附件一

出國報告摘要

一、出國計畫名稱：參加 2016 年第 32 屆國際土壤、底泥、水和能源會議

二、出國人員：土污基管會王子欣環境技術師

三、出國日期：105 年 10 月 16 日至 105 年 10 月 22 日

四、出國行程與內容概要：

日期	工作內容概要
105.10.16	●臺北出發至美國麻州艾姆赫斯特
105.10.17	●參加研討會舉辦之環境鑑識訓練課程，由美國 University of Oklahoma 地質系教授 Paul Philip 主講環境污染責任的鑑識技術
105.10.18	●參加研討會綠色整治與現地整治技術講座及整治技術訓練課程，主講應用在困難地質條件（如黏土層與裂隙岩床）下的整治工具
105.10.19	●參加研討會環境鑑識與污染場址管理講座，發表海報論文，分享我國在環境鑑識技術的經驗
105.10.20	●參加研討會土壤與地下水污染影響室內空氣品質 (vapor intrusion)講座
105.10.21	●返程
105.09.22	●返抵臺灣

五、行程成果評估及心得建議：

（一） 本次研討會行程主要為了解國際間污染場址相關議題與技術的最新發展與應用現況，以作為國內未來技術發展規劃之參考。相關議題包括：

1. 發表海報論文，分享我國在環境鑑識領域的技術進展，以及穩定同位素鑑識技術的發展成果。主要分享內容包括：

(1)我國應用環境鑑識技術釐清污染責任的經驗。

(2)利用穩定同位素鑑識技術進行場址鑑識工作的學理依據。

其中，有多位美國從事環境鑑識工作的專家對於我方在學理面提出系統性的探討與結果極為讚賞；整治領域的專家則建議我們可將穩定同位素技術應用在生物整治成效的鑑定。

2. 參加研討會講座，了解國際環保議題的進展，包括綠色整治觀念、整

治技術、環境鑑識、場址管理、土壤與地下水污染影響室內空氣品質(vapor intrusion)等議題，內容摘錄如下：

(1)綠色整治是種決策過程，不是項技術。美國環保署為推行綠色整治，於 2013 年公布 ASTM E2893，制定綠色整治的實施指引，並在全美推廣，讓資源損耗與碳足跡也成為整治決策過程的考量因素之一。美國麻州州政府結合該州於 1993 年建立的證照制度(licensed site professionals, LSP)，經由教育訓練要求 LSP 遵照 ASTM E2893 方法，將綠色整治與場址管理結合，作為綠色整治推廣的主要管道。

(2)在綠色整治的潮流之下，整治技術朝向結合場址當地的環境特色與需求，做既有整治技術的調整與整合。同時，在整治藥劑的選擇與施作上，亦以永續與長效為主要考量。

(3)環境鑑識技術仍以特徵比對為主，包括元素組成分析、油品指紋分析、穩定同位素特徵，技術發展的面向包括針對低濃度樣品的分析偵測極限突破（如前濃縮技術）、多元素同時分析及即時分析等。

(4)污染場址整治產業從 20 年前整治技術的推陳出新，轉變至今日重視場址管理工具的建立，尤其是跨領域技術的應用，包括分子診斷技術（如分子生物技術與穩定同位素特徵）、物質流與高解析場址調查。此外，整治決策也包括思考整治是否為必要？是否協商及管理手段就可提供最佳的風險控制？

(5)土壤或地下水中污染物經揮發與擴散過程進入到室內，造成室內空氣品質惡化是污染場址衍伸的另一個環境議題，並已影響到居住安全與房地產買賣。由於污染物在室內空間與時間分布上的變異性，導致採樣手法容易影響評估結果，同時也必須排除該污染來自於室內其他來源而非土壤或地下水，因此主要的研究課題包括採樣評估技術以及來源鑑識技術。

3. 參加訓練課程，包括環境鑑識技術與困難地質（黏土層與裂隙岩床）之整治技術，各課程重點包括：

(1)環境鑑識技術訓練課程以講授穩定同位素為主。穩定同位素可鑑識來源，包括食品（龍舌蘭酒 Tequila、啤酒、蜂蜜）、底泥或水污

染的來源或產源鑑定。環境領域的相關應用包括地下水污染來源相關性、污染責任釐清與比例分配、油品洩漏（柴油或汽油）污染責任鑑定、多環性芳香化合物、多氯聯苯污染來源鑑定、過氯酸鹽來源鑑定、室內空氣污染來源鑑定、污染物在現地是否進行降解以及其降解機制等。

(2)困難地質之整治技術係針對污染範圍內具有低透水地質（如黏土層、坋土層或腐泥岩等）或具有裂隙的基岩。較常使用的整治技術或工法包括特定深度加壓注藥(Jet Injection)、搭配特殊灌注方式之生物整治、熱處理法、電動力法等。

（二） 心得及建議事項：

1. 國內在油品特徵指紋、穩定同位素鑑識技術及整治技術的發展已有國際技術水平，但跨領域及綜合應用的層面尚未多元。以穩定同位素鑑識技術為例，除了應用於含氯碳氫污染場址之外，未來應進一步評估國內環境問題的需求，拓展該項技術之應用面。
2. 國內污染場址經過多年的盤查，已進入到整治為主的階段，建議可參考國外經驗，學習國外對於場址整治管理上做決策的思維，從思考整治是否為必要？是否協商及管理手段就可提供最佳的風險控制？至尋求控制風險之最綠色方式，與國內正推行中的綠色整治概念相互結合等。

附件二

公務出國期間國外人士個人資料彙整表

會議活動名稱	姓名	單位及職稱	國別	專長領域	會晤日期	聯絡電話	電子郵件	我方接洽者姓名職稱	交流內容
2016 年第 32 屆國際土壤、底泥、水和能源會議	Aaron Peacock	Pace Analytical General Manager 總經理	USA	Superfund 管理、污染整治、綠色整治	10/17~20		aaron.peacock@pacelabs.com	王子欣 環境技術師	CSIA
	Yi Wang 王毅	Pace Analytical CSIA Center Director 同位素中心主任	USA	污染場址管理	10/17~20		yi.wang@ pacelabs.com	王子欣 環境技術師	CSIA
	David Rich	Geotech President 董事長	USA	污染整治	10/17~20		drdave@geotech.com	王子欣 環境技術師	廠商展示高解析調查
	Philip Tackett	FLIR Product Manager 產品部經理	USA	SuRF UK 推廣、污染場址管理、永續整治	10/17~20		Philip.tackett@flir.com	王子欣 環境技術師	廠商展示污染即時偵測
	Carol de Groot Bois	Bois Consulting Company President 董事長	USA	污染整治技術、永續整治	10/17~20		cb@boisconsulting.com	王子欣 環境技術師	CSIA
	Robert Haddad	Exponent Vice President 副董事長	USA	污染整治技術、永續整治	10/17~20		bhaddad@exponent.com	王子欣 環境技術師	CSIA
	David Cash	University of Massachusetts Boston McCormack Graduate School Dean 院長	USA	SuRF UK 推廣、永續整治	10/17~20		david.cash@umb.edu	王子欣 環境技術師	CSIA

附件三、海報論文摘要資料

Fractionation Effects on C, H and Cl Stable Isotopes of Chlorinated Solvents during Dissolution, Adsorption and Evaporation

I-Hsing Chen[1], Zih-Sin Wang[1], Chia-Pei Li[2], Hsin-Lan Hsu[2,*]

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Environmental forensics of contaminated sites is a critical issue over the recent decades in order to resolve the liability. For the sites contaminated by chlorinated solvents, compound specific isotope analysis is an emerging and useful tool for investigators to trace the original sources of contaminants. When interpreting the isotopic signatures, it is essential to understand what could cause changes in these signatures, especially the mass transfer processes that contaminants often experience in the environment. Previous studies indicated that mass transfer processes could cause isotope fractionation effects on the stable isotope ratios of some contaminants of environmental concern. However, most studies were focused on the carbon stable isotope and some certain compounds such as trichloroethylene. Impacts on many other contaminants and other stable isotopes still remained unknown. The purpose of this work was to systematically investigate the fractionation effects on carbon, hydrogen and chlorine stable isotopic compositions of the chlorinated organic compounds during adsorption, dissolution and evaporation. The studied chlorinated organic compounds included tetrachloroethylene, trichloroethylene, 1,1-dichloroethene, vinyl chloride, 1,2-dichloroethane and dichloromethane, all of which were among the target chlorinated contaminants in Taiwan and other countries such as the United States. Results of this research were also compared with other studies and implications on environmental forensics were discussed.

Fractionation Effects on C, H and Cl Stable Isotopes of Chlorinated Solvents during Dissolution, Adsorption and Evaporation

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1 Environmental Protection Administration, Executive Yuan. No. 83, Zhonghua Rd. Sec. 1, Zhongzheng District, Taipei, 10042, Taiwan.
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Introduction

Background

Chlorinated solvents, such as PCE, TCE, EDC, DCM etc., are used widely during industrial processes. The cracks of storage tank or improper disposal of waste liquid let these solvents contaminate soil and groundwater, and pose threats to ecosystem and human health. Chlorinated solvents are dense non-aqueous phase liquid (DNAPL). It's difficult to find their pure phases in the contaminated site because contaminated soil has low mobility and DNAPL will deposit on the bottom of saturated aquifer with low rates of dissolution. It's a big issue on environmental forensics.

Compound specific isotope analysis (CSIA)

Compound specific isotope analysis (CSIA) is a state-of-the-art and useful tool in the field of environmental forensics. A process making the relative abundance of isotopes of a compound changed is called as isotope fractionation. Solvents produced from different manufacturing processes have their own specific isotope signatures ($\delta^{h}E$). Accordingly, contaminants' stable isotope signatures obtained from CSIA could be applied on tracing the original sources of contaminants and clarifying the responsibilities.

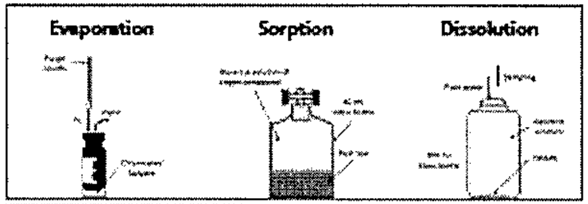
As expressed by eq. 1, an element's isotope signature of a compound in the sample is calculated by using the isotope ratio ($^{h}E/^{l}E$) of sample and that of international standard. ^{h}E and ^{l}E represent heavy isotope and light isotope of element (E), respectively. During fractionation processes of natural environment, the isotope ratio variation of compounds is generally revealed by fractionation factor (α) or enrichment factor (ε_{E}) and described through Rayleigh equation (eq. 2), where f is the ratio of remaining concentration and initial concentration of the target compound (C/C_0).

$$\delta^{h}E = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000‰ \quad \text{(eq. 1)} \qquad R = R_0 f^{(\alpha-1)} = R_0 f^{\frac{\varepsilon}{1000}} \quad \text{(eq. 2)}$$

Objective

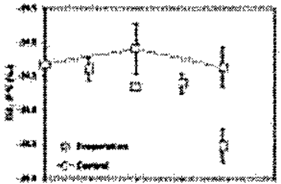
Before applying CSIA on environmental forensics, it's necessary to realize the fractionation effects of important natural transformation processes on isotopes of those chlorinated compounds. Most previous studies were focus on $\delta^{13}C$ variations of PCE, TCE, and c-DCE during evaporation or sorption.[1, 2-4] Merely few of them probed into $\delta^{2}H$ or $\delta^{37}Cl$ and the isotope fractionation effect of dissolution for a few chlorinated contaminants [5, 6]. Therefore, the objective of this work is to investigate carbon, chlorine and hydrogen isotope compositions of PCE, TCE, 1,1-dichloroethene (1,1-DCE), vinyl chloride (VC), EDC and DCM during the processes of evaporation, sorption and dissolution by GC/MS and GC/IRMS.

Experimental Method



Result

Evaporation experiments' results showed that carbon and chlorine stable isotope signature of all target compounds changed centrally (as Table). Those results indicated that during the evaporations of chlorinated solvents, molecules with ^{12}C and/or ^{35}Cl were evaporated earlier than those with ^{13}C and/or ^{37}Cl did. In the aspect of hydrogen stable isotope signature, TCE and EDC's $\delta^{2}H$ value declined as the evaporative percentage increased. However, the $\delta^{2}H$ values of 11DCE and DCM solvent residuals became enriched as the evaporation progressed. The evaporation enrichment factors of each target compound were presented in Table.



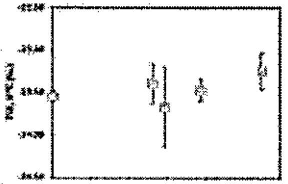
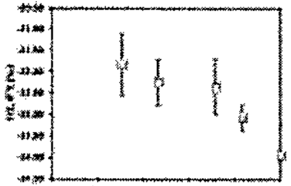


Table. The C, Cl and H isotope enrichment factors of target compounds evaporation, sorption and dissolution experiment; the uncertainty was characterized using the standard uncertainty of the slope of the regression line; N.S. means that there was no significant isotope effect during experiment.

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	ε_{13C}	1.08±0.29	0.76±0.18	0.83±0.12	0.99±0.48	1.21±0.25
	ε_{37Cl}	-0.17±0.20	-1.23±0.06	-2.03±0.13	-1.40±0.30	-1.72±0.13
	ε_{2H}	NA	17.53±11.36	13.09±12.89	-13.15±13.39	-32.42±9.93
[illegible]	ε_{13C}	-1.01±0.42	N.S.	N.S.	N.S.	N.S.
	ε_{37Cl}	N.S.	-5.16±2.21	N.S.	N.S.	N.S.
	ε_{2H}	N.A.	N.S.	N.S.	N.S.	N.S.
[illegible]	ε_{13C}	0.43±0.33	0.77±0.19	N.S.	N.S.	-1.32±0.34
	ε_{37Cl}	N.S.	N.S.	N.S.	N.S.	N.S.
	ε_{2H}	N.A.	18.58±8.42	N.S.	N.S.	N.S.

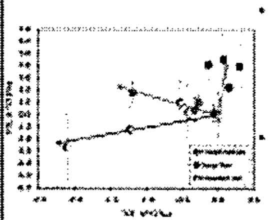
Sorption experiments' results showed that sorption only caused significant isotope effect on PCE's $\delta^{13}C$ and TCE's $\delta^{37}Cl$ with an enrichment factor of -1.01±0.42 and -5.16±2.21, respectively. This result indicated that TCE molecules with ^{37}Cl might prefer to be partitioned into organic matters, comparing to those molecules with ^{35}Cl; likewise, PCE molecules with ^{12}C tended to dissolve in organic matters. There were no significant isotope effect observed on other target compounds' $\delta^{13}C$, $\delta^{2}H$ and $\delta^{37}Cl$ values.

In the dissolution study, the CSIA were conducted with aqueous samples. Dissolution caused significant isotope effect on PCE, TCE, DCM's $\delta^{13}C$ and TCE's $\delta^{2}H$ in 95% confidence interval. Their enrichment factors were shown in Table.



In addition, dissolution did not cause isotope effect on the chlorine stable isotope signatures of all target compounds because the variation of their $\delta^{37}Cl$ values was not significant in 95% confidence interval and the difference of each signature was within the precision of analysis (1 ‰).

Conclusion



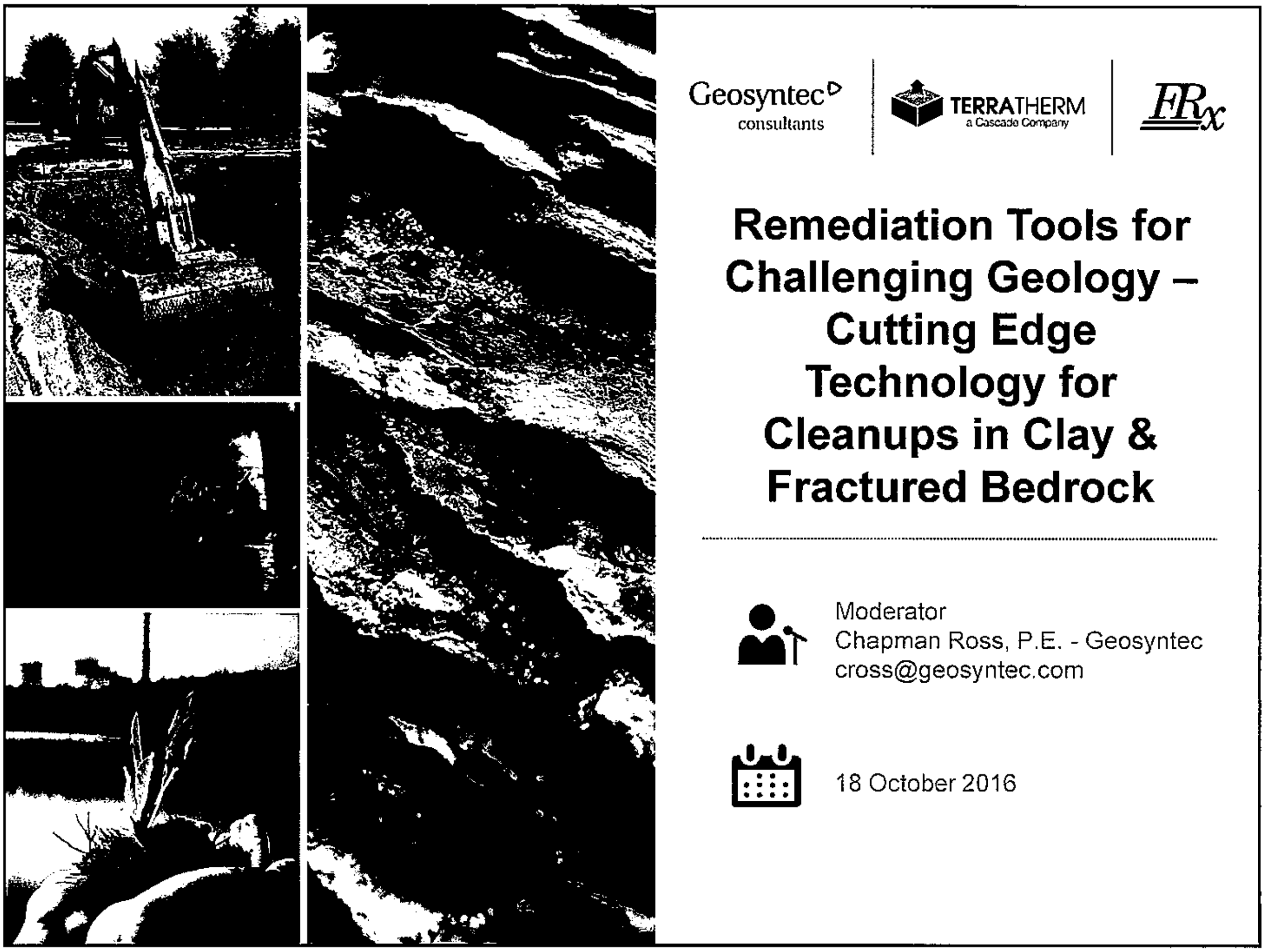
- The isotope effect could be ignored interpreting isotope signatures at most cases because the isotope signature of chlorinated contaminants in the environment changes significantly, when they are affected at least 50% by evaporation, sorption and dissolution.
- Two-dimensional carbon and chlorine isotope analysis could help to discriminate between evaporation, sorption and dissolution, even biodegradation, owing to the isotope fractionation difference of each mechanism.

Reference

1. Yu, T.; Gan, Y.; Zhou, A.; Yu, K.; Liu, Y., Investigation of Stable C and Cl isotope effects of trichloroethene and tetrachloroethylene during evaporation at different temperatures. *Journal of Earth Science* 2014, 25, (4), 735-740.
2. Huang, L.; Sturchio, N.; Abrajano, T.; Heraty, L.; Holt, B., Carbon and chlorine isotope fractionation of chlorinated aliphatic hydrocarbons by evaporation. *Organic Geochemistry* 1999, 30, (8), 777-785.
3. Slater, G. F.; Dempster, H. S.; Sherwood Lollar, B.; Ahad, J., Headspace analysis: a new application for isotopic characterization of dissolved organic contaminants. *Environ. Sci. Technol.* 1999, 33, (1), 190-194.
4. Schüth, C.; Taubald, H.; Bolaño, N.; Maciejczyk, K., Carbon and hydrogen isotope effects during sorption of organic contaminants on carbonaceous materials. *Journal of Contaminant Hydrology* 2003, 64, (3), 269-281.
5. Höhener, P.; Yu, X., Stable carbon and hydrogen isotope fractionation of dissolved organic groundwater pollutants by equilibrium sorption. *Journal of contaminant hydrology* 2012, 129, 54-61.
6. Poulson, S. R.; Drever, J. I., Stable isotope (C, Cl, and H) fractionation during vaporization of trichloroethylene. *Environ. Sci. Technol.* 1999, 33, (20), 3689-3694.

