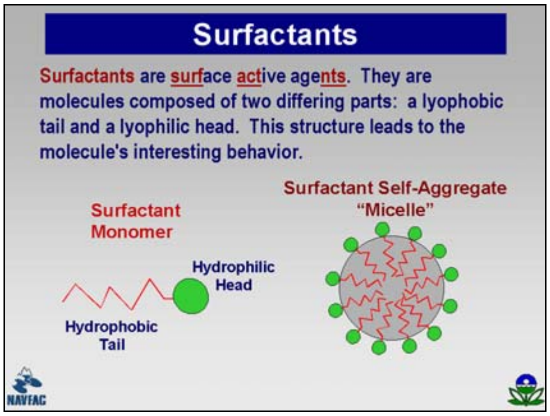
Outline

- Overview of Chemical Flooding Technologies
- Performance Assessment (PA) Issues & Methods
- Surfactant flooding PA example: Camp Lejeune demonstration
- Conclusions



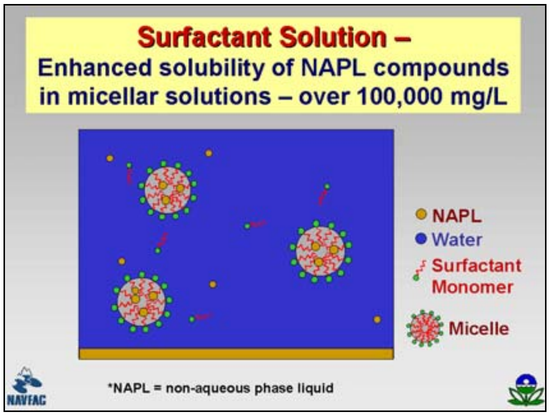
Surfactant Flushing/Flooding

- SEAR stands for:
  Surfactant Enhanced Aquifer Remediation
- SEAR involves the injection of surfactants to recover NAPL-contaminants by either enhanced solubilization or mobilization due to interfacial tension reduction.
- May result in a single-phase solution or multi-phase fluid



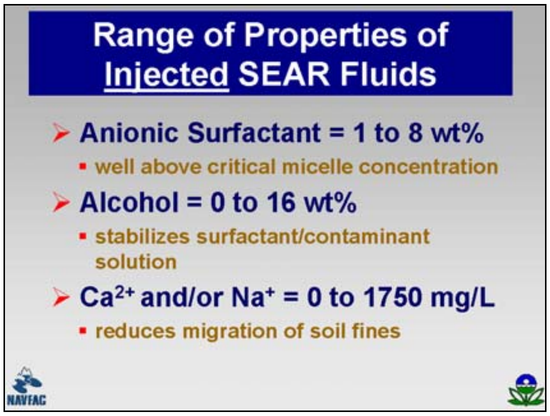
Surfactants

Surfactants are surface active agents. They are molecules composed of two differing parts: a lyophobic tail and a lyophilic head. This structure leads to the molecule's interesting behavior.



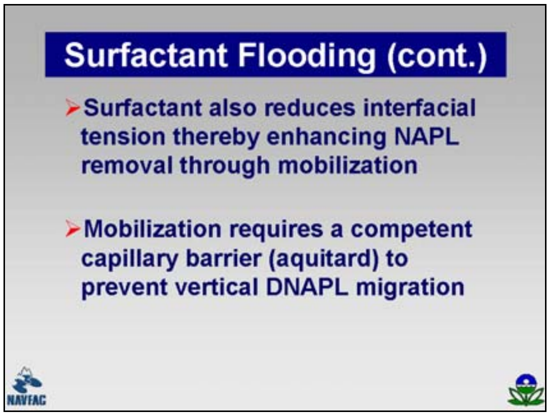
Surfactant Solution – Enhanced solubility of NAPL compounds in micellar solutions – over 100,000 mg/L

*NAPL = non-aqueous phase liquid



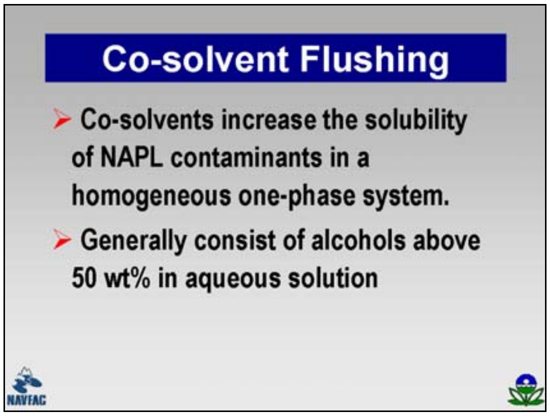
Range of Properties of Injected SEAR Fluids

- Anionic Surfactant = 1 to 8 wt%
  - well above critical micelle concentration
- Alcohol = 0 to 16 wt%
  - stabilizes surfactant/contaminant solution
- Ca^{2+} and/or Na^{+} = 0 to 1750 mg/L
  - reduces migration of soil fines



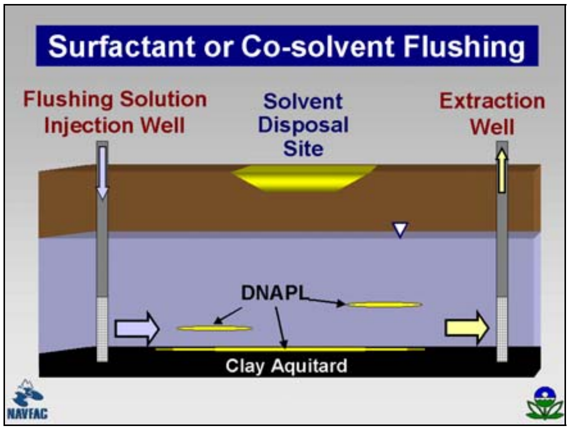
Surfactant Flooding (cont.)

- Surfactant also reduces interfacial tension thereby enhancing NAPL removal through mobilization
- Mobilization requires a competent capillary barrier (aquitard) to prevent vertical DNAPL migration

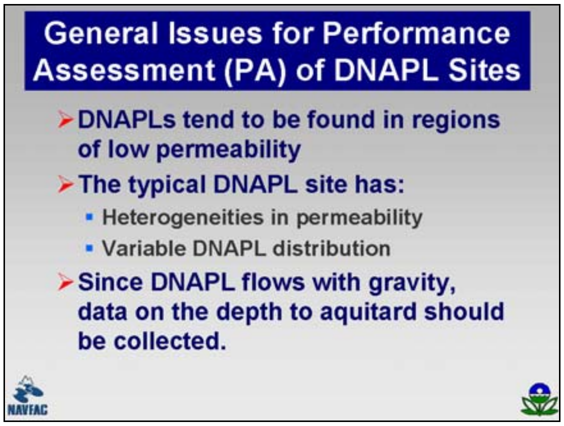


Co-solvent Flushing

- Co-solvents increase the solubility of NAPL contaminants in a homogeneous one-phase system.
- Generally consist of alcohols above 50 wt% in aqueous solution

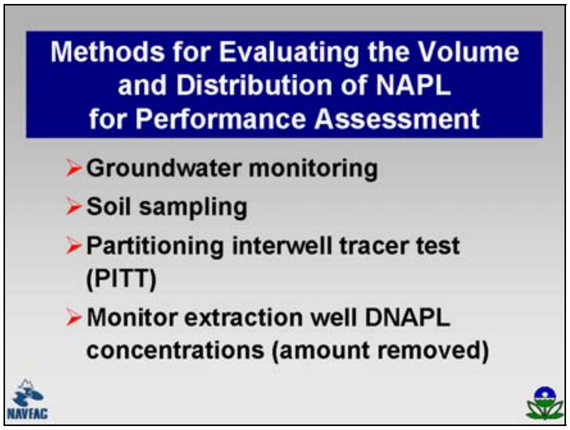


Surfactant or Co-solvent Flushing



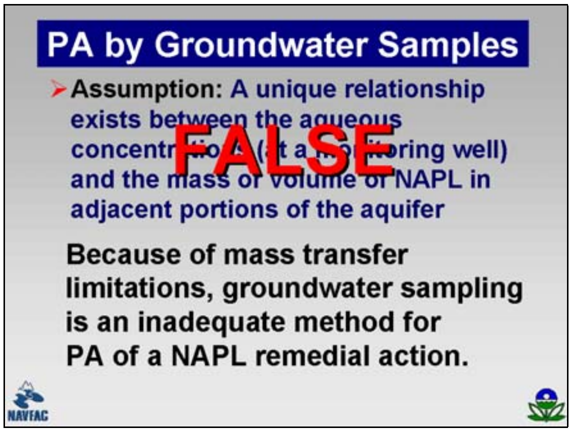
General Issues for Performance Assessment (PA) of DNAPL Sites

- DNAPLs tend to be found in regions of low permeability
- The typical DNAPL site has:
  - Heterogeneities in permeability
  - Variable DNAPL distribution
- Since DNAPL flows with gravity, data on the depth to aquitard should be collected.



Methods for Evaluating the Volume and Distribution of NAPL for Performance Assessment

- Groundwater monitoring
- Soil sampling
- Partitioning interwell tracer test (PITT)
- Monitor extraction well DNAPL concentrations (amount removed)

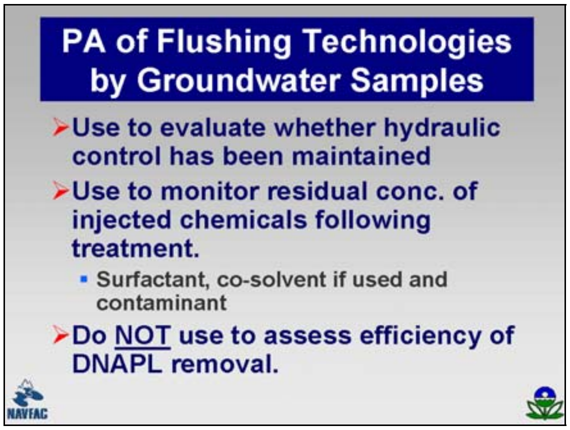


PA by Groundwater Samples

- Assumption: A unique relationship exists between the aqueous concentration (at a monitoring well) and the mass or volume of NAPL in adjacent portions of the aquifer

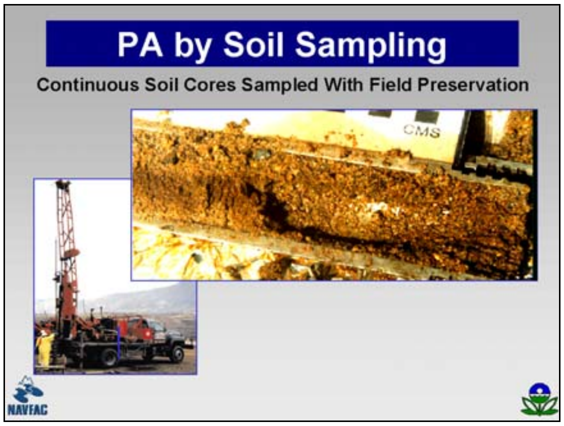
FALSE

Because of mass transfer limitations, groundwater sampling is an inadequate method for PA of a NAPL remedial action.



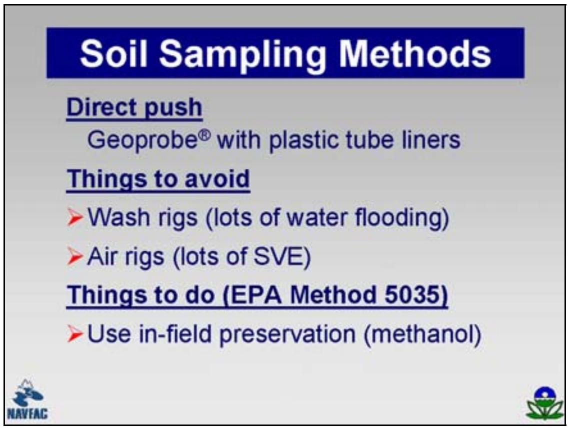
PA of Flushing Technologies by Groundwater Samples

- Use to evaluate whether hydraulic control has been maintained
- Use to monitor residual conc. of injected chemicals following treatment.
  - Surfactant, co-solvent if used and contaminant
- Do NOT use to assess efficiency of DNAPL removal.



PA by Soil Sampling

Continuous Soil Cores Sampled With Field Preservation



Soil Sampling Methods

Direct push

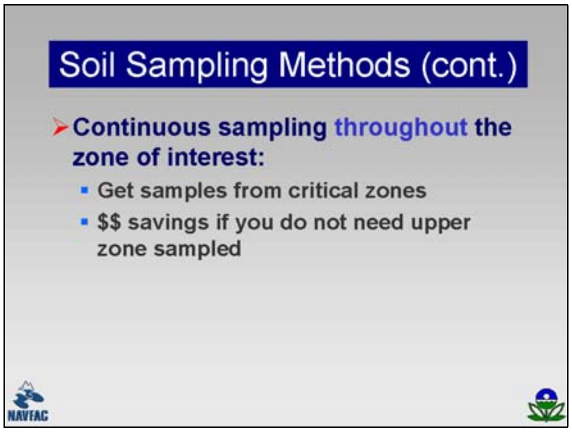
Geoprobe® with plastic tube liners

Things to avoid

- Wash rigs (lots of water flooding)
- Air rigs (lots of SVE)

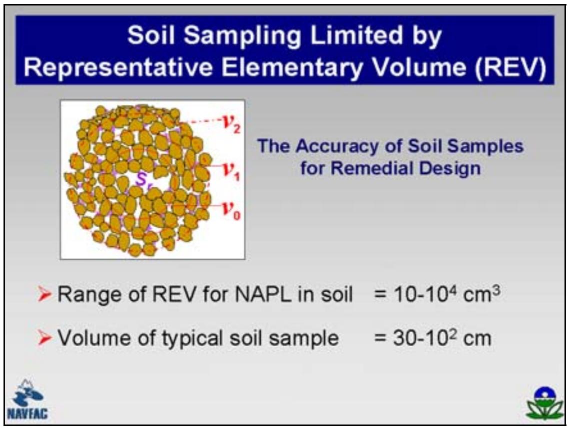
Things to do (EPA Method 5035)

- Use in-field preservation (methanol)



Soil Sampling Methods (cont.)

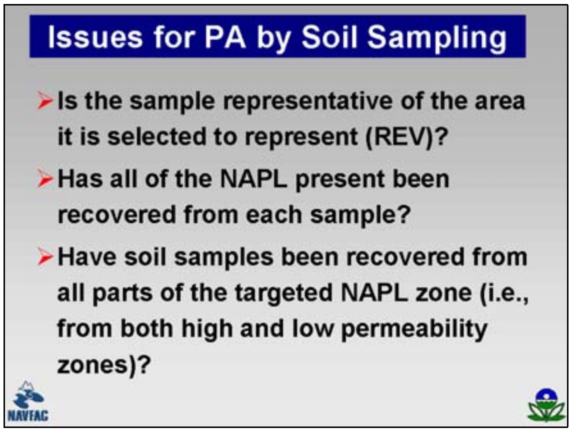
- Continuous sampling throughout the zone of interest:
  - Get samples from critical zones
  - $$ savings if you do not need upper zone sampled



Soil Sampling Limited by Representative Elementary Volume (REV)

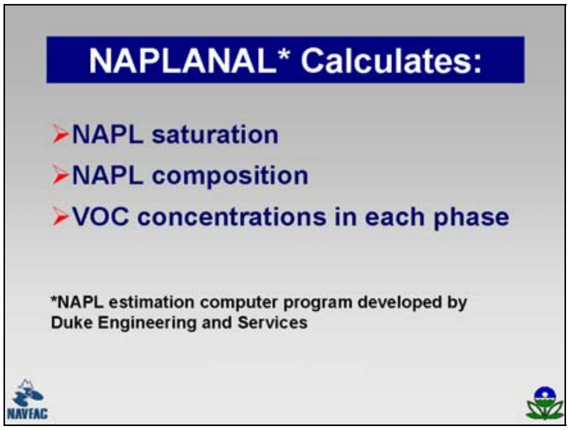
The Accuracy of Soil Samples for Remedial Design

- Range of REV for NAPL in soil = 10-10^4 cm^3
- Volume of typical soil sample = 30-10^2 cm



Issues for PA by Soil Sampling

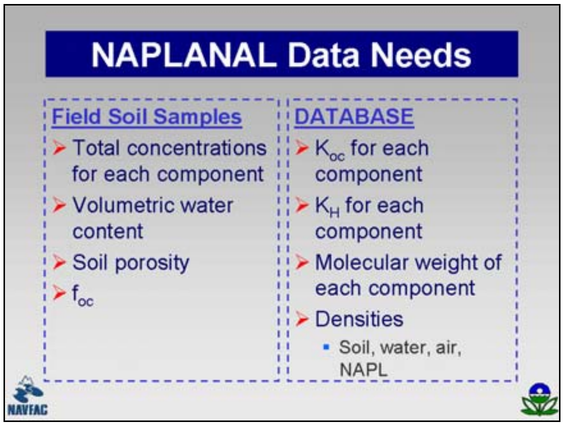
- Is the sample representative of the area it is selected to represent (REV)?
- Has all of the NAPL present been recovered from each sample?
- Have soil samples been recovered from all parts of the targeted NAPL zone (i.e., from both high and low permeability zones)?



NAPLANAL* Calculates:

- NAPL saturation
- NAPL composition
- VOC concentrations in each phase

*NAPL estimation computer program developed by Duke Engineering and Services



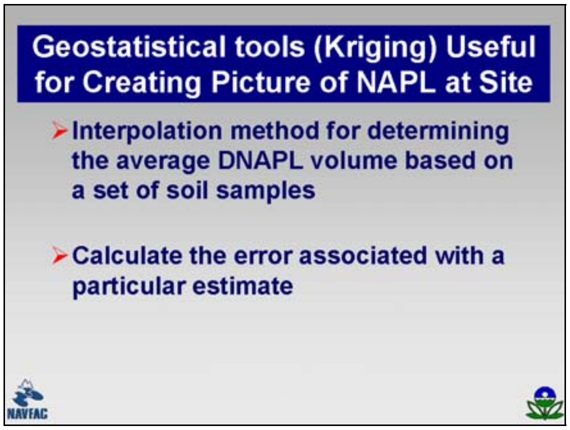
NAPLANAL Data Needs

Field Soil Samples

- Total concentrations for each component
- Volumetric water content
- Soil porosity
- f_{oc}

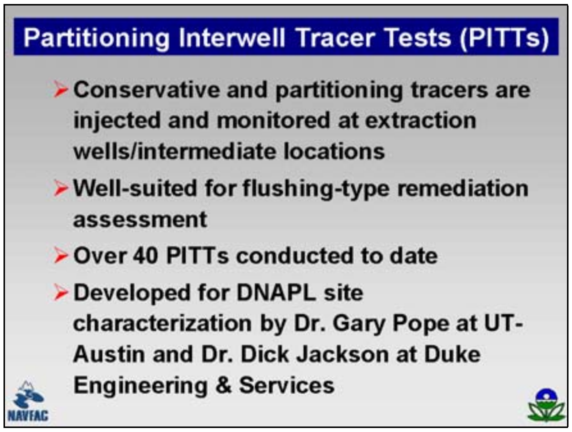
DATABASE

- K_{oc} for each component
- K_H for each component
- Molecular weight of each component
- Densities
  - Soil, water, air, NAPL



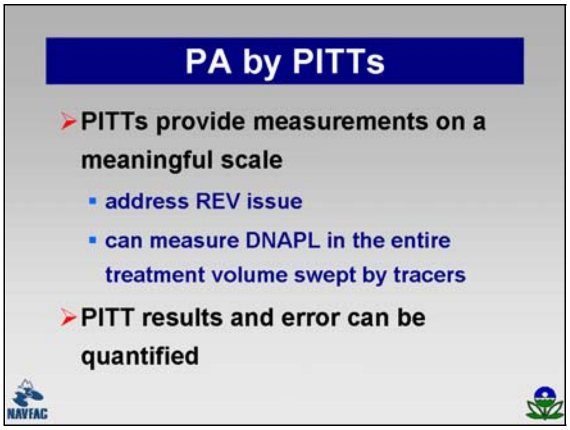
Geostatistical tools (Kriging) Useful for Creating Picture of NAPL at Site

- Interpolation method for determining the average DNAPL volume based on a set of soil samples
- Calculate the error associated with a particular estimate



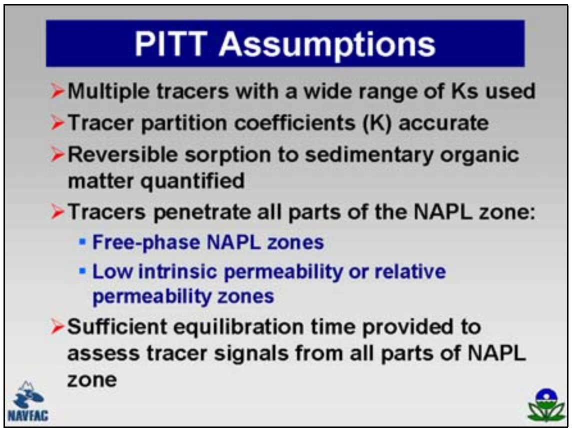
Partitioning Interwell Tracer Tests (PITTs)

- Conservative and partitioning tracers are injected and monitored at extraction wells/intermediate locations
- Well-suited for flushing-type remediation assessment
- Over 40 PITTs conducted to date
- Developed for DNAPL site characterization by Dr. Gary Pope at UT-Austin and Dr. Dick Jackson at Duke Engineering & Services



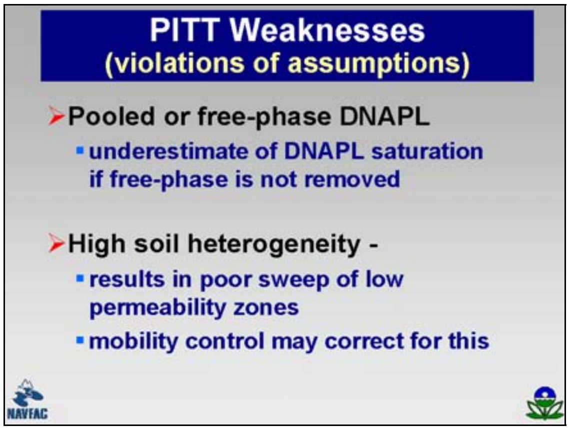
PA by PITTS

- PITTs provide measurements on a meaningful scale
  - address REV issue
  - can measure DNAPL in the entire treatment volume swept by tracers
- PITT results and error can be quantified



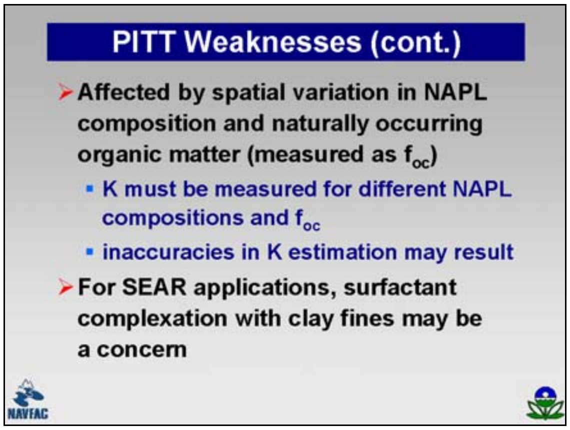
PITT Assumptions

- Multiple tracers with a wide range of Ks used
- Tracer partition coefficients (K) accurate
- Reversible sorption to sedimentary organic matter quantified
- Tracers penetrate all parts of the NAPL zone:
  - Free-phase NAPL zones
  - Low intrinsic permeability or relative permeability zones
- Sufficient equilibration time provided to assess tracer signals from all parts of NAPL zone



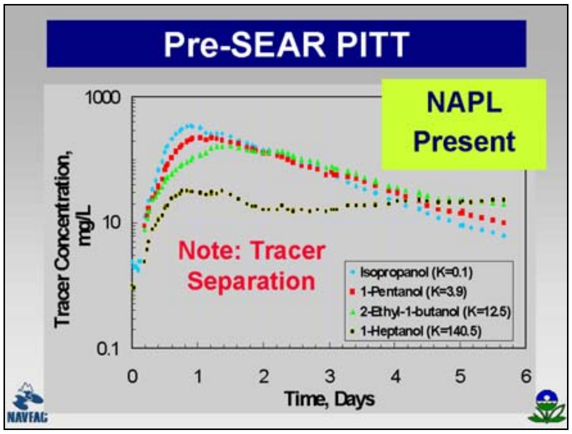
PITT Weaknesses (violations of assumptions)

- Pooled or free-phase DNAPL
  - underestimate of DNAPL saturation if free-phase is not removed
- High soil heterogeneity -
  - results in poor sweep of low permeability zones
  - mobility control may correct for this



PITT Weaknesses (cont.)

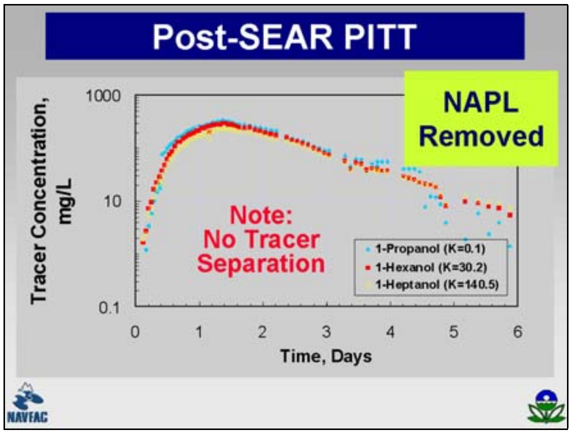
- Affected by spatial variation in NAPL composition and naturally occurring organic matter (measured as f_{oc})
  - K must be measured for different NAPL compositions and f_{oc}
  - inaccuracies in K estimation may result
- For SEAR applications, surfactant complexation with clay fines may be a concern



Pre-SEAR PITT

NAPL Present

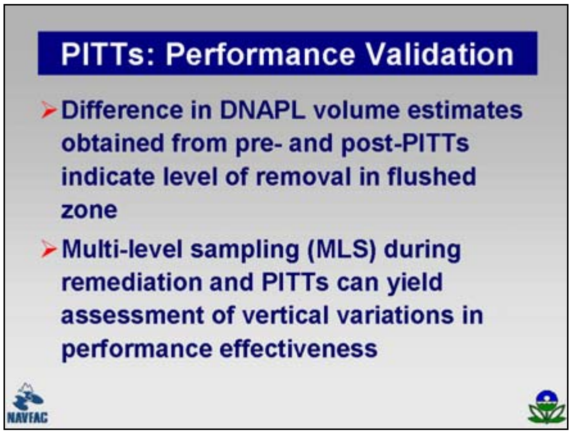
Note: Tracer Separation



Post-SEAR PITT

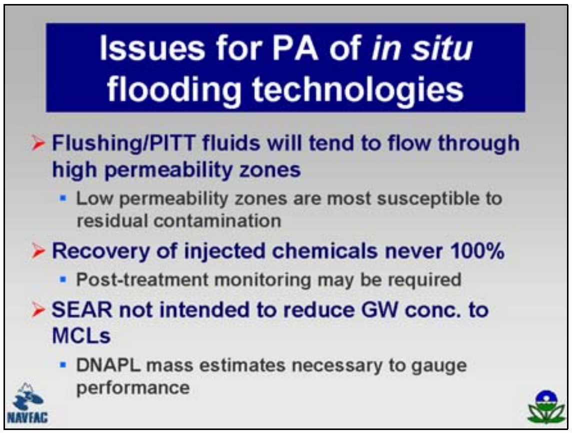
NAPL Removed

Note: No Tracer Separation



PITTs: Performance Validation

- Difference in DNAPL volume estimates obtained from pre- and post-PITTs indicate level of removal in flushed zone
- Multi-level sampling (MLS) during remediation and PITTs can yield assessment of vertical variations in performance effectiveness

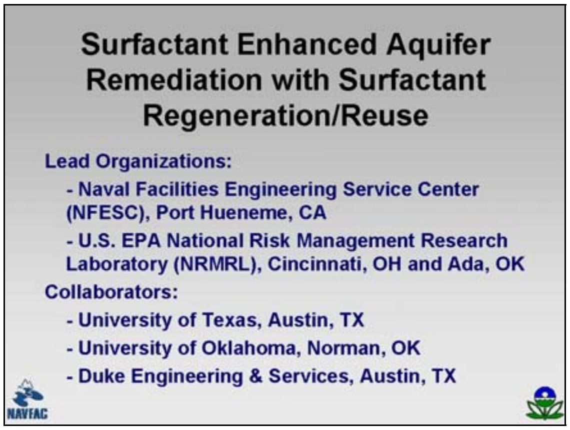


Issues for PA of *in situ* flooding technologies

- Flushing/PITT fluids will tend to flow through high permeability zones
  - Low permeability zones are most susceptible to residual contamination
- Recovery of injected chemicals never 100%
  - Post-treatment monitoring may be required
- SEAR not intended to reduce GW conc. to MCLs
  - DNAPL mass estimates necessary to gauge performance

Example Site

- U.S. Marine Corps Base Camp Lejeune
  - Soil contaminated with dry cleaning solvent (PCE) – Site 88



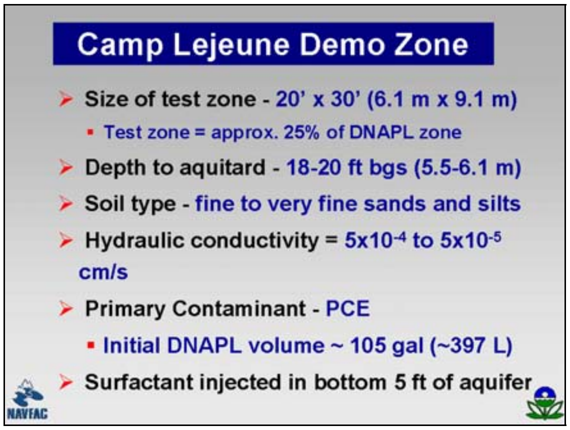
Surfactant Enhanced Aquifer Remediation with Surfactant Regeneration/Reuse

Lead Organizations:

- Naval Facilities Engineering Service Center (NFESC), Port Hueneme, CA
- U.S. EPA National Risk Management Research Laboratory (NRMRL), Cincinnati, OH and Ada, OK

Collaborators:

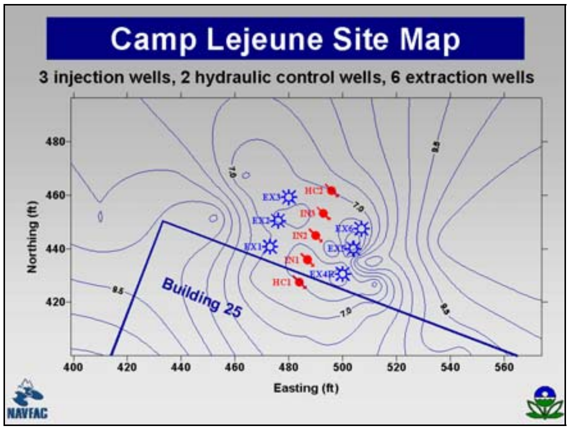
- University of Texas, Austin, TX
- University of Oklahoma, Norman, OK
- Duke Engineering & Services, Austin, TX