附件四、訓練課程講義資料

Workshop 7



Geosyntec consultants | TERRATHERM a Cascade Company | FRx

Remediation Tools for Challenging Geology – Cutting Edge Technology for Cleanups in Clay & Fractured Bedrock

Moderator
Chapman Ross, P.E. - Geosyntec
cross@geosyntec.com

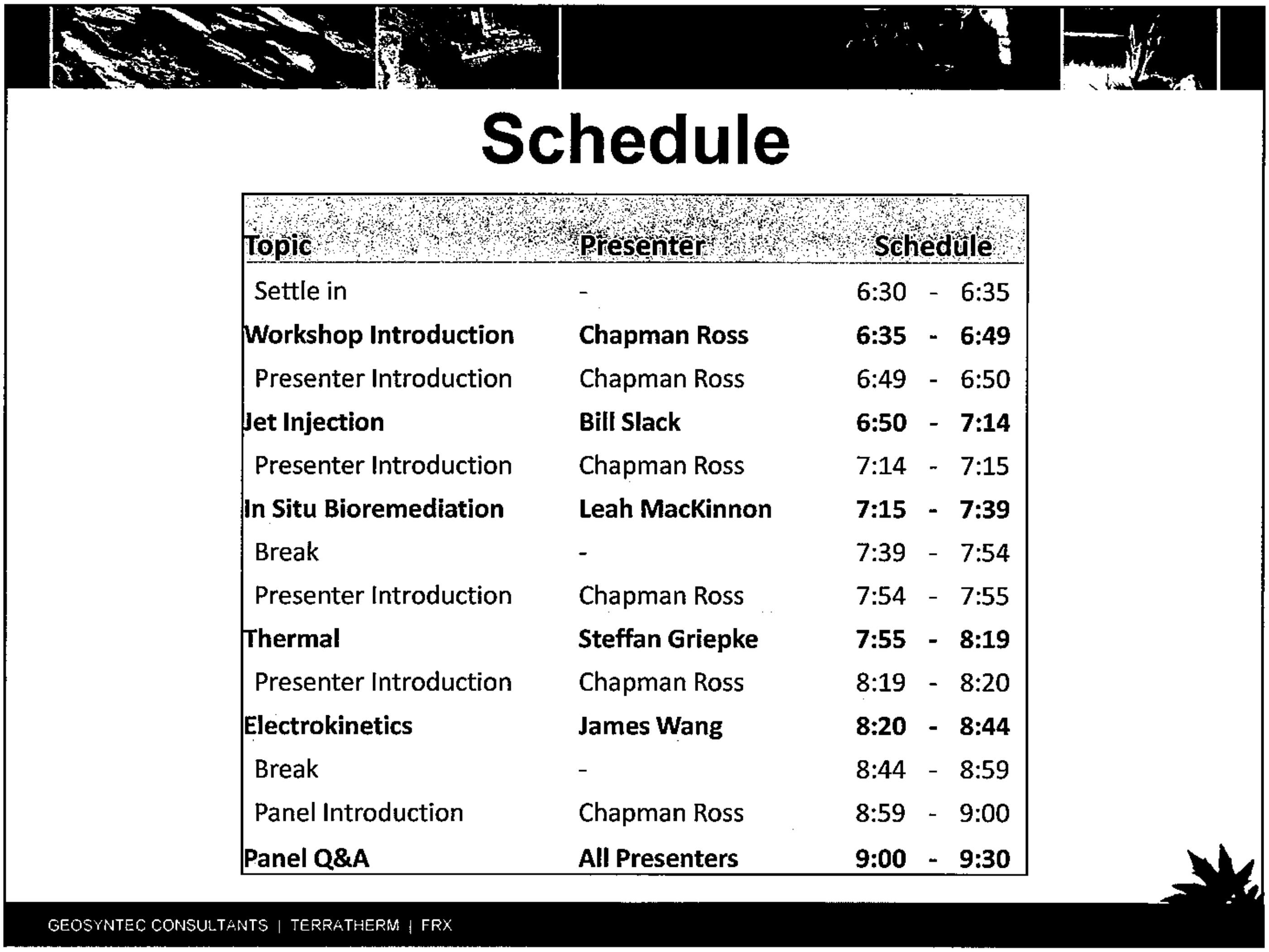
18 October 2016

32nd Annual International Conference on Soils, Sediments, Water, and Energy

University of Massachusetts

Amherst, MA

Workshop 7



Schedule

Topic	Presenter	Schedule
Settle in	-	6:30 - 6:35
Workshop Introduction	**Chapman Ross**	**6:35 - 6:49**
Presenter Introduction	Chapman Ross	6:49 - 6:50
Jet Injection	**Bill Slack**	**6:50 - 7:14**
Presenter Introduction	Chapman Ross	7:14 - 7:15
In Situ Bioremediation	**Leah MacKinnon**	**7:15 - 7:39**
Break	-	7:39 - 7:54
Presenter Introduction	Chapman Ross	7:54 - 7:55
Thermal	**Steffan Griepke**	**7:55 - 8:19**
Presenter Introduction	Chapman Ross	8:19 - 8:20
Electrokinetics	**James Wang**	**8:20 - 8:44**
Break	-	8:44 - 8:59
Panel Introduction	Chapman Ross	8:59 - 9:00
Panel Q&A	**All Presenters**	**9:00 - 9:30**

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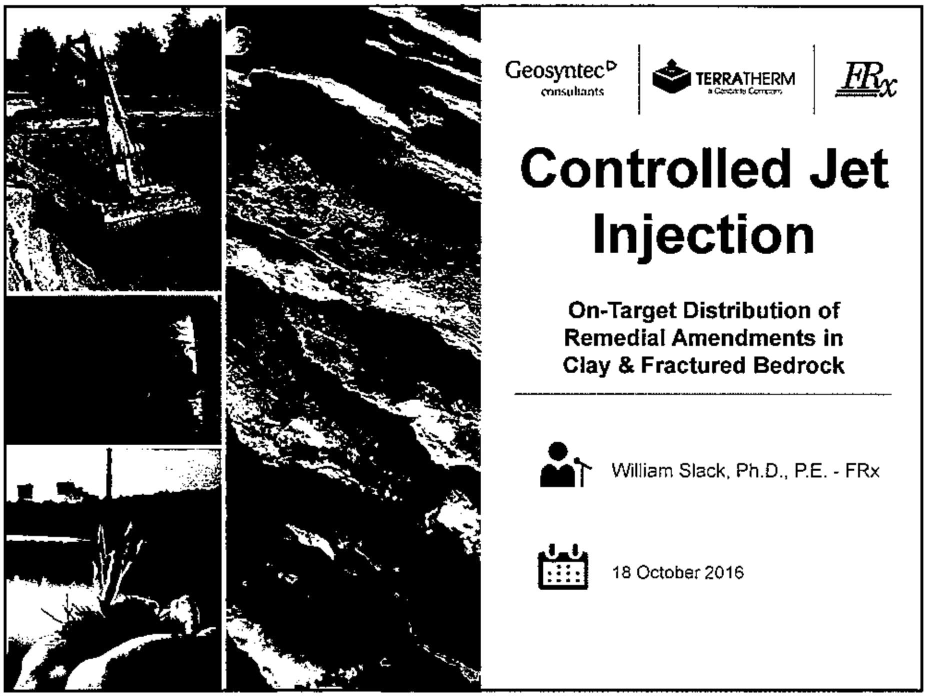
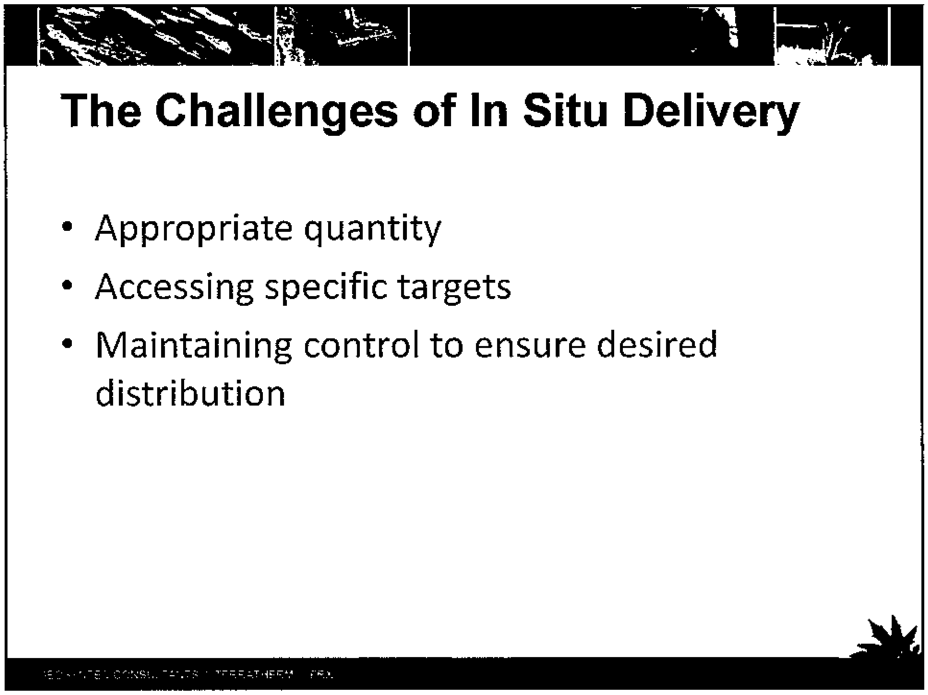


Controlled Jet Injection

On-Target Distribution of Remedial Amendments in Clay & Fractured Bedrock

William Slack, Ph.D., P.E. - FRx

18 October 2016



The Challenges of In Situ Delivery

- Appropriate quantity
- Accessing specific targets
- Maintaining control to ensure desired distribution

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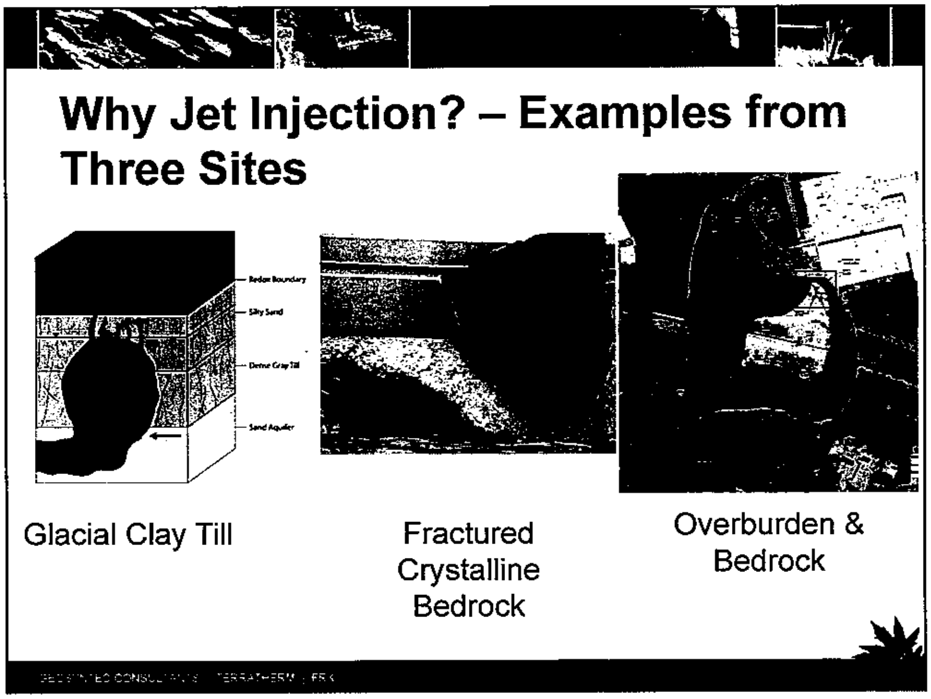
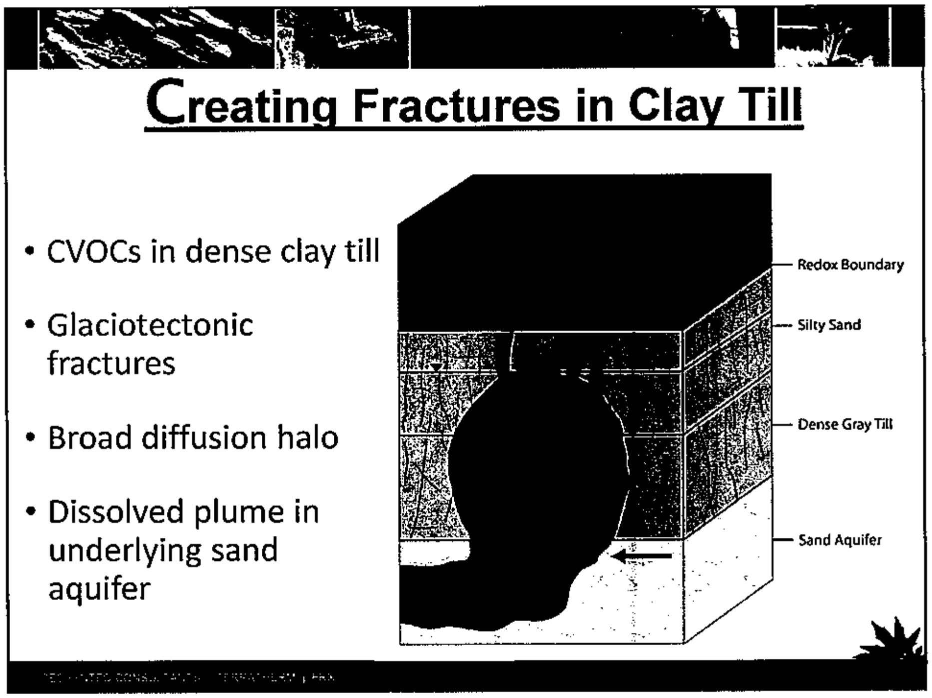


Why Jet Injection? – Examples from Three Sites

Glacial Clay Till

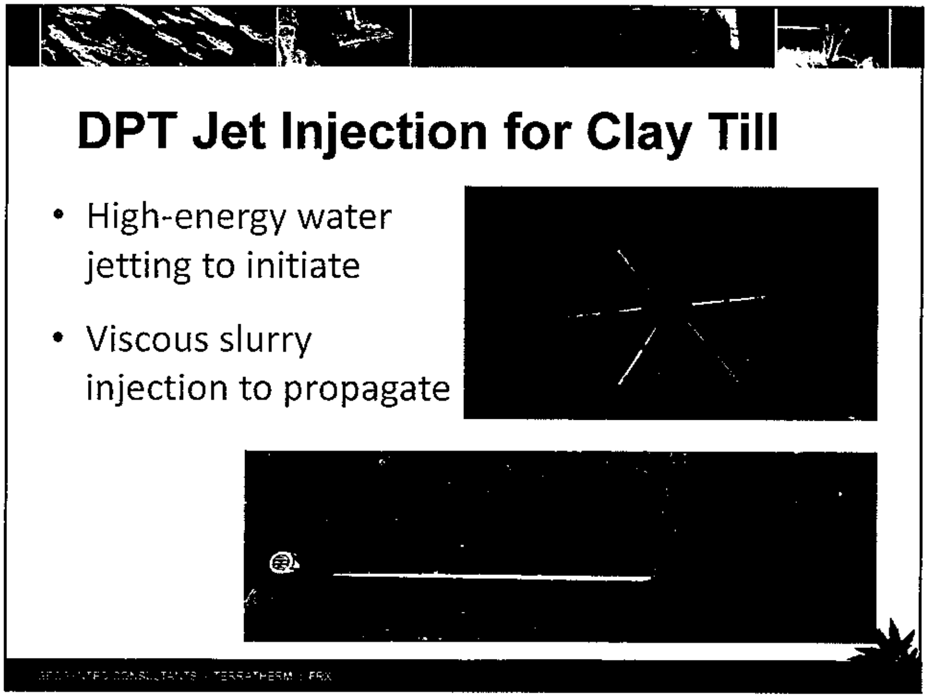
Fractured Crystalline Bedrock

Overburden & Bedrock



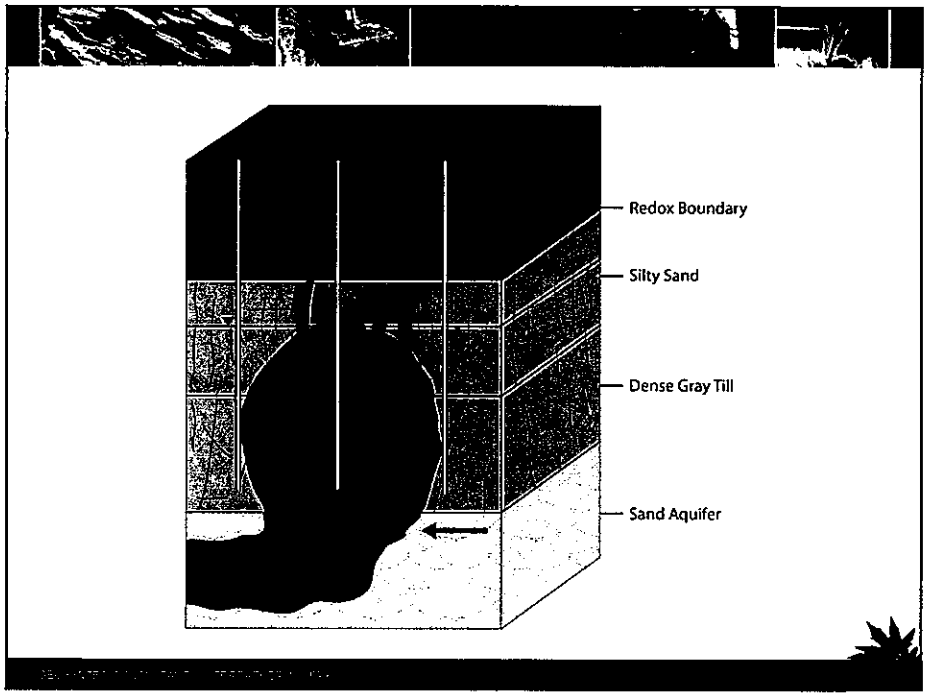
Creating Fractures in Clay Till

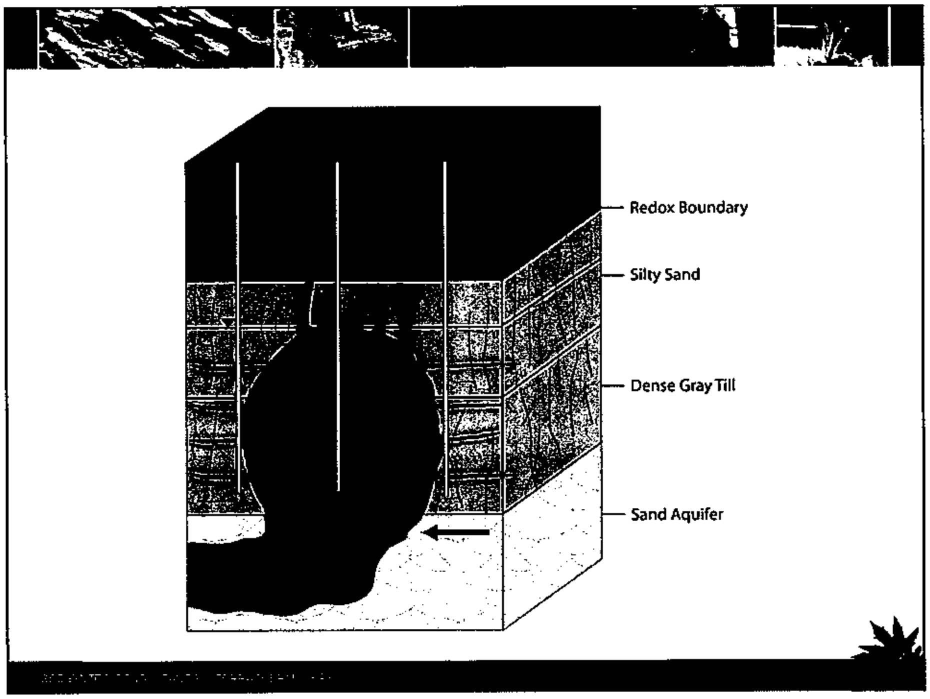
- CVOCs in dense clay till
- Glaciotectonic fractures
- Broad diffusion halo
- Dissolved plume in underlying sand aquifer

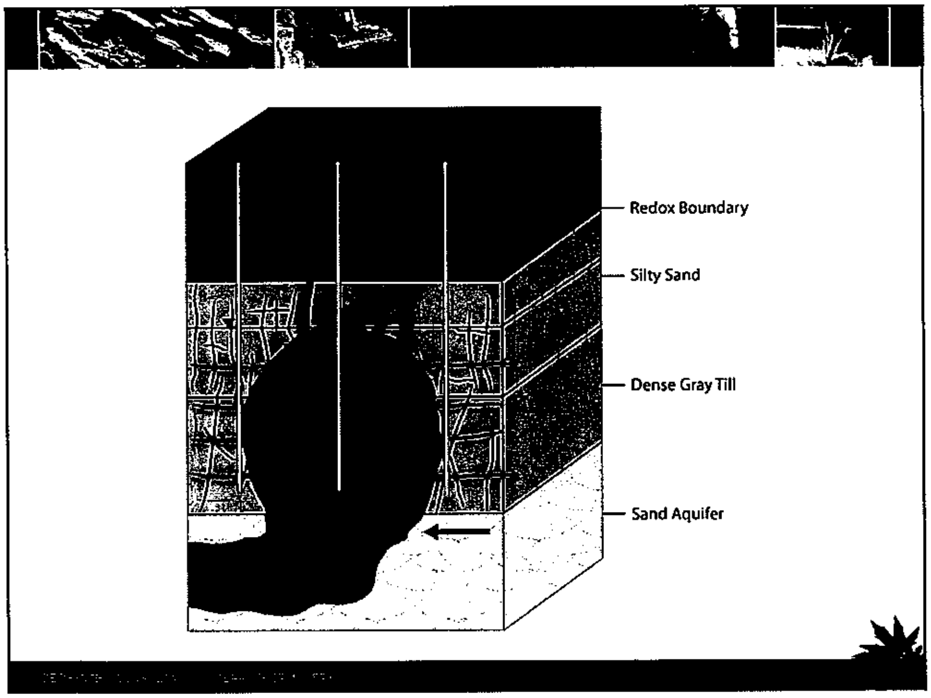


DPT Jet Injection for Clay Till

- High-energy water jetting to initiate
- Viscous slurry injection to propagate




Redox Boundary
Silty Sand
Dense Gray Till
Sand Aquifer


Redox Boundary
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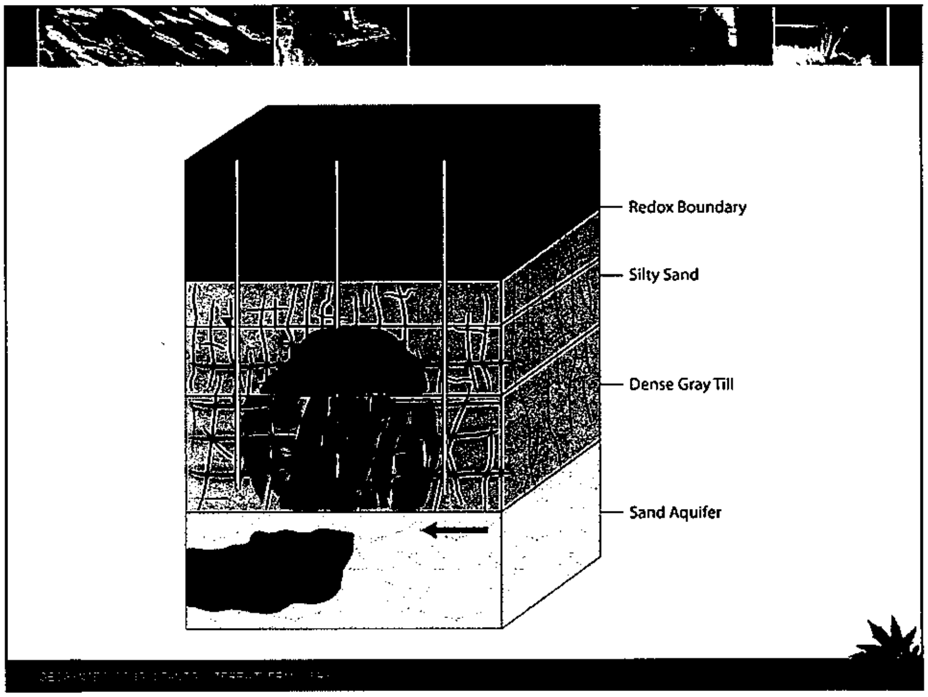
Redox Boundary
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Dense Gray Till
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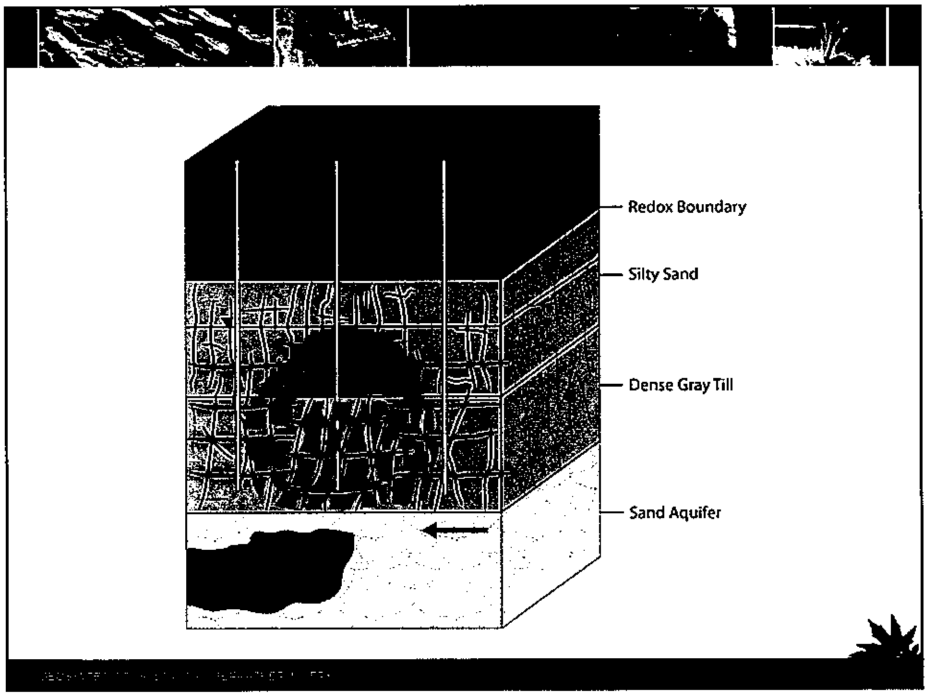
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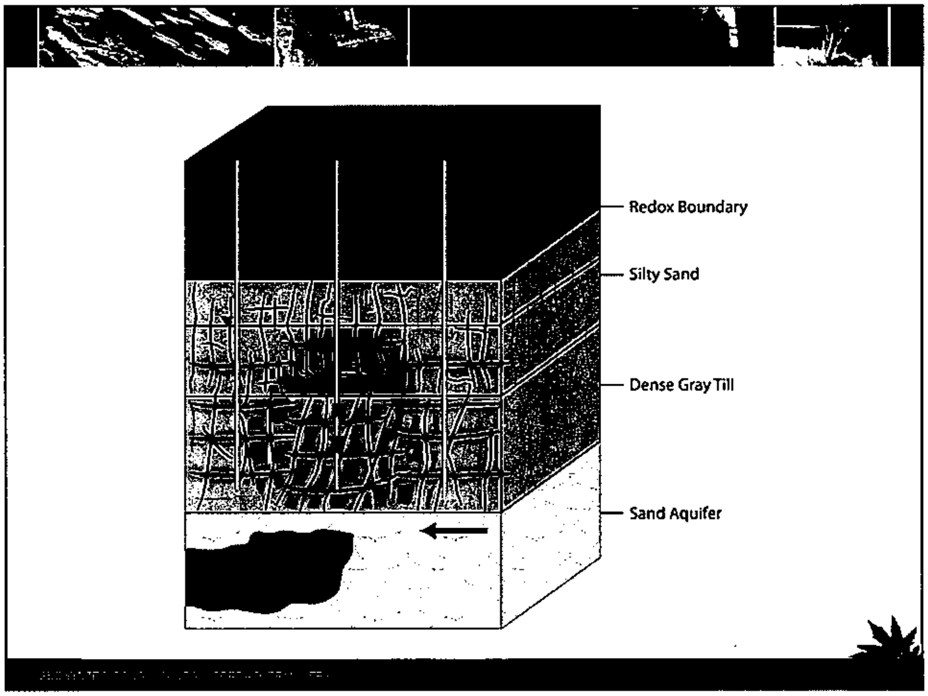
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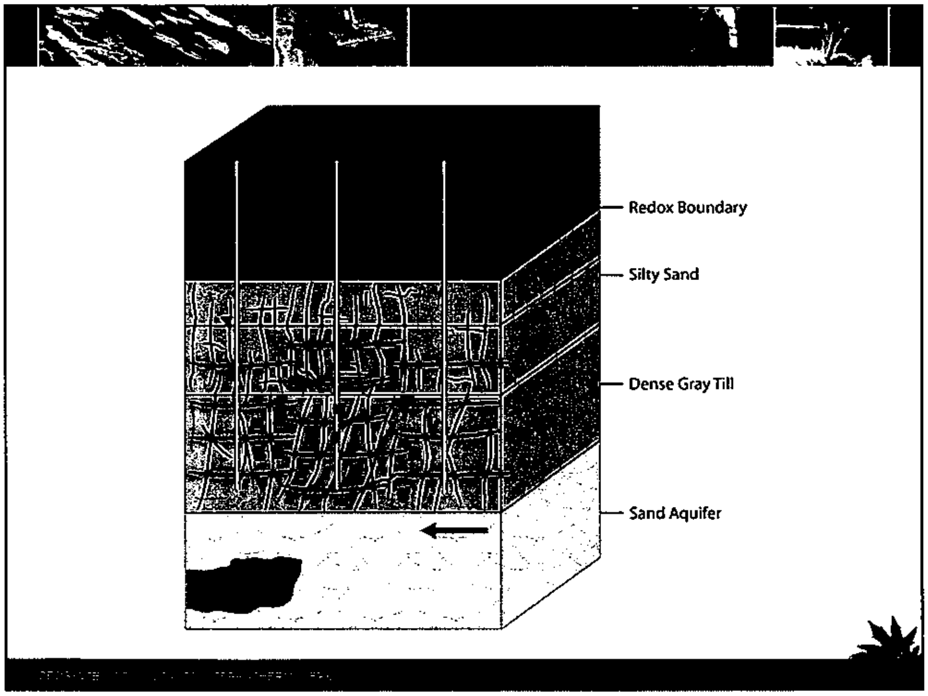
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Dense Gray Till
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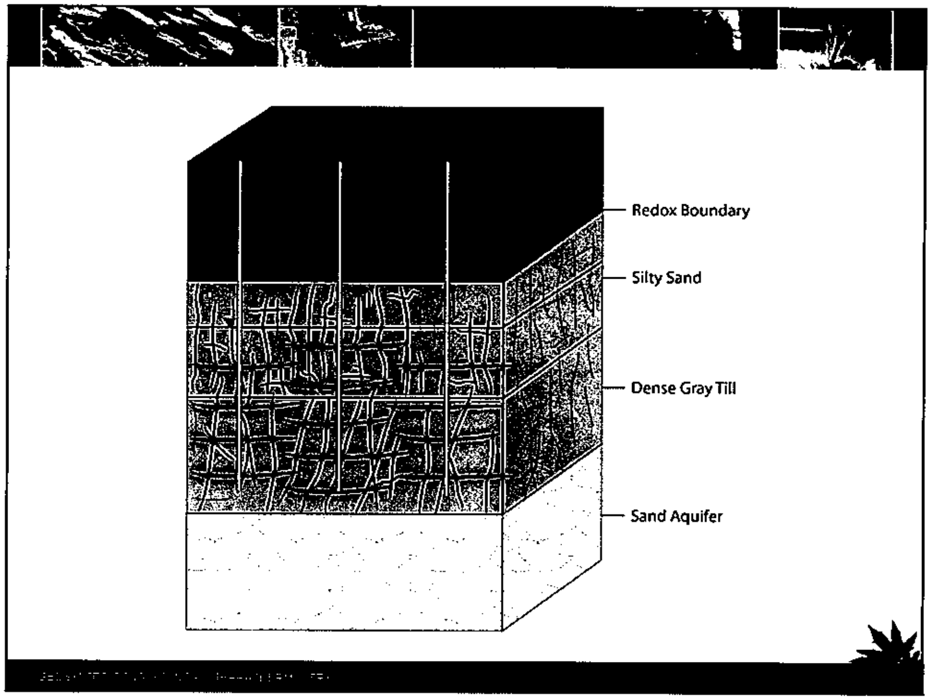
Redox Boundary
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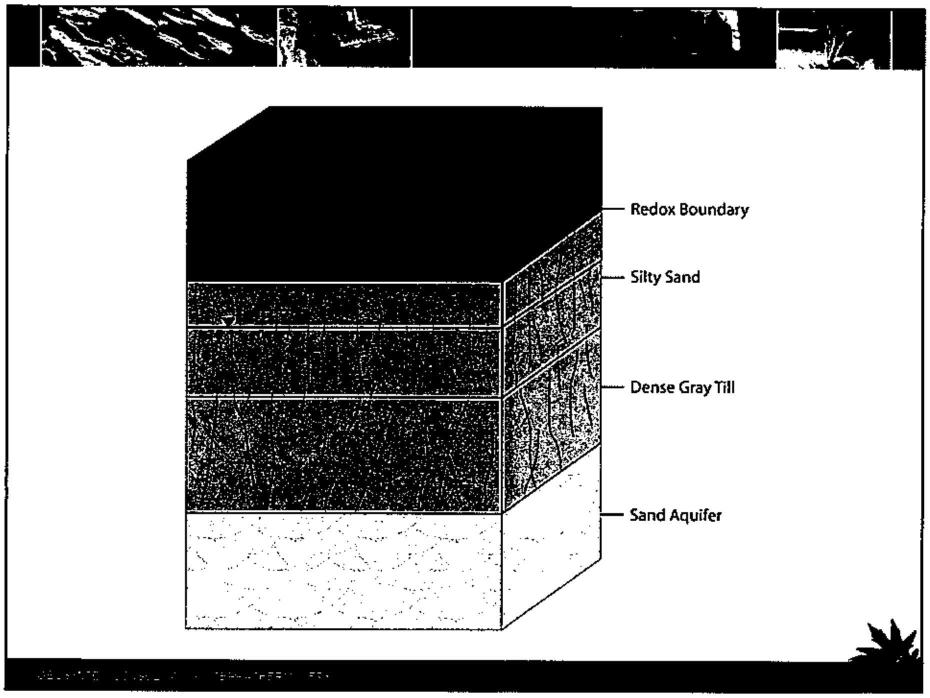
Redox Boundary
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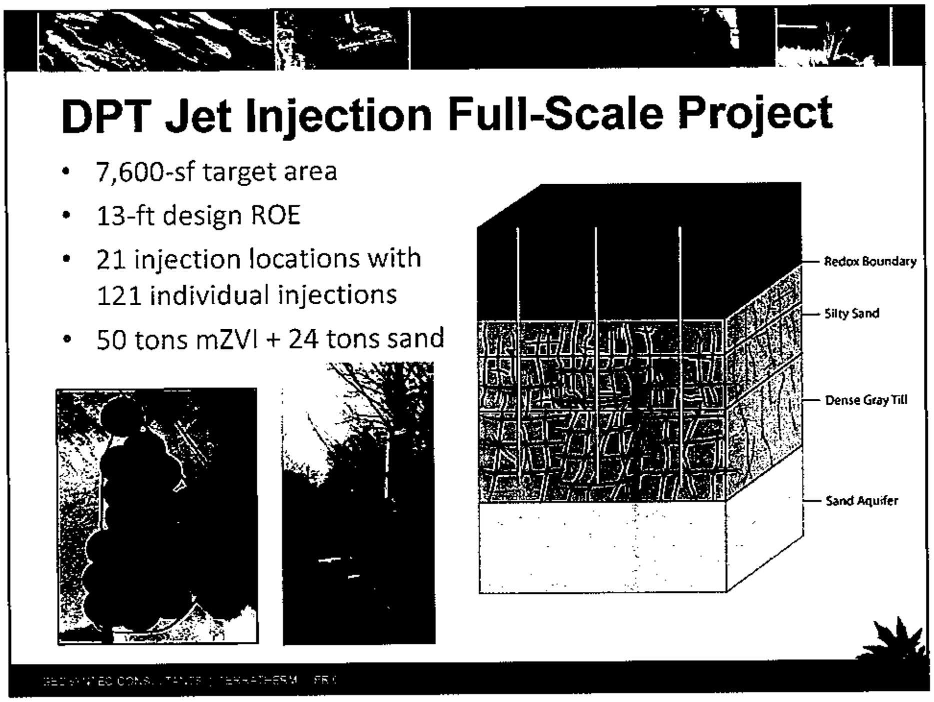
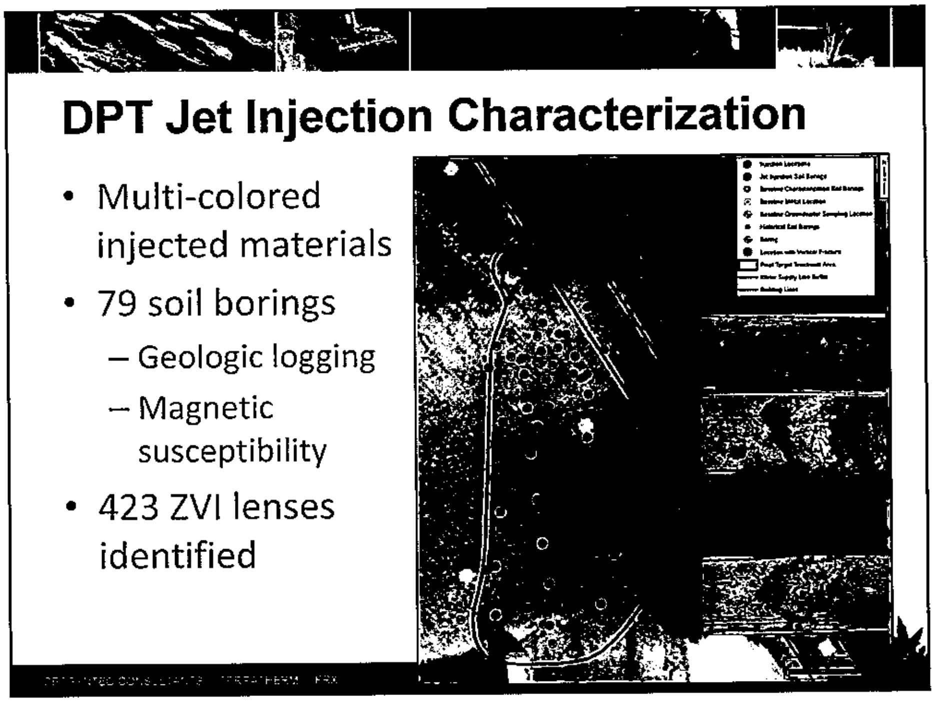
Dense Gray Till
Sand Aquifer



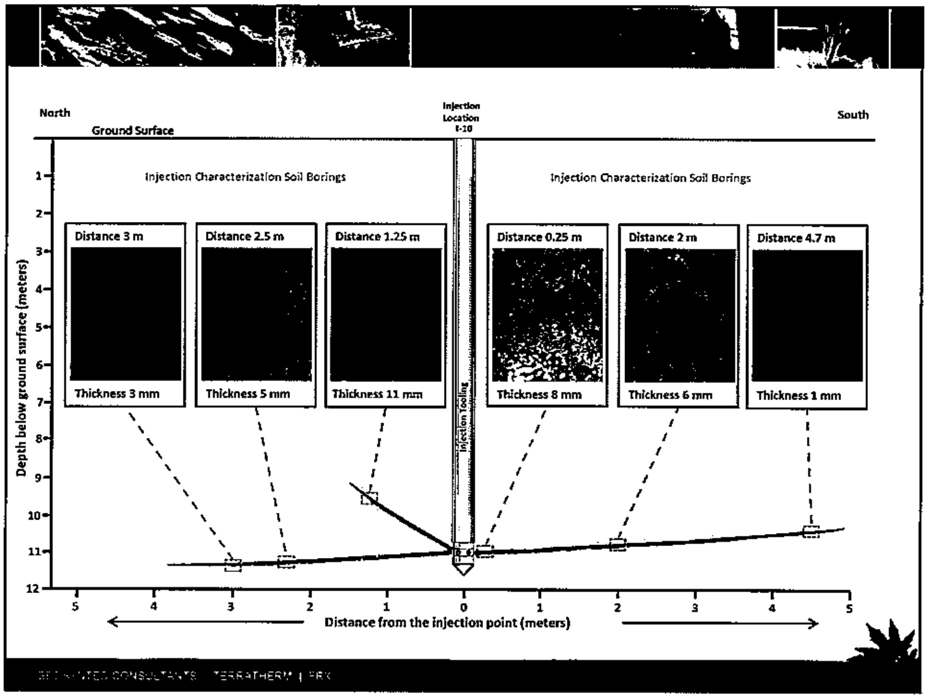
DPT Jet Injection Full-Scale Project

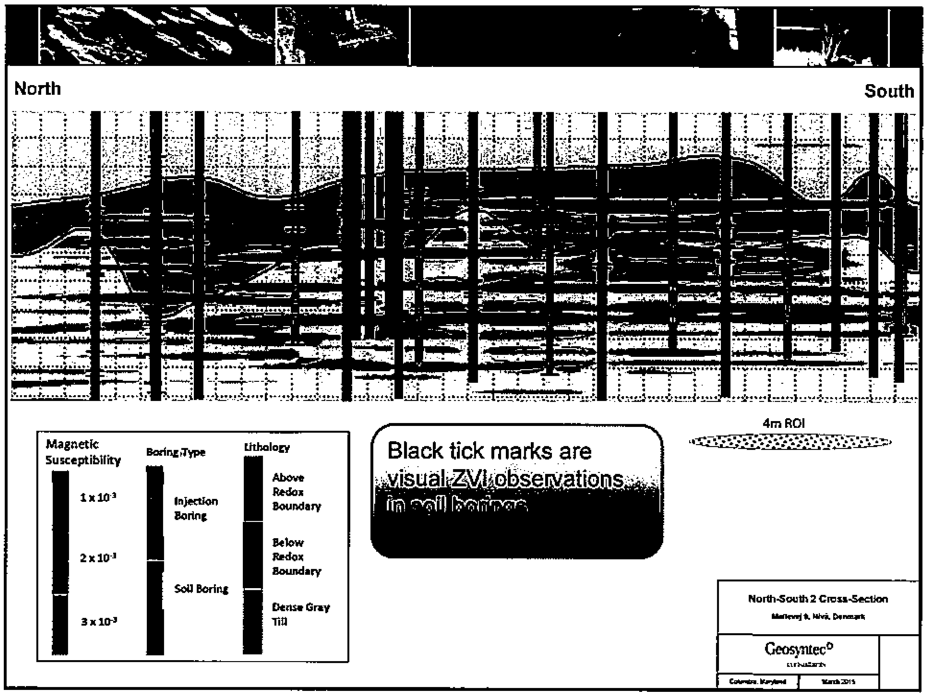
- 7,600-sf target area
- 13-ft design ROE
- 21 injection locations with 121 individual injections
- 50 tons mZVI + 24 tons sand