Camp Lejeune Demo Zone

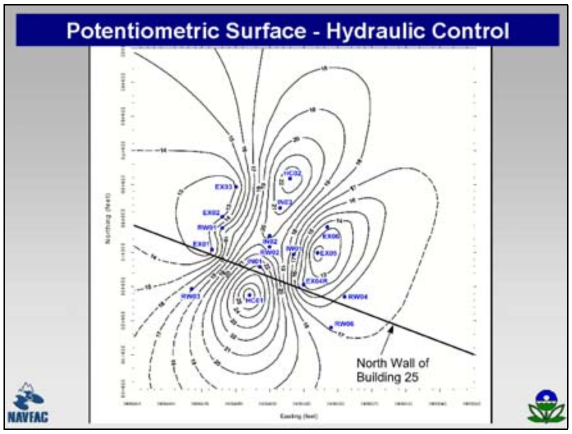
- Size of test zone - 20' x 30' (6.1 m x 9.1 m)
  - Test zone = approx. 25% of DNAPL zone
- Depth to aquitard - 18-20 ft bgs (5.5-6.1 m)
- Soil type - fine to very fine sands and silts
- Hydraulic conductivity = 5×10^{-4} to 5×10^{-5} cm/s
- Primary Contaminant - PCE
  - Initial DNAPL volume ~ 105 gal (~397 L)
- Surfactant injected in bottom 5 ft of aquifer

Camp Lejeune SEAR Well Field

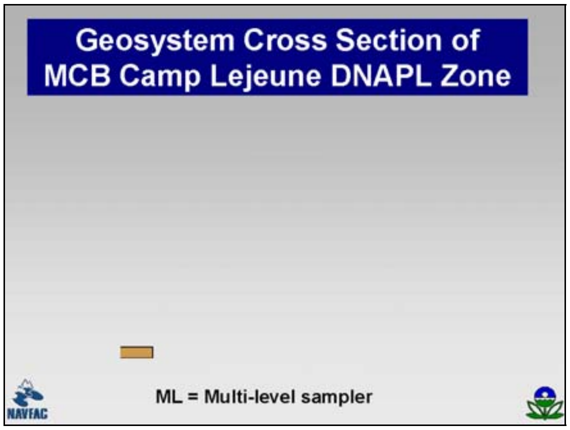


Camp Lejeune Site Map

3 injection wells, 2 hydraulic control wells, 6 extraction wells

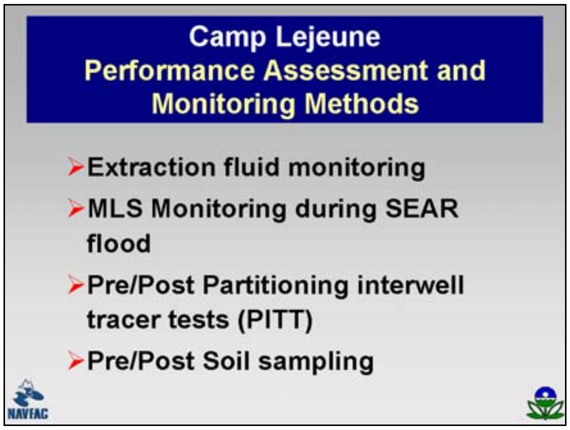


Potentiometric Surface - Hydraulic Control



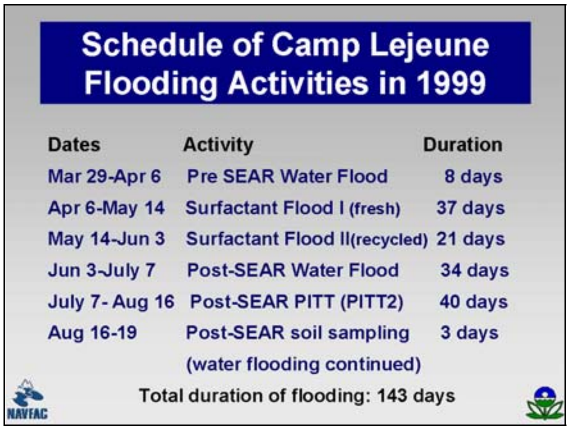
Geosystem Cross Section of MCB Camp Lejeune DNAPL Zone

ML = Multi-level sampler



Camp Lejeune Performance Assessment and Monitoring Methods

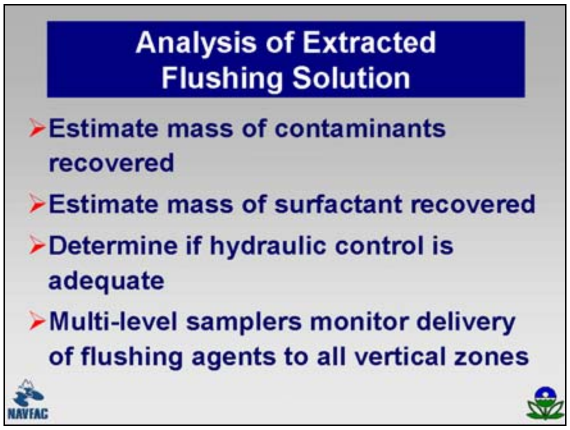
- Extraction fluid monitoring
- MLS Monitoring during SEAR flood
- Pre/Post Partitioning interwell tracer tests (PITT)
- Pre/Post Soil sampling



Schedule of Camp Lejeune Flooding Activities in 1999

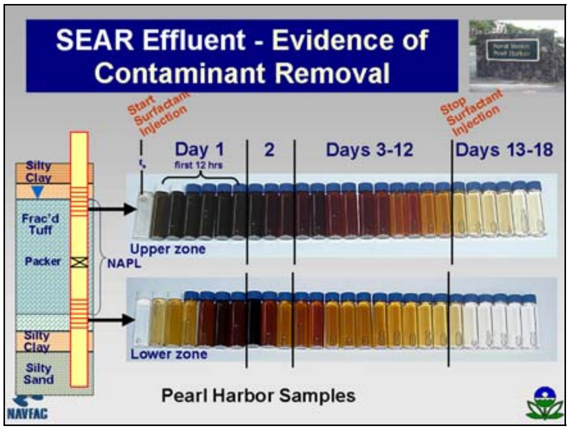
Dates	Activity	Duration
Mar 29-Apr 6	Pre SEAR Water Flood	8 days
Apr 6-May 14	Surfactant Flood I (fresh)	37 days
May 14-Jun 3	Surfactant Flood II(recycled)	21 days
Jun 3-July 7	Post-SEAR Water Flood	34 days
July 7- Aug 16	Post-SEAR PITT (PITT2)	40 days
Aug 16-19	Post-SEAR soil sampling (water flooding continued)	3 days

Total duration of flooding: 143 days



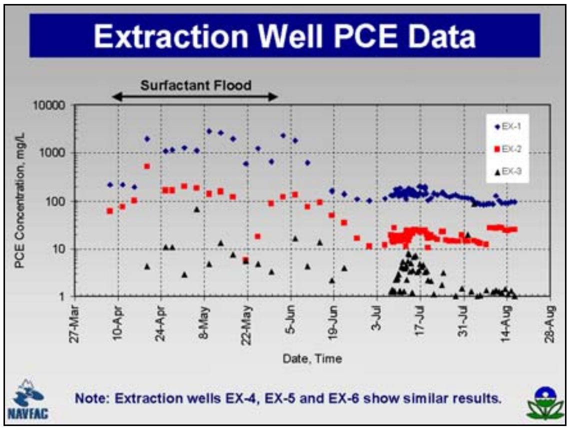
Analysis of Extracted Flushing Solution

- Estimate mass of contaminants recovered
- Estimate mass of surfactant recovered
- Determine if hydraulic control is adequate
- Multi-level samplers monitor delivery of flushing agents to all vertical zones



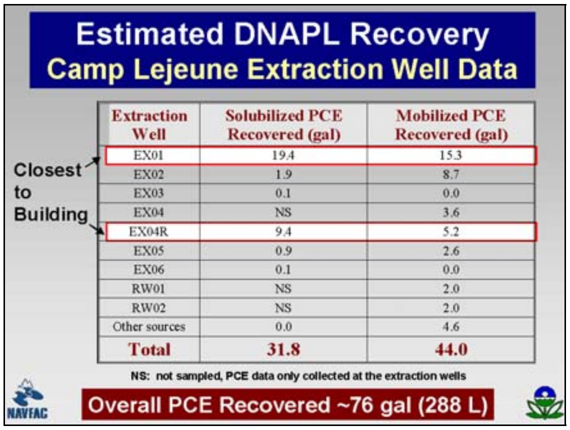
SEAR Effluent - Evidence of Contaminant Removal

Pearl Harbor Samples



Extraction Well PCE Data

Note: Extraction wells EX-4, EX-5 and EX-6 show similar results.



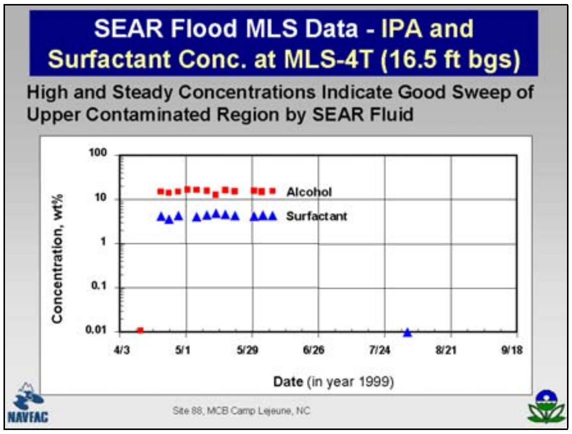
Estimated DNAPL Recovery Camp Lejeune Extraction Well Data

Closest to Building

Extraction Well	Solubilized PCE Recovered (gal)	Mobilized PCE Recovered (gal)
EX01	19.4	15.3
EX02	1.9	8.7
EX03	0.1	0.0
EX04	NS	3.6
EX04R	9.4	5.2
EX05	0.9	2.6
EX06	0.1	0.0
RW01	NS	2.0
RW02	NS	2.0
Other sources	0.0	4.6
Total	**31.8**	**44.0**

NS: not sampled, PCE data only collected at the extraction wells

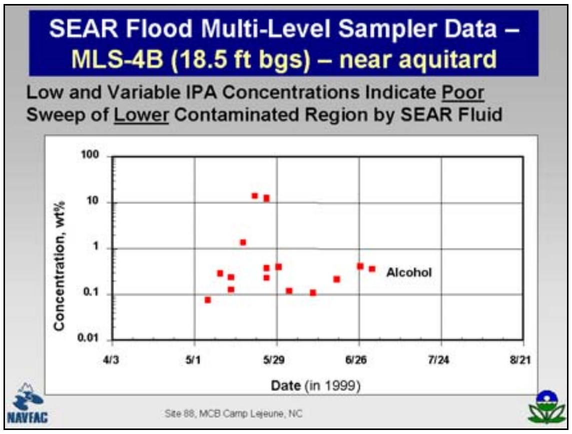
Overall PCE Recovered ~76 gal (288 L)



SEAR Flood MLS Data - IPA and Surfactant Conc. at MLS-4T (16.5 ft bgs)

High and Steady Concentrations Indicate Good Sweep of Upper Contaminated Region by SEAR Fluid

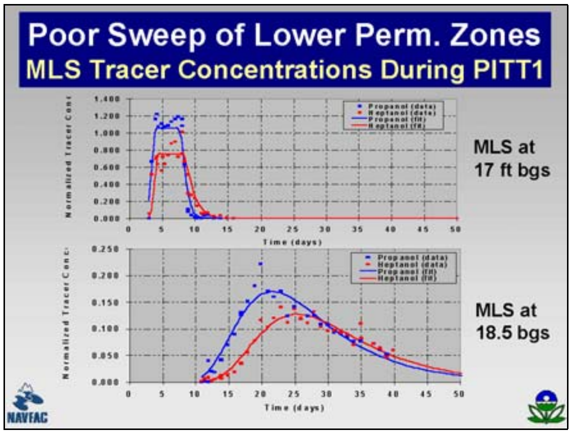
Site 88, MCB Camp Lejeune, NC



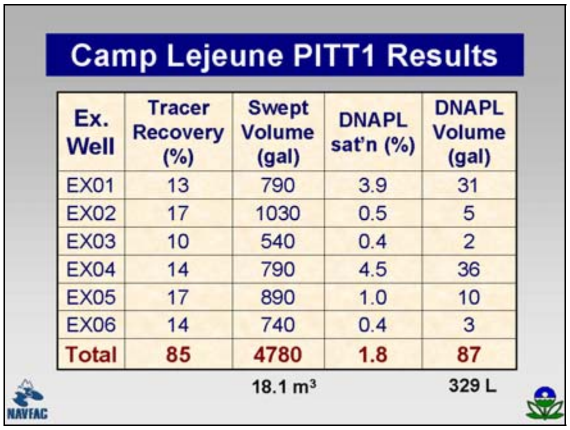
SEAR Flood Multi-Level Sampler Data – MLS-4B (18.5 ft bgs) – near aquitard

Low and Variable IPA Concentrations Indicate Poor Sweep of Lower Contaminated Region by SEAR Fluid

Site 88, MCB Camp Lejeune, NC

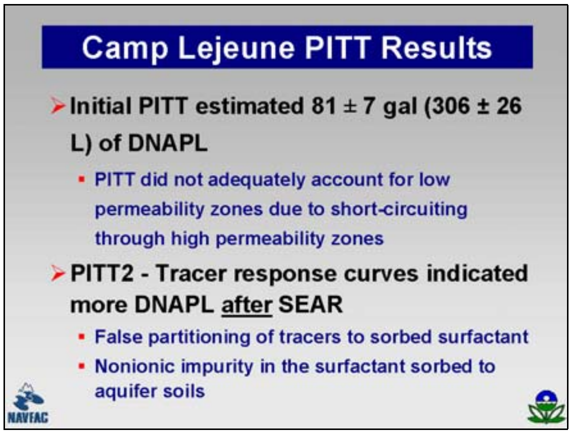


Poor Sweep of Lower Perm. Zones MLS Tracer Concentrations During PITT1



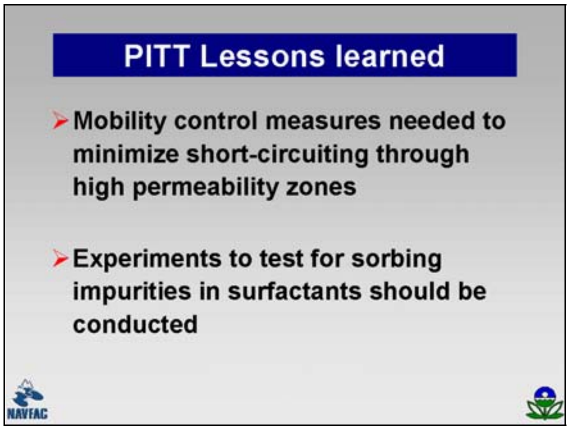
Camp Lejeune PITT1 Results

Ex. Well	Tracer Recovery (%)	Swept Volume (gal)	DNAPL sat'n (%)	DNAPL Volume (gal)
EX01	13	790	3.9	31
EX02	17	1030	0.5	5
EX03	10	540	0.4	2
EX04	14	790	4.5	36
EX05	17	890	1.0	10
EX06	14	740	0.4	3
Total	**85**	**4780**	**1.8**	**87**
		18.1 m³		329 L



Camp Lejeune PITT Results

- Initial PITT estimated 81 ± 7 gal (306 ± 26 L) of DNAPL
    - PITT did not adequately account for low permeability zones due to short-circuiting through high permeability zones
- PITT2 - Tracer response curves indicated more DNAPL after SEAR
    - False partitioning of tracers to sorbed surfactant
    - Nonionic impurity in the surfactant sorbed to aquifer soils

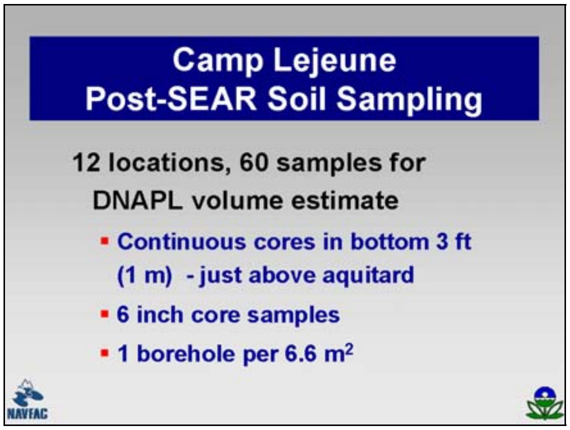


PITT Lessons learned

- Mobility control measures needed to minimize short-circuiting through high permeability zones
- Experiments to test for sorbing impurities in surfactants should be conducted

Estimated Costs (US$) for Camp Lejeune PITT

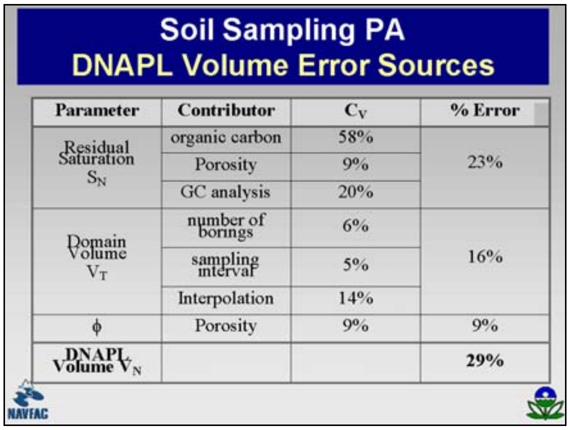
- Low Permeability Site, 40 days
  - Pre/post-PITT, 111 yd^3: ~$127,000 each
  - Pre-PITT, 463 yd^3: $182,100
  - Post-PITT, 463 yd^3: $164,500
- High Perm. Site, 23 days
  - Pre-PITT, 617 yd^3: $74,900
  - Post-PITT, 617 yd^3: $71,200



Camp Lejeune Post-SEAR Soil Sampling

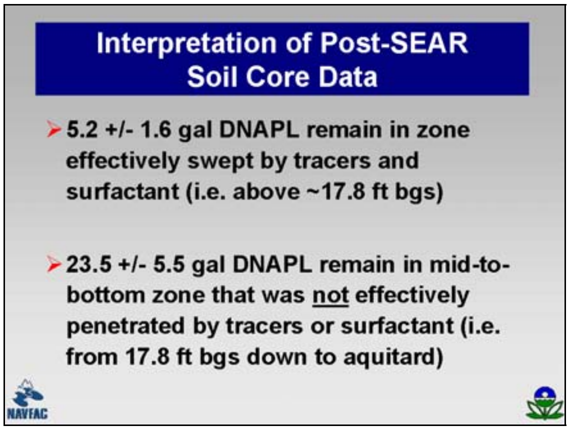
12 locations, 60 samples for DNAPL volume estimate

- Continuous cores in bottom 3 ft (1 m) - just above aquitard
- 6 inch core samples
- 1 borehole per 6.6 m^2



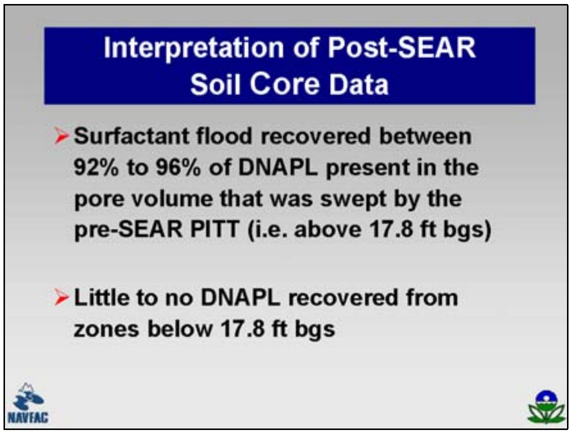
Soil Sampling PA DNAPL Volume Error Sources

Parameter	Contributor	C_V	% Error
Residual Saturation S_N	organic carbon	58%	23%
	Porosity	9%	
	GC analysis	20%	
Domain Volume V_T	number of borings	6%	16%
	sampling interval	5%	
	Interpolation	14%	
ϕ	Porosity	9%	9%
DNAPL Volume V_N			29%



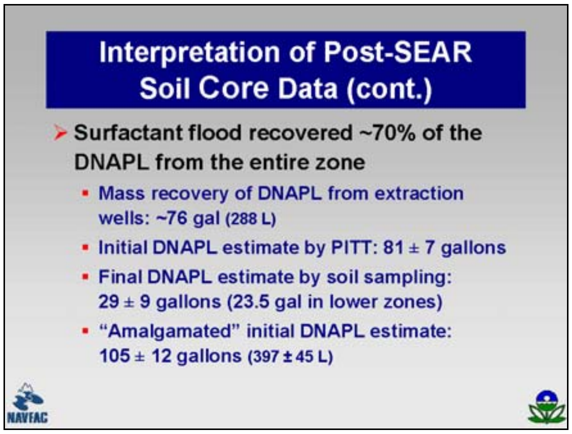
Interpretation of Post-SEAR Soil Core Data

- 5.2 +/- 1.6 gal DNAPL remain in zone effectively swept by tracers and surfactant (i.e. above ~17.8 ft bgs)
- 23.5 +/- 5.5 gal DNAPL remain in mid-to-bottom zone that was not effectively penetrated by tracers or surfactant (i.e. from 17.8 ft bgs down to aquitard)



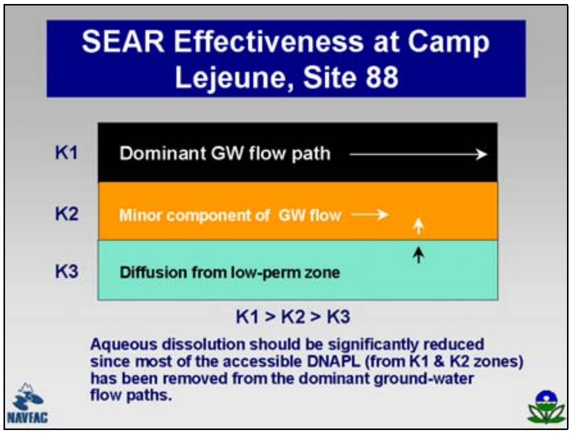
Interpretation of Post-SEAR Soil Core Data

- Surfactant flood recovered between 92% to 96% of DNAPL present in the pore volume that was swept by the pre-SEAR PITT (i.e. above 17.8 ft bgs)
- Little to no DNAPL recovered from zones below 17.8 ft bgs



Interpretation of Post-SEAR Soil Core Data (cont.)

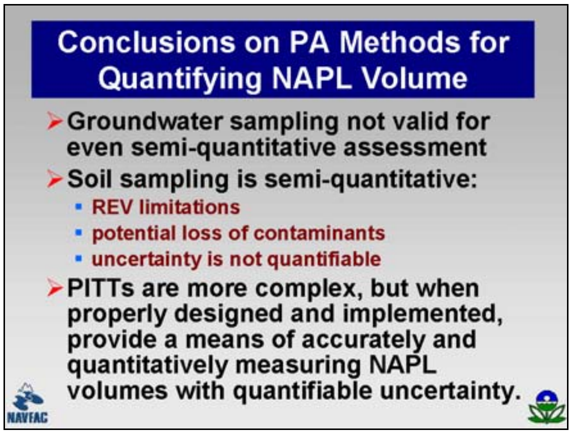
- Surfactant flood recovered ~70% of the DNAPL from the entire zone
  - Mass recovery of DNAPL from extraction wells: ~76 gal (288 L)
  - Initial DNAPL estimate by PITT: 81 ± 7 gallons
  - Final DNAPL estimate by soil sampling: 29 ± 9 gallons (23.5 gal in lower zones)
  - “Amalgamated” initial DNAPL estimate: 105 ± 12 gallons (397 ± 45 L)



SEAR Effectiveness at Camp Lejeune, Site 88

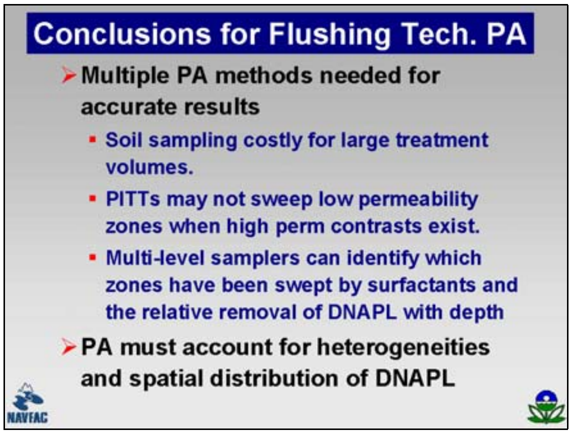
K1 > K2 > K3

Aqueous dissolution should be significantly reduced since most of the accessible DNAPL (from K1 & K2 zones) has been removed from the dominant ground-water flow paths.



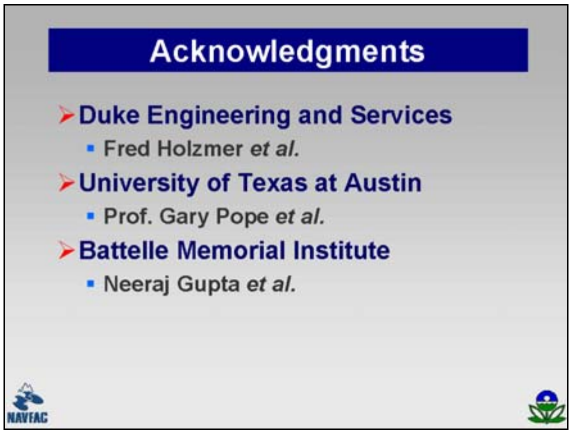
Conclusions on PA Methods for Quantifying NAPL Volume

- Groundwater sampling not valid for even semi-quantitative assessment
- Soil sampling is semi-quantitative:
  - REV limitations
  - potential loss of contaminants
  - uncertainty is not quantifiable
- PITTs are more complex, but when properly designed and implemented, provide a means of accurately and quantitatively measuring NAPL volumes with quantifiable uncertainty.



Conclusions for Flushing Tech. PA

- Multiple PA methods needed for accurate results
  - Soil sampling costly for large treatment volumes.
  - PITTs may not sweep low permeability zones when high perm contrasts exist.
  - Multi-level samplers can identify which zones have been swept by surfactants and the relative removal of DNAPL with depth
- PA must account for heterogeneities and spatial distribution of DNAPL



Acknowledgments

- Duke Engineering and Services
  - Fred Holzmer *et al.*
- University of Texas at Austin
  - Prof. Gary Pope *et al.*
- Battelle Memorial Institute
  - Neeraj Gupta *et al.*

SITE-SPECIFIC VERIFICATION OF IN SITU BIOREMEDIATION

Frank Volkering[1]

1. INTRODUCTION

Biological remediation strategies such as in-situ bioremediation, biobarriers and monitored natural attenuation require detailed knowledge of groundwater processes, and especially of biodegradation processes. The information obtained via traditional lines of evidence is not always conclusive or sufficient. Table 1 provides an overview of the traditional characterization methods.

Table 1: Strengths and weaknesses of traditional characterization methods.

Method	Strength	Weakness
Pollutant concentration	specific, quantitative	inconclusive
Degradation intermediates	conclusive, specific, quantitative	not for all pollutants
Mineralization products	conclusive, quantitative	not specific
Geochemical characterization	important process parameters	not specific, qualitative
Microcosm studies	conclusive, specific, semi-quantitative	lengthy, expensive
In situ experiments	conclusive, quantitative	lengthy, expensive

Biochemical techniques, such as DNA/RNA analysis may be used to obtain conclusive and specific evidence for biodegradation, but the evidence is mainly qualitative and as yet only applicable for a limited number of pollutants.

This paper presents a new line of evidence for bioremediation, based on the natural stable isotope composition of organic pollutants. Isotope analysis gives us a view into the pollutant molecules and offers conclusive, pollutant-specific, and possibly even quantitative information on biodegradation processes.

2. THEORY

Isotopes are elements with the same atomic number, but with a different atomic weight. Most elements on earth consist of two or more stable isotopes, as can be seen for the elements occurring in the most common organic pollutants in Table 1 below.

Table 2: Elements of the most common organic pollutants and their isotopes.

Element	Common isotope		Other stable isotopes	
	isotope	%	isotope	%
hydrogen (H)	^{1}H	99.985	^{2}H	0.015
carbon (C)	^{12}C	98.89	^{13}C	1.11
nitrogen (N)	^{14}N	99.63	^{15}N	0.37
oxygen (O)	^{16}O	99.759	^{17}O ^{18}O	0.037 0.204
chlorine (Cl)	^{35}Cl	75.53	^{37}Cl	24.47

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For analytical reasons, stable isotope concentrations are expressed using the δ-notation, relating the isotope ratio of a sample to that of a standard reference material. For ^{13}C, the standard material is Vienna PeeDee Belemnite (VPDB), a marine carbonate. The δ for ^{13}C is defined as:

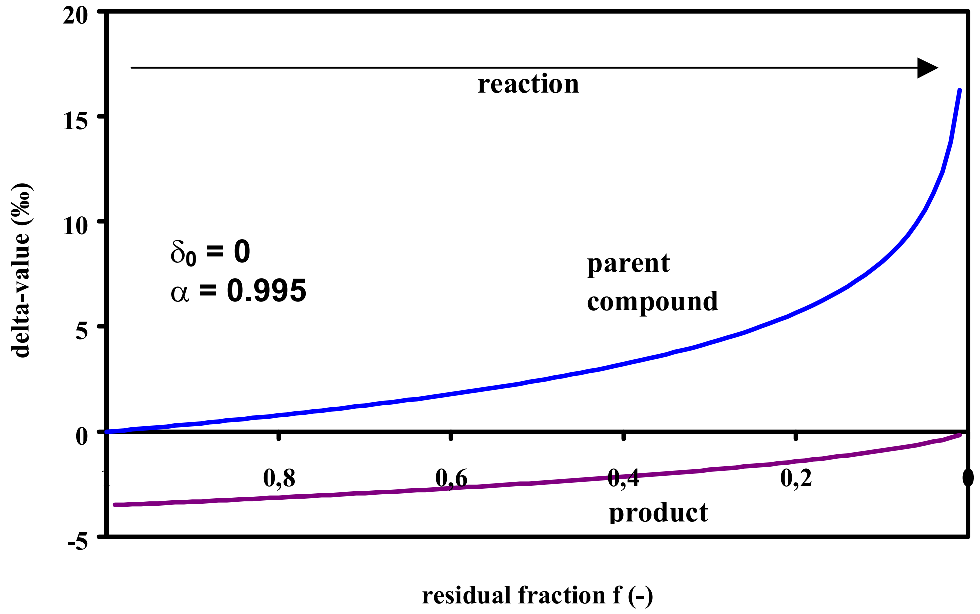
$$\delta^{13}\mathrm{C} = \left(\frac{(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{sample}}}{(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{VPDB}}} - 1 \right) \times 1000 \qquad (‰\ \mathrm{VPDB})$$

Due to difference in mass and size, stable isotopes of one element behave slightly different in many physical, chemical and biological processes. In most biodegradation processes, the lightest isotope is degraded preferentially. This causes a small, but usually significant change in the isotope composition of the residual pollutant. This so-called isotopic fractionation can be described with the Rayleigh equation:

$$R = R_0 \times f^{(\alpha - 1)}$$

in which R is the isotope ratio (e.g. ^{13}C/^{12}C), R_0 is the initial isotope ratio, f is the fraction residual substrate, and α is the fractionation factor. Figure 1 gives a theoretical example of the changes in isotopic composition (expressed as δ) of the parent compound (the pollutant) and the reaction product during a fractionating reaction.

Figure 1: Theoretical change in the stable isotope composition of reactant (parent compound) and reaction product during a fractionating reaction.



3. COMPOUND-SPECIFIC ISOTOPE ANALYSIS OF POLLUTANTS

Combination of a chromatrographical pretreatment to separate different compounds with continuous flow isotope ratio mass spectrometry makes it possible to measure the stable isotope composition of individual organic components in a mixture. This so-called compound-specific stable isotope analysis (CSIA) allows us to determine the isotopic composition of a single organic pollutant in groundwater. For carbon, this technique has already been applied since 1997. Recently, CSIA of deuterium (^{2}H) has also become available. In the near future, CSIA is expected to become applicable to other relevant isotopes.