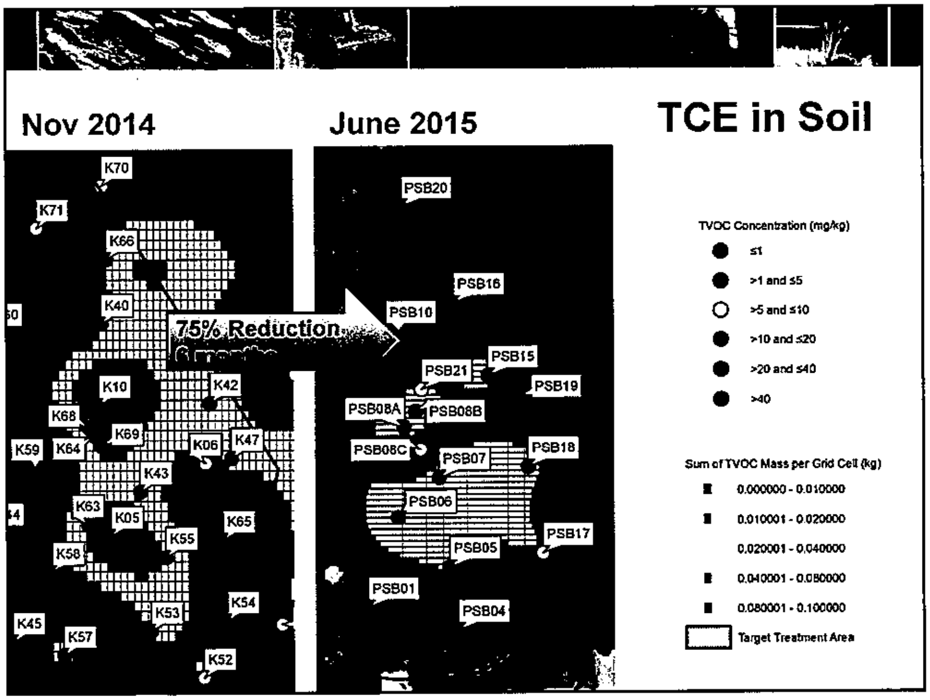
DPT Jet Injection Characterization

- Multi-colored injected materials
- 79 soil borings
  - Geologic logging
  - Magnetic susceptibility
- 423 ZVI lenses identified





Black tick marks are visual ZVI observations in soil borings



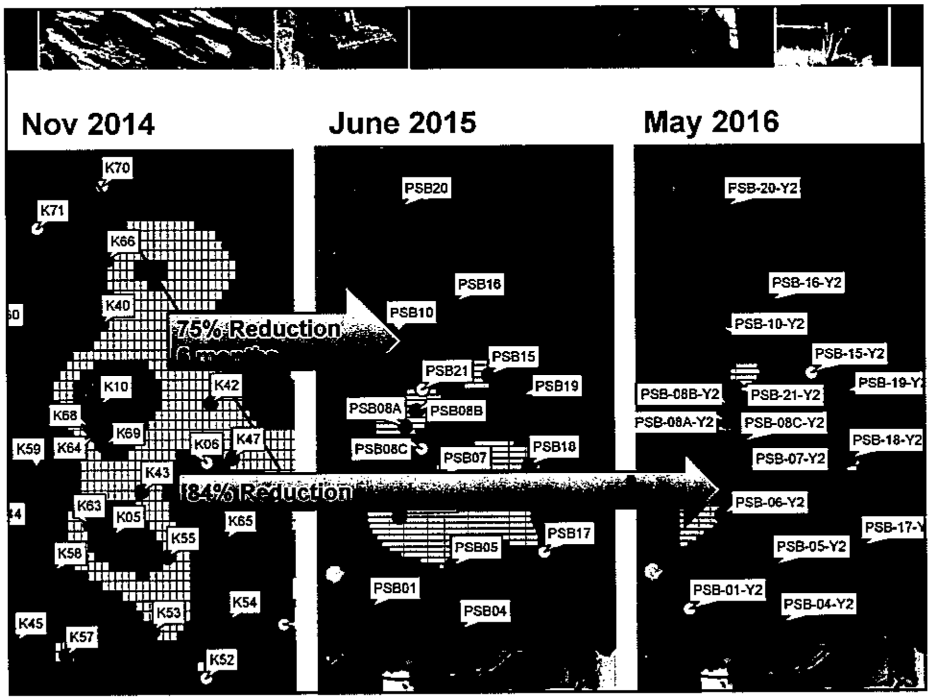
Nov 2014

June 2015

TCE in Soil

TVOC Concentration (mg/kg)
● ≤1
● >1 and ≤5
○ >5 and ≤10
● >10 and ≤20
● >20 and ≤40
● >40

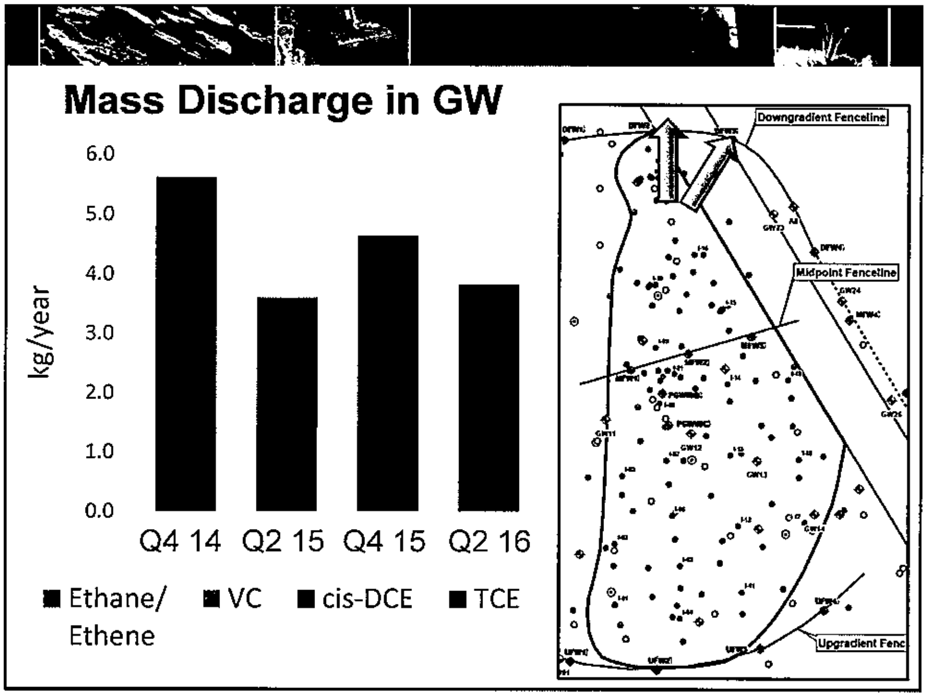
Sum of TVOC Mass per Grid Cell (kg)
▪ 0.000000 - 0.010000
▪ 0.010001 - 0.020000
0.020001 - 0.040000
▪ 0.040001 - 0.080000
▪ 0.080001 - 0.100000
☐ Target Treatment Area



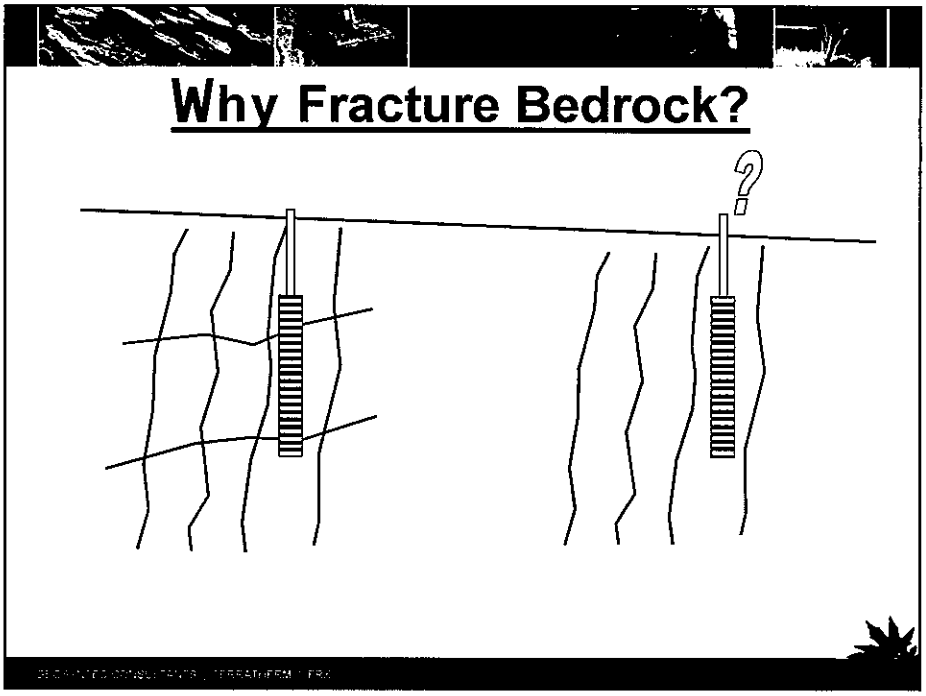
Nov 2014

June 2015

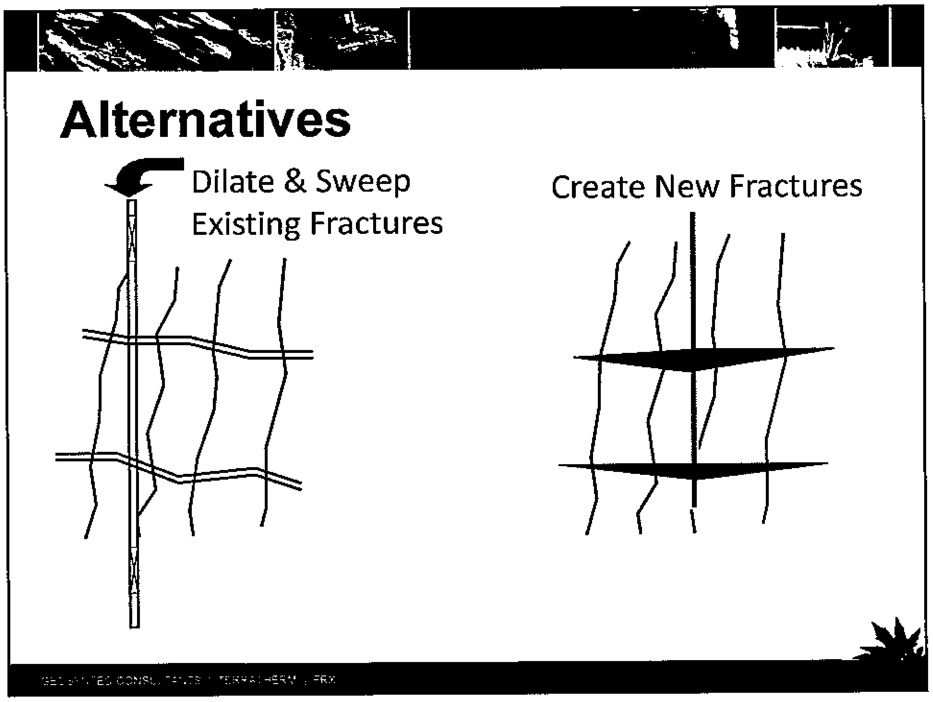
May 2016



Mass Discharge in GW



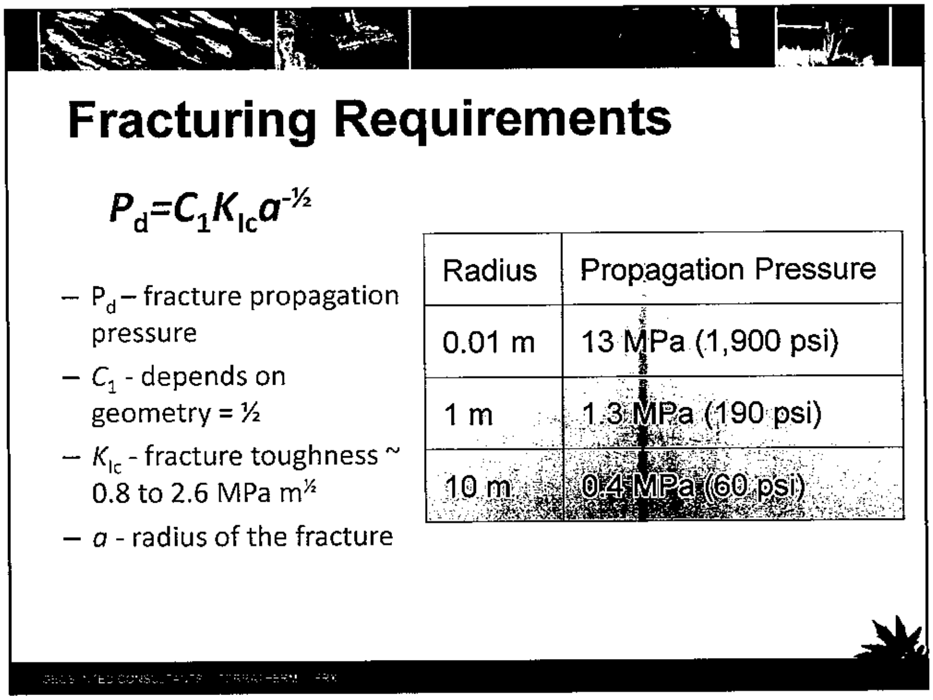
Why Fracture Bedrock?



Alternatives

Dilate & Sweep Existing Fractures

Create New Fractures

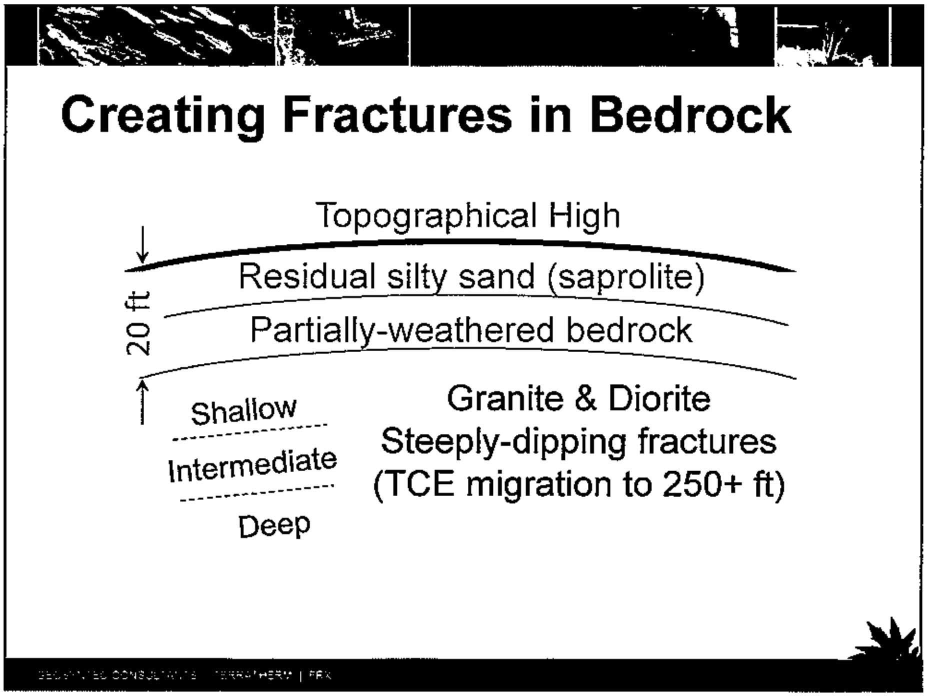


Fracturing Requirements

$$P_d = C_1 K_{Ic} a^{-½}$$

- P_d – fracture propagation pressure
- C_1 - depends on geometry = ½
- K_{Ic} - fracture toughness ~ 0.8 to 2.6 MPa $m^{½}$
- a - radius of the fracture

Radius	Propagation Pressure
0.01 m	13 MPa (1,900 psi)
1 m	1.3 MPa (190 psi)
10 m	0.4 MPa (60 psi)



Creating Fractures in Bedrock

Topographical High

Residual silty sand (saprolite)

Partially-weathered bedrock

20 ft

Shallow

Intermediate

Deep

Granite & Diorite
Steeply-dipping fractures
(TCE migration to 250+ ft)

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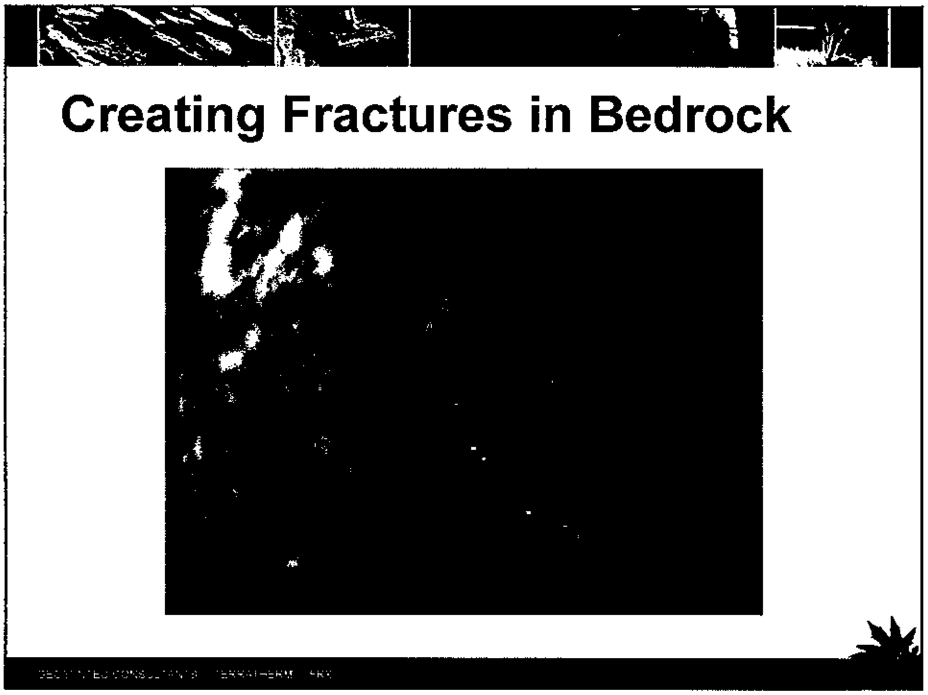

Creating Fractures in Bedrock

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Creating Fractures in Bedrock

- Cut kerfs with water jets
- Isolate kerfs with straddle packers
- Inject viscous gel to nucleate fracture
- Propagate the fracture with continued injection
- Monitor injection pressure and deformation of ground surface
- Examine wells with borehole camera

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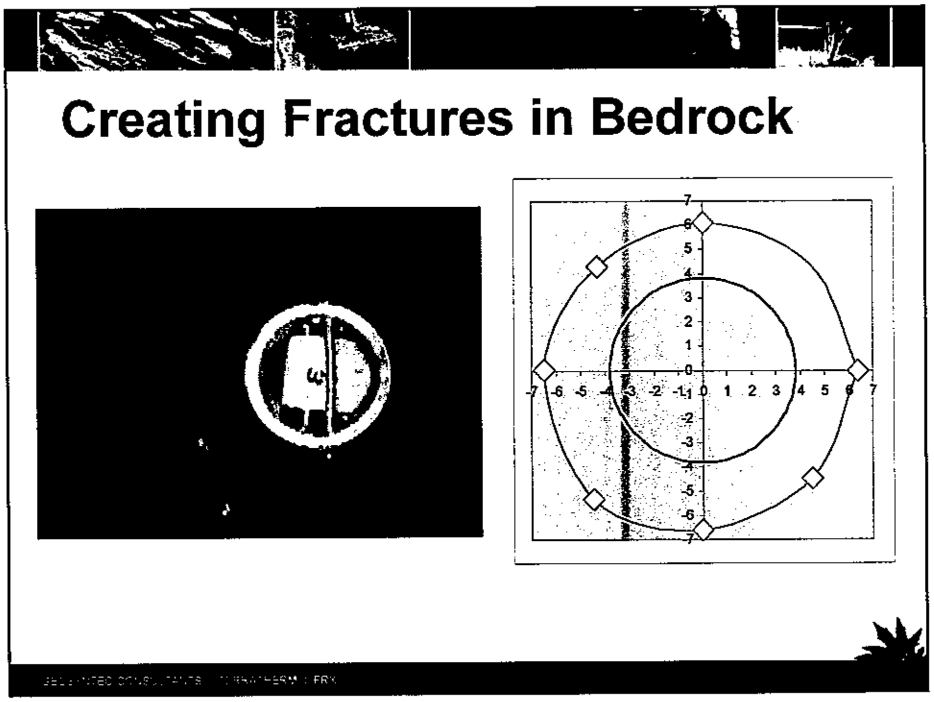

Creating Fractures in Bedrock

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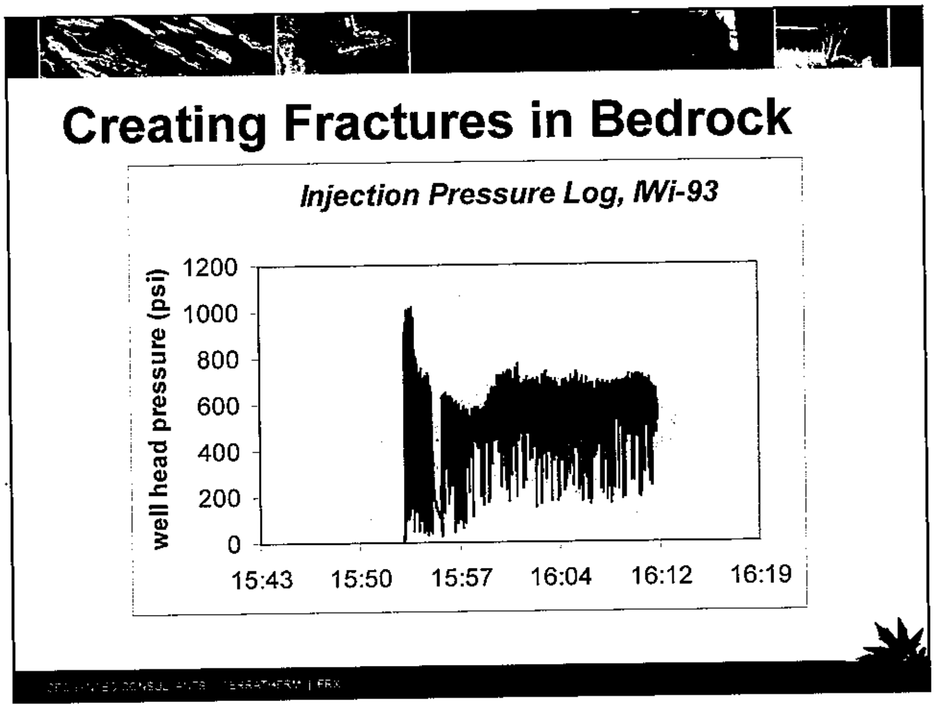
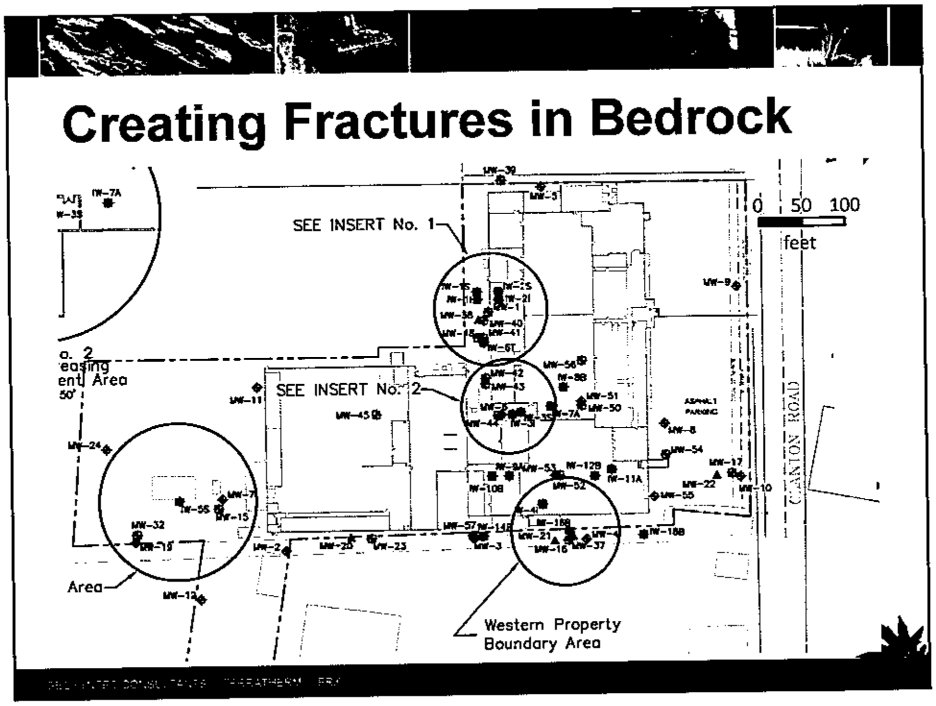
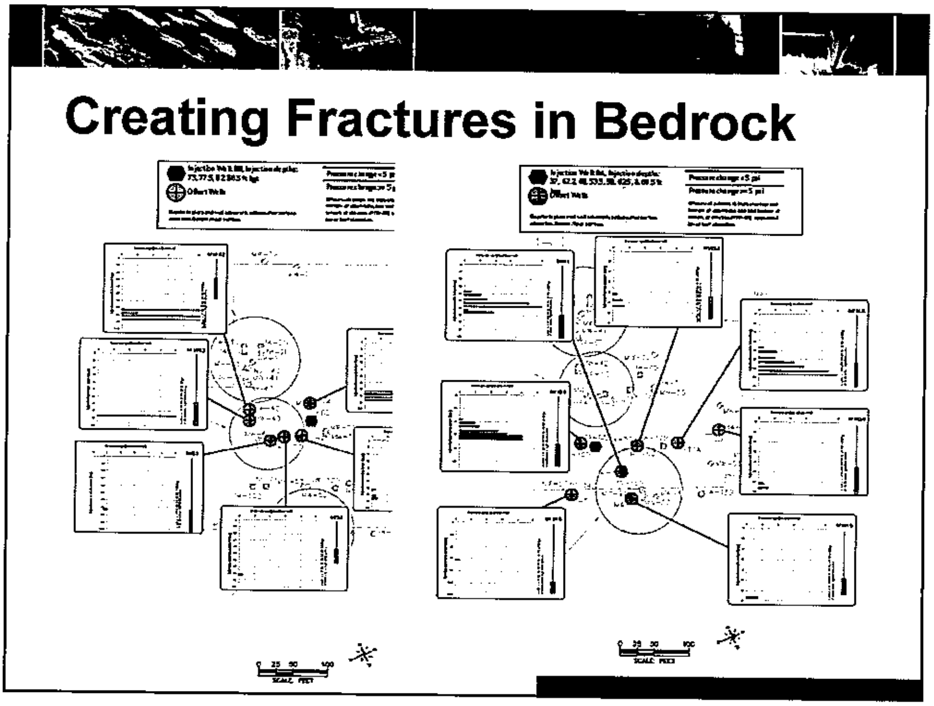


Creating Fractures in Bedrock

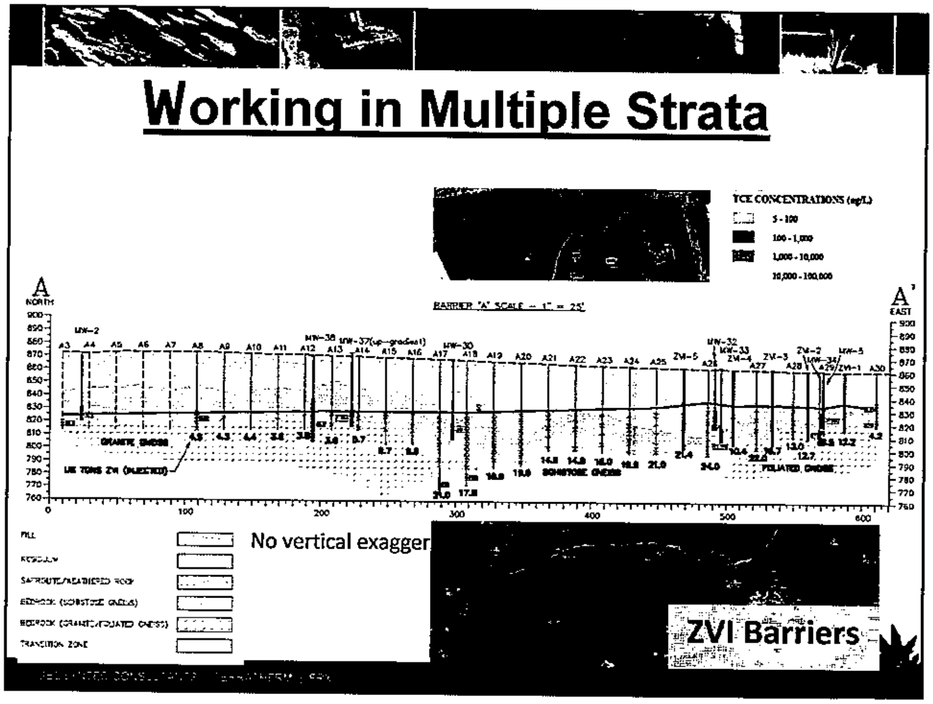
Injection Pressure Log, IWi-93



Creating Fractures in Bedrock



Creating Fractures in Bedrock



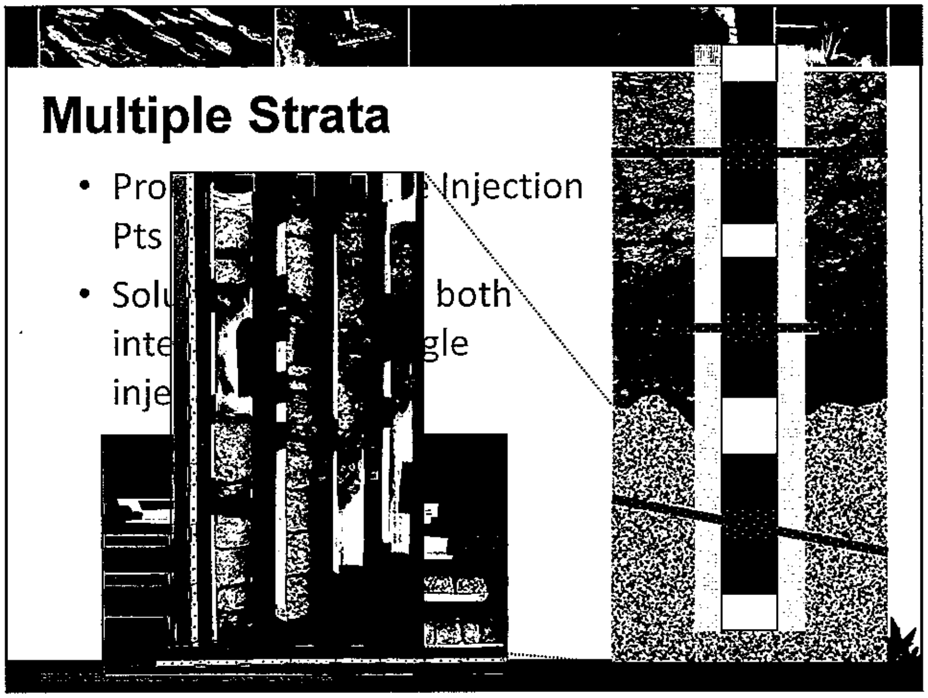
Working in Multiple Strata

TCE CONCENTRATIONS (ug/L)

- ▢ 5 - 100
- ■ 100 - 1,000
- ▨ 1,000 - 10,000
- 10,000 - 100,000

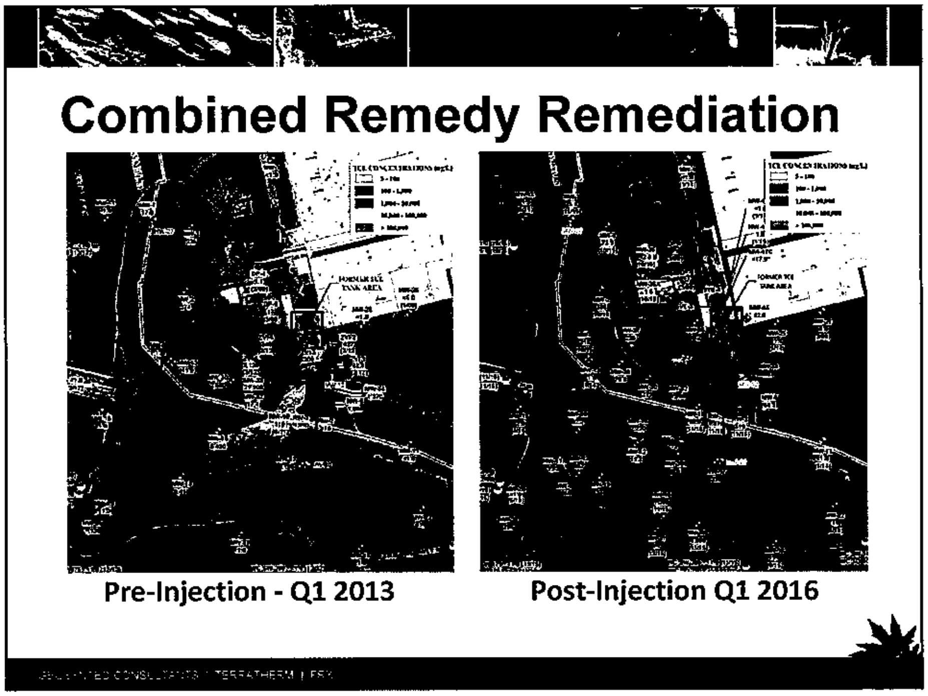
No vertical exagger

ZVI Barriers



Multiple Strata

- Pro Injection Pts
- Sol both inte gle inje



Combined Remedy Remediation

Pre-Injection - Q1 2013

Post-Injection Q1 2016

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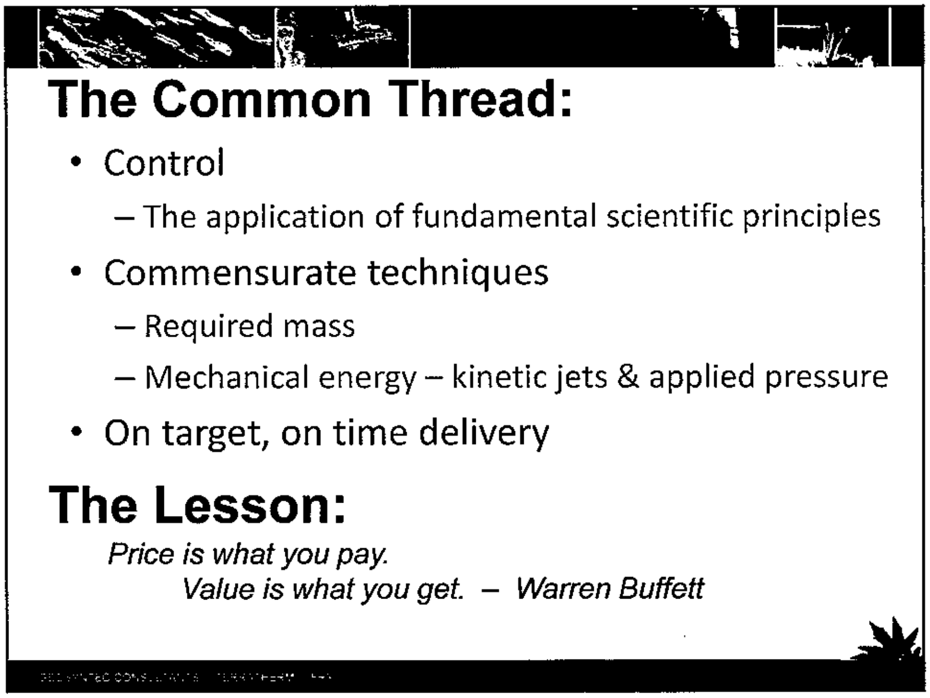
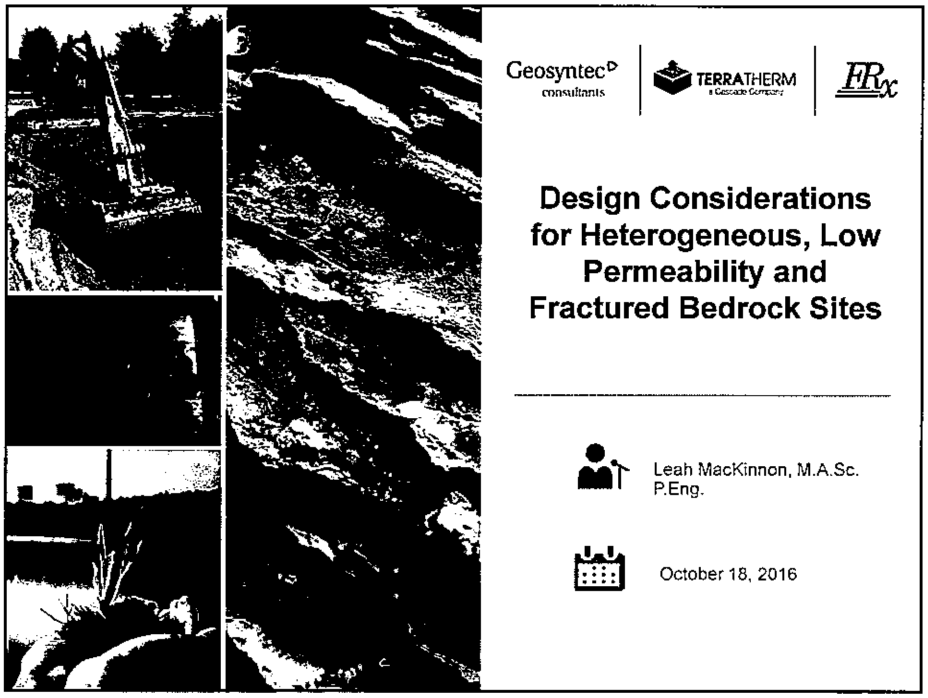


The Common Thread:

- Control
  - – The application of fundamental scientific principles
- Commensurate techniques
  - – Required mass
  - – Mechanical energy – kinetic jets & applied pressure
- On target, on time delivery

The Lesson:

Price is what you pay.
Value is what you get. – Warren Buffett



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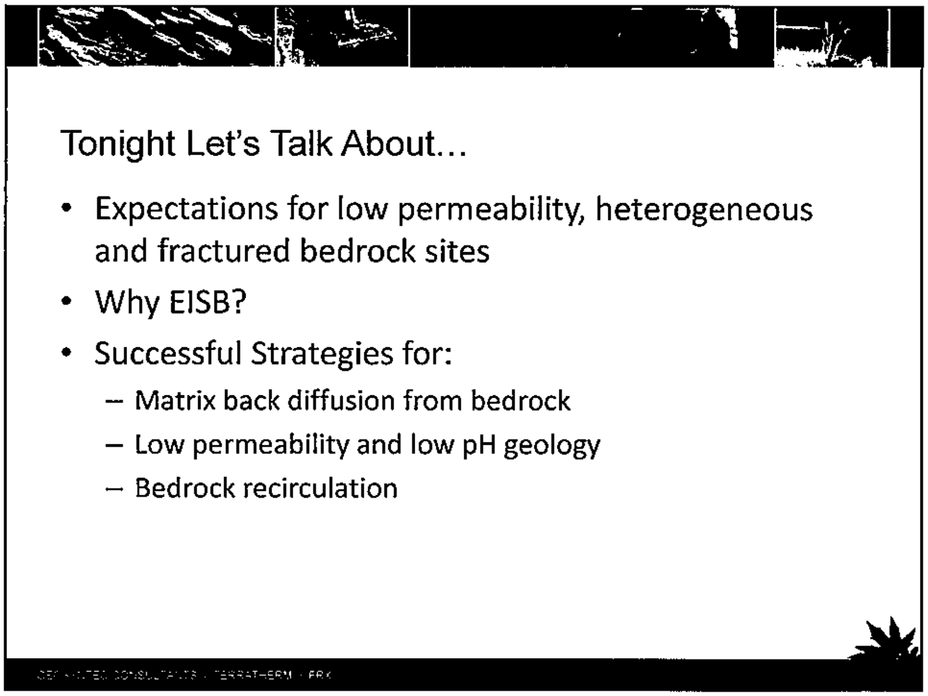
Design Considerations for Heterogeneous, Low Permeability and Fractured Bedrock Sites

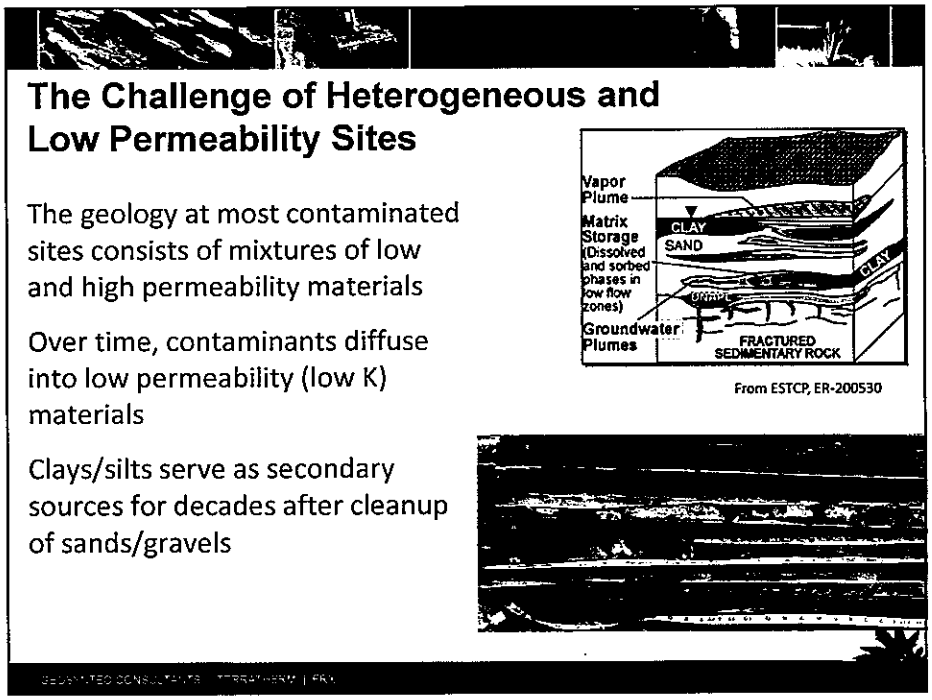
Leah MacKinnon, M.A.Sc.
P.Eng.