CSIA enables us to follow the isotopic composition of a pollutant during the course of biodegradation processes (parent compound in Figure 1). Laboratory studies have shown a strong isotopic fractionation of ^{13}C to occur during reductive and oxidative degradation of many chlorinated aliphatic hydrocarbons (e.g. PCE, TCE, DCE, VC, TCA, and DCA). For the degradation of aromatic hydrocarbons (BTEX, phenols) and MTBE, a small but significant ^{13}C-fractionation has been observed. Fractionation of ^{2}H has only been measured in a limited number of studies, but promises to offer very powerful evidence for biodegradation.

A literature example of the ^{13}C- fractionation during the reductive dechlorination of trichloroethylene (TCE) and the oxidation of 1,2 dichloroethane (DCA) is given in Figure 2 below. Table 2 presents a qualitative overview of the fractionation during different degradation processes, based on fractionation factors reported in the literature (laboratory studies).

Figure 2: Fractionating effect of trichloroethene (TCE) reduction and 1,2 dichloroethane (DCA) oxidation. TCE data from Sherwood-Lollar, et al., 1999; DCA data from Hunkeler and Aravena, 2000.

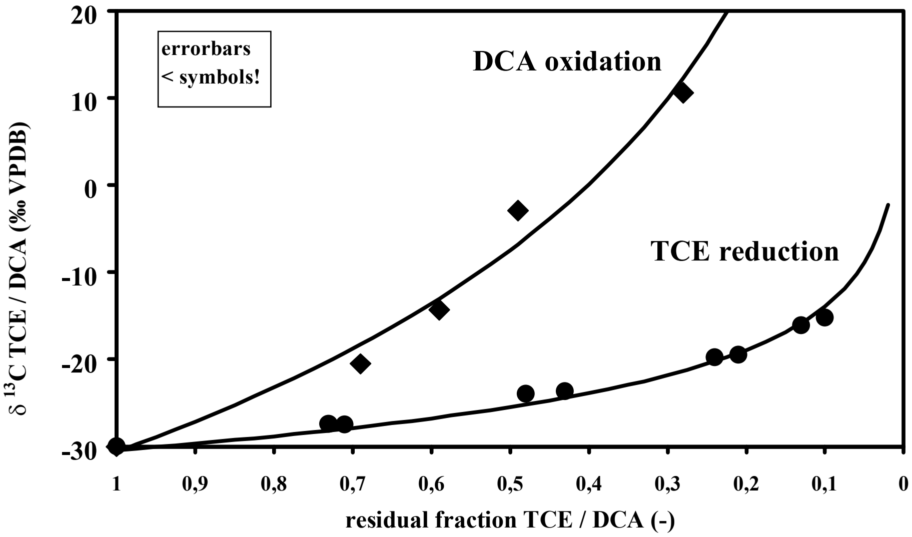


Table 3: Qualitative data on fractionation during different degradation processes.

Pollutant	Isotopic fractionation		
	Hydrogen	Carbon	Chlorine
chlorinated aliphatic hydrocarbons anaerobic			
tetrachloroethylene	n.a.	ooo	oo
trichloroethylene	oooo	ooo	oo
cis-dichloroethylene	?	ooo	?
vinyl chloride	?	oooo	?
chlorinated aliphatic hydrocarbons aerobic			
cis-dichloroethylene	?	oooo	?
dichloromethane	?	oooo	oo
aromatic hydrocarbons anaerobic			
benzene	ooo	o	n.a.
toluene	ooo	o	n.a.
ethylbenzene	ooo	o	n.a.
xylenes	?	o	n.a.
miscellaneous hydrocarbons			
MTBE (aerobic)	ooo	oo	n.a.

NOTES:

o	= limited fractionation	oo	= fractionation
ooo	= strong fractionation	oooo	= very strong fractionation
n.a.	= not applicable		

4. FIELD APPLICATION

To be able to use isotopic fractionation as evidence for biodegradation, it essential to exclude fractionation by other processes. Of the processes occurring in groundwater, only volatilization and chemical transformation may have a significant fractionating effect. Other processes, such as dissolution, transport of solute molecules and sorption, do not affect the isotopic composition of pollutants significantly. Unexpectedly, volatilization seems to reduce the ^{13}C-content of volatile organic compounds and thus has a fractionating effect contrary to that of biodegradation. Therefore, isotopic enrichment of the residual pollutant provides conclusive evidence for in situ (bio)degradation.

CSIA can be applied in two different strategies. In the first strategy, CSIA is performed on contaminated groundwater samples along the source-plume path from one sampling round. Assuming degradation to proceed with transport of pollutant from the source zone, a sort of fractionation curve as presented in Figure 1 can be constructed by plotting the isotopic composition against the pollutant concentration. It should be noted that this is not a true fractionation curve, since the disappearance of pollutant will at least be partly caused by dilution. An alternative way of presenting the data is to plot the isotopic composition against the distance from the source zone. Using the source-plume strategy, it should theoretically be possible to use a known fractionation factor to calculate the extent of biodegradation that has occurred. As yet, however, our knowledge of isotopic fractionation is too limited to allow translation of fractionation factors obtained in laboratory experiments to the field situation.

The second strategy in which CSIA can be used is to include the analysis in a monitoring series. For analytical reasons, comparison of δ-values is best done within one measurement series. This implies that time-series of isotopic data from single monitoring wells are likely to have limited value. However, the comparison of isotopic trends within different sampling rounds can be very useful and can be used to provide evidence for ongoing biodegradation and to correct for seasonal fluctuations in pollutant concentrations.

4.1 Fractionation of Chlorinated Aliphatic Hydrocarbons

As can bee seen in Table 3, the reductive and oxidative degradation of chlorinated hydrocarbons have a strong fractionating effect on both ^{13}C and ^{2}H. Therefore, CSIA is a good method for obtaining evidence for these degradation processes. However, the formation of less chlorinated intermediates during reductive dechlorination provides straightforward and conclusive evidence for degradation, diminishing the need for a more advanced technique such as isotope analysis. In complex cases with several source zones or with several different CAH present, additional evidence may be necessary. Recent field studies have shown CSIA of ^{13}C in PCE and TCE to be an effective characterization method (Sherwood Lollar et al. 2001).

4.2 Fractionation of Aromatic Hydrocarbons

With traditional techniques, it is very hard to obtain evidence for the (an)aerobic degradation of individual aromatic hydrocarbons in a mixture. Therefore, CSIA offers unique possibilities for aromatic hydrocarbons.

The source-plume strategy described above was applied in a recent research project at the site of Dow Benelux NV, Terneuzen, and The Netherlands. In this study, CSIA of both ^{13}C and ^{2}H have been used to investigate the natural attenuation of a contamination with benzene and ethylbenzene in an anaerobic aquifer (Mancini et al., 2001). From previous groundwater investigations, including a geochemical groundwater characterization, degradation of ethylbenzene was concluded to occur. Degradation of benzene, however, could not be ascertained. The results of the CSIA study are shown in the Figures 3 and 4 below.

Figure 3: Stable isotope composition (^{13}C, ^{2}H) of ethylbenzene in samples from the source zone (■) and the contaminant plume (◆).

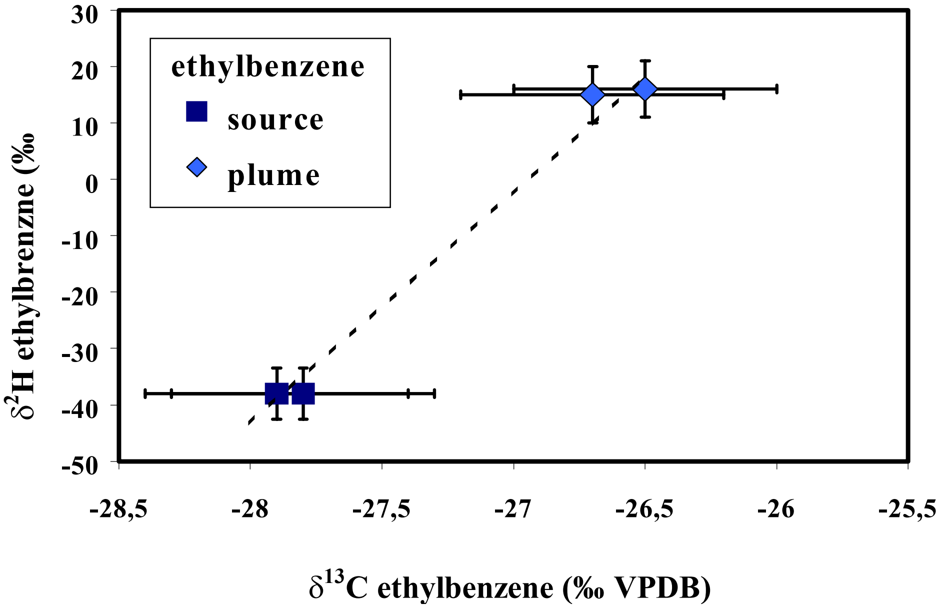
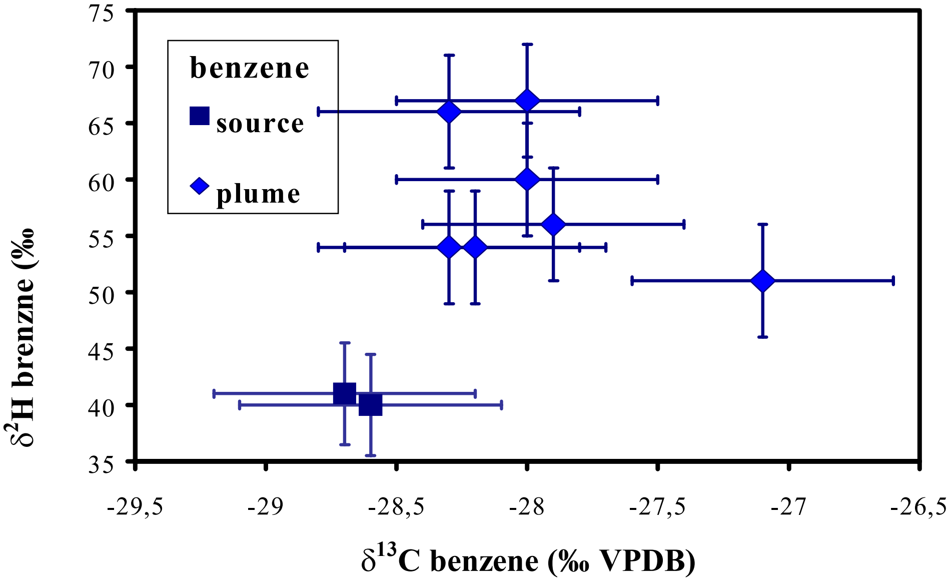


Figure 4: Stable isotope composition (^{13}C, ^{2}H) of benzene in samples from the source zone (■) and the contaminant plume (◆).



For both ethylbenzene and benzene, the data showed a small enrichment of ^{13}C (1-2‰) in samples from the plume compared to samples from the source zone. However, for the isotopic shift to become significant, a concentration reduction of approximately 80-90% was required. This need for samples in which degradation is in an advanced stage limits the applicability of ^{13}C CSIA. Therefore, the study also included CSIA of ^{2}H in ethylbenzene and benzene. The ^{2}H results showed a much stronger fractionating effect (fractionation of up to 60‰ for ethylbenzene and up to 28‰ for benzene) and provided conclusive evidence for the biodegradation of benzene, even in downgradient samples that still have relatively high pollutant concentrations. To our knowledge this is the first time field evidence for anaerobic degradation of benzene is obtained without the use of microcosm studies.

5. CONCLUSIONS

CSIA presents a new and very promising line of evidence for in-situ biodegradation. It has several advantages over existing methods in terms of specificity, conclusiveness, and cost-effectiveness. At present, CSIA is especially useful for degradation processes for which no other conclusive lines of evidence exist, such as the anaerobic degradation of benzene in a BTEX pollution. For other degradation processes, such as the reductive dechlorination of CAH, CSIA may be useful in complex situations or as an independent alternative line of evidence.

The practical application of CSIA in field studies is rather straightforward. Standard techniques can be used for groundwater sampling,, and after a simple conservation step, samples can be sent to a specialized isotope laboratory. The most crucial steps in the process are the selection of the samples and the interpretation of the results.

CSIA still has some drawbacks, such as the limited number of laboratories able to perform the analyses, the high detection limits, the rather long turnover times and the relatively high analysis costs (especially for elements other than carbon) However, compound-specific isotope analysis is a rapidly developing technique, and it is expected that most of these drawbacks will be overcome soon.

6. AKNOWLEDGEMENTS

The results presented here are obtained in a research project that was partly financed by the Dutch Soil Research Program (SKB), by Dow Benelux nv, and by the Dutch provinces of Drenthe, Gelderland, and Noord-Brabant

Compound-specific isotope analyses of ^{13}C and ^{2}H for the study a the site of Dow Benelux NV, Terneuzen have been performed by Silvia Mancini form the Stable Isotope Laboratory of the University of Toronto.

7. REFERENCES

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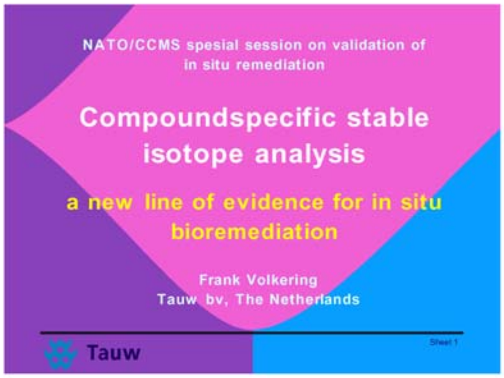
8. PRESENTATION VISUALS ~ *presented by Frank Volkering*

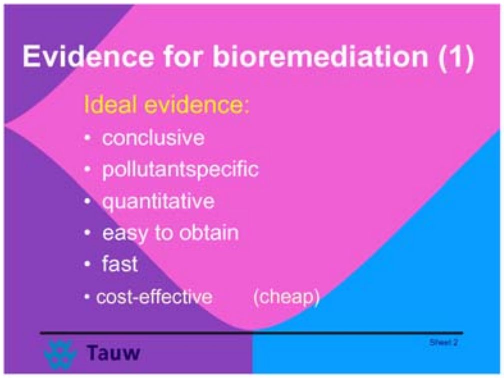


NATO/CCMS spesial session on validation of in situ remediation

Compoundspecific stable isotope analysis

a new line of evidence for in situ bioremediation

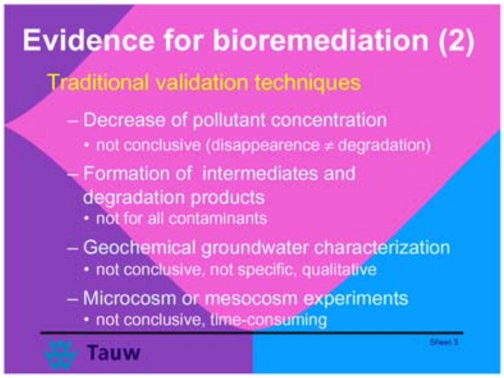
Frank Volkering
Tauw bv, The Netherlands



Evidence for bioremediation (1)

Ideal evidence:

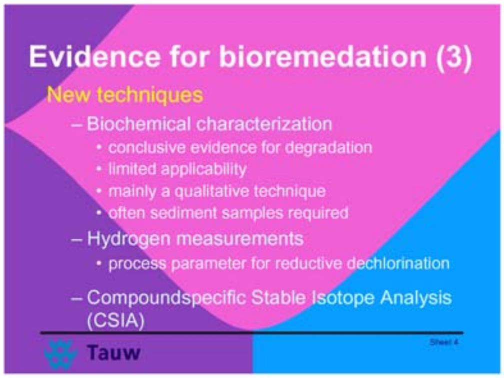
- conclusive
- pollutantspecific
- quantitative
- easy to obtain
- fast
- cost-effective (cheap)



Evidence for bioremediation (2)

Traditional validation techniques

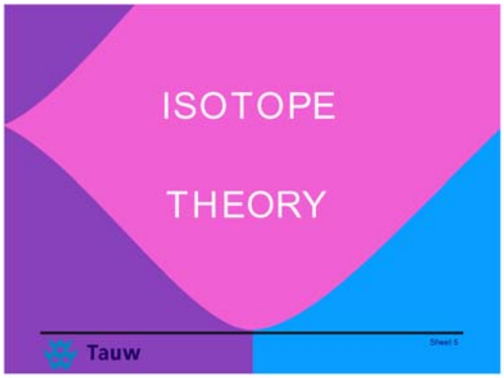
- Decrease of pollutant concentration
  - not conclusive (disappearence ≠ degradation)
- Formation of intermediates and degradation products
  - not for all contaminants
- Geochemical groundwater characterization
  - not conclusive, not specific, qualitative
- Microcosm or mesocosm experiments
  - not conclusive, time-consuming



Evidence for bioremedation (3)

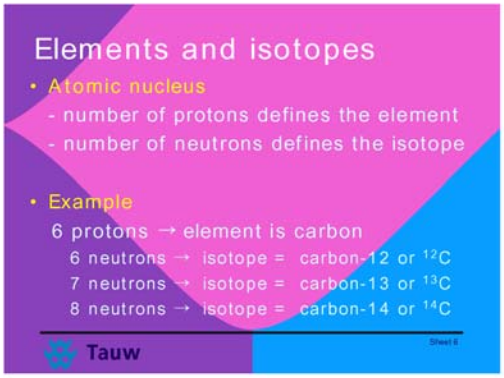
New techniques

- Biochemical characterization
  - conclusive evidence for degradation
  - limited applicability
  - mainly a qualitative technique
  - often sediment samples required
- Hydrogen measurements
  - process parameter for reductive dechlorination
- Compoundspecific Stable Isotope Analysis (CSIA)



ISOTOPE

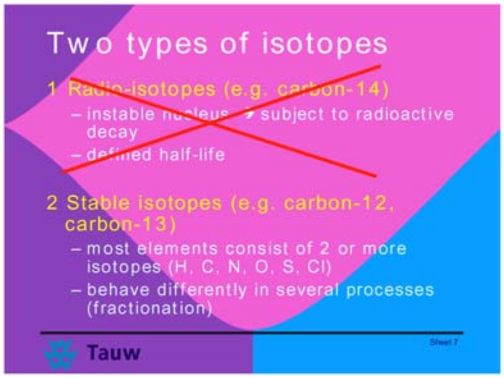
THEORY



Elements and isotopes

- Atomic nucleus
  - number of protons defines the element
  - number of neutrons defines the isotope
- Example

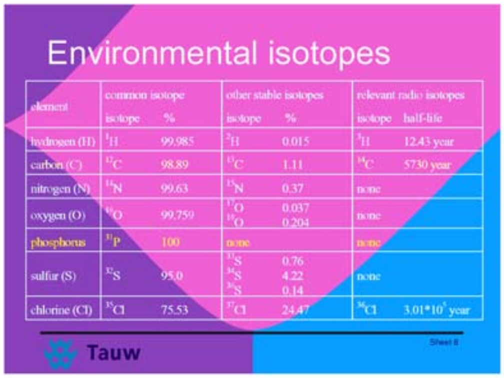
6 protons → element is carbon
6 neutrons → isotope = carbon-12 or ^{12}C
7 neutrons → isotope = carbon-13 or ^{13}C
8 neutrons → isotope = carbon-14 or ^{14}C



Two types of isotopes

1 ~~Radio-isotopes (e.g. carbon-14)~~
- ~~instable nucleus → subject to radioactive decay~~
- ~~defined half-life~~

2 Stable isotopes (e.g. carbon-12, carbon-13)
- most elements consist of 2 or more isotopes (H, C, N, O, S, Cl)
- behave differently in several processes (fractionation)

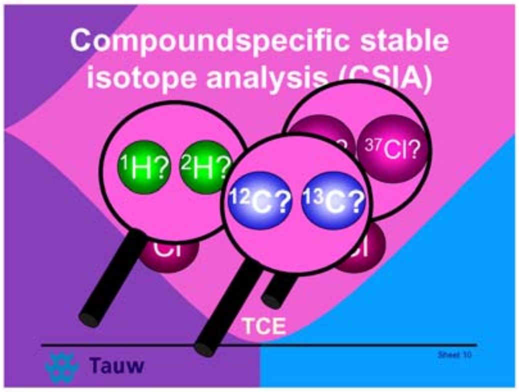


Environmental isotopes

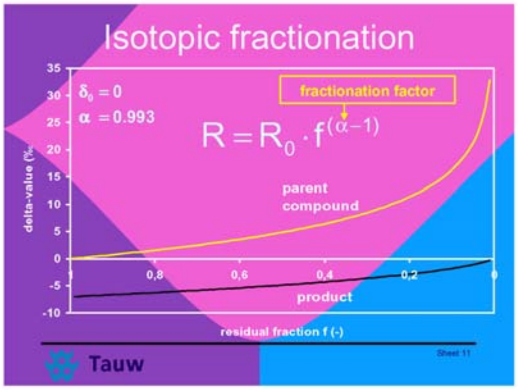
element	common isotope		other stable isotopes		relevant radio isotopes	
	isotope	%	isotope	%	isotope	half-life
hydrogen (H)	^{1}H	99.985	^{2}H	0.015	^{3}H	12.43 year
carbon (C)	^{12}C	98.89	^{13}C	1.11	^{14}C	5730 year
nitrogen (N)	^{14}N	99.63	^{15}N	0.37	none	
oxygen (O)	^{16}O	99.759	^{17}O ^{18}O	0.037 0.204	none	
phosphorus	^{31}P	100	none		none	
sulfur (S)	^{32}S	95.0	^{33}S ^{34}S ^{36}S	0.76 4.22 0.14	none	
chlorine (Cl)	^{35}Cl	75.53	^{37}Cl	24.47	^{36}Cl	$3.01*10^{5}$ year

Environmental isotopes

element	common isotope		other stable isotopes		relevant radio isotopes	
	isotope	%	isotope	%	isotope	half-life
hydrogen (H)	^{1}H	99.985	^{2}H	0.015	^{3}H	12.43 year
carbon (C)	^{12}C	98.89	^{13}C	1.11	^{14}C	5730 year
nitrogen (N)	^{14}N	99.63	^{15}N	0.37	none	
oxygen (O)	^{16}O	99.759	^{17}O ^{18}O	0.037 0.204	none	
phosphorus	^{31}P	100	none		none	
sulfur (S)	^{32}S	95.0	^{33}S ^{34}S ^{36}S	0.76 4.22 0.14	none	
chlorine (Cl)	^{35}Cl	75.53	^{37}Cl	24.47	^{36}Cl	$3.01*10^{5}$ year



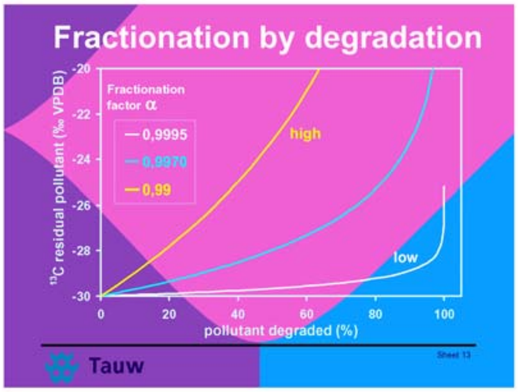
Compoundspecific stable isotope analysis (CSIA)



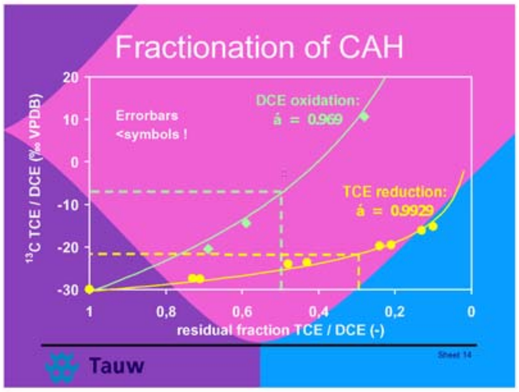
Isotopic fractionation

Fractionation of residual pollutant

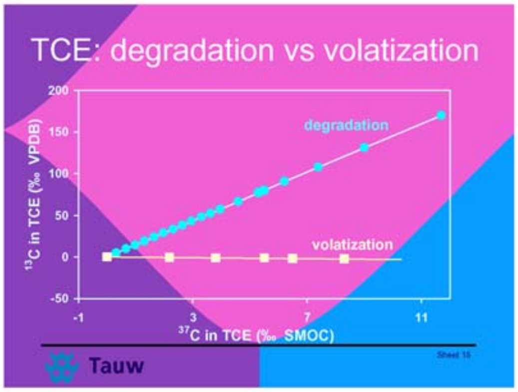
- preferential degradation lighter isotope ➡ residual pollutant enriched in heavy isotope
- applicable for:
  - chlorinated aliphatic hydrocarbons
  - aromatic hydrocarbons (BTEX)
  - MTBE
  - etc.



Fractionation by degradation

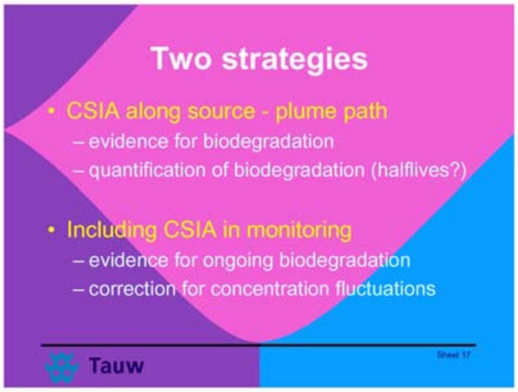


Fractionation of CAH



TCE: degradation vs volatization

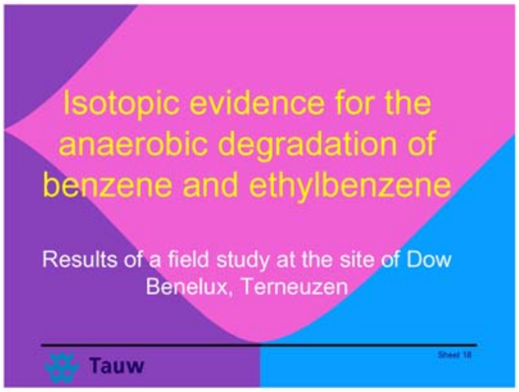
FIELD APPLICATION



Two strategies

- CSIA along source - plume path
  - evidence for biodegradation
  - quantification of biodegradation (halflives?)
- Including CSIA in monitoring
  - evidence for ongoing biodegradation
  - correction for concentration fluctuations

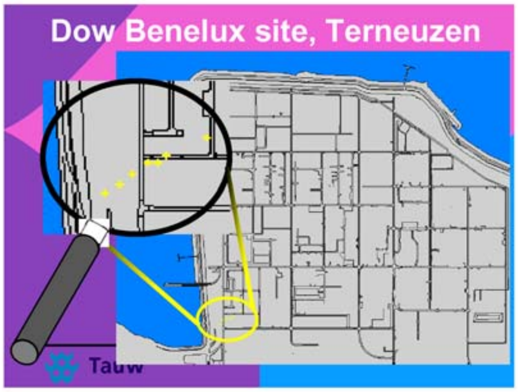
Tauw



Isotopic evidence for the anaerobic degradation of benzene and ethylbenzene

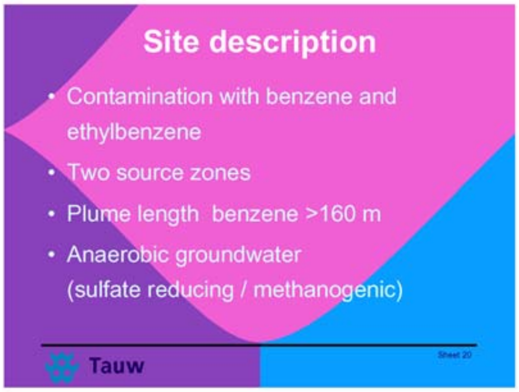
Results of a field study at the site of Dow Benelux, Terneuzen

Tauw



Dow Benelux site, Terneuzen

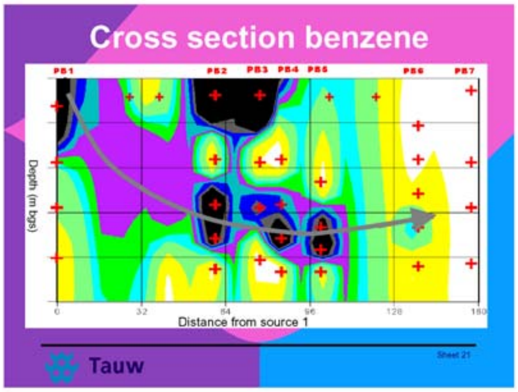
Tauw



Site description

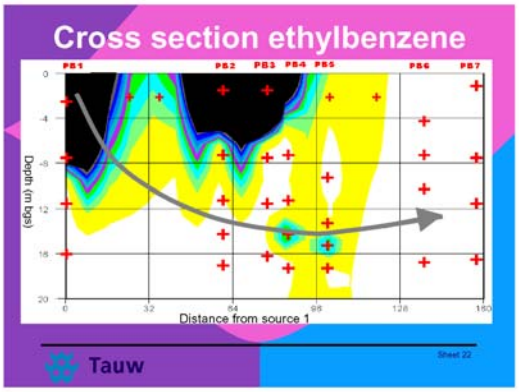
- Contamination with benzene and ethylbenzene
- Two source zones
- Plume length benzene >160 m
- Anaerobic groundwater (sulfate reducing / methanogenic)

Tauw



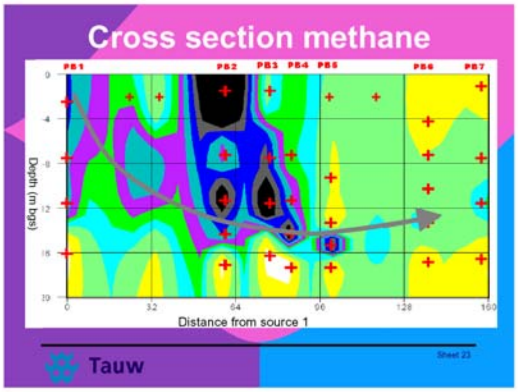
Cross section benzene

Tauw



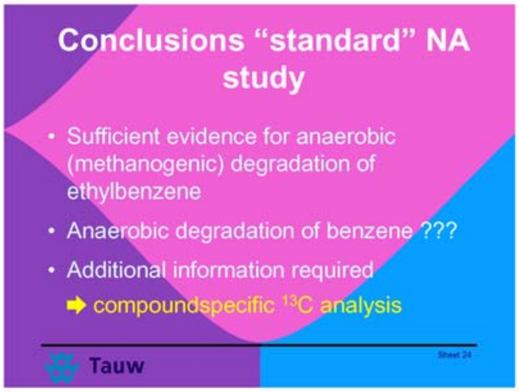
Cross section ethylbenzene

Tauw



Cross section methane

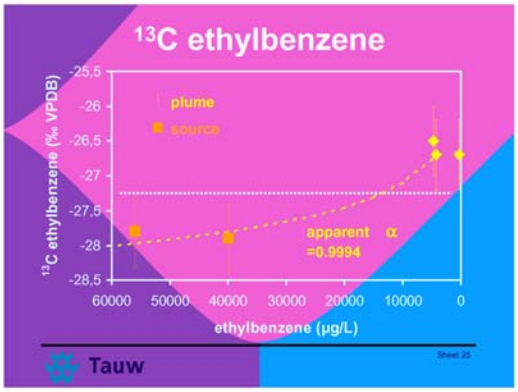
Tauw



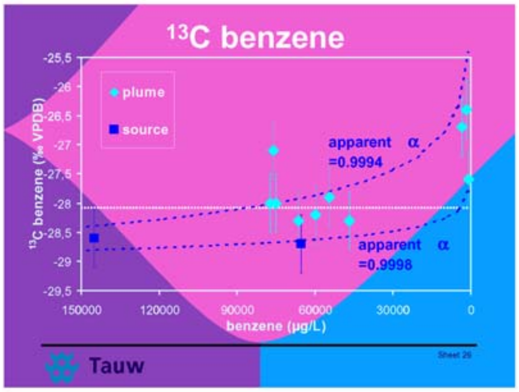
Conclusions “standard” NA study

- Sufficient evidence for anaerobic (methanogenic) degradation of ethylbenzene
- Anaerobic degradation of benzene ???
- Additional information required
  ➡ compoundspecific ^{13}C analysis