October 18, 2016



Tonight Let's Talk About...

- Expectations for low permeability, heterogeneous and fractured bedrock sites
- Why EISB?
- Successful Strategies for:
  - Matrix back diffusion from bedrock
  - Low permeability and low pH geology
  - Bedrock recirculation



The Challenge of Heterogeneous and Low Permeability Sites

The geology at most contaminated sites consists of mixtures of low and high permeability materials

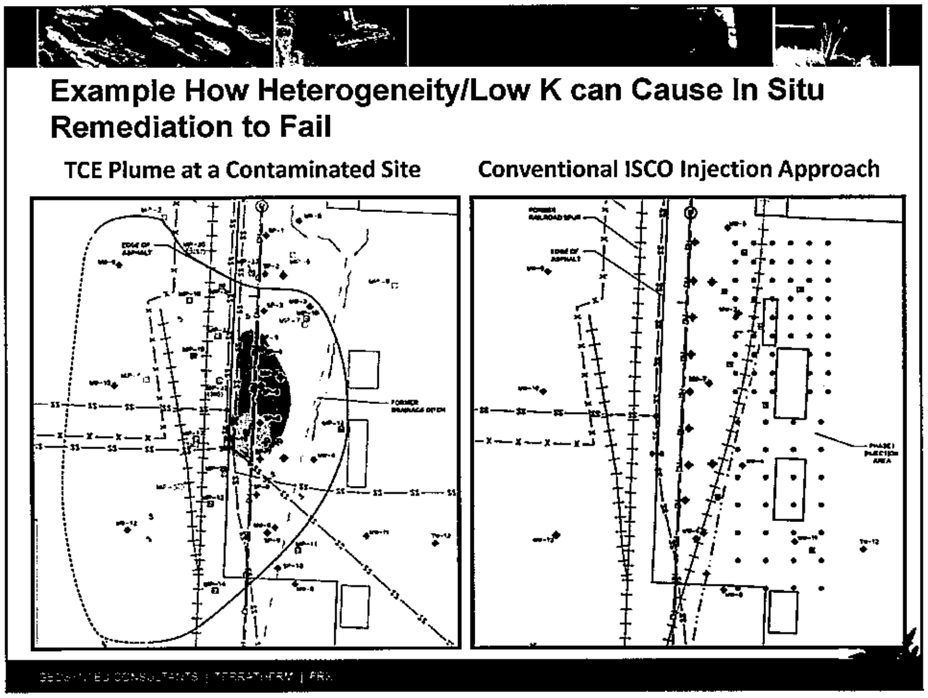
Over time, contaminants diffuse into low permeability (low K) materials

Clays/silts serve as secondary sources for decades after cleanup of sands/gravels

From ESTCP, ER-200530

Impact of Heterogeneous and Low K Conditions on EISB

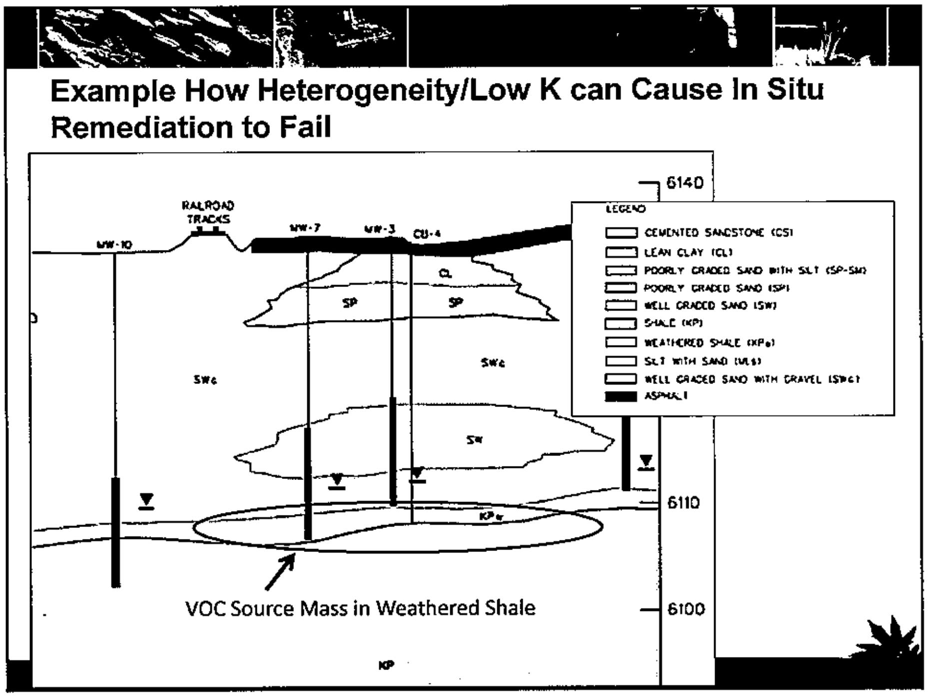
- In low K and heterogeneous sites, COC distribution is likely to be less well understood
- Remedial behavior will be less predictable, pilot testing recommended
- Back-diffusion is likely to require longer remedial duration
- Expect:
  - Injections into isolated zones, dense injection grids
  - Use of longer term amendments to reduce rebound
  - Repeat injections, adaptive management
- Consider alternative delivery techniques:
  - Fracturing, EK, In situ mixing
  - Hydraulic control, push-pull, pull-push
  - Horizontal biobarriers



Example How Heterogeneity/Low K can Cause In Situ Remediation to Fail

TCE Plume at a Contaminated Site

Conventional ISCO Injection Approach

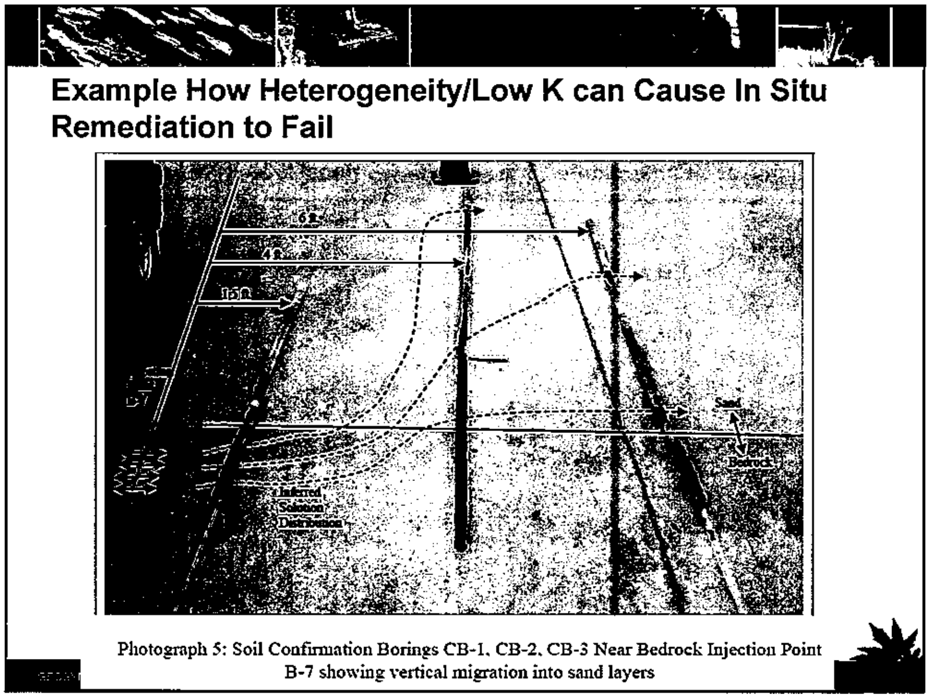


Example How Heterogeneity/Low K can Cause In Situ Remediation to Fail

LEGEND

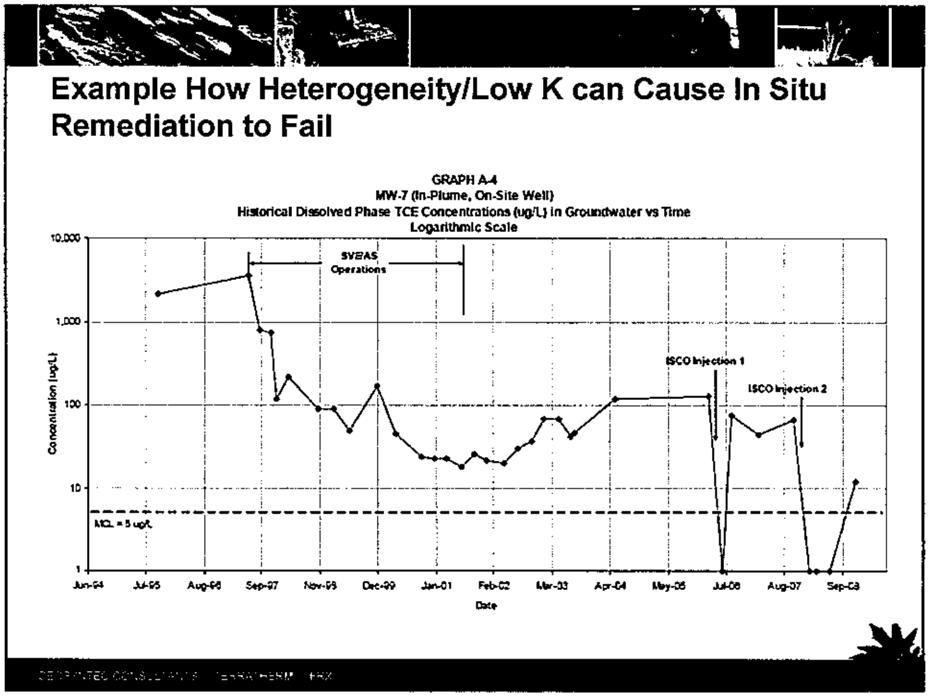
- ▭ CEMENTED SANDSTONE (CS)
- ▭ LEAN CLAY (CL)
- ▭ POORLY GRADED SAND WITH SILT (SP-SM)
- ▭ POORLY GRADED SAND (SP)
- ▭ WELL GRADED SAND (SW)
- ▭ SHALE (KP)
- ▭ WEATHERED SHALE (KPw)
- ▭ SILT WITH SAND (MLS)
- ▭ WELL GRADED SAND WITH GRAVEL (SWG)
- ■ ASPHALT

VOC Source Mass in Weathered Shale



Example How Heterogeneity/Low K can Cause In Situ Remediation to Fail

Photograph 5: Soil Confirmation Borings CB-1, CB-2, CB-3 Near Bedrock Injection Point B-7 showing vertical migration into sand layers



Example How Heterogeneity/Low K can Cause In Situ Remediation to Fail

GRAPH A-4
MW-7 (In-Plume, On-Site Well)
Historical Dissolved Phase TCE Concentrations (ug/L) in Groundwater vs Time
Logarithmic Scale

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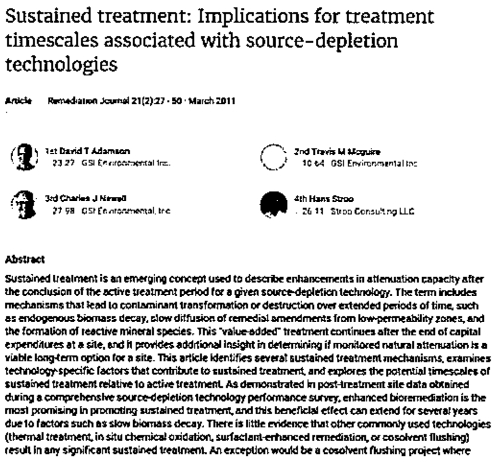
Why EISB?

- Provides long term treatment
- Amendments and bacteria can diffuse into matrix
- Easily implemented in an adaptive manner
- Can be used sequentially with other technologies to provide remedial and cost efficiency
  - SVE/MPE, Thermal, ISCO
- Combines naturally with low cost polishing techniques
  - MNA
  - Natural source zone depletion

EISB Sustains Long Term Treatment

- Long term electron donors (EVO, EHC, etc.) last for years in situ
- Endogenous cell decay extends treatment period
- Bacterial growth and accumulation of reduced minerals sustains treatment and reduces occurrence of rebound



Sustained treatment: Implications for treatment timescales associated with source-depletion technologies

Article Remediation Journal 21(2):27 - 50 · March 2011

1st David T Adamson 23.27 GSI Environmental Inc.

2nd Travis M Mcguire 10.64 GSI Environmental Inc

3rd Charles J Newell 27.98 GSI Environmental, Inc

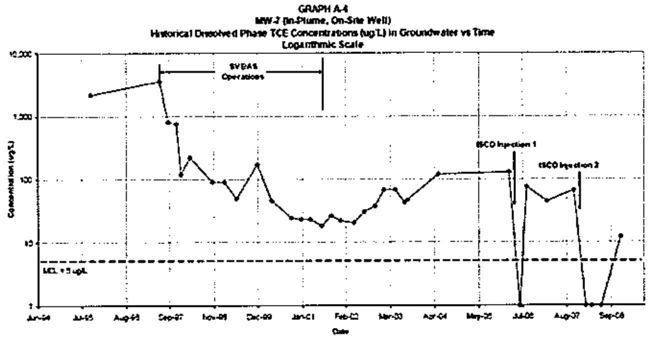
4th Hans Stroo 26.11 Stroo Consulting LLC

Abstract

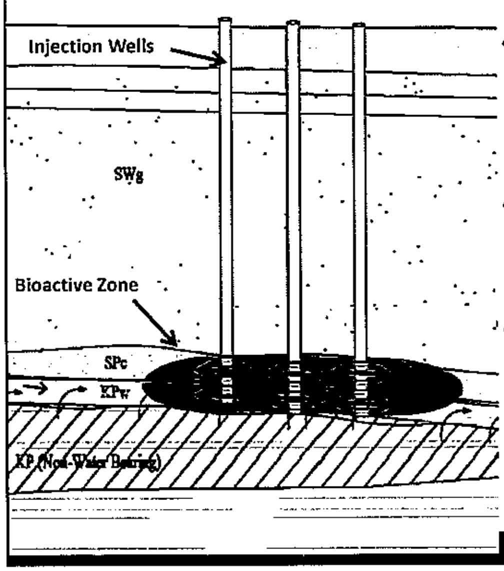
Sustained treatment is an emerging concept used to describe enhancements in attenuation capacity after the conclusion of the active treatment period for a given source-depletion technology. The term includes mechanisms that lead to contaminant transformation or destruction over extended periods of time, such as endogenous biomass decay, slow diffusion of remedial amendments from low-permeability zones, and the formation of reactive mineral species. This "value-added" treatment continues after the end of capital expenditures at a site, and it provides additional insight in determining if monitored natural attenuation is a viable long-term option for a site. This article identifies several sustained treatment mechanisms, examines technology-specific factors that contribute to sustained treatment, and explores the potential timescales of sustained treatment relative to active treatment. As demonstrated in post-treatment site data obtained during a comprehensive source-depletion technology performance survey, enhanced bioremediation is the most promising in promoting sustained treatment, and this beneficial effect can extend for several years due to factors such as slow biomass decay. There is little evidence that other commonly used technologies (thermal treatment, in situ chemical oxidation, surfactant-enhanced remediation, or cosolvent flushing) result in any significant sustained treatment. An exception would be a cosolvent flushing project where

Case Study:

Revisiting the Low K / Heterogeneous Site

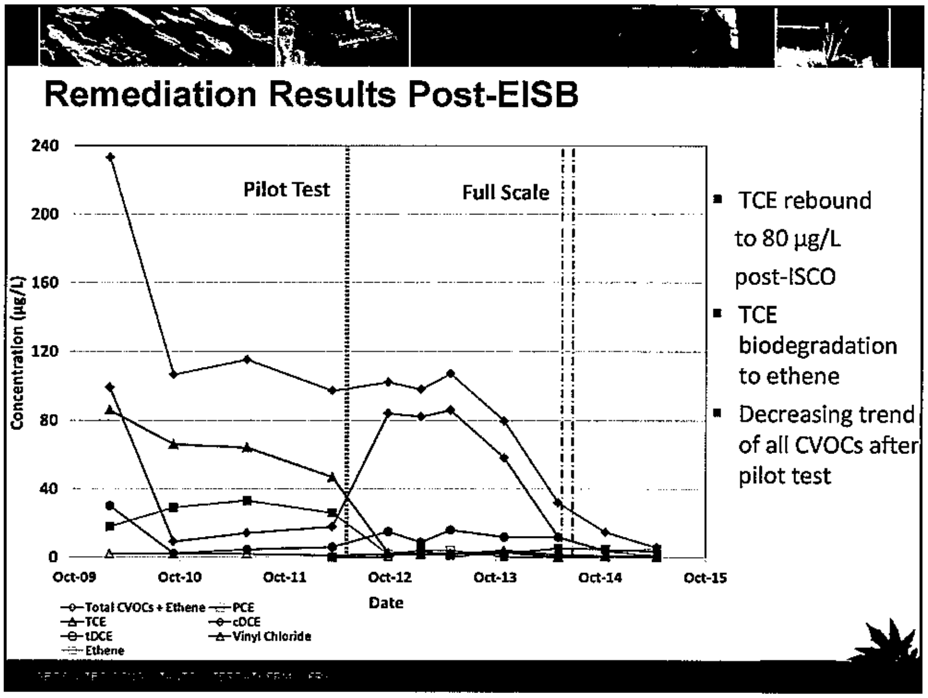


Horizontal Biobarrier for Low K / Heterogeneous Site



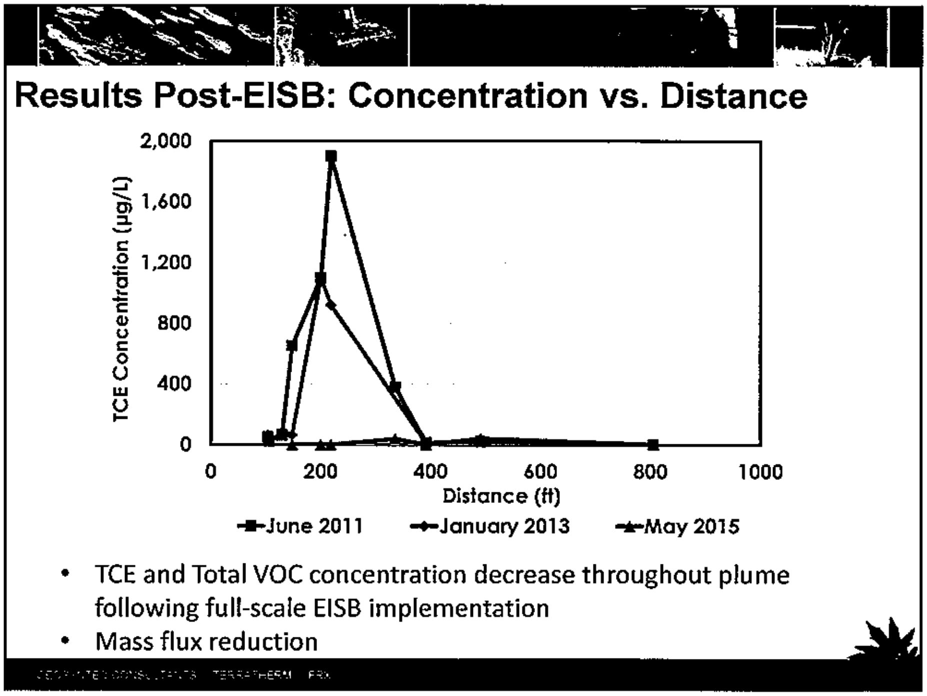
- Goal - Establish long-lasting bioactive zone to treat VOCs diffusing from weathered shale and bedrock into sand zone
- Use low-solubility electron donor to provide long term treatment
- Potential donor/DHC diffusion into bedrock
- Low pressure injections to better deliver to target interval

low P. - to let diffuse ~~so~~ slowly



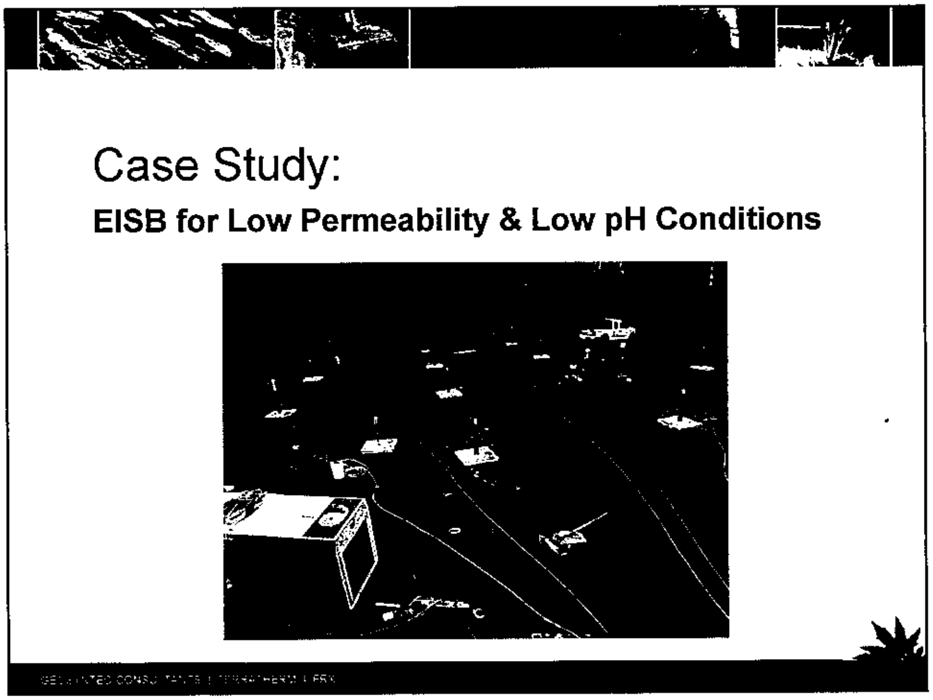
Remediation Results Post-EISB

- TCE rebound to 80 µg/L post-ISCO
- TCE biodegradation to ethene
- Decreasing trend of all CVOCs after pilot test



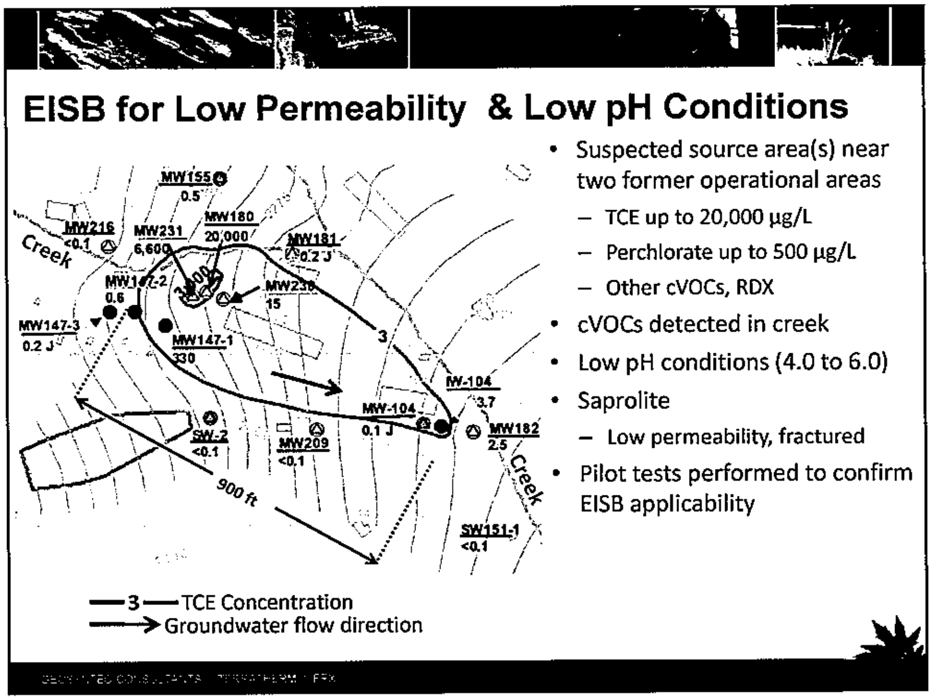
Results Post-EISB: Concentration vs. Distance

- TCE and Total VOC concentration decrease throughout plume following full-scale EISB implementation
- Mass flux reduction



Case Study:

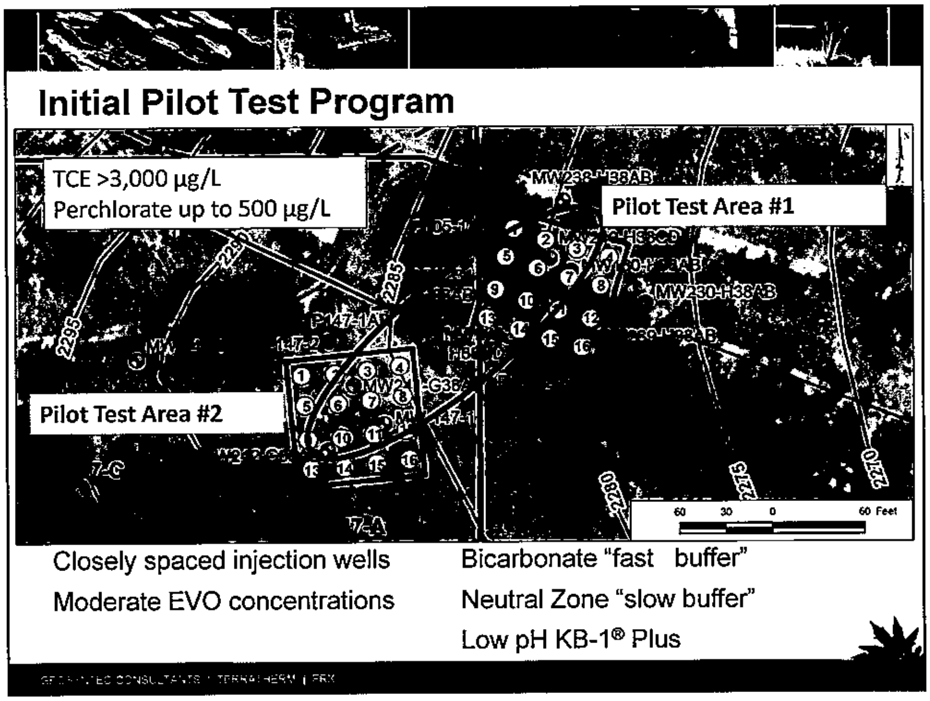
EISB for Low Permeability & Low pH Conditions



EISB for Low Permeability & Low pH Conditions

- Suspected source area(s) near two former operational areas
  - TCE up to 20,000 µg/L
  - Perchlorate up to 500 µg/L
  - Other cVOCs, RDX
- cVOCs detected in creek
- Low pH conditions (4.0 to 6.0)
- Saprolite
  - Low permeability, fractured
- Pilot tests performed to confirm EISB applicability

—3— TCE Concentration
——> Groundwater flow direction

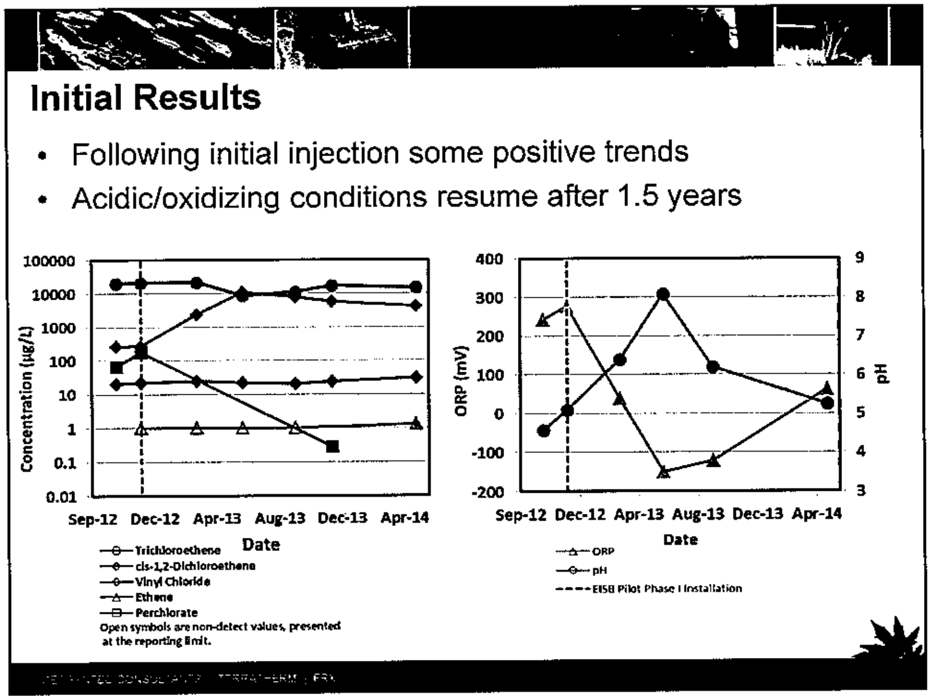


Initial Pilot Test Program

TCE >3,000 µg/L
Perchlorate up to 500 µg/L

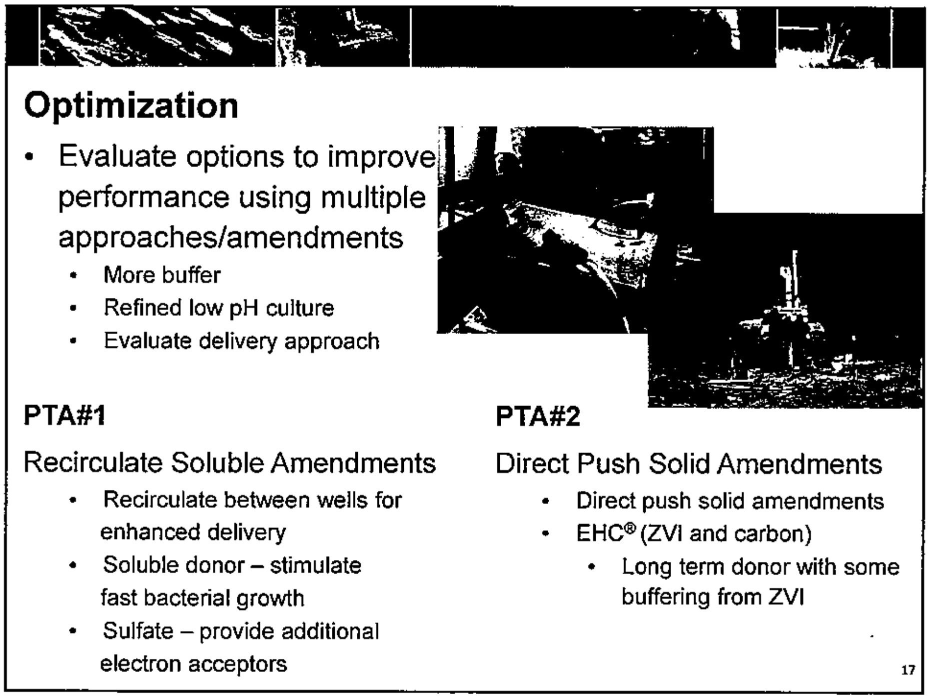
Closely spaced injection wells
Moderate EVO concentrations

Bicarbonate "fast buffer"
Neutral Zone "slow buffer"
Low pH KB-1® Plus



Initial Results

- Following initial injection some positive trends
- Acidic/oxidizing conditions resume after 1.5 years



Optimization

- Evaluate options to improve performance using multiple approaches/amendments
  - More buffer
  - Refined low pH culture
  - Evaluate delivery approach

PTA#1

Recirculate Soluble Amendments

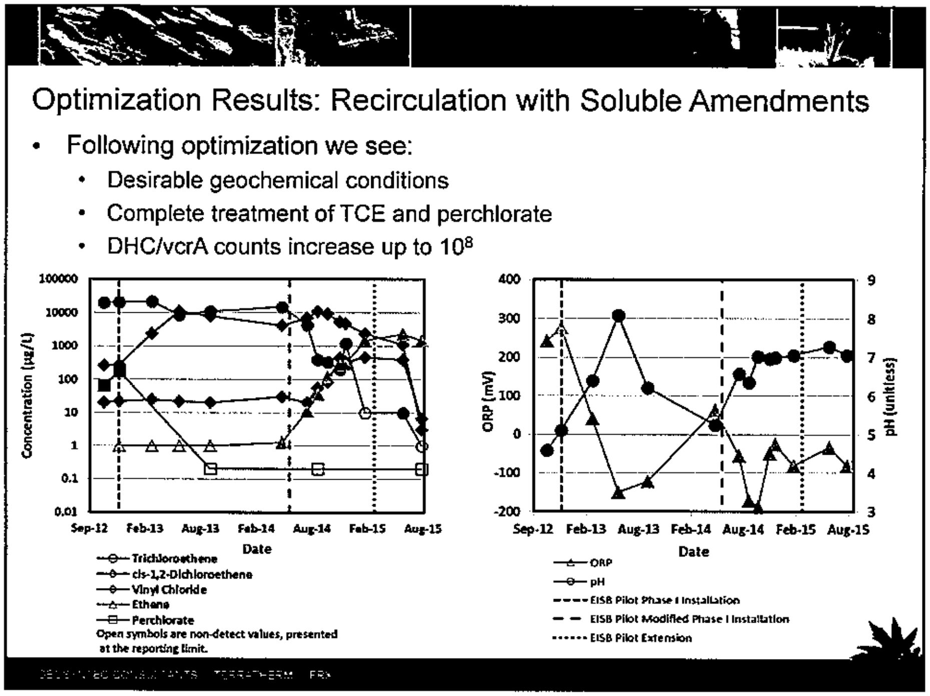
- Recirculate between wells for enhanced delivery
- Soluble donor – stimulate fast bacterial growth
- Sulfate – provide additional electron acceptors

PTA#2

Direct Push Solid Amendments

- Direct push solid amendments
- EHC® (ZVI and carbon)
  - Long term donor with some buffering from ZVI

17



Optimization Results: Recirculation with Soluble Amendments

- Following optimization we see:
  - Desirable geochemical conditions
  - Complete treatment of TCE and perchlorate
  - DHC/vcrA counts increase up to 10^8

Open symbols are non-detect values, presented at the reporting limit.

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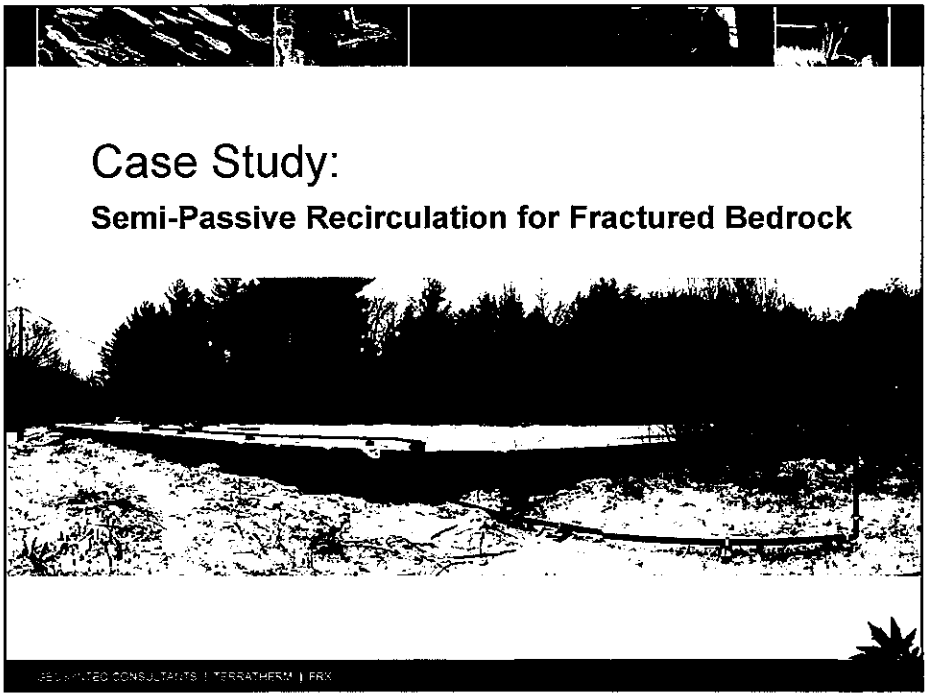

Case Study:

Semi-Passive Recirculation for Fractured Bedrock

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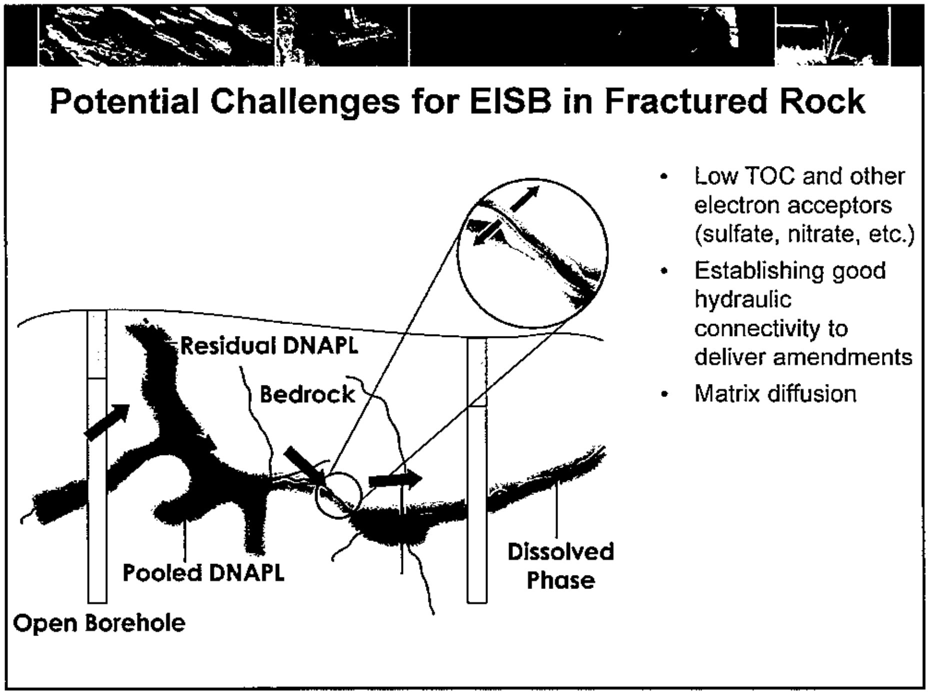
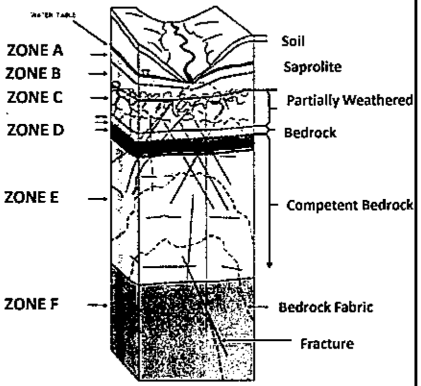


Potential Challenges for EISB in Fractured Rock

- Low TOC and other electron acceptors (sulfate, nitrate, etc.)
- Establishing good hydraulic connectivity to deliver amendments
- Matrix diffusion

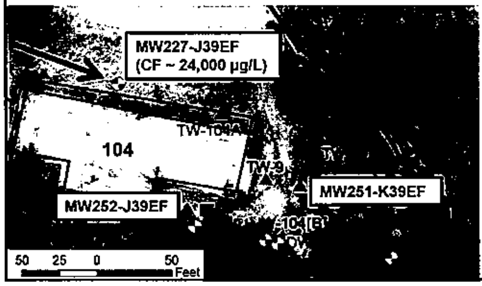
Geology

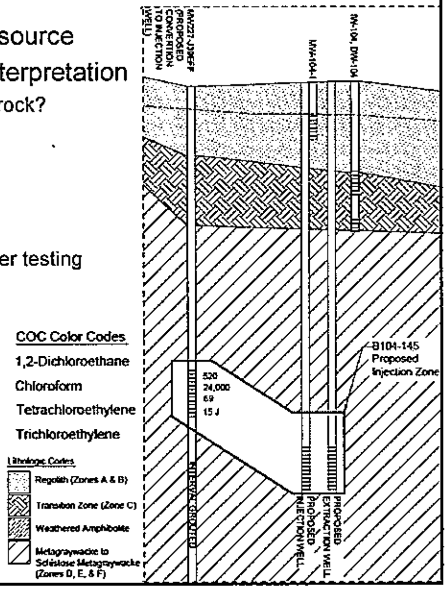
- Crystalline Bedrock
  - Metagraywacke, Schistose Metagraywacke or Amphibolite
  - Discrete Fractures
  - Sub-vertical Fractures

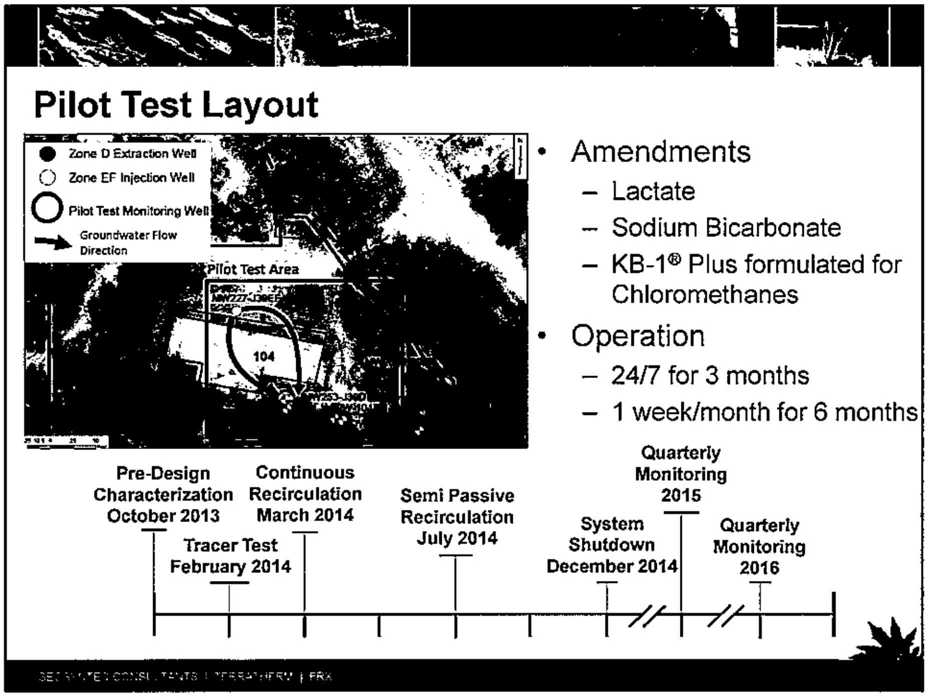


Pre-Pilot Characterization

- Address data gaps/uncertainty of CF source
- Support pilot test implementation & interpretation
  - Is the source in the overburden or the bedrock?
  - How deep are the impacts to bedrock?
  - Connectivity?
  - How do vertical fractures play a role?
- Characterization tools
  - Transducer deployment, geophysics, packer testing
  - Tracer testing