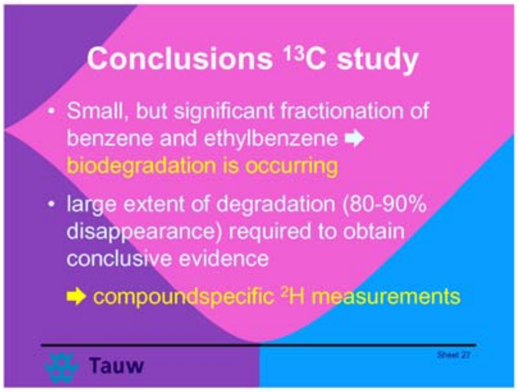
Tauw



^{13}C ethylbenzene



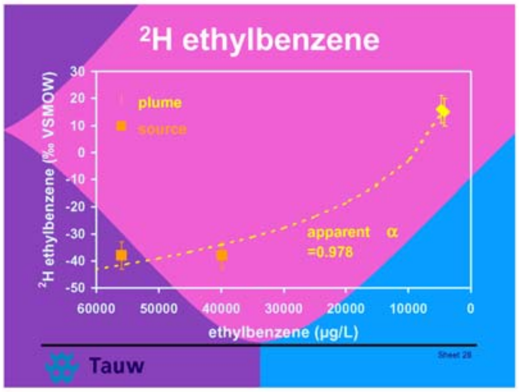
^{13}C benzene



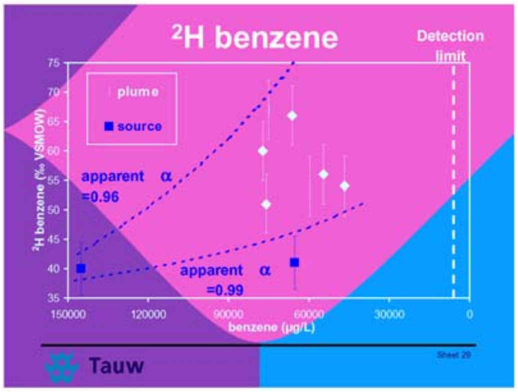
Conclusions ^{13}C study

- Small, but significant fractionation of benzene and ethylbenzene ➡ biodegradation is occurring
- large extent of degradation (80-90% disappearance) required to obtain conclusive evidence

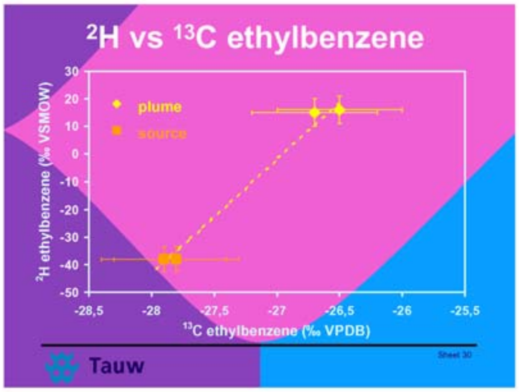
➡ compoundspecific ^{2}H measurements



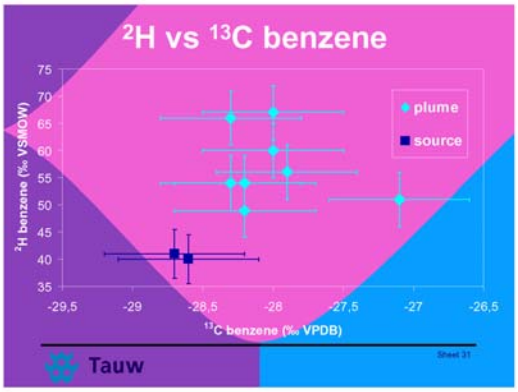
^{2}H ethylbenzene



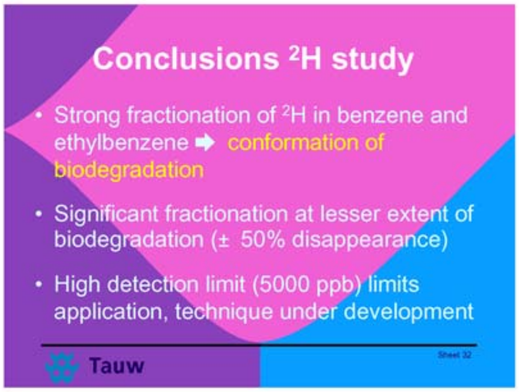
^{2}H benzene



^{2}H vs ^{13}C ethylbenzene

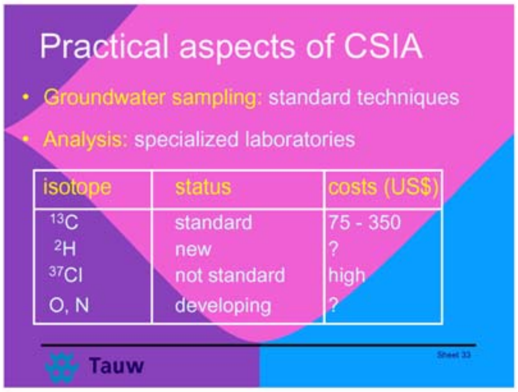


^{2}H vs ^{13}C benzene



Conclusions ^{2}H study

- Strong fractionation of ^{2}H in benzene and ethylbenzene ➡ conformation of biodegradation
- Significant fractionation at lesser extent of biodegradation (± 50% disappearance)
- High detection limit (5000 ppb) limits application, technique under development

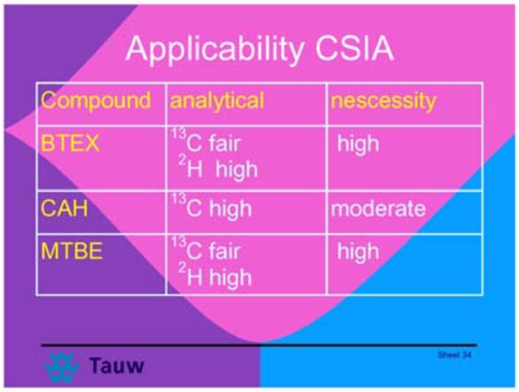


Practical aspects of CSIA

- Groundwater sampling: standard techniques
- Analysis: specialized laboratories

isotope	status	costs (US$)
^{13}C	standard	75 - 350
^{2}H	new	?
^{37}Cl	not standard	high
O, N	developing	?

Tauw Sheet 33



Applicability CSIA

Compound	analytical	nescessity
BTEX	^{13}C fair ^{2}H high	high
CAH	^{13}C high	moderate
MTBE	^{13}C fair ^{2}H high	high

Tauw Sheet 34

Acknowledgements

- Rik Jonker, Boris van Breukelen, Koos Groen (Vrije Universitieit Amsterdam)
- Silvia Mancini, Barbara Sherwood-Lollar (University of Toronto)
- SKB for funding

Tauw Sheet 35

Interested in isotopes?

Attend the symposium

"Natural isotope analysis in soil and groundwater pollution research"

October 10, Amsterdam

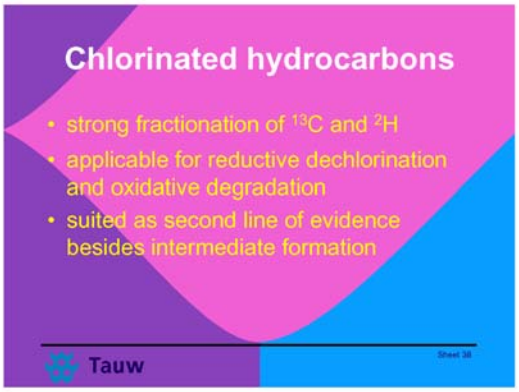
Tauw Sheet 36

For everything you always wanted to know about isotopes and more:

State-of-the-art on isotope analysis

(available soon)

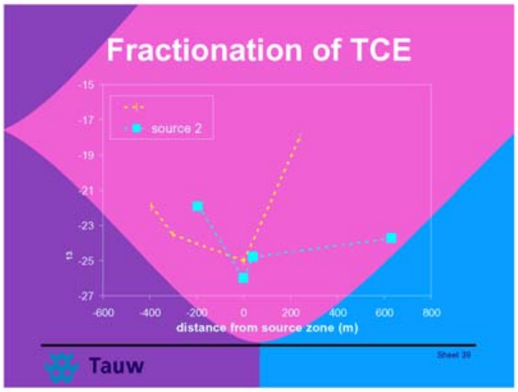
Tauw Sheet 37



Chlorinated hydrocarbons

- strong fractionation of ^{13}C and ^{2}H
- applicable for reductive dechlorination and oxidative degradation
- suited as second line of evidence besides intermediate formation

Tauw Sheet 38



Fractionation of TCE

Tauw Sheet 39

SITE-SPECIFIC VERIFICATION OF IN SITU CHEMICAL OXIDATION

Eric Hood[1], Robert L. Siegrist[2] and Neil Thomson[3]

1. INTRODUCTION

During the 1990's, in situ chemical oxidation (ISCO) emerged as a promising method for remediation of contaminated sites. As a site remediation technology, the goal of ISCO has been to destroy target organic chemicals present in soil and groundwater systems and thereby reduce the mass, mobility, and/or toxicity of contamination. Fundamental and applied laboratory research has elucidated many aspects of the reaction stoichiometry, degradation pathways, and kinetics for common organic chemicals in aqueous systems as well as the effects of temperature, pH, and matrix composition. Laboratory research has also explored the transport processes affecting oxidant delivery and dispersal in a porous medium like soil or aquifer sediments. Pilot-scale demonstrations and full-scale applications have attempted *in situ* treatment of aqueous and sorbed phase levels of organic contaminants, and to a lesser degree, dense nonaqueous phase liquids (DNAPLs). Oxidant delivery and distribution in the subsurface has been accomplished using injection probes, deep soil mixing, hydraulic fracturing, and vertical or horizontal groundwater wells. The literature now contains numerous research articles and technical reports, as well as several recent guidance documents that describe ISCO using hydrogen peroxide (or Fenton's reagent), ozone, and permanganate for treatment of organics in soil and ground water (e.g., USEPA 1998b, ESTCP 1999, Yin and Allen 1999, Siegrist *et al.* 2000, Siegrist *et al.* 2001).

Chlorinated solvents (as DNAPLs) are frequently released into the subsurface environment from industrial sources through both intentional disposal, and accidental leaks and spills. The United States Environmental Protection Agency (USEPA) reported in 1997 that DNAPLs may be present at up to 60% of the Superfund National Priorities List (NPL) sites (USEPA 1997). Of the 622 NPL sites reported in 1996, the chlorinated solvents trichloroethene (TCE) and perchloroethene (PCE) were detected in groundwater at 336 and 167 of these sites, respectively (USEPA 1998a). TCE and PCE are of particular concern because of the potential risks that they pose to human health; accordingly, the concentrations of these compounds have stringent regulatory levels.

At many sites, attempts to manage groundwater contamination associated with the presence of DNAPLs have met with limited success. The depth and areal distribution of DNAPLs often precludes any attempts at excavation while the effectiveness of pump-and-treat is limited by the low solubility of these contaminants, the weakness of dispersive mixing processes, and mass transfer limitations from the DNAPL into the dissolved phase. Increasingly, source removal technologies such as in situ chemical oxidation are being aggressively employed to remove DNAPL mass and/or reduce the concentration of the target contaminants below regulatory criteria with little knowledge of the expected performance of this technology. Only a limited number of controlled field trials that provide an indication of ISCO performance at DNAPL sites have been reported in the literature.

Several oxidizing agents are commonly used for ISCO including Fenton's reagent (Fe^{2+}/H_2O_2), and permanganate (MnO_4^-) (USEPA 1998b, Gates-Anderson *et al.* 2001, Siegrist *et al.* 2001). Fenton's reagent and permanganate can rapidly mineralize both TCE and PCE to inorganic products including chloride and carbon dioxide. The rapid degradation reactions enhance the removal of the DNAPL by increasing the concentration gradient that drives the rate of mass transfer. However, this technology is limited by the ability to advectively deliver the active oxidant (hydroxyl radicals in the case of Fenton's reagent) to the DNAPL in the subsurface. Oxidant delivery is complicated by both geologic heterogeneity and secondary oxidation reactions between the reagent and the reduced organic and inorganic phases within the natural aquifer matrix.

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[2] Colorado School of Mines, Golden, Colorado, USA. Email: siegrist@mines.edu
[3] University of Waterloo, Waterloo, Ontario, Canada.

A number of factors can limit DNAPL removal by ISCO. While the DNAPL mass present in regions of the aquifer where oxidant delivery is dominated by advection may be readily removed, the rate of mass transfer from DNAPL mass in stagnant zones is limited by diffusion of the contaminant and oxidant through the water surrounding the DNAPL. Oxidant delivery though diffusion and the degradation of TCE in low permeability zones has been demonstrated (Siegrist *et al.* 1999, Struse *et al.* 2001). However, oxidant delivery by diffusive transport alone is less likely to result in a significant mass transfer and degradation enhancement (Hood and Thomson 2000).

2. REMEDIATION EFFECTIVENESS

As observed in a controlled field trial evaluating the performance of ISCO using permanganate (Schnarr *et al.* 1998) the most optimistic result is complete DNAPL removal. Since the DNAPL resulting in the formation of a groundwater plume is removed, the concentration of the contaminant in groundwater will decrease over time and eventually should reach background levels.

The most likely outcome of an ISCO treatment approach at a DNAPL site, is partial DNAPL mass removal accompanied by a reduction in the average concentration of DNAPL organics in the groundwater plume. In the short-term, residual oxidant (e.g., permanganate) in the treatment zone following the period of active oxidant injection will continue to degrade dissolved phase compounds to non-detectable concentrations. However, as oxidant is flushed from the treatment zone by groundwater flow and/or reacts with naturally occurring reductants within the soil matrix, the DNAPL organic concentrations may increase, but remain at a level that is less than pre-treatment concentrations.

3. PERFORMANCE INDICATORS

Various criteria may be used to assess the performance of in situ remediation technologies such as ISCO. These performance indicators are described below, particularly as they apply to DNAPL sites.

3.1 Contaminant Mass

The total mass of DNAPL present at a site may be estimated though interpolation and extrapolation of the spatial distribution of contaminant concentrations in soil; however, this approach is complicated by the high degree of heterogeneity frequently observed in the distribution of DNAPL in natural geologic environments. The number of samples required to adequately estimate the DNAPL mass is sufficiently large that the costs of sample collection and analysis are prohibitive.

3.2 Groundwater Concentration

The most common performance assessment approach is the comparison of pre- and post-treatment volatile organic compound (VOC) concentrations in a network monitoring wells. In comparison to DNAPL mass, this approach more closely represents the exposure risks typically associated with groundwater contamination (i.e., direct ingestion of groundwater containing VOCs). As previously discussed, VOC concentrations in the monitoring wells measured immediately following the oxidant injection period are likely to be biased low due to the presence of residual oxidant in the treated zone. Further, the presence of any amount of DNAPL following ISCO will result in groundwater concentrations exceeding regulatory criteria since the solubility of these compounds is greater than the criteria by several orders of magnitude. As a result, monitoring wells located immediately adjacent to the remaining DNAPL may provide results that are biased high and are not reflective of the overall impact of ISCO treatment.

A number of potential limitations to this performance assessment approach should be considered during the design of a post-treatment monitoring program. Since residual oxidant will tend to negatively bias the post-treatment estimate of the average plume VOC concentrations, monitoring efforts should emphasize characterizing the long-term, steady-state VOC concentration in the monitoring network. Since the DNAPL remaining following treatment will result in local zones of high VOC concentrations that may positively bias the average post-treatment plume concentration, the number of sampling points must be sufficiently large to reflect a representative spatially averaged VOC concentration.

3.3 Groundwater Flux

The ideal performance assessment criterion is the rate of mass removal (expressed as a flux multiplied by the DNAPL:water interfacial surface area) from the DNAPL source into the groundwater plume. At steady-state, this rate (termed the plume load with units of $M\ T^{-1}$), is equivalent to 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. The plume load is distinguished from plume flux that is the rate of mass flow per unit area with units of $M\ T^{-1}\ L^{-2}$. In some sense, the collection of a sufficiently large number of samples randomly located within the groundwater plume will provide an adequate data set for determination of plume load; however, more cost-effective approaches may be employed to collect plume load data. In the simplest approach, steady-state VOC concentration data may be collected from an extraction well pumped at a continuous rate that is sufficient to create a steady-state capture zone that encompasses the entire groundwater plume. Using the flow rate and average VOC concentration, the plume load may be directly calculated. While the time required to achieve a steady-state VOC concentration in the extraction well is a potential constraint, the ease of data collection makes this a potentially attractive approach. Alternatively, plume load may be determined using an approach made feasible by the advent of inexpensive multilevel sampling piezometers and drivepoint profiling tools. Using a closely spaced transect of groundwater samples from a plane intersecting the groundwater plume and oriented at a right angle to the direction of groundwater flow, the plume load may be calculated using an estimate of the Darcy velocity and spatial interpolation of the concentration distribution across the sampling transect. While requiring complex data interpolation and relatively high sample collection and analysis costs, this approach is rapid in comparison to continuous pumping from an extraction well.

4. FIELD APPLICATIONS

4.1 Features and Performance Observations

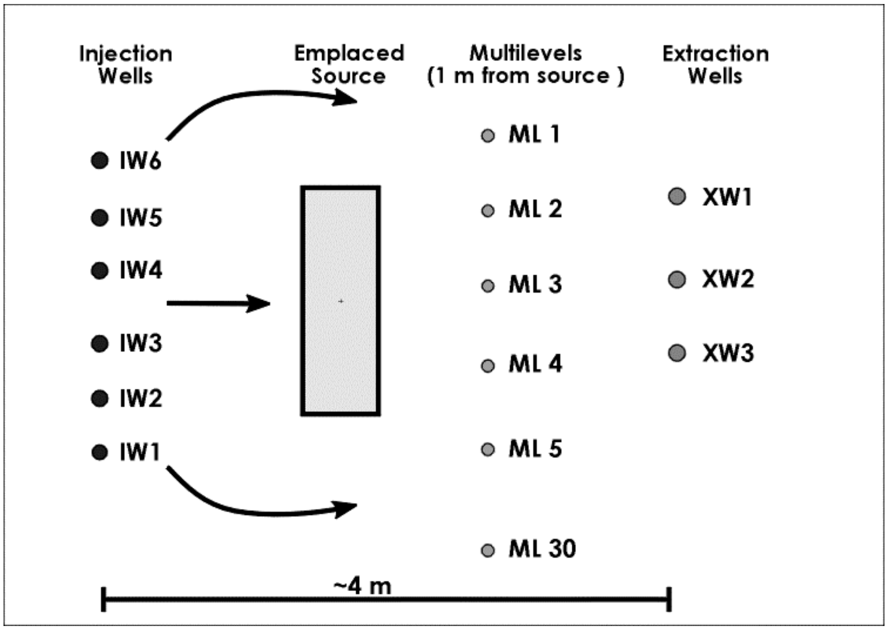
Field applications of ISCO are growing rapidly in the U.S. and abroad as highlighted in recent articles and reports (e.g., Jerome *et al.* 1997, Schnarr *et al.* 1998, ESTCP 1999, Lowe *et al.* 2001, USEPA 1998b, Siegrist *et al.* 1999, Yin and Allen 1999, Siegrist *et al.* 2001). In general, ISCO systems have been shown to be capable of achieving high treatment efficiencies (e.g., >90 to 99%) for common COCs such as chlorinated ethenes (e.g., TCE, PCE) and aromatic compounds (e.g., benzene, phenols, naphthalene), with very fast reaction rates (e.g., >90% destruction in minutes). Field applications have demonstrated that ISCO can achieve destruction of COCs and achieve clean-up goals at some contaminated sites However, field-scale applications can also have uncertain or poor in situ treatment performance. Uncertain or poor performance is often attributed to poor uniformity of oxidant delivery caused by low permeability zones and site heterogeneity, excessive oxidant consumption by natural subsurface materials, presence of large DNAPL masses, and incomplete degradation. Assessment of treatment efficiency is commonly based on sampling and analysis of soil and/or groundwater to enable comparison of post-treatment concentrations to those present prior to ISCO. These approaches are fraught with problems due to heterogeneities in the subsurface and the limited number of samples from which inferences are to be made. In addition, simply characterizing the treated region may not provide the proper information regarding performance as it does not specifically address changes in contaminant flux that may result from partial cleanup of a source zone feeding a plume. The following case study illustrates alternative performance assessment approaches as evaluated during a field trial.

4.2 Case Study Illustrating Performance Assessment Approaches

A pilot demonstration of ISCO using permanganate was conducted in a shallow sandy aquifer (Hood *et al.* 2000). The DNAPL source zone consisted of mixture of TCE and PCE as a residual; the dimensions of the source zone were 1.5 m x 1.0 m x 0.5 m. The groundwater monitoring and oxidant delivery system consisted of six injection and three extraction wells, along with a fence of multilevel piezometers containing sample points spaced ~0.5 m horizontally and 0.2 m vertically (Figure 1). The DNAPL source was flushed with potassium permanganate at a concentration of 8 g/L for 480 days.

The performance assessment approach at the demonstration site utilized a comparison of the three indicators previously described (DNAPL mass, peak plume concentration, and plume load). DNAPL mass reduction was based on pre-treatment DNAPL mass estimated using a modeling approach and post-treatment soil sampling (>300 samples). Peak concentrations in the pre- and post-treatment groundwater plume were measured as the maximum concentration detected from the multilevel transect. The spatial distribution of VOC concentrations in the multilevel transect was used to calculate pre- and post-treatment plume loads. In addition, the steady-state VOC concentrations in the extraction wells were used as a comparative plume load measurement.

Figure 1: Plan view of test site, including injection wells (IW), multilevel piezometers (ML), and extraction wells (XW). The shaded box represents the location of the DNAPL source zone.



The results of the performance assessment are summarized in Table 1. During post-treatment soil sampling, DNAPL was not detected in any of the soil samples and only a few detections of sorbed TCE or PCE were observed, suggesting that the DNAPL was entirely removed. In contrast, the peak plume concentrations of both TCE and PCE observed in the multilevel transect located immediately down-gradient of the source zone decreased by factors of only 70 and 2, respectively, relative to pre-treatment conditions. This relatively minor decrease was consistent with a positive bias in concentration resulting from the presence of DNAPL, in spite of the detailed soil sampling efforts suggesting the DNAPL was not present. In contrast to these contradictory results, the observed reductions in the TCE and PCE plume loads (decreased from the pre-treatment plume loads by approximate factors of 100 and 10, respectively) measured using both the transect and continuous extraction methods were consistent between measurement methods.

Table 1: Summary of chemical oxidation performance assessment data.

Performance Indicator	Pre-treatment (TCE/PCE)	Post-treatment (TCE/PCE)
DNAPL Mass (kg)	1.6 / 9.0	ND / ND
Peak Concentration (ug/L)	142 / 61	2 / 31
Transect Plume Load (mg/day)	836 / 854	7 / 98
Extraction Plume Load (mg/day)	2,099 / 2,218	17 / 222

ND = non-detectable.

5. SUMMARY

Short-term monitoring programs using a sparse monitoring network to assess the impact of in situ chemical oxidation on remediation performance can be inadequate and misleading. This is particularly true for DNAPL sources of groundwater contamination, where such approaches can be subject to either negative or positive bias. Design of such programs should focus on determining the post-treatment reduction achieved over a sufficiently long monitoring period so that residual oxidant does not interfere with the observed COC concentrations. In addition, assessments should rely on steady-state reductions observed in multiple monitoring wells within the former extent of the groundwater plume rather than reductions observed in a single monitoring point that could be easily biased. Plume flux is a valuable performance assessment tool, although its applicability at some industrial sites may be limited by the time and cost required to complete these measurements using rigorous methodologies.

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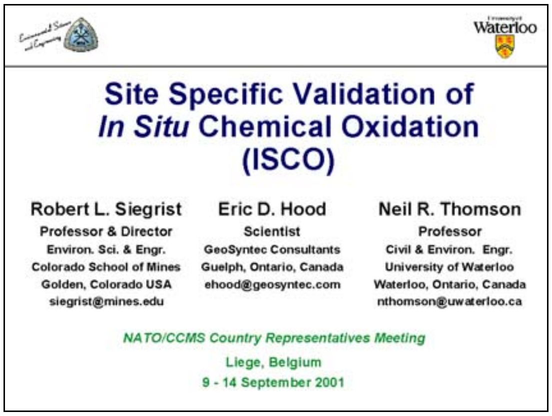
7. PRESENTATION VISUALS ~ *presented by Robert L. Siegrist*



Site Specific Validation of *In Situ* Chemical Oxidation (ISCO)

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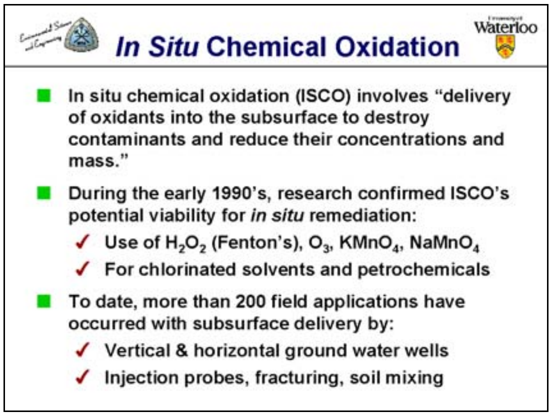
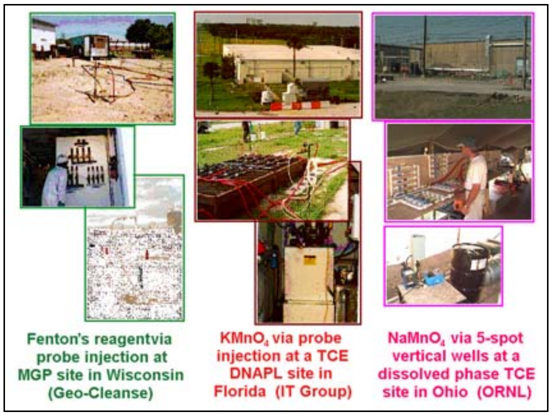
NATO/CCMS Country Representatives Meeting
Liege, Belgium
9 - 14 September 2001



In Situ Chemical Oxidation

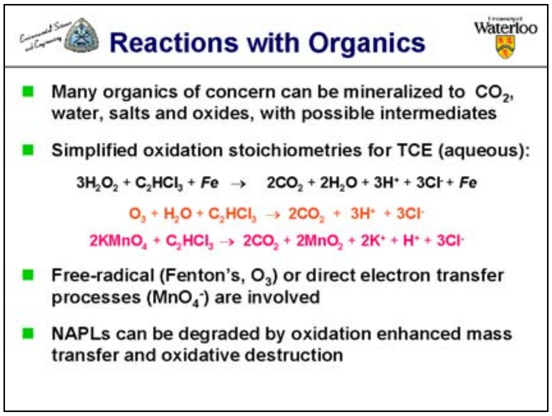
- In situ chemical oxidation (ISCO) involves "delivery of oxidants into the subsurface to destroy contaminants and reduce their concentrations and mass."
- During the early 1990's, research confirmed ISCO's potential viability for *in situ* remediation:
  - ✓ Use of H_2O_2 (Fenton's), O_3, $KMnO_4$, $NaMnO_4$
  - ✓ For chlorinated solvents and petrochemicals
- To date, more than 200 field applications have occurred with subsurface delivery by:
  - ✓ Vertical & horizontal ground water wells
  - ✓ Injection probes, fracturing, soil mixing



Fenton's reagentvia probe injection at MGP site in Wisconsin (Geo-Cleanse)

$KMnO_4$ via probe injection at a TCE DNAPL site in Florida (IT Group)

$NaMnO_4$ via 5-spot vertical wells at a dissolved phase TCE site in Ohio (ORNL)



Reactions with Organics

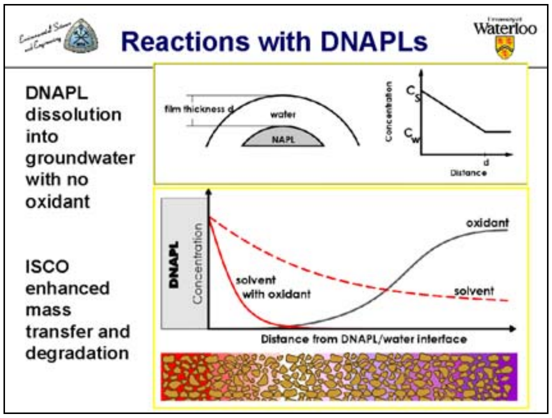
- Many organics of concern can be mineralized to CO_2, water, salts and oxides, with possible intermediates
- Simplified oxidation stoichiometries for TCE (aqueous):

$$3H_2O_2 + C_2HCl_3 + Fe \rightarrow 2CO_2 + 2H_2O + 3H^+ + 3Cl^- + Fe$$

$$O_3 + H_2O + C_2HCl_3 \rightarrow 2CO_2 + 3H^+ + 3Cl^-$$

$$2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_2 + 2K^+ + H^+ + 3Cl^-$$

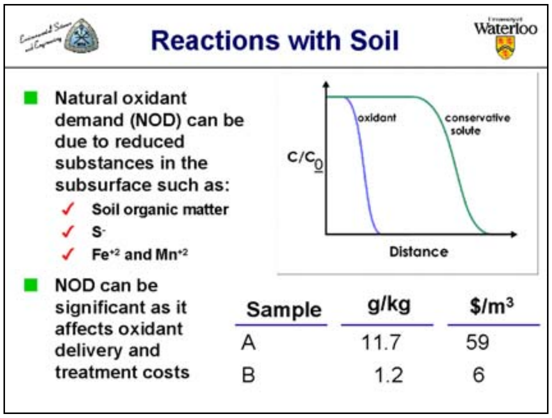
- Free-radical (Fenton's, O_3) or direct electron transfer processes (MnO_4^-) are involved
- NAPLs can be degraded by oxidation enhanced mass transfer and oxidative destruction



Reactions with DNAPLs

DNAPL dissolution into groundwater with no oxidant

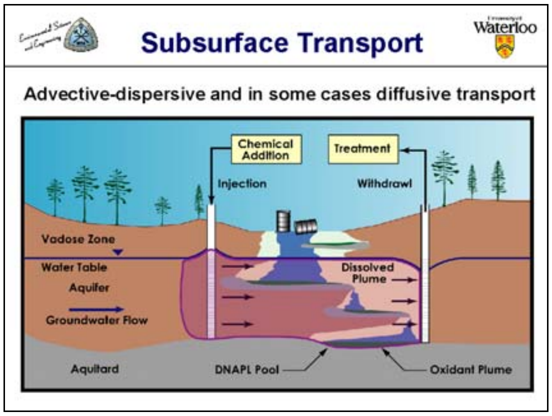
ISCO enhanced mass transfer and degradation



Reactions with Soil

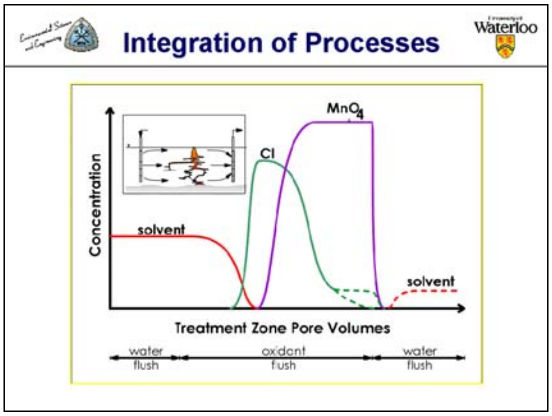
- Natural oxidant demand (NOD) can be due to reduced substances in the subsurface such as:
  - ✓ Soil organic matter
  - ✓ S^-
  - ✓ Fe^{+2} and Mn^{+2}
- NOD can be significant as it affects oxidant delivery and treatment costs

Sample	g/kg	$/m³
A	11.7	59
B	1.2	6



Subsurface Transport

Advective-dispersive and in some cases diffusive transport



Integration of Processes

Site-Specific Validation

- Validation of ISCO performance goal achievement at a specific site can include:
  - Soil and/or groundwater sampling to define:
    - Concentrations in soil and/or groundwater ($M L^{-3}$)
    - Contaminant mass before and after ISCO (M)
  - Plume mass flux ($M T^{-1} L^{-1}$) or plume load ($M T^{-1}$)
  - Estimates of total mass destruction (%)
  - Toxicity assays (via bioassay methods)
  - Other measures of ISCO function
    - Subsurface geophysical mapping
    - Soil/groundwater reaction byproducts (Cl^-)
    - Soil/groundwater chemistry (oxidant, pH, Eh, D.O.,...)

Site-Specific Validation

- Validation of ISCO performance goal achievement at a specific site normally can not include:
  - Measurements of mass recovered as in mass recovery based methods
  - At present, the use of multicomponent partitioning tracers is still under study

Examples

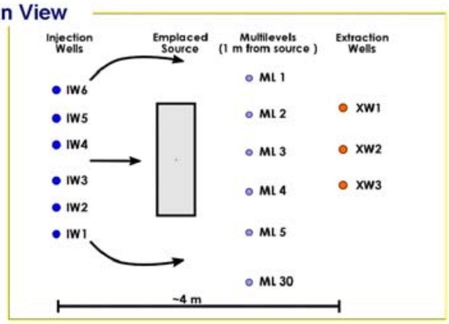
➊ Field Trial in Canada

Application Description

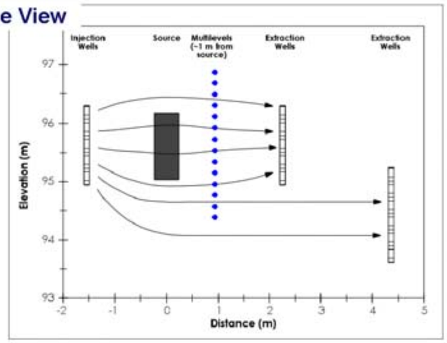
- ✓ Well-characterized, homogeneous sand aquifer
- ✓ Residual DNAPL source zone containing TCE and PCE
- ✓ Highly instrumented
- ✓ ISCO using $KMnO_4$ in a horizontal flushing mode

Hood, 2000; Hood and Thomson, 2001

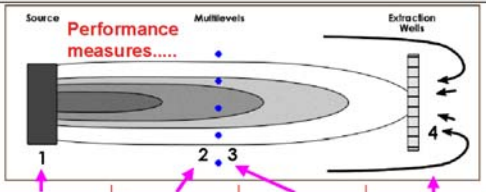
Plan View



Profile View



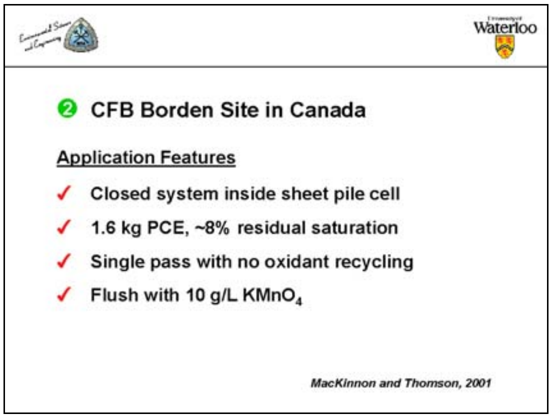
Operation mode	Objectives	Monitoring
Pre-oxidation water flush (75 days)	-characterize flow -plume load	VOCs, Br^-
Oxidant flush (484+177 days)	-remove DNAPL -monitor performance	Cl^-, $KMnO_4$
Post-oxidation water flush (119 days)	-residence time -plume load	VOCs, Br^-
Source coring	-mass of DNAPL, MnO_2	VOCs, Mn



1. DNAPL mass destruction	2. Peak concentration	3. Transect plume load	4. Extraction plume load
difficult to measure	spatial variability	many samples, velocity?	req. 100% capture

Results

Measure	Pre-ISCO (TCE or PCE)	Post-ISCO (TCE or PCE)
DNAPL mass (kg)	1.6 / 9.0	ND / ND
Peak concentration (ug/L)	142 / 61	2 / 31
Transect plume load (mg/d)	836 / 854	7 / 98
Extraction plume load (mg/d)	2099 / 2218	17 / 222

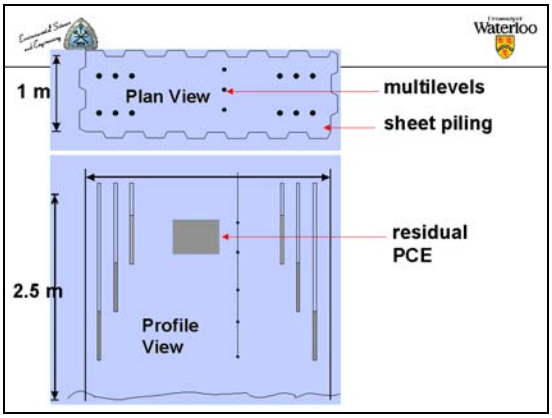


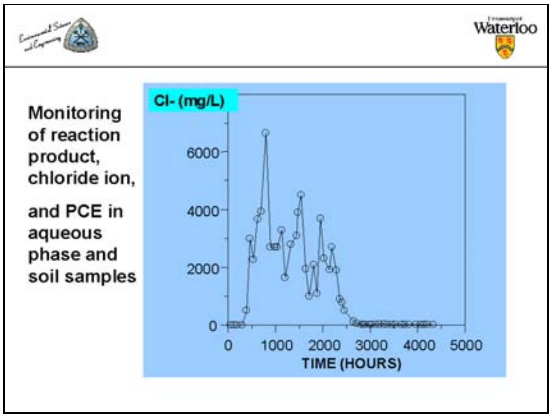
❷ CFB Borden Site in Canada

Application Features

- ✓ Closed system inside sheet pile cell
- ✓ 1.6 kg PCE, ~8% residual saturation
- ✓ Single pass with no oxidant recycling
- ✓ Flush with 10 g/L $KMnO_4$

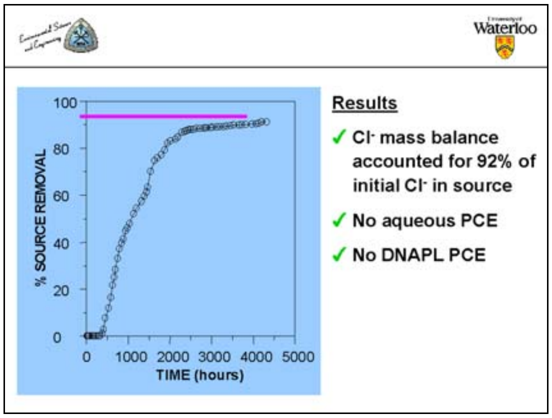
MacKinnon and Thomson, 2001





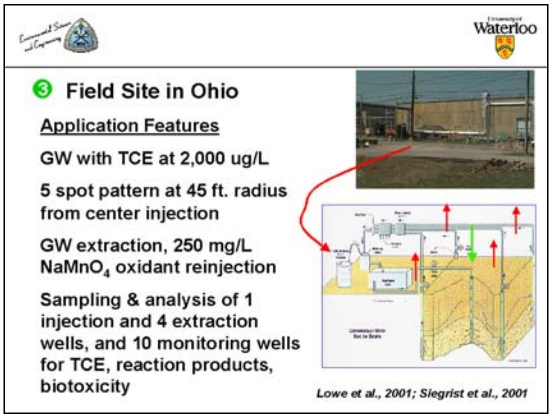
Monitoring of reaction product, chloride ion,

and PCE in aqueous phase and soil samples



Results

- ✓ Cl$^-$ mass balance accounted for 92% of initial Cl$^-$ in source
- ✓ No aqueous PCE
- ✓ No DNAPL PCE



❸ Field Site in Ohio

Application Features

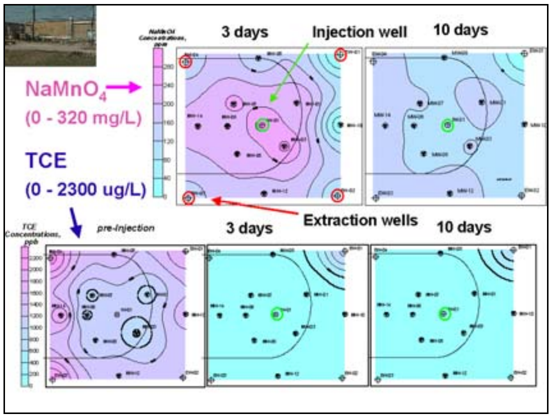
GW with TCE at 2,000 ug/L

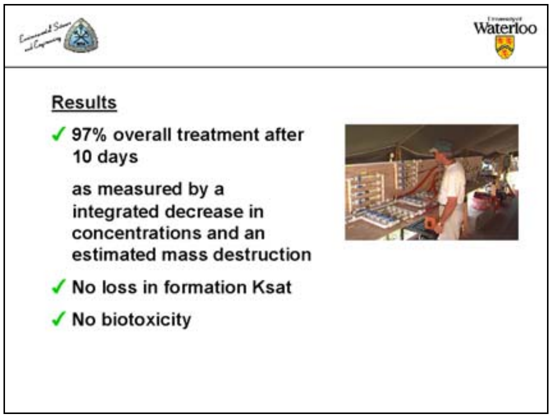
5 spot pattern at 45 ft. radius from center injection

GW extraction, 250 mg/L $NaMnO_4$ oxidant reinjection

Sampling & analysis of 1 injection and 4 extraction wells, and 10 monitoring wells for TCE, reaction products, biotoxicity

Lowe et al., 2001; Siegrist et al., 2001

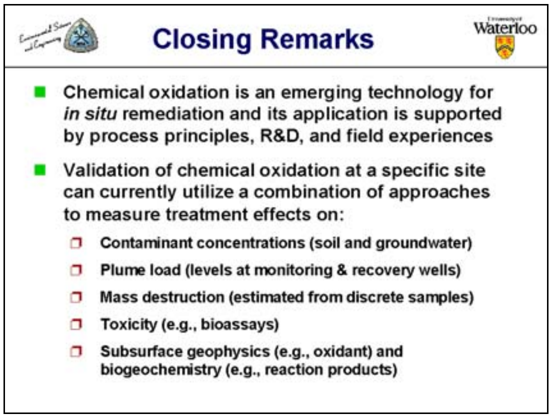




Results

- ✓ 97% overall treatment after 10 days

  as measured by a integrated decrease in concentrations and an estimated mass destruction
- ✓ No loss in formation Ksat
- ✓ No biotoxicity



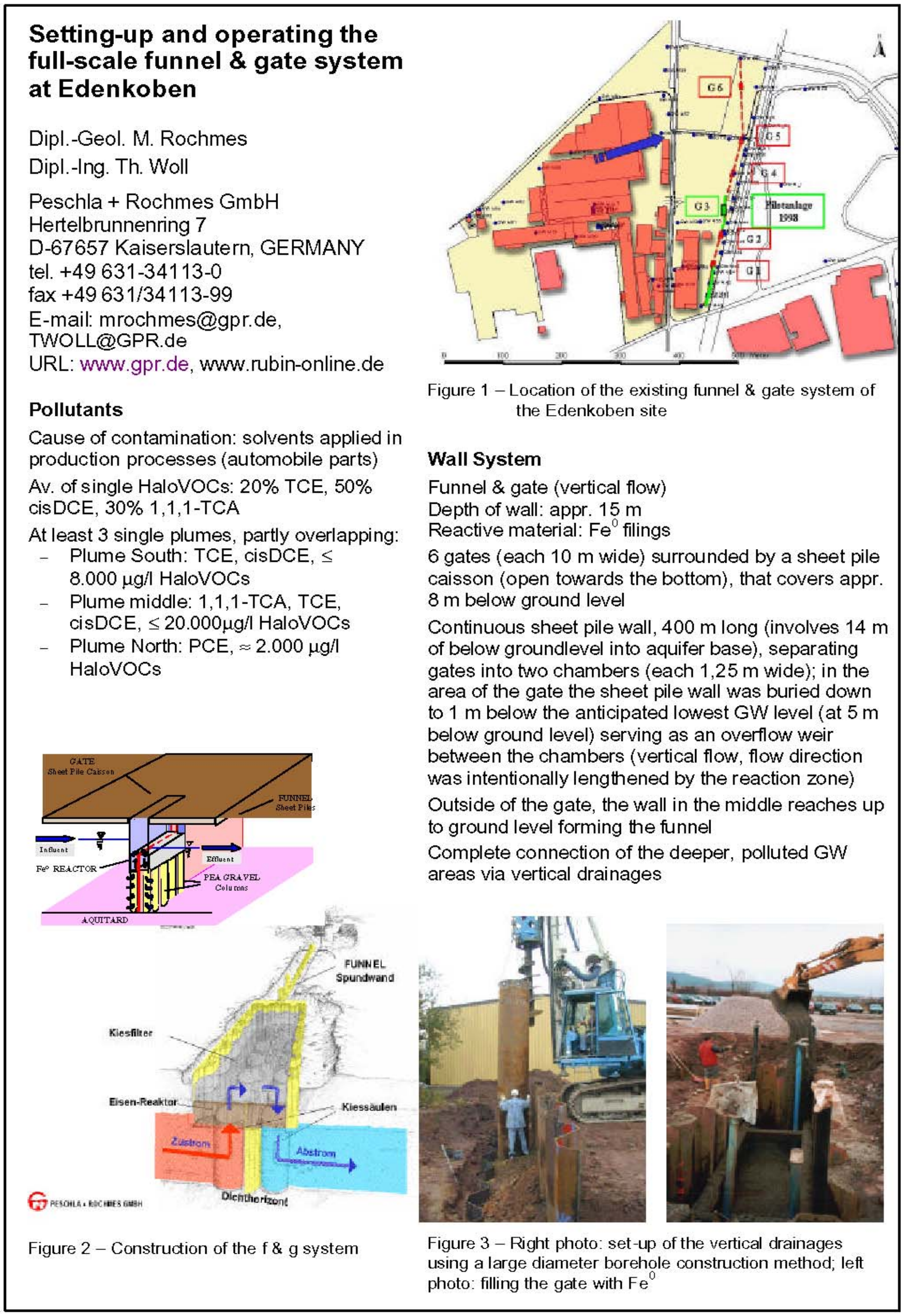
Closing Remarks

- Chemical oxidation is an emerging technology for *in situ* remediation and its application is supported by process principles, R&D, and field experiences
- Validation of chemical oxidation at a specific site can currently utilize a combination of approaches to measure treatment effects on:
  - ❐ Contaminant concentrations (soil and groundwater)
  - ❐ Plume load (levels at monitoring & recovery wells)
  - ❐ Mass destruction (estimated from discrete samples)
  - ❐ Toxicity (e.g., bioassays)
  - ❐ Subsurface geophysics (e.g., oxidant) and biogeochemistry (e.g., reaction products)

SITE-SPECIFIC VERIFICATION OF IN SITU PERMIABLE REACTIVE BARRIERS

Volker Birke[1]

1. THE FUNNEL & GATE SYSTEM AT EDENKOBEN



Setting-up and operating the full-scale funnel & gate system at Edenkoben

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Pollutants

Cause of contamination: solvents applied in production processes (automobile parts)

Av. of single HaloVOCs: 20% TCE, 50% cisDCE, 30% 1,1,1-TCA

At least 3 single plumes, partly overlapping:

- Plume South: TCE, cisDCE, ≤ 8.000 µg/l HaloVOCs
- Plume middle: 1,1,1-TCA, TCE, cisDCE, ≤ 20.000µg/l HaloVOCs
- Plume North: PCE, ≈ 2.000 µg/l HaloVOCs

Figure 1 – Location of the existing funnel & gate system of the Edenkoben site

Wall System

Funnel & gate (vertical flow)
Depth of wall: appr. 15 m
Reactive material: Fe^0 filings

6 gates (each 10 m wide) surrounded by a sheet pile caisson (open towards the bottom), that covers appr. 8 m below ground level

Continuous sheet pile wall, 400 m long (involves 14 m of below groundlevel into aquifer base), separating gates into two chambers (each 1,25 m wide); in the area of the gate the sheet pile wall was buried down to 1 m below the anticipated lowest GW level (at 5 m below ground level) serving as an overflow weir between the chambers (vertical flow, flow direction was intentionally lengthened by the reaction zone)

Outside of the gate, the wall in the middle reaches up to ground level forming the funnel

Complete connection of the deeper, polluted GW areas via vertical drainages

Figure 2 – Construction of the f & g system

Figure 3 – Right photo: set-up of the vertical drainages using a large diameter borehole construction method; left photo: filling the gate with Fe^0

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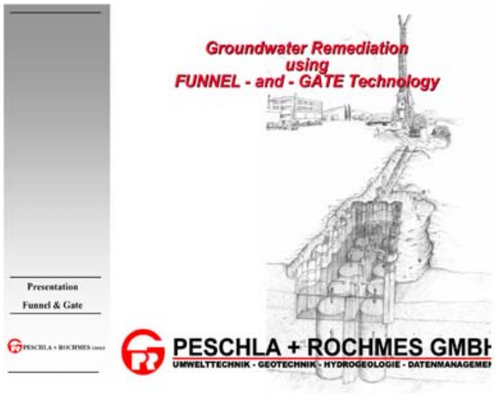
[1] Kaiserslautern, Germany. *www.gpr.de.www.rubin-online.de*.

2. PRESENTATION VISUALS ~ *presented by Volker Birke*

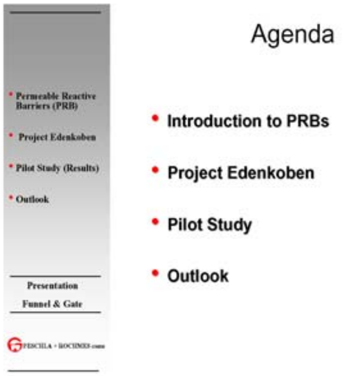


Groundwater Remediation using FUNNEL - and - GATE Technology

PESCHLA + ROCHMES GMBH
UMWELTTECHNIK - GEOTECHNIK - HYDROGEOLOGIE - DATENMANAGEMENT

Presentation
Funnel & Gate

PESCHLA + ROCHMES GMBH



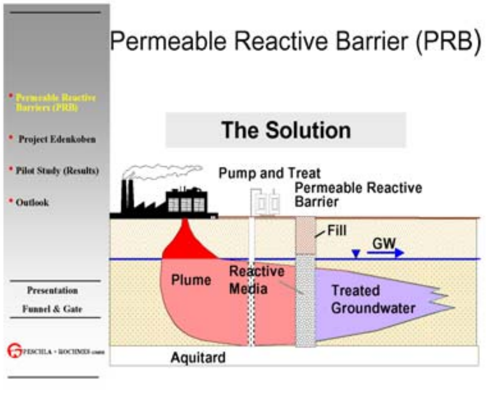
Agenda

- Introduction to PRBs
- Project Edenkoben
- Pilot Study
- Outlook

- Permeable Reactive Barriers (PRB)
- Project Edenkoben
- Pilot Study (Results)
- Outlook

Presentation
Funnel & Gate

PESCHLA + ROCHMES GMBH



Permeable Reactive Barrier (PRB)

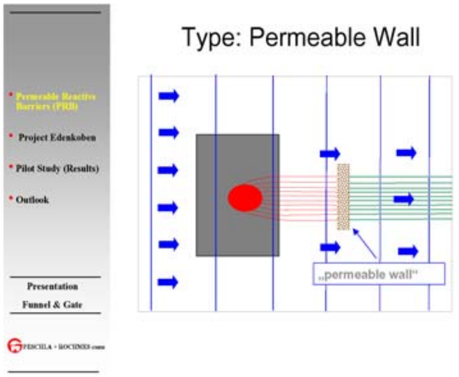
The Solution

Pump and Treat
Permeable Reactive Barrier
Fill
GW
Plume
Reactive Media
Treated Groundwater
Aquitard

- Permeable Reactive Barriers (PRB)
- Project Edenkoben
- Pilot Study (Results)
- Outlook

Presentation
Funnel & Gate

PESCHLA + ROCHMES GMBH



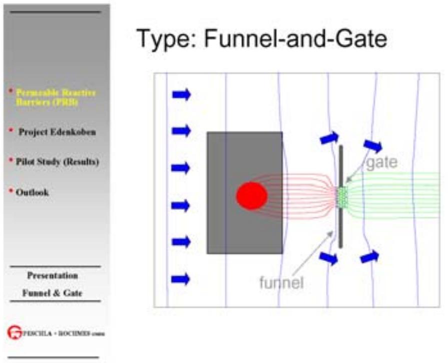
Type: Permeable Wall

„permeable wall"

- Permeable Reactive Barriers (PRB)
- Project Edenkoben
- Pilot Study (Results)
- Outlook

Presentation
Funnel & Gate

PESCHLA + ROCHMES GMBH



Type: Funnel-and-Gate

gate
funnel

- Permeable Reactive Barriers (PRB)
- Project Edenkoben
- Pilot Study (Results)
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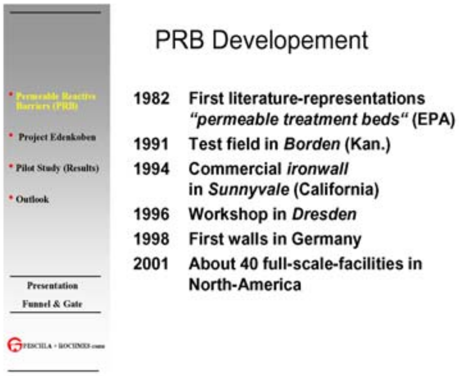
Presentation
Funnel & Gate

PESCHLA + ROCHMES GMBH



PRB Developement

1982	First literature-representations *"permeable treatment beds"* (EPA)
1991	Test field in *Borden* (Kan.)
1994	Commercial *ironwall* in *Sunnyvale* (California)
1996	Workshop in *Dresden*
1998	First walls in Germany
2001	About 40 full-scale-facilities in North-America

- Permeable Reactive Barriers (PRB)
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Presentation
Funnel & Gate

PESCHLA + ROCHMES GMBH

Iron Filings (Fe°)

- Permeable Reactive Barriers (PRB)
- Project Edenkoben
- Pilot Study (Results)
- Outlook

Presentation
Funnel & Gate

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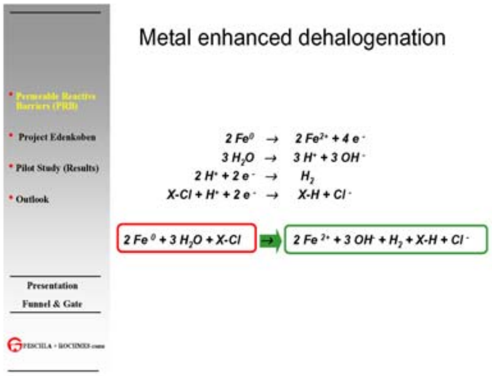

Metal enhanced dehalogenation

$$\begin{aligned} 2\,Fe^0 &\rightarrow 2\,Fe^{2+} + 4\,e^- \\ 3\,H_2O &\rightarrow 3\,H^+ + 3\,OH^- \\ 2\,H^+ + 2\,e^- &\rightarrow H_2 \\ X\text{-}Cl + H^+ + 2\,e^- &\rightarrow X\text{-}H + Cl^- \end{aligned}$$

$$\boxed{2\,Fe^0 + 3\,H_2O + X\text{-}Cl} \rightarrow \boxed{2\,Fe^{2+} + 3\,OH^- + H_2 + X\text{-}H + Cl^-}$$

- Permeable Reactive Barriers (PRB)
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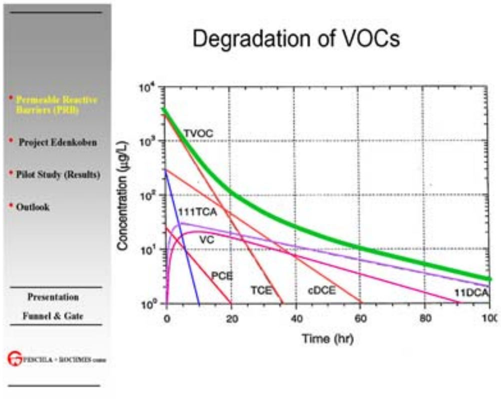
Presentation
Funnel & Gate

PESCHLA + ROCHMES GMBH



Degradation of VOCs

- Permeable Reactive Barriers (PRB)
- Project Edenkoben
- Pilot Study (Results)
- Outlook

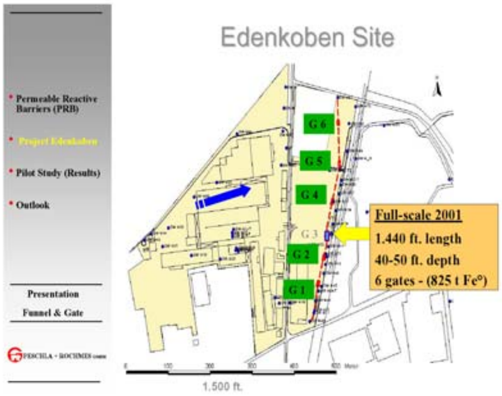
Presentation
Funnel & Gate

Case Study - Edenkoben

- Permeable Reactive Barriers (PRB)
- Project Edenkoben
- Pilot Study (Results)
- Outlook

Presentation
Funnel & Gate

Site:	**Automotive Industrial Plant**
Contaminants:	**VOCs (PCE, TCE, cDCE, 111TCA)**
Constr. Type:	**Funnel-and-Gate** **Funnel: sealed sheet piles** **Gates: sheet pile caisson vertical flowthrough**
Reactive Media:	**Zero-Valent Iron**

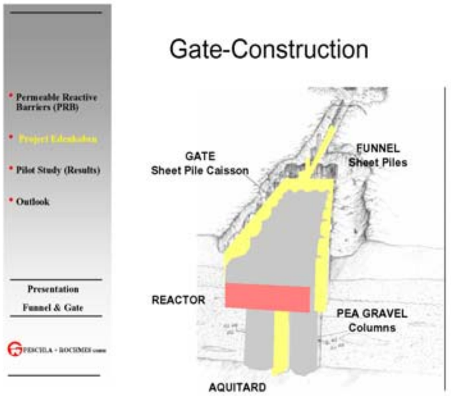


Edenkoben Site

- Permeable Reactive Barriers (PRB)
- Project Edenkoben
- Pilot Study (Results)
- Outlook

Presentation
Funnel & Gate

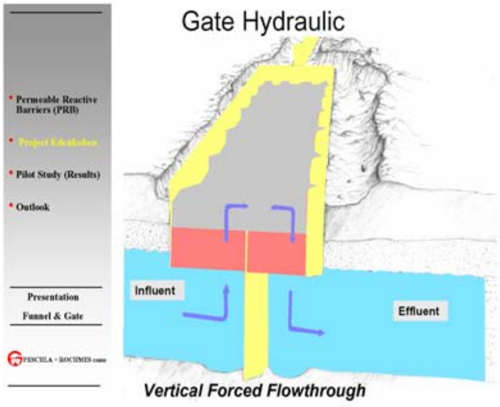
Full-scale 2001
1.440 ft. length
40-50 ft. depth
6 gates - (825 t Fe°)



Gate-Construction

- Permeable Reactive Barriers (PRB)
- Project Edenkoben
- Pilot Study (Results)
- Outlook

Presentation
Funnel & Gate

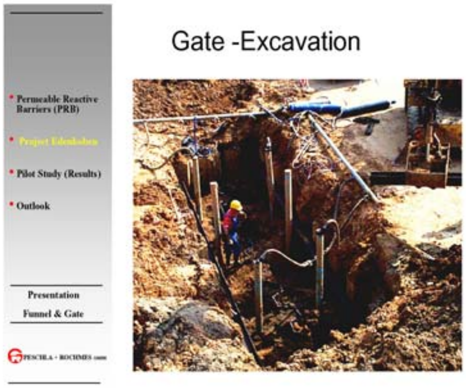


Gate Hydraulic

- Permeable Reactive Barriers (PRB)
- Project Edenkoben
- Pilot Study (Results)
- Outlook

Presentation
Funnel & Gate

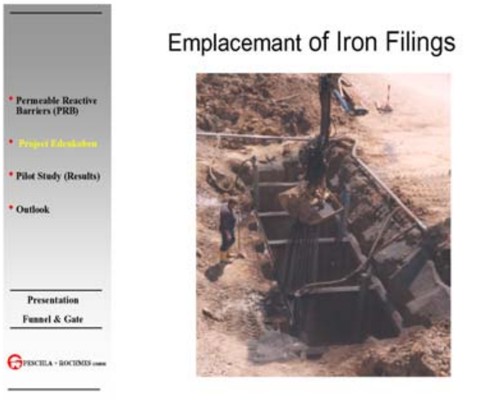
Vertical Forced Flowthrough



Gate -Excavation

- Permeable Reactive Barriers (PRB)
- Project Edenkoben
- Pilot Study (Results)
- Outlook

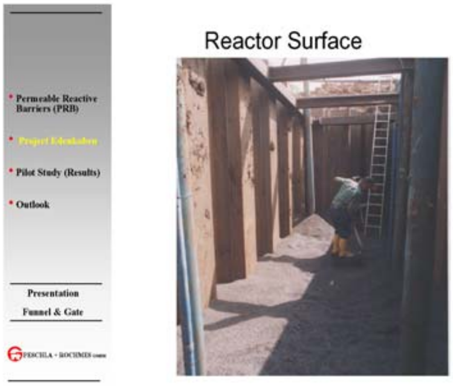
Presentation
Funnel & Gate



Emplacemant of Iron Filings

- Permeable Reactive Barriers (PRB)
- Project Edenkoben
- Pilot Study (Results)
- Outlook

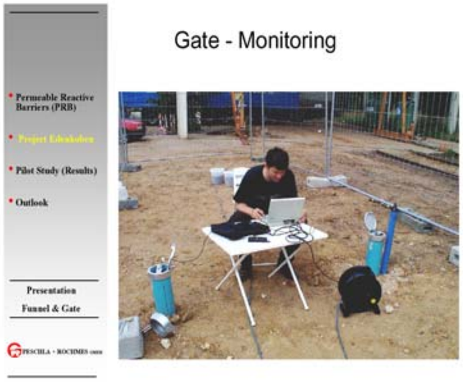
Presentation
Funnel & Gate



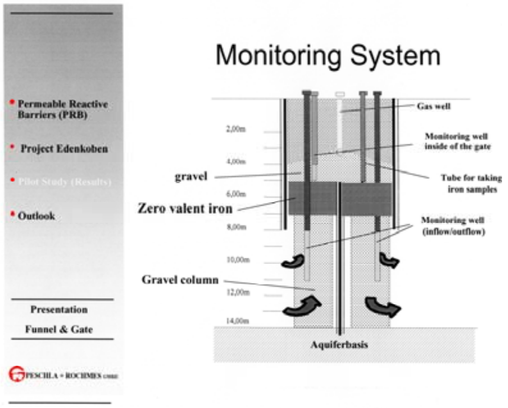
Reactor Surface

- Permeable Reactive Barriers (PRB)
- Project Edenkoben
- Pilot Study (Results)
- Outlook

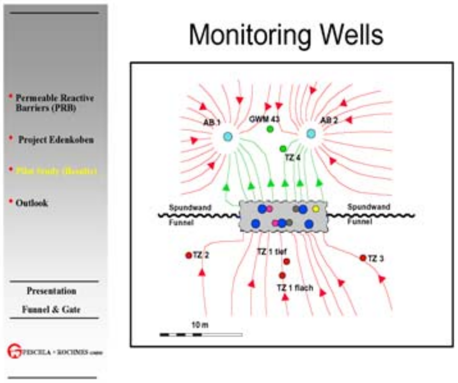
Presentation
Funnel & Gate



Gate - Monitoring



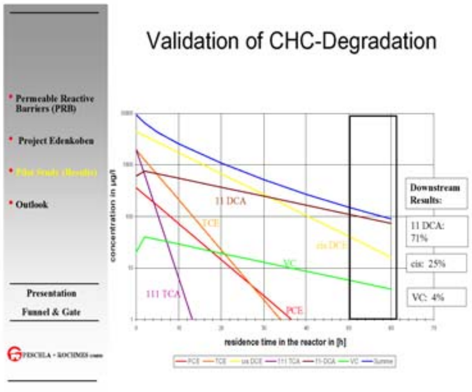
Monitoring System



Monitoring Wells

Monitoring Objectives

1. Degradation of CHC
2. Hydrochemical Parameters
3. Hydraulic Function
4. Precipitations
5. Gasproduction



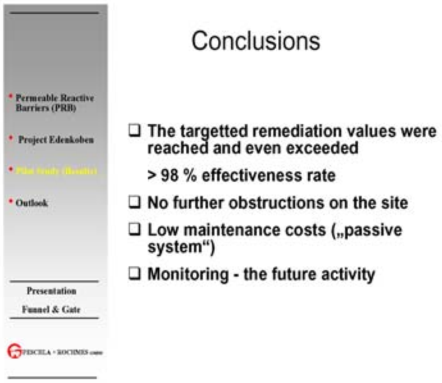
Validation of CHC-Degradation

Downstream Results:

11 DCA: 71%

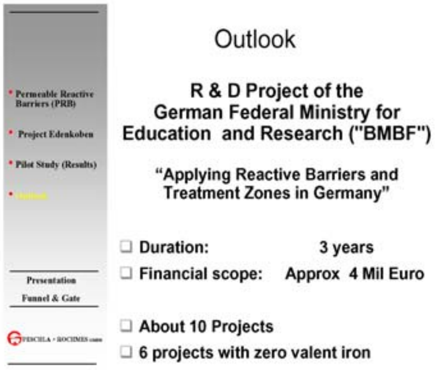
cis: 25%

VC: 4%



Conclusions

- ☐ The targetted remediation values were reached and even exceeded
  > 98 % effectiveness rate
- ☐ No further obstructions on the site
- ☐ Low maintenance costs („passive system“)
- ☐ Monitoring - the future activity



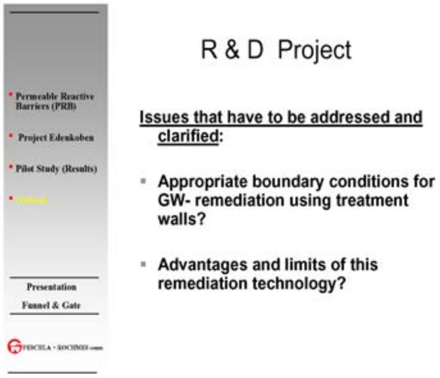
Outlook

R & D Project of the German Federal Ministry for Education and Research ("BMBF")

“Applying Reactive Barriers and Treatment Zones in Germany”

- ☐ Duration: 3 years
- ☐ Financial scope: Approx 4 Mil Euro

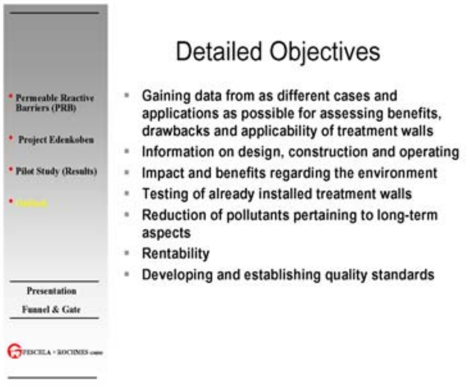
- ☐ About 10 Projects
- ☐ 6 projects with zero valent iron



R & D Project

Issues that have to be addressed and clarified:

- Appropriate boundary conditions for GW- remediation using treatment walls?
- Advantages and limits of this remediation technology?



- Permeable Reactive Barriers (PRB)
- Project Edenkoben
- Pilot Study (Results)
- Outlook

Presentation
Funnel & Gate

Detailed Objectives

- Gaining data from as different cases and applications as possible for assessing benefits, drawbacks and applicability of treatment walls
- Information on design, construction and operating
- Impact and benefits regarding the environment
- Testing of already installed treatment walls
- Reduction of pollutants pertaining to long-term aspects
- Rentability
- Developing and establishing quality standards

- Permeable Reactive Barriers (PRB)
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Presentation
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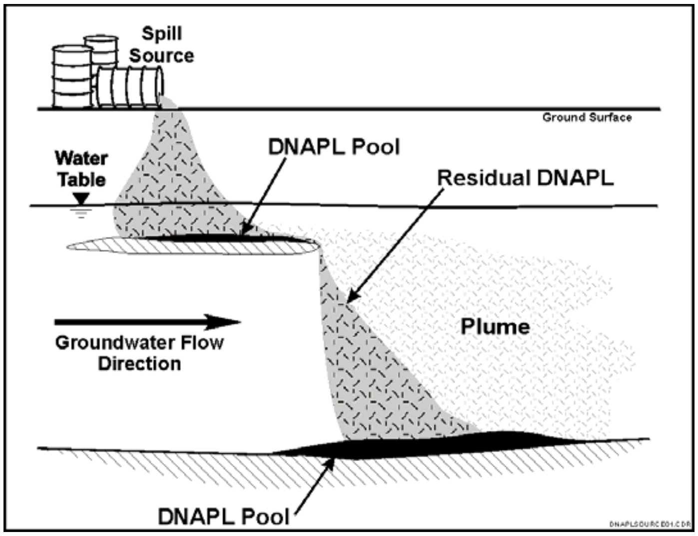
SITE-SPECIFIC VERIFICATION OF IN SITU REMEDIATION OF DNAPLS

Arun Gavaskar[1]

Dense nonaqueous-phase liquid (DNAPL) contamination is turning out to be more widespread than first imagined, especially as site owners and their representatives get better at finding DNAPL source zones. DNAPL is most commonly encountered at sites contaminated with chlorinated solvents, such as trichloroethylene (TCE) and perchloroethylene (PCE). These solvents were used in many industrial activities, such as metal finishing, dry cleaning, and maintenance. Past use and disposal practices have led to the appearance of these solvents in the subsurface. Because many of these solvents are denser than water, they often penetrate the water table and continue to migrate downward until they encounter a low-permeability layer. Depending on the nature of its saturation of the soil pores, DNAPL is considered either mobile or residual. Mobile DNAPL can be displaced from the pores that it occupies by a strong hydraulic gradient. Residual DNAPL, on the other hand, cannot be displaced by hydraulic gradient alone, no matter how strong. Therefore, it cannot be pumped out of extraction wells, as in the case of mobile DNAPL.

Figure 1: Illustration of a DNAPL Source Zone Forming.



Many of these solvents are resistant to natural degradation in the solvent phase and are only sparingly soluble in water. In addition, their mass transfer to the dissolved phase is often further retarded by an array of factors, such as complex soil pore geometries. Therefore, even a spill or leak of one drum of solvent can continue to dissolve and contaminate an aquifer for several years or decades. In many aquifers, the dissolved phase or plume generated encounters little retardation (from factors such as adsorption or degradation). Therefore, these plumes can often travel long distances and threaten drinking water sources and other receptors.

1. CHANGES IN DNAPL SITE CHARACTERIZATION

One challenge in finding DNAPL source zones is that their downward migration is governed by geologic heterogeneities and preferential pathways, rather than the hydraulic gradient. In addition, many sites have suffered spills and leaks in multiple and often unknown locations. This has led to the presence of multiple subsurface sources on a single property, resulting in multiple overlapping plumes. At such sites, DNAPL

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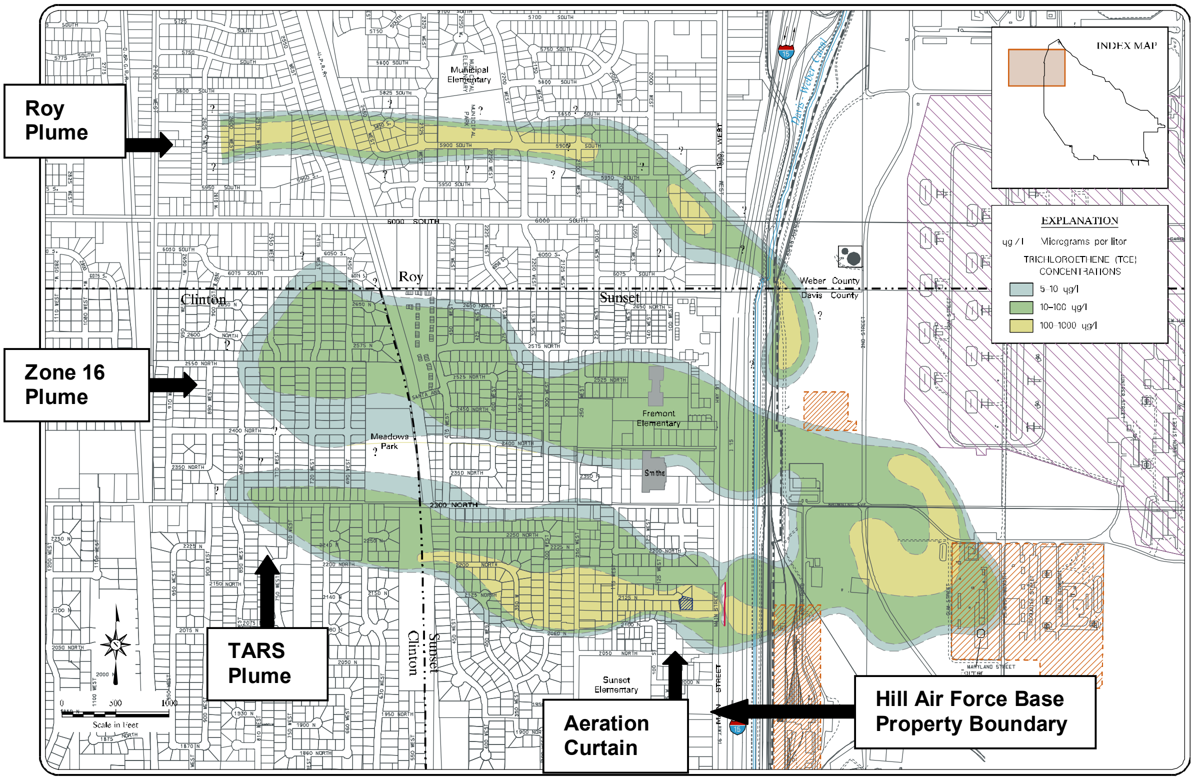
sometimes may occur in counterintuitive locations. At many sites, even those with an apparent plethora of monitoring wells, the monitoring well density may not be enough to distinguish between multiple plumes, let alone multiple sources. For example, at one of the most challenging sites, Operable Unit 5 in Hill Air Force Base, Utah, fairly extensive initial monitoring led to the discovery of what was thought to be only one plume (see Figure 2). Subsequently, additional monitoring led to the identification of three plumes. An expert panel that recently reviewed the abundant monitoring data could not be sure whether the three plumes originated from a single source or multiple sources. Multiple wells and soil borings over approximately one square mile of suspected source area have failed to reveal any definite sources. Whether or not a source, if it is narrowly defined as DNAPL or solvent phase, still exists at this site is not yet clear. If such a source exists, the DNAPL mass is probably relatively small, but diffuse.

Figure 2: TCE Plumes at Operable Unit 5, Hill Air Force Base, Utah (Source: Montgomery Watson, 2001).



2. CHALLENGES IN DNAPL SITE REMEDIATION

There are two schools of thought on how to deal with DNAPL sites; both schools represent thoughtful and valid arguments, indicating that the learning process still continues.

One school of thought argues that most DNAPL source zones are recalcitrant to characterization and treatment. In this school, success is ultimately measured by an improvement in downgradient groundwater quality (reduction in dissolved contaminant concentrations to target cleanup levels at a downgradient compliance boundary, which is often the property boundary). Proponents of this school use three arguments:

(a) The practical difficulties encountered in finding and delineating DNAPL sources
(b) The technical and economic limitations in removing 100% of the DNAPL mass at a site

(c) Modeling simulations, which show that DNAPL mass removal would have to be nearly 100%, before any significant improvement in groundwater quality is encountered at the compliance boundary (Freeze and McWhorter, 1997; Cherry et al., 1996).

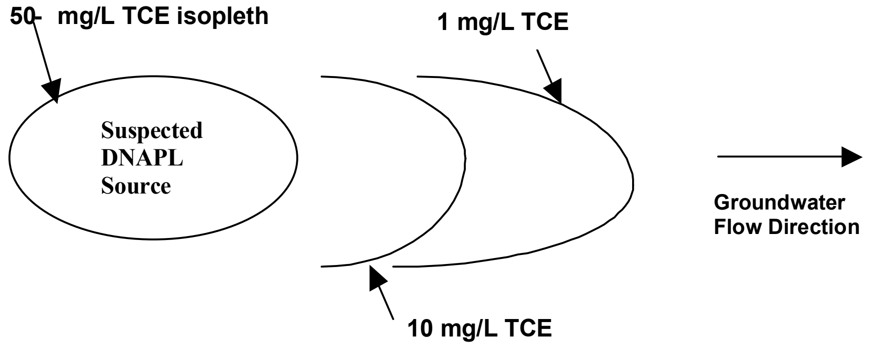
The first school argues that at many sites, because of the complex nature of the DNAPL distribution, even the best characterization efforts may fail to completely delineate the source and some parts of the DNAPL source could fall outside the zone targeted for remediation. Therefore, not only is DNAPL remediation limited by the technical and economic limitations posed by the asymptotic nature of DNAPL mass recovery encountered during most remediation applications, but that the intrinsic complexity of the DNAPL distribution at most sites assures an outcome that is less than 100% successful in removing the source. This would lead to the continued presence of a dissolved contaminant plume that the site owner would have to address. A better approach at many sites would be to leave the source alone and focus the remedy on containing the plume.

The second school of thought primarily argues that any DNAPL mass removal is welcome. Success need not be defined so absolutely. Site owners are getting better at characterization and at finding and delineating DNAPL source zones. As long as DNAPL source zones are reasonably well defined and remediation technologies are able to remove a reasonable amount (say, 60 to 90%) of DNAPL mass from the affected aquifer, there is a good chance that the resulting plume is weakened to the point where natural attenuation may be sufficient to achieve target cleanup levels at a downgradient compliance boundary. Even if an active remedy, such as a pump-and-treat system, is required to contain a post-source remediation plume, the life of the plume would probably have been greatly reduced by the weakening of the source that feeds it. In addition, this school argues that models showing persisting downgradient plume concentrations, following substantial DNAPL mass removal, are based on homogeneous aquifers. In most aquifers, which are heterogeneous to varying degrees, removal of some DNAPL mass (probably from the more permeable regions of the aquifer, where most remediation technologies are particularly effective) would cause the bulk of the groundwater flow to encounter less DNAPL. Most of the remaining DNAPL would be trapped in pores that are inaccessible to the bulk flow. Therefore, in most cases, downgradient contaminant concentrations should be lower, following substantial DNAPL mass removal.

3. IMPLICATIONS FOR SITE OWNERS

Because both schools of thought present valid arguments backed by theoretical simulations and practical experience, it appears that DNAPL sites will have to be approached on a case-by-case basis. The first school's argument is strengthened by the fact that at many sites, such as former NAS Moffett Field and Dover AFB, passive plume containment remedies, such as natural attenuation or permeable barrier have been found to be effective and economical (Gavaskar et al., 2000; Gavaskar et al., 1998). Even an active remedy, such as a pump-and-treat system, is not as uneconomical as it used to be. With the development of concepts, such as slow pump and treat (Cherry et al., 1996), in which pumping is conducted at the lowest rate necessary to contain a plume, at many sites, it may be possible to contain fairly large plumes with relatively small pump-and-treat operations (1 to 5 gal/min). Previously, more aggressive pump-and-treat operations aimed at treating and removing the plume were much more costly. In addition, at some sites, pump-and-treat systems are already installed as an interim remedy and could be optimized for more effective containment and favorable economics. The development of high capacity and more compact "low-profile" or tray-type air strippers has also contributed to reducing the space and cost requirements of pump-and-treat systems (Battelle and Duke Engineering & Services, 2001). In addition, as seen at Operable Unit 5, Hill Air Force Base, the probability of even finding the DNAPL source may be minimal. However, there are also sites where the technical feasibility and economics may favor source delineation and remediation. For example, at some sites, such as Naval Air Station Pensacola, Florida, the source zone has been more broadly defined as the area inside the isopleth with the highest concentration of the contaminant (see illustration of this type of site in Figure 3). Because this high-dissolved phase concentration area identified was relatively small, source remediation efforts were focused in this *suspected* source area without additional effort to find actual DNAPL phase. Therefore, DNAPL site characterization and remediation is as much an art as a science; much is left to the collective judgment of site owners and their representatives (scientific consultants and attorneys), regulators, and other stakeholders.

Figure 3: Suspected Source Area Ringed by Highest Identified Groundwater Concentration.



At Launch Complex 34, Cape Canaveral Air Station, Florida, for example, TCE has entered the subsurface in such large quantities that a moderate characterization effort (relative to the size of the site) was able to find and adequately delineate the source. In addition, the large mass of DNAPL, perched on a relatively thin clay aquitard underlying the surficial aquifer, was threatening the confined aquifer below. Although there are signs that over the last 30 to 40 years, some DNAPL has progressed to the confined aquifer in areas where the aquitard is particularly thin, removal of DNAPL mass from the surficial aquifer has greatly reduced the risk to the confined aquifer. Significant contamination of confined aquifers due to DNAPL present in surficial aquifers is a risk that potentially threatens drinking water supplies and increases the potential costs of any future remediation or plume containment efforts.

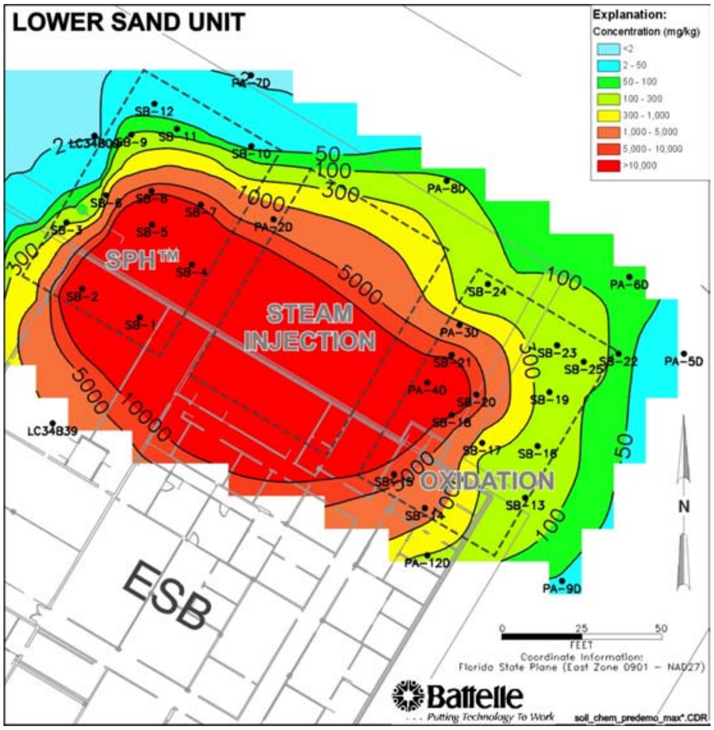
The first school would argue that remediation of the source zone increases the risk of DNAPL migration – downwards or to the sides; this may increase the contamination in the aquitard or the cleaner confined aquifer below or it may lead to a widening of the source, and hence, the plume in the surficial aquifer. Therefore, remediation of the DNAPL in the surficial aquifer would have to be done in a way that minimizes the potential for further downward migration of DNAPL due to the remediation technology application itself. This would seem to favor technologies that promote destruction of the DNAPL in the subsurface, rather than those that promote mobilization and extraction of the DNAPL to the surface for aboveground treatment. Much better hydraulic control would be required for DNAPL mobilization technologies, although engineering controls are necessary for any source remediation effort.

4. CHALLENGES IN DEFINING AND VALIDATING THE SUCCESS OF DNAPL SITE REMEDIATION

DNAPL is a relatively new problem. The widespread nature of this problem was first recognized in the 1990s. Remediation and monitoring approaches for this problem are still evolving. One shortcoming in several DNAPL remediation technology demonstrations has been inadequate monitoring and/or the limitations of the monitoring instruments themselves. Two demonstrations in the U.S. that have attempted more comprehensive monitoring of DNAPL source zones and the effects of the remediation efforts are the Interagency DNAPL Consortium's (IDC) demonstration of three remediation technologies—chemical oxidation, resistive heating, and steam injection – at Cape Canaveral Air Station (Battelle, 2001 a and b) and the Environmental Security Technologies Certification Program's (ESTCP) demonstration of surfactant flushing at Marine Corps Base at Camp Lejeune, North Carolina (Duke Engineering &

Services, 2000). Although different monitoring tools were used in the two demonstrations, considerable effort was made in both demonstrations to track, not just the reduction in groundwater concentrations and any aboveground DNAPL recovery (as is typical in previous remediation efforts), but also the initial mass and fate of the DNAPL in the aquifer.

Figure 4: DNAPL Source Zone (300 mg/kg and higher contours) at Cape Canaveral Air Station Identified through Extensive Soil Sampling.



The apparent success or failure of DNAPL treatment can sometimes be a matter of data collection and interpretation. As an example, Table 1 presents a restricted data set from the resistive heating demonstration at Cape Canaveral Air Station representative of the level of monitoring and data collection conducted at many remediation sites. All the data in Table 1 indicate success at removing DNAPL mass (1,947 kg of TCE recovered aboveground) and improving groundwater quality (as much as 99% decline in groundwater TCE concentrations). Much of the remaining TCE appears to have been degraded by the treatment, as evidenced by the increase in chloride.

On the other hand, Table 2 shows the results of more comprehensive monitoring conducted at the Cape Canaveral site, through characterization and estimation of the pretreatment DNAPL mass, installation and monitoring of depth-discrete perimeter wells, and analysis of the pre- and post-treatment groundwater geochemistry. Extensive soil sampling and kriging (statistical analysis) were used to obtain a range of estimates for the pre-treatment and post-treatment TCE mass, at the 80% confidence level. Spatial coverage of the heterogeneous DNAPL distribution was improved by collecting nearly 300 soil samples during each event from the 75 ft long x 50 ft wide x 45 ft deep test plot in the DNAPL source zone. Methanol extraction procedures for the soil samples were modified to allow extraction of larger aliquots of soil, thus allowing the entire subsurface soil column to be extracted and analyzed at each of 12 locations in the test plot. The main advantage of depth-discrete groundwater and soil sampling over some other tools is that spatial coverage is not dependent on geologic heterogeneities in the aquifer or on specific DNAPL properties. Collecting a sufficiently high number of soil samples, with the number being determined by the expected variability of the TCE distribution and the desired level of statistical confidence, gave the site owner reasonably good estimates of the pre- and post-demonstration TCE masses. Of course, this degree of characterization and monitoring is not likely to be economically feasible for most full-scale remediation sites. However, in the early stages of development of DNAPL source remediation options, comprehensive monitoring is necessary to identify potential shortcomings of the remediation approach and design improved applications at future sites.

Table 1: Interpretation of DNAPL Remediation by Resistive Heating at Cape Canaveral Air Station with a Basic Monitoring Scheme Typical of Many Remediation Projects.

Monitoring Parameter	Pre-Treatment Level	Post-Treatment Level	Change
TCE in Source Zone Well PA-13I	1,070,000 µg/L	60,200 µg/L	- 94 %
TCE in Source Zone Well PA-14I	960,000 µg/L	174,000 µg/L	- 82%
TCE in Source Zone Well PA-14D	868,000 µg/L	2,730 µg/L	- 99%
TCE Mass Recovered Aboveground in Extracted Vapor	--	1,947 kg	--
Chloride in source zone well PA-13D	774 mg/L	3,610 mg/L	+ 366%
Chloride in source zone well PA-14D	774 mg/L	4,790 mg/L	+ 519%

The more comprehensive data in Table 2 now indicate a strong probability that the DNAPL mass recovered aboveground is a fraction of the DNAPL mass that was initially in the subsurface. Because the TCE mass recovered aboveground does not account for the entire difference between the pre- and post-demonstration TCE masses, it is probable that substantial amounts of TCE either degraded or migrated from the treatment plot. Possible pathways for TCE degradation include enhanced biodegradation (due to the enhanced action of microbes at elevated temperatures) and/or abiotic reduction (due to reaction with cast iron shot used in the heating electrodes). However, chloride, which could have been a key indicator of the degradation pathway, loses some significance due to the fact that the substantial increase in groundwater chloride was accompanied by a similar increase in other dissolved ions, namely, sodium, potassium, calcium, and carbonate (alkalinity), which are all seawater constituents.

Given the closeness of this site to the ocean and the presence of relatively high salinity in the pre-treatment groundwater at the base of the surficial aquifer, the possibility that the treatment somehow enhanced saltwater intrusion into the test plot cannot be ruled out. This leads to the possibility that some DNAPL migrated out of the test plot during the treatment. Possible pathways for migration include heat-induced volatilization to the vadose zone and atmosphere and the sideways spread of the deeper TCE caused by an intermediate silt layer in the otherwise sandy aquifer. Although the resistive heating technology successfully heated even the more difficult parts of the target aquifer, such as the soil immediately above the clay aquitard at 45 ft below ground surface and the portion of the aquifer under a building, more engineering controls will be required at future site to manage the collection of mobilized TCE, especially in difficult geologic settings.

At Cape Canaveral Air Station, the demonstration of chemical (permanganate) oxidation treatment of the DNAPL in a separate test plot was more conclusive. As seen in Table 3, the disappearance of TCE mass from aquifer in the test plot (treated portion of the DNAPL source zone) and the monitored changes in groundwater present a more integrated picture of TCE oxidation as the major pathway of DNAPL mass removal. The significant increase in chloride in the treated aquifer was not accompanied by a consistent increase in sodium, another major seawater constituent. At the same time, alkalinity (carbonate) levels in the groundwater increased, as would be expected when carbon dioxide generation (oxidation of organic species) occurs in the surficial aquifer. Visual evidence of purple discoloration of soil and groundwater in the treatment zone indicated good distribution of the potassium permanganate oxidant. Pre- and post-treatment slug tests did not indicate any changes in hydraulic conductivity of the aquifer following treatment. Monitoring of deeper wells and soil cores showed no evidence of DNAPL in the confined aquifer below. Levels of some trace metals (chromium, nickel, and thallium) that were present in the industrial grade potassium permanganate injected in the aquifer rose temporarily, but are expected to subside, once the treatment zone re-equilibrates with the groundwater flow.

Table 2: Interpretation of DNAPL Remediation by Resistive Heating at Cape Canaveral Air Station with a More Comprehensive Monitoring Scheme.

Monitoring Parameter	Pre-Treatment Level	Post-Treatment Level	Change
TCE in Source Zone Well PA-13I	1,070,000 µg/L	60,200 µg/L	- 94 %
TCE in Source Zone Well PA-14I	960,000 µg/L	174,000 µg/L	- 82%
TCE in Source Zone Well PA-14D	868,000 µg/L	2,730 µg/L	- 99%
TCE Mass in Aquifer (80% confidence interval)	7,498 to 15,677 kg	1,031 to 1,535 kg	- 80 to 93%
TCE Mass Removed from Aquifer (80% confidence interval)	--	5,963 to 14,646 kg *	--
TCE Mass Recovered Aboveground in Extracted Vapor	--	1,947 kg	--
Chloride in source zone well PA-13D	774 mg/L	3,610 mg/L	+ 366%
Chloride in source zone well PA-14D	774 mg/L	4,790 mg/L	+ 519%
Sodium in Source Zone Well PA-13D	369 mg/L	2,070 mg/L	+ 461%
Sodium in Source Zone Well PA-14D	325 mg/L	3,130 mg/L	+ 863%

* Estimated as the difference between the pre-treatment and post-treatment TCE mass estimates in the aquifer. This TCE mass removed estimate is significantly higher than the TCE mass of 1,947 kg recovered aboveground

Therefore, at least during the continuing developmental phase of in-situ DNAPL remediation technologies, a comprehensive characterization of pre-treatment and post-treatment contaminant mass, aquifer geochemistry and hydrology, and the regions surrounding the treated source zone is desirable to understand the true effectiveness of the treatment. Once these remediation technologies are proven and the level of engineering controls appropriate for each class of technology has been identified, it is anticipated that characterization and monitoring requirements will gradually recede. For a well-engineered treatment system, the primary pre-treatment characterization objective would be identification of the boundaries of the DNAPL source zone and distribution of the hot spots in the zone, not the exact DNAPL mass. This would ensure that the treatment is targeted where it is most needed, and minimize (but not fully eliminate) the potential for unidentified pockets of DNAPL pockets outside the treatment zone. The primary post-treatment monitoring objective would be a reduction in groundwater concentrations of the contaminants to target cleanup levels at the compliance boundary. Long-term monitoring would be required to ascertain that the cleanup levels are sustainable and are not subject to a rebound in groundwater contaminant concentrations, once a new post-treatment equilibrium is established in the aquifer.

If the target (regulation-mandated or risk-based) cleanup level is not achieved or achievable in the long term at the compliance boundary, a secondary treatment would be required. The secondary treatment could take any one of several forms – natural attenuation, pump-and-treat system (albeit for a shorter future period and for a weaker plume), or secondary source treatment (probably, some form of enhanced bioremediation). In this sense, three time-based goals are envisioned for remediation of a DNAPL source zone:

Table 3: Interpretation of DNAPL Remediation by Chemical Oxidation at Cape Canaveral Air Station with a More Comprehensive Monitoring Scheme.

Monitoring Parameter	**Pre-Treatment Level**	**Post-Treatment Level**	**Change**
TCE in Source Zone Well BAT-2S	1,110,000 µg/L	< 5 µg/L	- 99 %
TCE in Source Zone Well BAT-2D	1,160,000 µg/L	220,000 µg/L	- 81%
TCE Mass in Test Plot Aquifer (80% confidence interval)	6,217 to 9,182 kg	1,511 to 2,345 kg [a]	- 62 to - 84%
	Same as above	2,980 to 3,182 kg [b]	- 49 to - 68%
Chloride in source zone well BAT-2S	53 mg/L	126 mg/L	+ 138%
Chloride in source zone well BAT-2D	722 mg/L	5,070 mg/L	+ 602%
Sodium in Source Zone Well BAT-2S	28 mg/L	68 mg/L	+ 143%
Sodium in Source Zone Well BAT-2D	305 mg/L	91 mg/L	- 70%
Alkalinity (carbonate[c]) in Source Zone Well BAT-2S	316	1,500 mg/L	+ 375%
Alkalinity (carbonate[c]) in Source Zone Well BAT-2D	208	1,300 mg/L	+ 525%

[a] TCE mass based on soil sampling conducted immediately following end of oxidant injection treatment.
[b] TCE mass based on soil sampling conducted nine months after the end of oxidant injection treatment. The differences between the TCE mass change estimated at the two time points are indicative of sampling variability.
[c] Carbonate buildup is indicative of carbon dioxide production through oxidation of organic species.

- A *short-term goal*, which targets maximum achievable DNAPL mass removal. This goal is generally determined by economic considerations and represents an end point for the primary treatment when the short-term cost of achieving incremental DNAPL mass removal becomes excessive. Achievement of this goal can be verified through the use of groundwater and soil sampling or other tools, as well as analysis of any side-streams recovered aboveground.

- An *intermediate-term goal*, which targets achievement of desired cleanup levels at the compliance boundary. It may take a year or several years for flow to re-equilibrate and for extraneous factors (such as diffusion of sequestered contaminants from downgradient fine-grained aquifer media) to subside, before the site owner can even make a determination that the target cleanup level has been achieved at the compliance boundary. It should be noted that the same is the case when source or plume containment, rather than source remediation, is the selected option at a site. For example, in Figure 2, an aeration trench has been implemented near the property boundary as a permeable barrier inside the TARS plume, for the last two years. Although this treatment is effective in terms of the quality of the treated water emerging from the interceptor trench, the downgradient portion of the TARS plume in Figure 2 shows no sign of receding or detaching from the upgradient plume or source. This persistence of downgradient contamination is probably because of the abundance of silty clay lenses, from which contaminants continue to diffuse slowly over time, thus re-contaminating the treated water. Similar persistence of downgradient contamination for several years following effective containment of the plume at the treatment point has been noted at former NAS Moffett Field (Gavaskar, et al. 1998), a site which has a somewhat similar composition of sand channels and clay deposits. Therefore, irrespective of the approach, be it source remediation or plume containment, at many sites, achievement (or non-achievement) of the intermediate goal, which is generally the most important goal that site owners and regulators are interested in, may not be apparent for a year or several years after implementation of the selected remedy.

- The *long-term goal* of any remediation ultimately would be achievement of regulatory cleanup levels or maximum contaminant levels (MCLs) in the source zone and plume, which would indicate that long-term monitoring and/or plume control measures can be dismantled.

The process seems formidable, but as each goal is reached, the costs of managing a site probably decline. The decision making process involved in selecting the appropriate remedy or chain of remedies and for selecting the tools for characterization and monitoring is driven by a mix of technical, regulatory, and economic factors that is determined on a site-specific basis.

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6. ACKNOWLEDGEMENTS

The DNAPL remediation demonstration at Cape Canaveral Air Station was funded by the Interagency DNAPL Consortium (IDC) led by the U.S. Department of Energy, Environmental Protection Agency's Superfund Innovative Technology Evaluation (SITE) Program, Naval Facilities Engineering Service Center (NFESC), and National Aeronautic and Space Administration (NASA). The permeable barrier projects, at former NAS Moffett Field and Dover Air Force Base, were funded by the Environmental Security Technologies Certification Program (ESTCP) through NFESC. The Hill Air Force Base information was provided by the U.S. Air Force and Montgomery Watson to the author as part of an expert panel review and advisory process to identify characterization and remediation strategies for Operable Unit 5.

7. PRESENTATION VISUALS ~ *presented by Arun Gavaskar*

Site-Specific Validation of In-Situ Remediation of DNAPL

Presented at NATO Special Session
September 11, 2001

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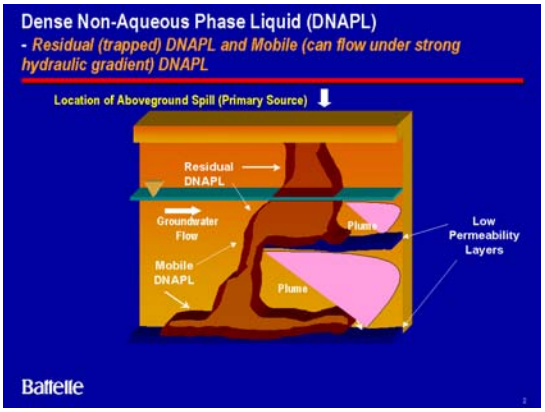
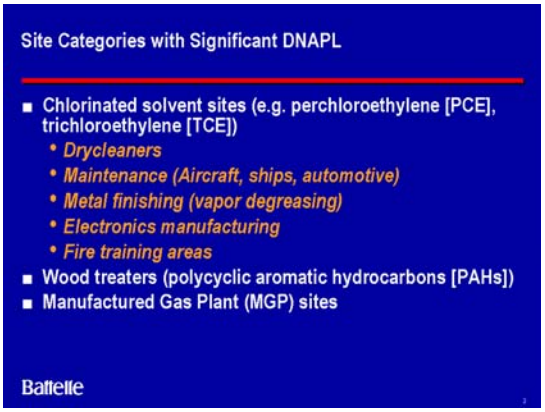


Dense Non-Aqueous Phase Liquid (DNAPL)

- Residual (trapped) DNAPL and Mobile (can flow under strong hydraulic gradient) DNAPL



Site Categories with Significant DNAPL

- Chlorinated solvent sites (e.g. perchloroethylene [PCE], trichloroethylene [TCE])
  - *Drycleaners*
  - *Maintenance (Aircraft, ships, automotive)*
  - *Metal finishing (vapor degreasing)*
  - *Electronics manufacturing*
  - *Fire training areas*
- Wood treaters (polycyclic aromatic hydrocarbons [PAHs])
- Manufactured Gas Plant (MGP) sites

DNAPL Site Strategies

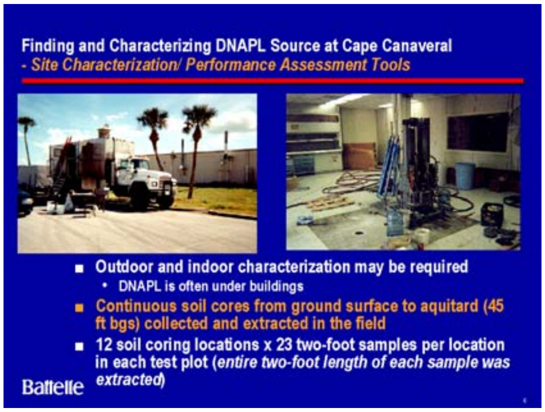
- What are the Remediation Options Available?

- Source Identification and Remediation (growing interest)
  - Excavation/ Soil Vapor Extraction
  - Heating (Resistive or Steam)
  - Chemical Oxidation (Permanganate or Fenton's reagent)
  - Surfactant flushing
- Source/Plume Containment (most commonly done)
  - Natural attenuation
  - Pump and treat (slow)
  - Permeable barriers (e.g., zerovalent iron, air sparging, biological)
- Plume Treatment (becoming rare)
  - Pump and treat (aggressive)
  - Enhanced bioremediation or bioaugmentation
- Secondary Treatment of DNAPL (becoming an issue)
  - Treating the residuals left behind by primary treatment

DNAPL Remediation at Cape Canaveral Air Station

- Interagency DNAPL Consortium

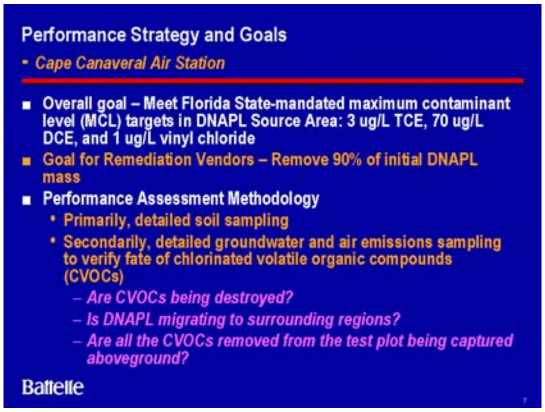
- DNAPL source characterization and in-situ treatment (75 ft x 50 ft test plots)
  - *Six-Phase Heating*
  - *Chemical Oxidation*
  - *Steam Injection*



Finding and Characterizing DNAPL Source at Cape Canaveral

- Site Characterization/ Performance Assessment Tools

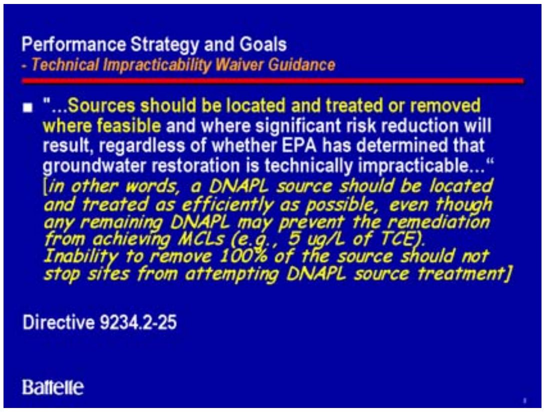
- Outdoor and indoor characterization may be required
  - DNAPL is often under buildings
- Continuous soil cores from ground surface to aquitard (45 ft bgs) collected and extracted in the field
- 12 soil coring locations x 23 two-foot samples per location in each test plot (*entire two-foot length of each sample was extracted*)



Performance Strategy and Goals

- Cape Canaveral Air Station

- Overall goal – Meet Florida State-mandated maximum contaminant level (MCL) targets in DNAPL Source Area: 3 ug/L TCE, 70 ug/L DCE, and 1 ug/L vinyl chloride
- Goal for Remediation Vendors – Remove 90% of initial DNAPL mass
- Performance Assessment Methodology
  - Primarily, detailed soil sampling
  - Secondarily, detailed groundwater and air emissions sampling to verify fate of chlorinated volatile organic compounds (CVOCs)
    - *Are CVOCs being destroyed?*
    - *Is DNAPL migrating to surrounding regions?*
    - *Are all the CVOCs removed from the test plot being captured aboveground?*

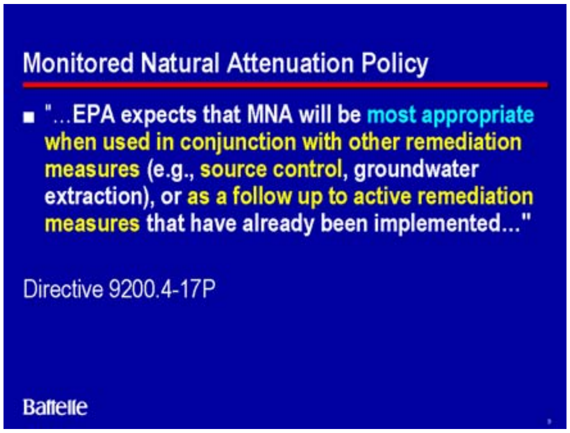


Performance Strategy and Goals

- Technical Impracticability Waiver Guidance

- "…Sources should be located and treated or removed where feasible and where significant risk reduction will result, regardless of whether EPA has determined that groundwater restoration is technically impracticable…" *[in other words, a DNAPL source should be located and treated as efficiently as possible, even though any remaining DNAPL may prevent the remediation from achieving MCLs (e.g., 5 ug/L of TCE). Inability to remove 100% of the source should not stop sites from attempting DNAPL source treatment]*

Directive 9234.2-25



Monitored Natural Attenuation Policy

- "...EPA expects that MNA will be most appropriate when used in conjunction with other remediation measures (e.g., source control, groundwater extraction), or as a follow up to active remediation measures that have already been implemented..."

Directive 9200.4-17P

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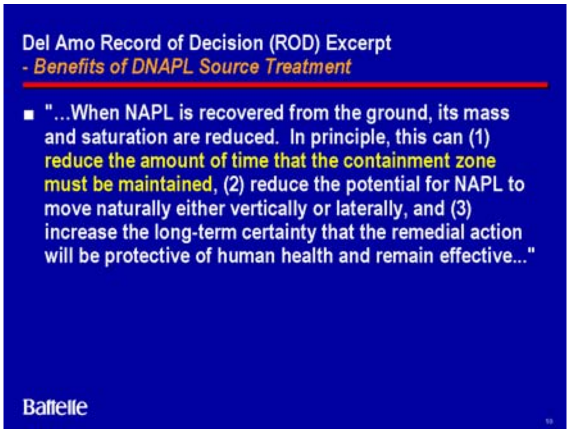

Del Amo Record of Decision (ROD) Excerpt
- Benefits of DNAPL Source Treatment

- "...When NAPL is recovered from the ground, its mass and saturation are reduced. In principle, this can (1) reduce the amount of time that the containment zone must be maintained, (2) reduce the potential for NAPL to move naturally either vertically or laterally, and (3) increase the long-term certainty that the remedial action will be protective of human health and remain effective..."

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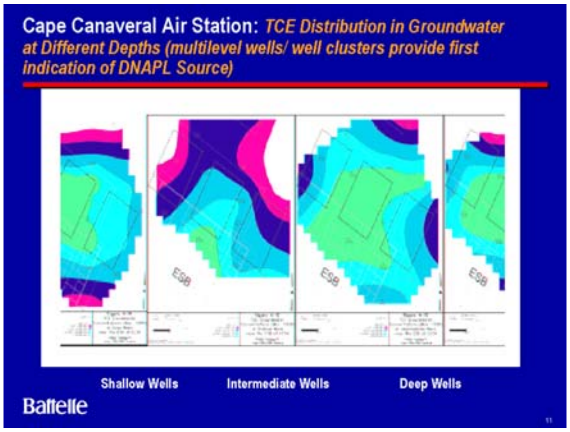

Cape Canaveral Air Station: *TCE Distribution in Groundwater at Different Depths (multilevel wells/ well clusters provide first indication of DNAPL Source)*

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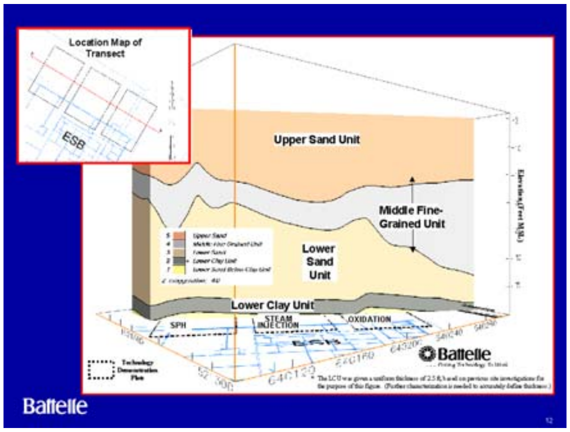

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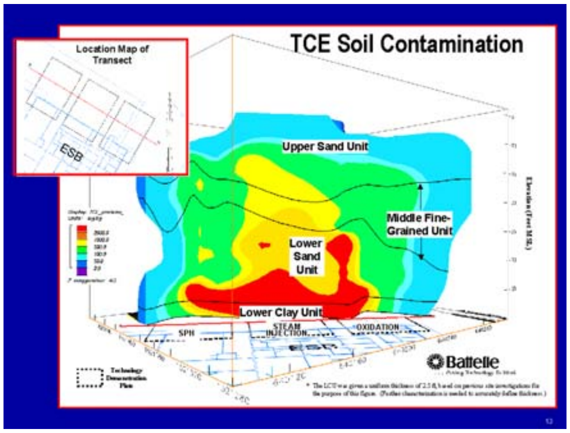

TCE Soil Contamination

Industrial Site in USA
- Six-Phase Heating Under a Building

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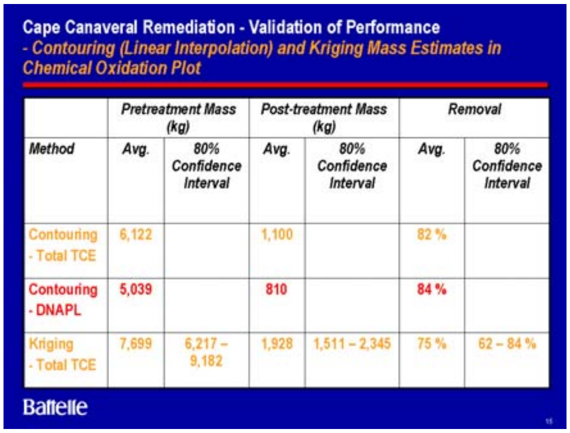

Cape Canaveral Remediation - Validation of Performance
- Contouring (Linear Interpolation) and Kriging Mass Estimates in Chemical Oxidation Plot

	Pretreatment Mass (kg)		*Post-treatment Mass (kg)*		*Removal*	
Method	*Avg.*	*80% Confidence Interval*	*Avg.*	*80% Confidence Interval*	*Avg.*	*80% Confidence Interval*
Contouring - Total TCE	6,122		1,100		82 %	
Contouring - DNAPL	5,039		810		84 %	
Kriging - Total TCE	7,699	6,217 – 9,182	1,928	1,511 – 2,345	75 %	62 – 84 %

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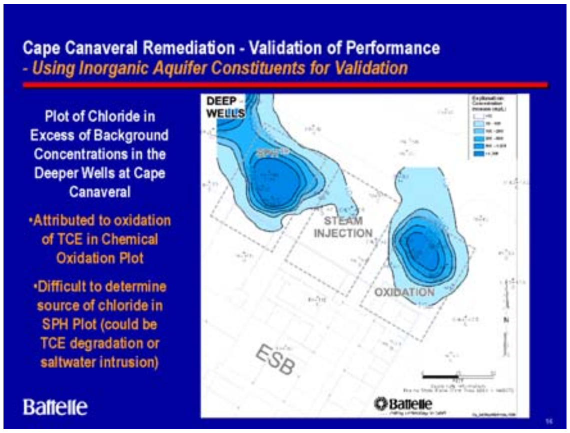

Cape Canaveral Remediation - Validation of Performance
- Using Inorganic Aquifer Constituents for Validation

Plot of Chloride in Excess of Background Concentrations in the Deeper Wells at Cape Canaveral

- Attributed to oxidation of TCE in Chemical Oxidation Plot
- Difficult to determine source of chloride in SPH Plot (could be TCE degradation or saltwater intrusion)

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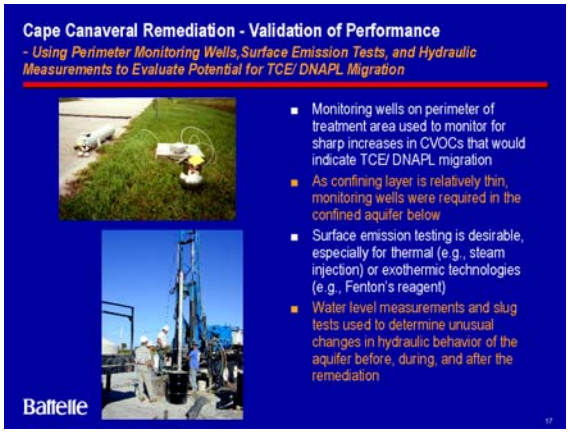

Cape Canaveral Remediation - Validation of Performance

- Using Perimeter Monitoring Wells, Surface Emission Tests, and Hydraulic Measurements to Evaluate Potential for TCE/ DNAPL Migration

- Monitoring wells on perimeter of treatment area used to monitor for sharp increases in CVOCs that would indicate TCE/ DNAPL migration
- As confining layer is relatively thin, monitoring wells were required in the confined aquifer below
- Surface emission testing is desirable, especially for thermal (e.g., steam injection) or exothermic technologies (e.g., Fenton's reagent)
- Water level measurements and slug tests used to determine unusual changes in hydraulic behavior of the aquifer before, during, and after the remediation

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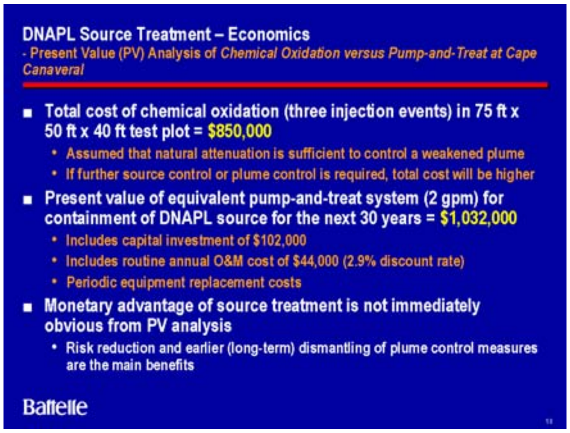

DNAPL Source Treatment – Economics

- Present Value (PV) Analysis of Chemical Oxidation versus Pump-and-Treat at Cape Canaveral

- Total cost of chemical oxidation (three injection events) in 75 ft x 50 ft x 40 ft test plot = $850,000
  - Assumed that natural attenuation is sufficient to control a weakened plume
  - If further source control or plume control is required, total cost will be higher
- Present value of equivalent pump-and-treat system (2 gpm) for containment of DNAPL source for the next 30 years = $1,032,000
  - Includes capital investment of $102,000
  - Includes routine annual O&M cost of $44,000 (2.9% discount rate)
  - Periodic equipment replacement costs
- Monetary advantage of source treatment is not immediately obvious from PV analysis
  - Risk reduction and earlier (long-term) dismantling of plume control measures are the main benefits

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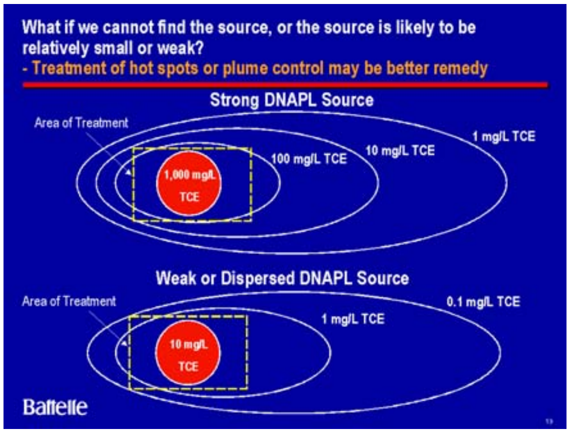

What if we cannot find the source, or the source is likely to be relatively small or weak?

- Treatment of hot spots or plume control may be better remedy

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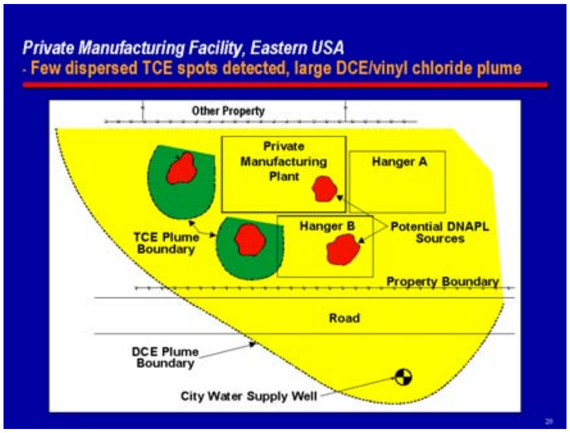
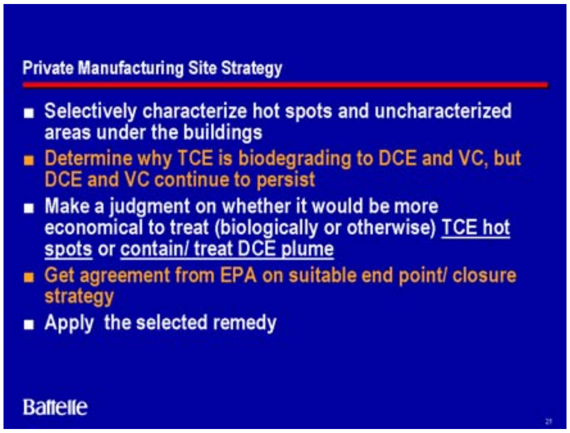


Private Manufacturing Facility, Eastern USA

- Few dispersed TCE spots detected, large DCE/vinyl chloride plume



Private Manufacturing Site Strategy

- Selectively characterize hot spots and uncharacterized areas under the buildings
- Determine why TCE is biodegrading to DCE and VC, but DCE and VC continue to persist
- Make a judgment on whether it would be more economical to treat (biologically or otherwise) TCE hot spots or contain/ treat DCE plume
- Get agreement from EPA on suitable end point/ closure strategy
- Apply the selected remedy

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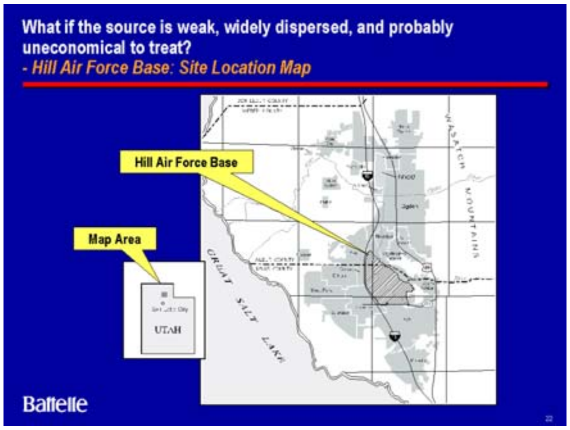

What if the source is weak, widely dispersed, and probably uneconomical to treat?

- Hill Air Force Base: Site Location Map

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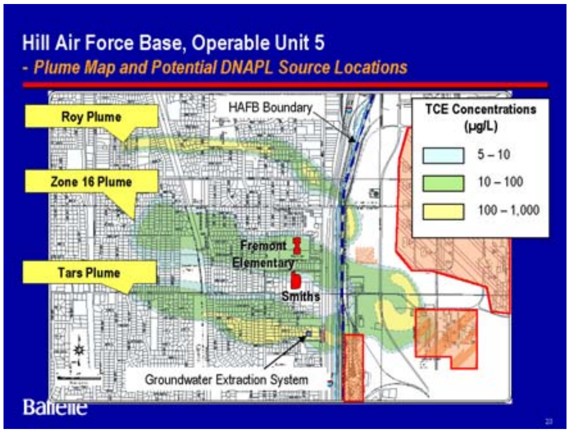

Hill Air Force Base, Operable Unit 5

- Plume Map and Potential DNAPL Source Locations

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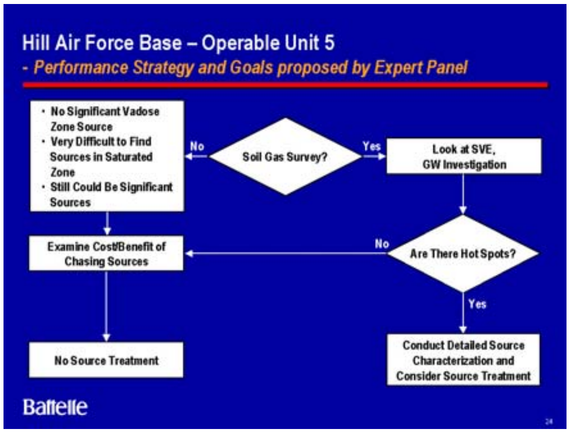

Hill Air Force Base – Operable Unit 5

- Performance Strategy and Goals proposed by Expert Panel

Soil Gas Survey?

No

- No Significant Vadose Zone Source
- Very Difficult to Find Sources in Saturated Zone
- Still Could Be Significant Sources

Examine Cost/Benefit of Chasing Sources

No Source Treatment

Yes

Look at SVE, GW Investigation

Are There Hot Spots?

No

Yes

Conduct Detailed Source Characterization and Consider Source Treatment

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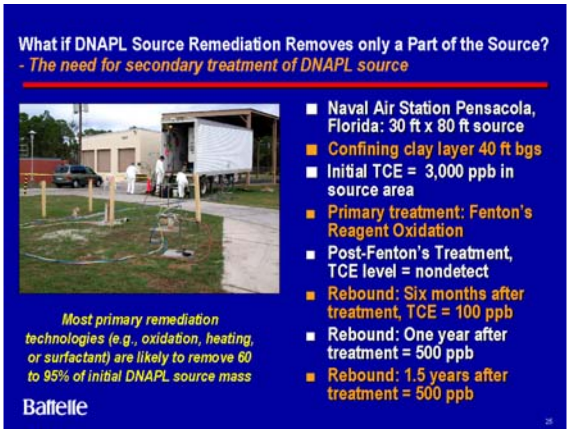

What if DNAPL Source Remediation Removes only a Part of the Source?
- The need for secondary treatment of DNAPL source

- Naval Air Station Pensacola, Florida: 30 ft x 80 ft source
- Confining clay layer 40 ft bgs
- Initial TCE = 3,000 ppb in source area
- Primary treatment: Fenton's Reagent Oxidation
- Post-Fenton's Treatment, TCE level = nondetect
- Rebound: Six months after treatment, TCE = 100 ppb
- Rebound: One year after treatment = 500 ppb
- Rebound: 1.5 years after treatment = 500 ppb

Most primary remediation technologies (e.g., oxidation, heating, or surfactant) are likely to remove 60 to 95% of initial DNAPL source mass

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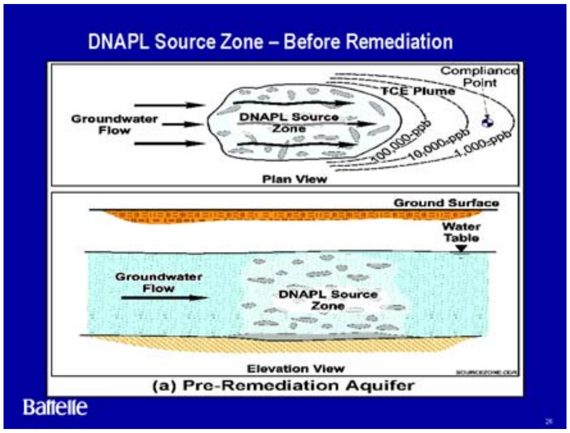

DNAPL Source Zone – Before Remediation

(a) Pre-Remediation Aquifer

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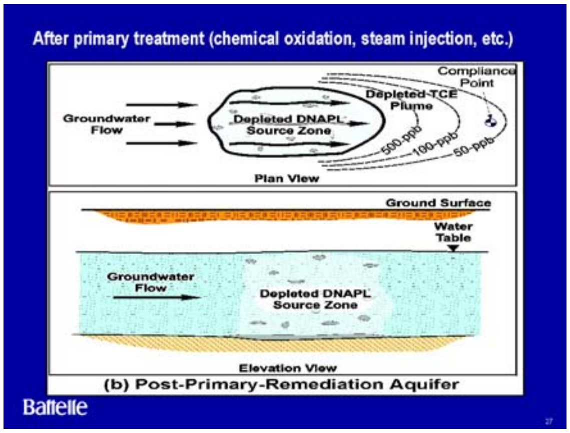

After primary treatment (chemical oxidation, steam injection, etc.)

(b) Post-Primary-Remediation Aquifer

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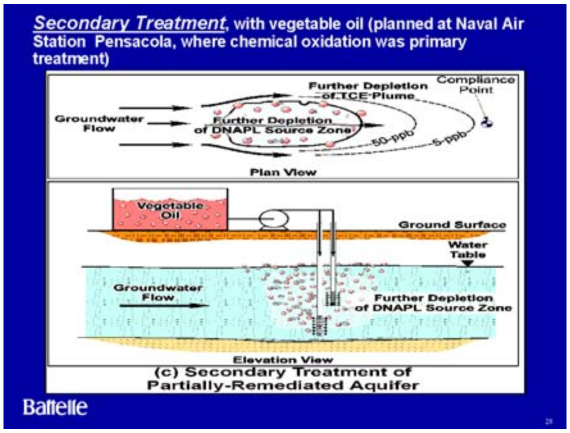

Secondary Treatment, with vegetable oil (planned at Naval Air Station Pensacola, where chemical oxidation was primary treatment)

(c) Secondary Treatment of Partially-Remediated Aquifer

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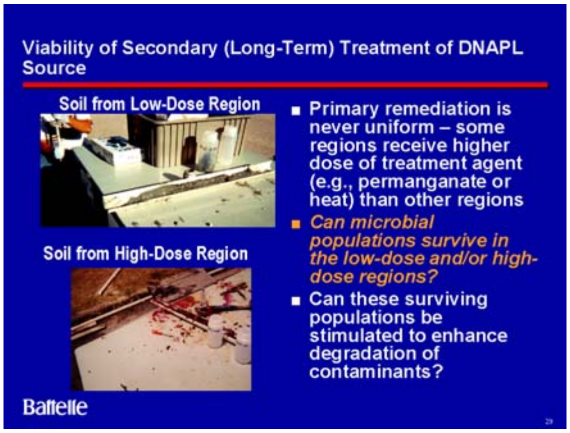

Viability of Secondary (Long-Term) Treatment of DNAPL Source

Soil from Low-Dose Region

Soil from High-Dose Region

- Primary remediation is never uniform – some regions receive higher dose of treatment agent (e.g., permanganate or heat) than other regions
- *Can microbial populations survive in the low-dose and/or high-dose regions?*
- Can these surviving populations be stimulated to enhance degradation of contaminants?

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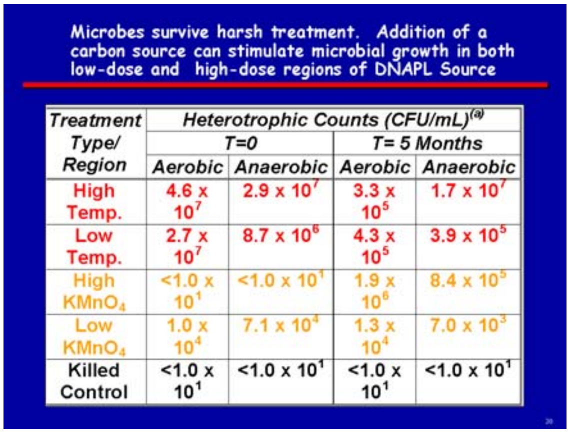
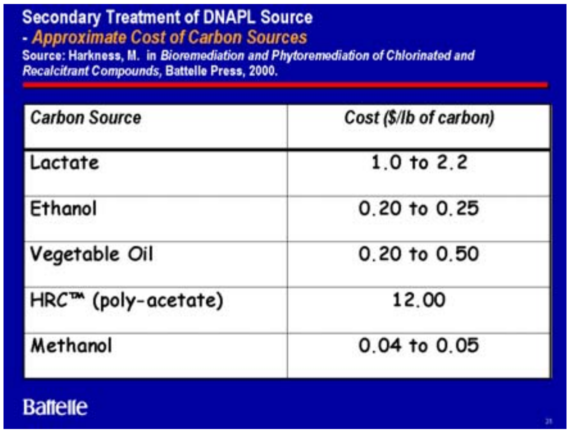


Microbes survive harsh treatment. Addition of a carbon source can stimulate microbial growth in both low-dose and high-dose regions of DNAPL Source

Treatment Type/ Region	*Heterotrophic Counts (CFU/mL)*[(a)]			
	T=0		*T= 5 Months*	
	Aerobic	*Anaerobic*	*Aerobic*	*Anaerobic*
High Temp.	4.6×10^7	2.9×10^7	3.3×10^5	1.7×10^7
Low Temp.	2.7×10^7	8.7×10^6	4.3×10^5	3.9×10^5
High $KMnO_4$	$<1.0 \times 10^1$	$<1.0 \times 10^1$	1.9×10^6	8.4×10^5
Low $KMnO_4$	1.0×10^4	7.1×10^4	1.3×10^4	7.0×10^3
Killed Control	$<1.0 \times 10^1$	$<1.0 \times 10^1$	$<1.0 \times 10^1$	$<1.0 \times 10^1$



Secondary Treatment of DNAPL Source
- Approximate Cost of Carbon Sources

Source: Harkness, M. in *Bioremediation and Phytoremediation of Chlorinated and Recalcitrant Compounds*, Battelle Press, 2000.

Carbon Source	*Cost ($/lb of carbon)*
Lactate	1.0 to 2.2
Ethanol	0.20 to 0.25
Vegetable Oil	0.20 to 0.50
HRC™ (poly-acetate)	12.00
Methanol	0.04 to 0.05

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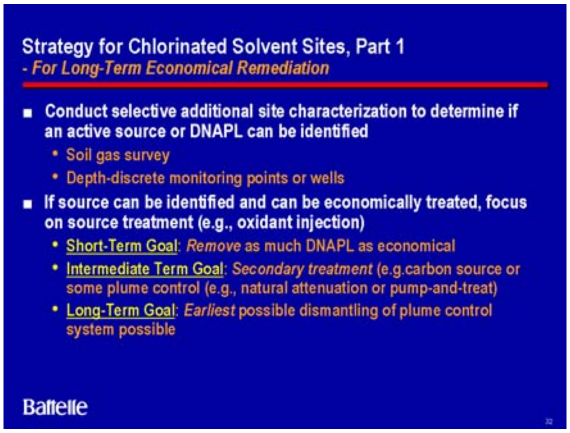

Strategy for Chlorinated Solvent Sites, Part 1
- For Long-Term Economical Remediation

- Conduct selective additional site characterization to determine if an active source or DNAPL can be identified
  - Soil gas survey
  - Depth-discrete monitoring points or wells
- If source can be identified and can be economically treated, focus on source treatment (e.g., oxidant injection)
  - Short-Term Goal: *Remove* as much DNAPL as economical
  - Intermediate Term Goal: *Secondary treatment* (e.g.carbon source or some plume control (e.g., natural attenuation or pump-and-treat)
  - Long-Term Goal: *Earliest* possible dismantling of plume control system possible

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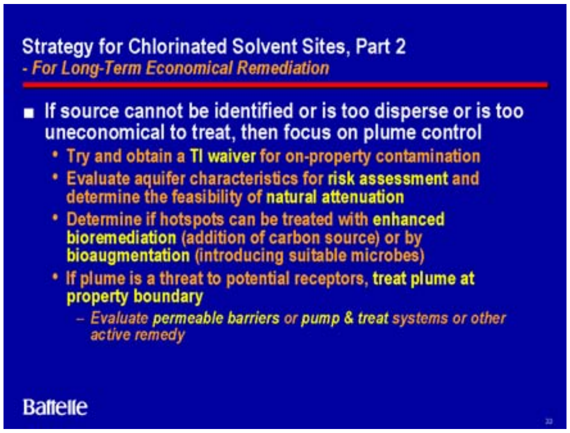

Strategy for Chlorinated Solvent Sites, Part 2

- For Long-Term Economical Remediation

- If source cannot be identified or is too disperse or is too uneconomical to treat, then focus on plume control
  - Try and obtain a **TI waiver** for on-property contamination
  - Evaluate aquifer characteristics for **risk assessment** and determine the feasibility of **natural attenuation**
  - Determine if hotspots can be treated with **enhanced bioremediation** (addition of carbon source) or by **bioaugmentation** (introducing suitable microbes)
  - If plume is a threat to potential receptors, **treat plume at property boundary**
    - *Evaluate **permeable barriers** or **pump & treat** systems or other active remedy*

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Site-Specific Validation of In-Situ Remediation of DNAPL

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- Battelle, 505 King Avenue, Columbus, Ohio 43201, USA
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FURURE DEVELOPMENTS IN VERIFICATION OF IN SITU PERFORMANCE: EXPECTATIONS, INSTRUMENTS, AND GOALS

Bert Satijn[1]

1. KEY ISSUES OF TECHNICAL PRESENTATIONS

The second day of the NATO/CCMS special session is dedicated to the technical issues of in situ technologies and validation aspects. This last presentation reviews technical contributions and picking up the key issues. These will be used as a base for a presentation of future developments in the field of performance testing and validation processes.

1.1 Soil Vapor Extraction- Michael Altenbockum

In Germany a large-scale review of executed soil vapor extraction projects has been executed. It became clear that in many cases the project team was not very well aware of the processes in subsoil. The overall conclusion of the reviewer was “They don’t know what they are doing”. Performance testing and validation was not done properly due to lack of experience and knowledge of the actual geochemical phenomena in the soil.

Energy consumption seemed to be a good parameter for cost efficiency. Energy is not only the important factor for the costs, but in relation with the total quantity of removed contaminants, it provides a good indication for the removal efficiency and environmental efficiency of the whole operation.

Conclusions of the study were, that Quality Assurance as integral part of the project needs more emphasis. The preparation of adequate guidelines in a kind of handbook or checklist could be an important aid to improve the performance of soil vapor extraction systems. In Germany they are working on these guidelines.

Validation should not only after the project being an issue. Especially during operation validation tools can provide the necessary information to modify the system and to adapt operation.

1.2. Surfactant/Cosolvent Flushing- Leland Vane

Validation of the performance of surfactant and cosolvent flushing is complicated, due to the complicated processes in subsoil. Although in many cases used, it is clear that groundwater monitoring is not the only and right validation tool. Concentrations in groundwater do not show the overall impact of the desorbing or mobilizing effect of the adsorbed contaminants on soil particles. No information will be gathered from the fate of the contaminants still (partly) adsorbed on the soil particles. It only provides evidence of the mass, diluted in the groundwater. To get more information of the residual bound contaminants on soil particles other methods are needed. Partitioning interwell tracer tests, PITT, are one of the promising new techniques. In fact with this technique the fate of the contaminants in the subsoil is “photographed”, by injecting a tracer into the hot spot and recovering it down stream. The recovery curve in the monitoring wells provides information on mass and location of NAPLs. PITT is fitting as characterization and validation tool.

But it is clear that to do a good validation a combination of different validation tools is required to provide evidence, that performance of the remediation system is adequate.

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1.3 Validation of In Situ Bioremediation by Applying Isotopes- Frank Volkering

Before validation of in situ bioremediation it is required to consider the parameters and criteria used. Next to the traditional parameters (concentrations in soil and groundwater, mass removal, etc.), last year's new lines of evidence have been developed, like hydrogen concentrations, DNA/RNA and isotopes.

Microorganisms do prefer to start with the lighter isotopes before cracking the heavier ones, as has been proven in many laboratories in batch tests. This phenomenon is called *fractionating of stable isotopes.* In one of the SKB-projects at the industrial site of DOW Chemicals in the Netherlands this method has been used successfully to validate the anaerobic degradation of benzene. It is expected that the application of analysis of stable isotopes will provide in future more possibilities for validation of the complex subsoil processes.

1.4 In Situ Chemical Oxidation- Robert Siegrist

In situ chemical oxidation is a new emerging technology for the elimination of hot spots. Also for this technique performance tests and validation tools are badly needed. Given the complex processes dealing with multiple evidence is needed for validation. Each method is providing us some part of the subsoil puzzle. One can think of a combination plume load measurements, mass destruction balances, bioassays and surface geophysics.

Compared to the traditional methods, it seems to be necessary to provide more evidence to prove that the new remediation system will be successful. But how much certainty do we have to give?

1.5 In Situ Permeable Reactive Barriers- Volker Birke

In Germany there are several experiences with reactive barriers. Reactive barriers are techniques on the boundary of in situ and ex situ. Validation of the performance is therefore a little bit easier than in case of the real in situ techniques. Installation of monitoring wells upstream, in the wall and downstream will provide the information on process conditions, efficiency and side effects. The technology is focused on an efficient removal of contaminants in the barrier without too much difficulty during exploitation. In many cases the barrier is designed to accommodate geochemical processes, for example the iron walls to eliminate the Tri and Per. But the anomaly in the subsoil is promoting biochemical processes, which easily creates clogging. The performance of active barriers might therefore be endangered due to bacterial growth in the barrier material or at the interface between soil and barrier.

In Germany the RUBIN network is established to develop and exchange knowledge on active barriers.

1.6 In Situ Remediation of DNAPLS- Arun Gavaskar

DNAPLs are made *not* to be discovered and *not* to be removed. This is the conclusion after studying so many projects on remediation of DNAPLs. The traditional approach of Pump and Treat is seldom successful. Pump & Treat becomes Pump & Spill due to the ever-lasting emissions from the source area. But the efficiency of source removal is sometimes disappointing. In sandy soils with new contaminants and retraceable source, there are possibilities of a removal rate of 90%. But in other cases it reaches up to 60 or 70%. So secondary treatment is normally necessary. It is also useful to realize that mobilizing the source and partial removing it, creates a situation in which the residue is normally more mobile than before. Without secondary treatment emissions to the plume will be bigger than before during a certain period after shaking up the source. The design of treatment system has to be based on a combination of primary and secondary treatment.

2. DEVELOPMENTS OF IN SITU TREATMENT

In situ remediation is a young science, only ten years old. The challenge of heterogeneity and complex biogeochemical processes makes the "remediator" a "geoartist". Site-specific circumstances influence the performance of techniques heavily. More understanding of processes by proper evaluation and research is needed. Better combinations of ex situ and in situ might provide solutions. Source boosting and plume management will be in many cases the right approach: better combinations of different in situ techniques with the right energy at the right time and place.

The consultants do not have enough knowledge and experience to propose such combinations. The contractors are normally specialized in one technique and are unable or unwilling to offer the right combination. This has also to do with the hardware; each technique requires its own system of hardware. But in future hardware has to be developed in such a way that the same equipment could be used for the subsequent phases in remediation.

The secondary treatment after partial removal of the source, is taking normally a long period. Therefore integration of clean up and redevelopment of the location could be thought over.

3. INSTRUMENTS AND GOALS FOR VALIDATION

Validation of in situ processes is based on the understanding of these processes. The available equipment is not sophisticated enough to provide the wanted evidence in many cases. More sophisticated monitoring tools are to be developed in the future, like cone penetration tests with specific probes for all relevant parameters to register the processes. Cheaper tools are needed in order to be able to get better spatial and time depending information.

Further development of sensors and effect related monitoring (bioassays) is important. But also the link to legislation should not be forgotten. Legislation is mainly based on concentrations, although risk based guidelines are becoming more and more important.

All these wishes do require quite some research funds. The economic developments and the political attention for soil quality is as such, that more money for these purposes is not to be expected. Therefore it is recommended to strengthen the international exchange of knowledge and data. An international performance database with information on the performance (well documented) of in situ techniques and methods to validate the performance could contribute to further development despite the recent developments in world society.

Although it will remain a challenge to be successful as "geoartists", the improvement of in situ techniques, hand in hand with its validation tools, has to contribute to a more predictable and cost efficient performance in soil quality management.

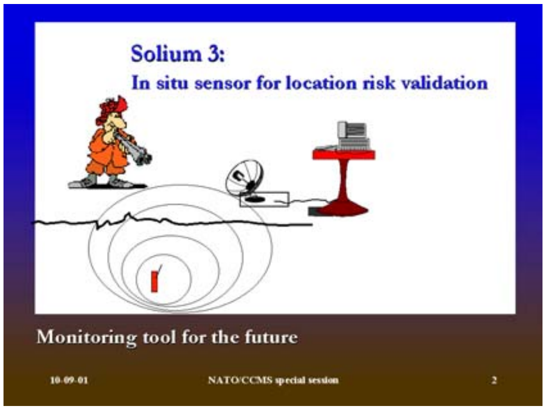
4. PRESENTATION VISUALS ~ *presented by Bert Satijn*

Future developments in validation of in situ performance, expectations, instruments & goals

Bert Satijn

SKB, Dutch Foundation for knowledge development and transfer on soil quality management

Nato/CCMS Special Session
Liege, 10 and 11 September 2001

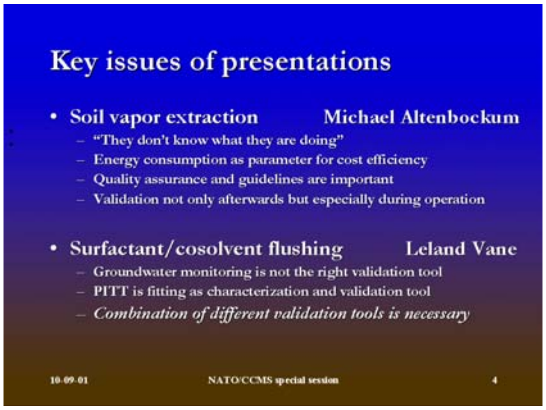


Solium 3:
In situ sensor for location risk validation

Monitoring tool for the future

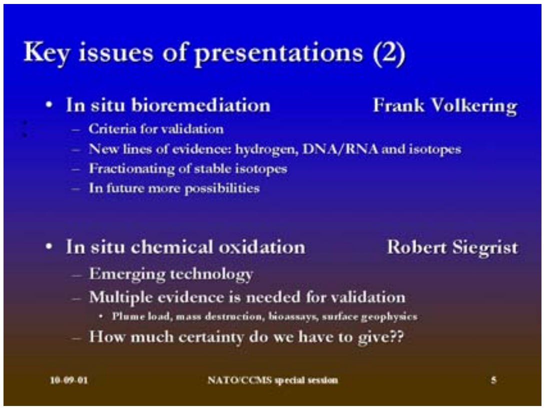
Outline of Presentation

- Recommendations of today's presentations
- Developments of in situ treatment
- Instruments and goals for validation
- Plenary discussion of field experiences and future developments



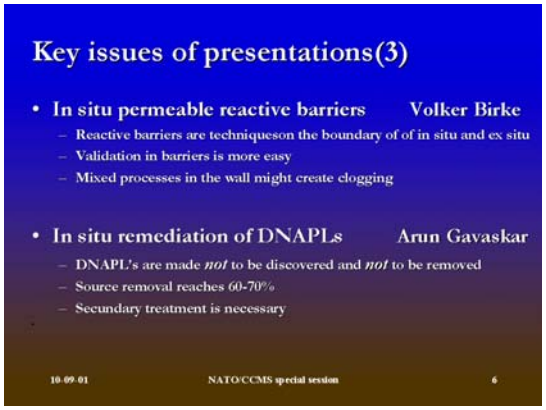
Key issues of presentations

- Soil vapor extraction **Michael Altenbockum**
  - "They don't know what they are doing"
  - Energy consumption as parameter for cost efficiency
  - Quality assurance and guidelines are important
  - Validation not only afterwards but especially during operation
- Surfactant/cosolvent flushing **Leland Vane**
  - Groundwater monitoring is not the right validation tool
  - PITT is fitting as characterization and validation tool
  - *Combination of different validation tools is necessary*



Key issues of presentations (2)

- In situ bioremediation **Frank Volkering**
  - Criteria for validation
  - New lines of evidence: hydrogen, DNA/RNA and isotopes
  - Fractionating of stable isotopes
  - In future more possibilities
- In situ chemical oxidation **Robert Siegrist**
  - Emerging technology
  - Multiple evidence is needed for validation
    - Plume load, mass destruction, bioassays, surface geophysics
  - How much certainty do we have to give??

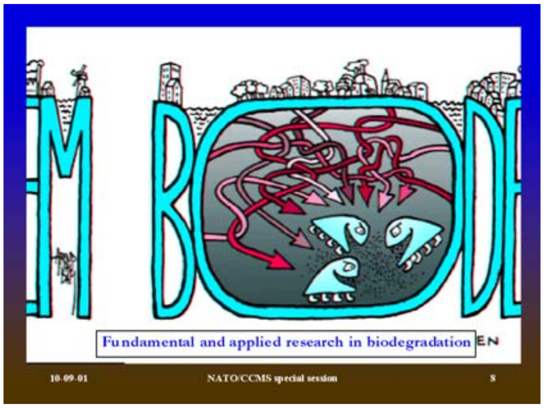


Key issues of presentations(3)

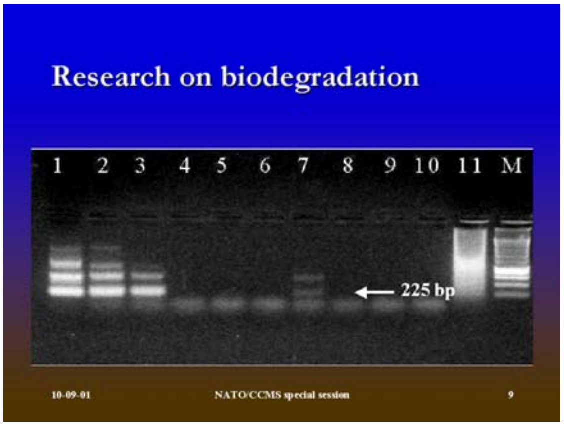
- In situ permeable reactive barriers **Volker Birke**
  - Reactive barriers are techniqueson the boundary of of in situ and ex situ
  - Validation in barriers is more easy
  - Mixed processes in the wall might create clogging
- In situ remediation of DNAPLs **Arun Gavaskar**
  - DNAPL's are made *not* to be discovered and *not* to be removed
  - Source removal reaches 60-70%
  - Secundary treatment is necessary

Developments of in situ treatment

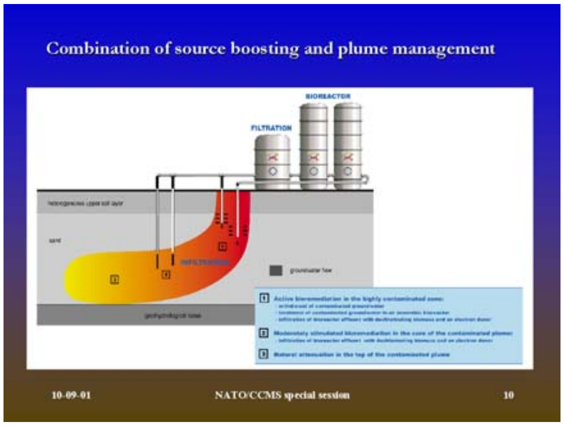
- More understanding of processes by proper evaluation and research
- Better combinations of ex situ and in situ
  - source boosting and plume management
- Better combinations of different in situ techniques
  - the right energy at the right time and place
- Integration of clean up and redevelopment



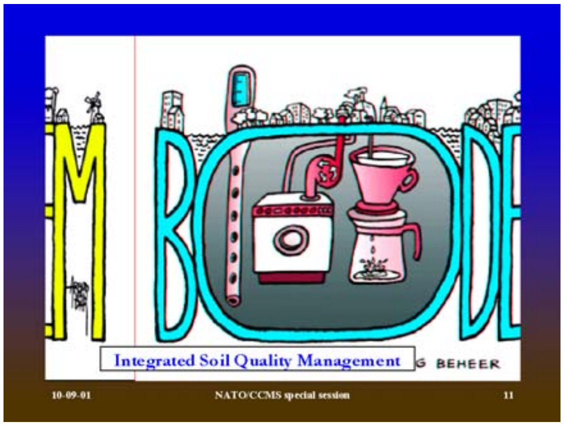
Fundamental and applied research in biodegradation



Research on biodegradation



Combination of source boosting and plume management



Developments of in situ treatment (2)

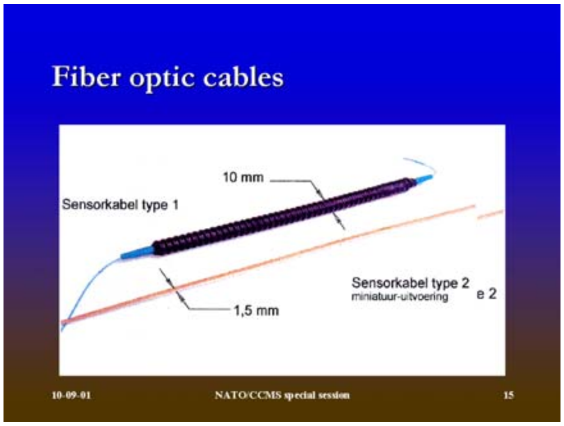
- More realistic goals by authorities and *geo-artists*
- Better understanding of risk reduction related to cost efficiency
- Better balance for uncertainties
- Function related risk criteria fitted on location scale (Solium 3)

Instruments and goals for validation

- More sophisticated monitoring tools
  - Cone penetration test with specific probes
    - more parameters
    - cheaper
    - 3D information
  - Further development of sensors and effect related monitoring (bioessays) including link to legislation
- International Performance Database

Cone penetration tests:

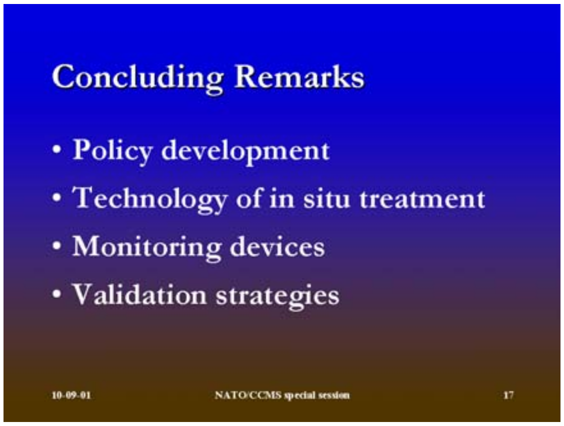
- •geotechnical data
- •watersampling
- •pH, temperature, Ec
- •redox profile
- •camera
- •ecotox-factor



Fiber optic cables

Instruments and goals for validation (2)

- Validation is an integral part of in situ technology
- Validation protocol is determined during planning phase
- Protocol is not denying heterogeneity



Concluding Remarks

- Policy development
- Technology of in situ treatment
- Monitoring devices
- Validation strategies

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PILOT STUDY MISSION

PHASE III C Continuation of NATO/CCMS Pilot Study: Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater

1. BACKGROUND TO PROPOSED STUDY

The problems of contamination resulting from inappropriate handling of wastes, including accidental releases, are faced to some extent by all countries. The need for cost-effective technologies to apply to these problems has resulted in the application of new/innovative technologies and/or new applications of existing technologies. In many countries, there is increasingly a need to justify specific projects and explain their broad benefits given the priorities for limited environmental budgets. Thus, the environmental merit and associated cost-effectiveness of the proposed solution will be important in the technology selection decision.

Building a knowledge base so that innovative and emerging technologies are identified is the impetus for the NATO/CCMS Pilot Study on "Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater." Under this current study, new technologies being developed, demonstrated, and evaluated in the field are discussed. This allows each of the participating countries to have access to an inventory of applications of individual technologies, which allows each country to target scarce internal resources at unmet needs for technology development. The technologies include biological, chemical, physical, containment, solidification/stabilization, and thermal technologies for both soil and groundwater. This current pilot study draws from an extremely broad representation and the follow up would work to expand this.

The current study has examined over fifty environmental projects. There were nine fellowships awarded to the study. A team of pilot study country representatives and fellows is currently preparing an extensive report of the pilot study activities. Numerous presentations and publications reported about the pilot study activities over the five-year period. In addition to participation from NATO countries, NACC and other European and Asian-Pacific countries participated. This diverse group promoted an excellent atmosphere for technology exchange. An extension of the pilot study will provide a platform for continued discussions in this environmentally challenging arena.

2. PURPOSE AND OBJECTIVES

The United States proposes a follow-up (Phase III) study to the existing NATO/CCMS study titled "Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater." The focus of Phase III would be the technical approaches for addressing the treatment of contaminated land and groundwater. This phase would draw on the information presented under the prior studies and the expertise of the participants from all countries. The output would be summary documents addressing cleanup problems and the array of currently available and newly emerging technical solutions. The Phase III study would be technologically orientated and would continue to address technologies. Issues of sustainability, environmental merit, and cost-effectiveness would be enthusiastically addressed. Principles of sustainability address the use of our natural resources. Site remediation addresses the management of our land and water resources. Sustainable development addresses the re-use of contaminated land instead of the utilization of new land. This appeals to a wide range of interests because it combines economic development and environmental protection into a single system. The objectives of the study are to critically evaluate technologies, promote the appropriate use of technologies, use information technology systems to disseminate the products, and to foster innovative thinking in the area of contaminated land. International technology verification is another issue that will enable technology users to be assured of minimal technology performance. This is another important issue concerning use of innovative technologies. This Phase III study would have the following goals:

a) In-depth discussions about specific types of contaminated land problems (successes and failures) and the suggested technical solutions from each country's perspective,

b) Examination of selection criteria for treatment and cleanup technologies for individual projects,

c) Expand mechanisms and channels for technology information transfer, such as the NATO/CCMS Environmental Clearinghouse System,

d) Examination/identification of innovative technologies, and

e) Examining the sustainable use of remedial technologies looking at the broad environmental significance of the project, thus the environmental merit and appropriateness of the individual project.

3. ESTIMATED DURATION

Meetings: November 1997 to May 2002
Completion of final report: June 2003

4. SCOPE OF WORK

First, the Phase III study would enable participating countries to continue to present and exchange technical information on demonstrated technologies for the cleanup of contaminated land and groundwater. During the Phase II study, these technical information exchanges benefited both the countries themselves and technology developers from various countries. This technology information exchange and assistance to technology developers would therefore continue. Emphasis would be on making the pilot study information available. Use of existing environmental data systems such as the NATO/CCMS Environmental Clearinghouse System will be pursued. The study would also pursue the development of linkages to other international initiatives on contaminated land remediation.

As in the Phase II study, projects would be presented for consideration and, if accepted by other countries, they would be discussed at the meetings and later documented. Currently, various countries support development of hazardous waste treatment/cleanup technologies by governmental assistance and private funds. This part of the study would report on and exchange information of ongoing work in the development of new technologies in this area. As with the current study, projects would be presented for consideration and if accepted, fully discussed at the meetings. Individual countries can bring experts to report on projects that they are conducting. A final report would be prepared on each project or category of projects (such as thermal, biological, containment, etc.) and compiled as the final study report.

Third, the Phase III study would identify specific contaminated land problems and examine these problems in depth. The pilot study members would put forth specific problems, which would be addressed in depth by the pilot study members at the meetings. Thus, a country could present a specific problem such as contamination at an electronics manufacturing facility, agricultural production, organic chemical facility, manufactured gas plant, etc. Solutions and technology selection criteria to address these problems would be developed based on the collaboration of international experts. These discussions would be extremely beneficial for the newly industrializing countries facing cleanup issues related to privatization as well as developing countries. Discussions should also focus on the implementation of incorrect solutions for specific projects. The documentation of these failures and the technical understanding of why the project failed will be beneficial for those with similar problems. Sustainability, environmental merit, and cost-benefit aspects would equally be addressed.

Finally, specific area themes for each meeting could be developed. These topics could be addressed in one-day workshops as part of the CCMS meeting. These topic areas would be selected and developed by the pilot study participants prior to the meetings. These areas would be excellent venues for expert speakers and would encourage excellent interchange of ideas.

5. NON-NATO PARTICIPATION

It is proposed that non-NATO countries be invited to participate or be observers at this NATO/CCMS Pilot Study. Proposed countries may be Brazil, Japan, and those from Central and Eastern Europe. It is proposed that the non-NATO countries (Austria, Australia, Sweden, Switzerland, New Zealand, Hungary, Slovenia, Russian Federation, etc.) participating in Phase II be extended for participation in Phase III of the pilot study. Continued involvement of Cooperation Partner countries will be pursued.

6. REQUEST FOR PILOT STUDY ESTABLISHMENT

It is requested of the Committee on the Challenges of Modern Society that they approve the establishment of the Phase III Continuation of the Pilot Study on the Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater.

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Lead Organization:	U.S. Environmental Protection Agency

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Participating Countries:	Australia, Austria, Belgium, Canada, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Ireland, Japan, New Zealand, Norway, Poland, Portugal, Slovenia, Sweden, Switzerland, The Netherlands, Turkey, United Kingdom, United States
Scheduled Meetings:	February 23-27, 1998, in Vienna, Austria May 9-14, 1999, in Angers, France June 26-30, 2000, in Wiesbaden, Germany September 9-14, 2001, in Liège, Belgium May 5-10, 2002, Rome, Italy