Pilot Test Layout

- Amendments
  - Lactate
  - Sodium Bicarbonate
  - KB-1® Plus formulated for Chloromethanes
- Operation
  - 24/7 for 3 months
  - 1 week/month for 6 months

Pre-Design Characterization October 2013

Tracer Test February 2014

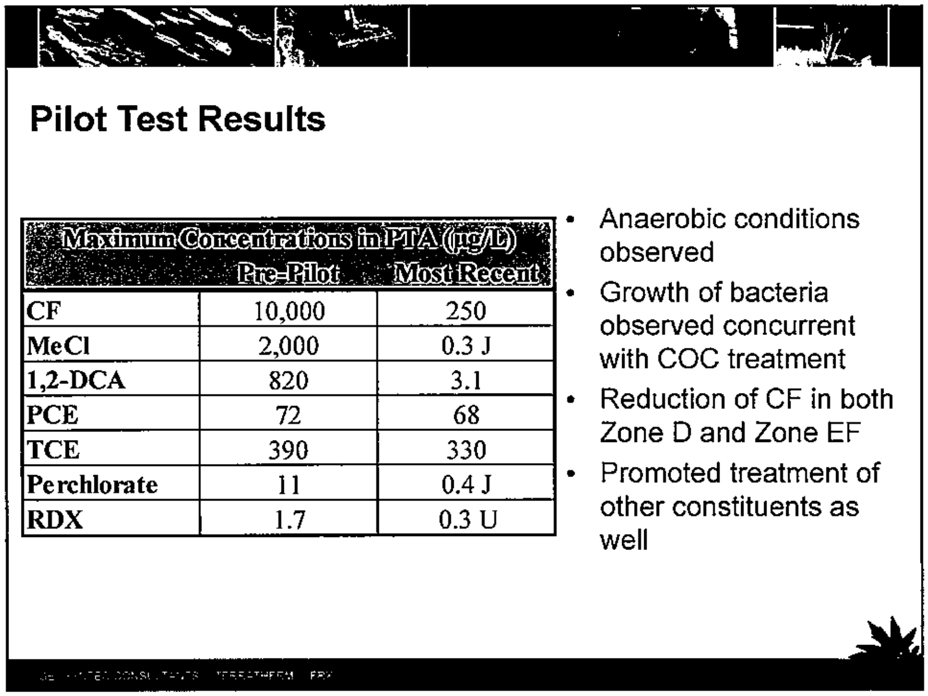
Continuous Recirculation March 2014

Semi Passive Recirculation July 2014

System Shutdown December 2014

Quarterly Monitoring 2015

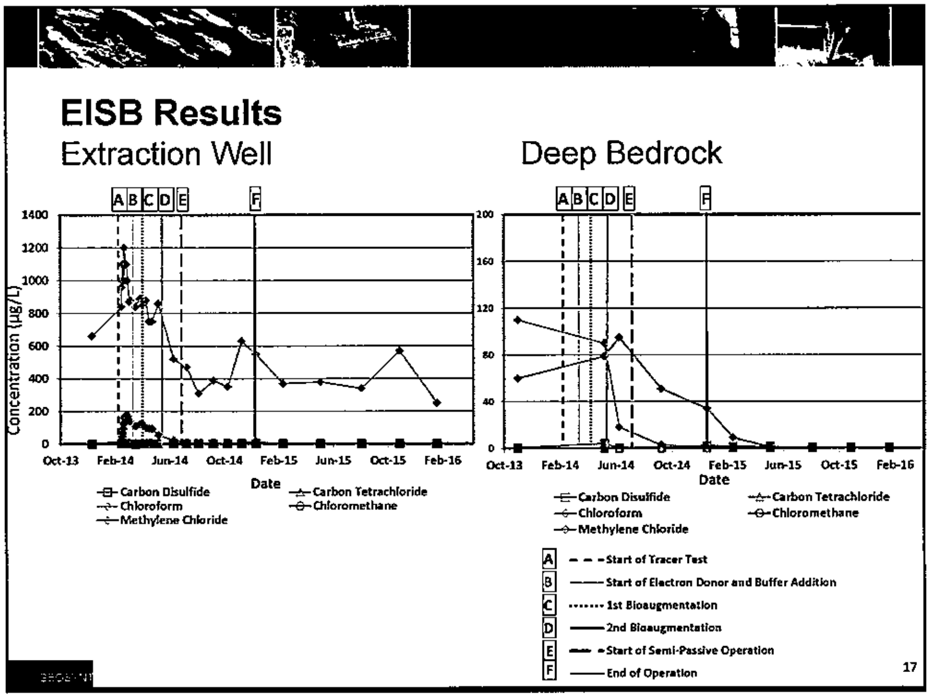
Quarterly Monitoring 2016



Pilot Test Results

Maximum Concentrations in PTA (µg/L)	Pre-Pilot	Most Recent
CF	10,000	250
MeCl	2,000	0.3 J
1,2-DCA	820	3.1
PCE	72	68
TCE	390	330
Perchlorate	11	0.4 J
RDX	1.7	0.3 U

- Anaerobic conditions observed
- Growth of bacteria observed concurrent with COC treatment
- Reduction of CF in both Zone D and Zone EF
- Promoted treatment of other constituents as well



EISB Results

Extraction Well

Deep Bedrock

A – – – Start of Tracer Test

B ——— Start of Electron Donor and Buffer Addition

C ······· 1st Bioaugmentation

D ——— 2nd Bioaugmentation

E ━ ━ Start of Semi-Passive Operation

F ——— End of Operation

Summary

- EISB well suited to address challenging geologies
- Good characterization and creativity key to achieve goals
- Pilot testing critical to finding optimal approach
- May need to evaluate multiple approaches, expect iterative approach in challenging conditions
- Hydraulic control is important to deliver amendment to target zone in both bedrock and low permeability media

Questions?

LMackinnon@
geosyntec.com

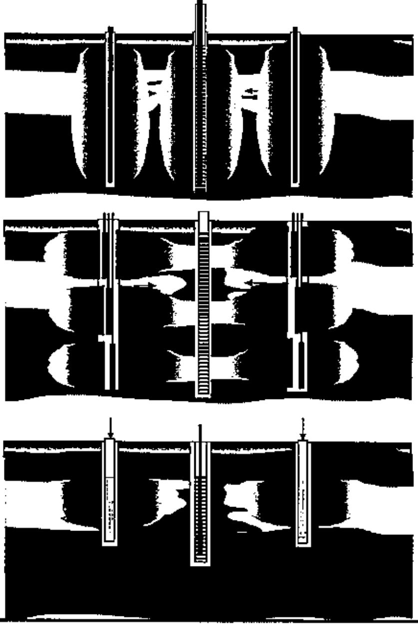
Geosyntec consultants | TERRATHERM a Cascade Company | FRx

Remediation Tools for Challenging Geology Thermal Remediation Workshop 7

Steffen Griepke,
TerraTherm

Tuesday October 18, 2016

Heating Methods



TCH/ISTD - Heating governed by **thermal conductivity**

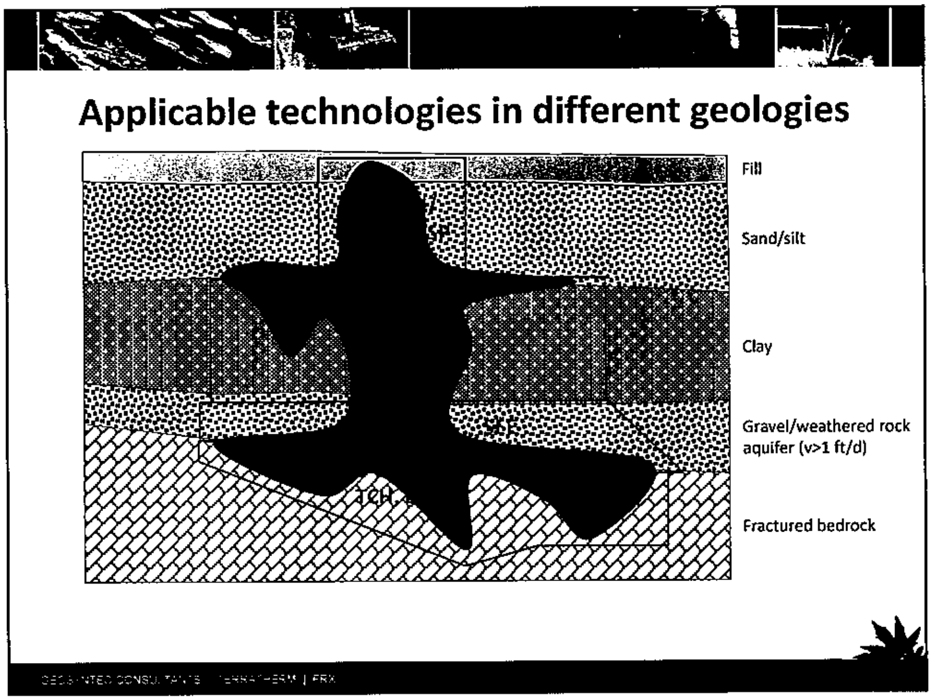
(f~5)

ERH - Heating governed by **electrical conductivity**

(f~200)

SEE - Heating governed by **hydraulic conductivity**

(f~10^6)



Applicable technologies in different geologies

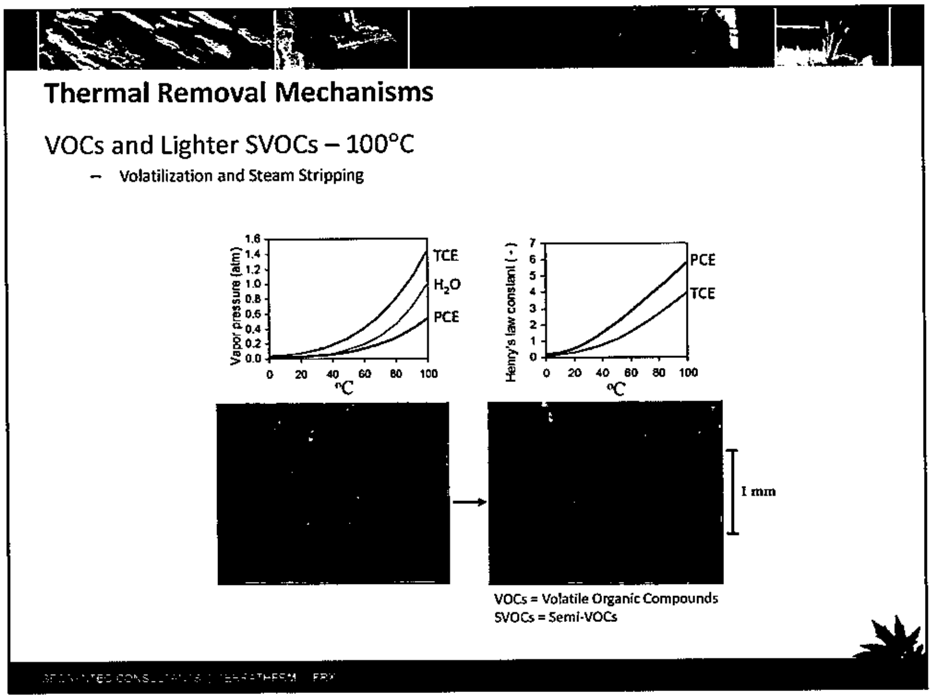
Fill

Sand/silt

Clay

Gravel/weathered rock aquifer (v>1 ft/d)

Fractured bedrock

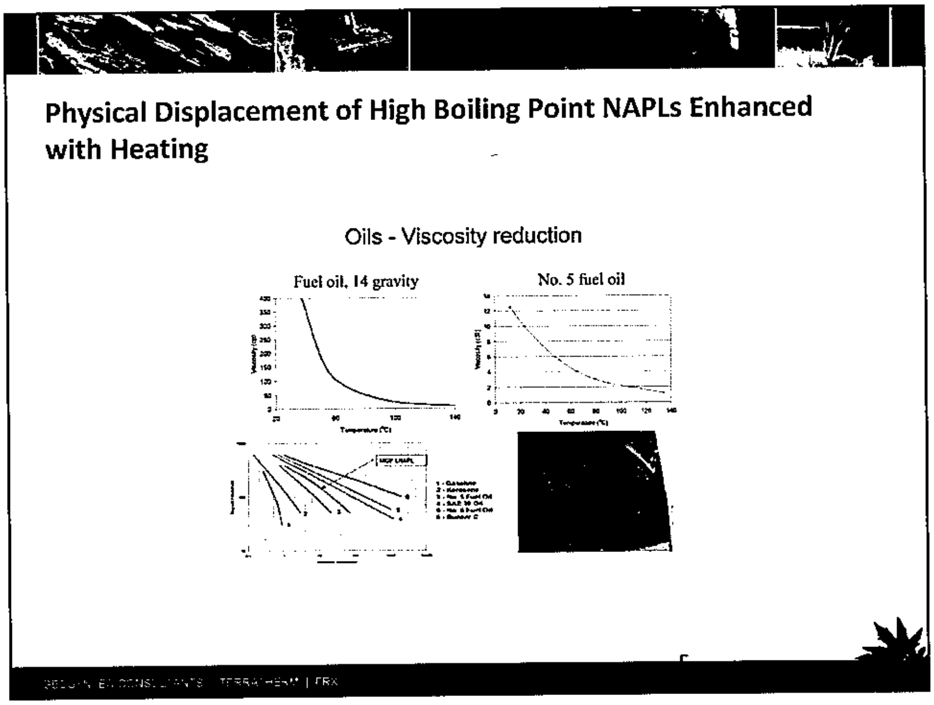


Thermal Removal Mechanisms

VOCs and Lighter SVOCs – 100°C

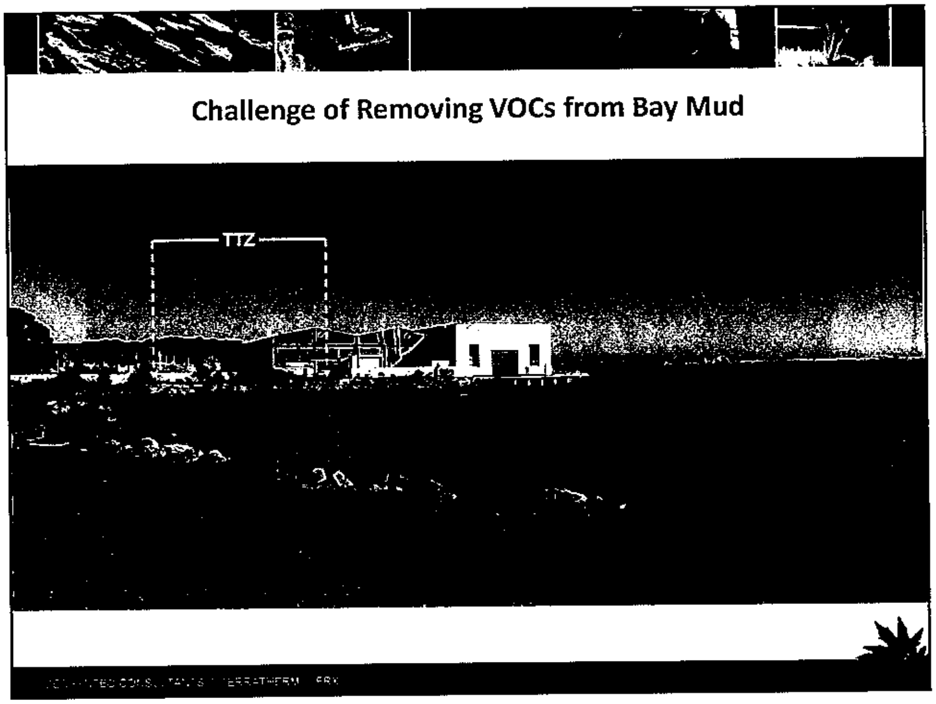
- Volatilization and Steam Stripping

VOCs = Volatile Organic Compounds
SVOCs = Semi-VOCs

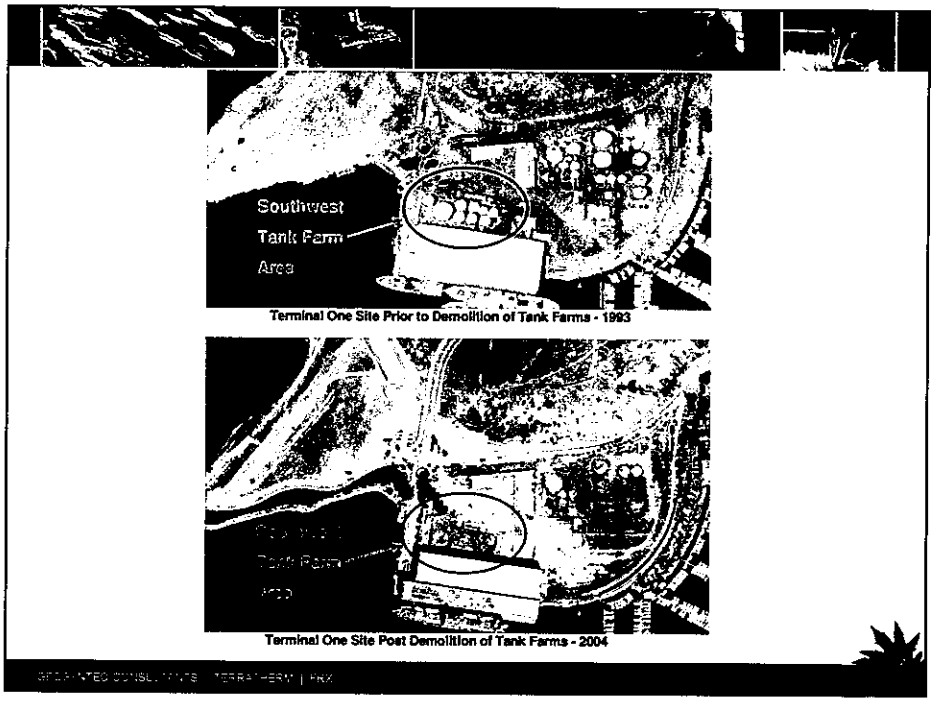


Physical Displacement of High Boiling Point NAPLs Enhanced with Heating

Oils - Viscosity reduction



Challenge of Removing VOCs from Bay Mud



Terminal One Site Prior to Demolition of Tank Farms - 1993

Terminal One Site Post Demolition of Tank Farms - 2004

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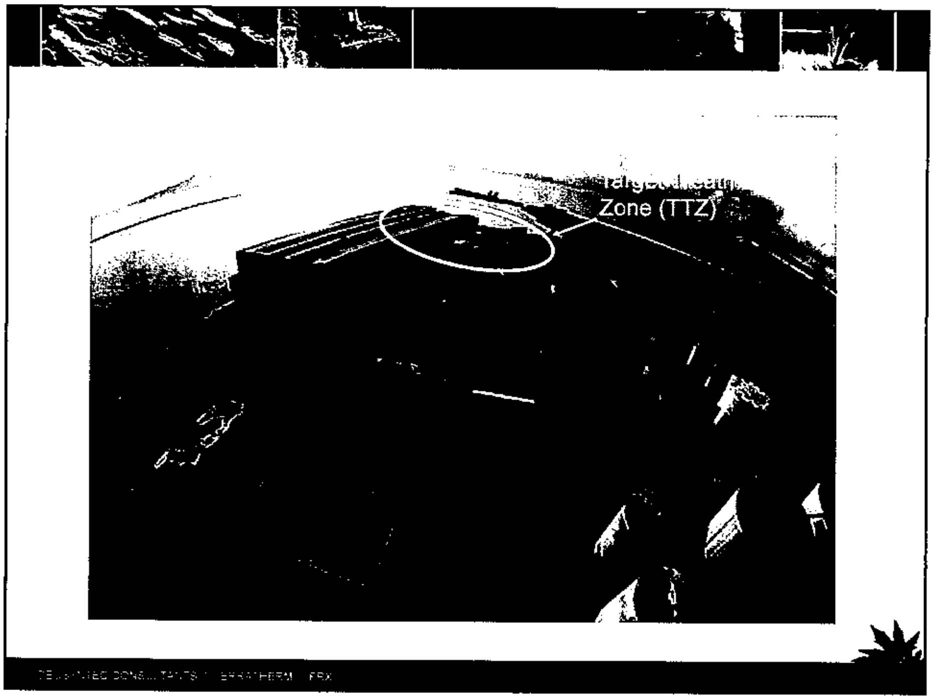

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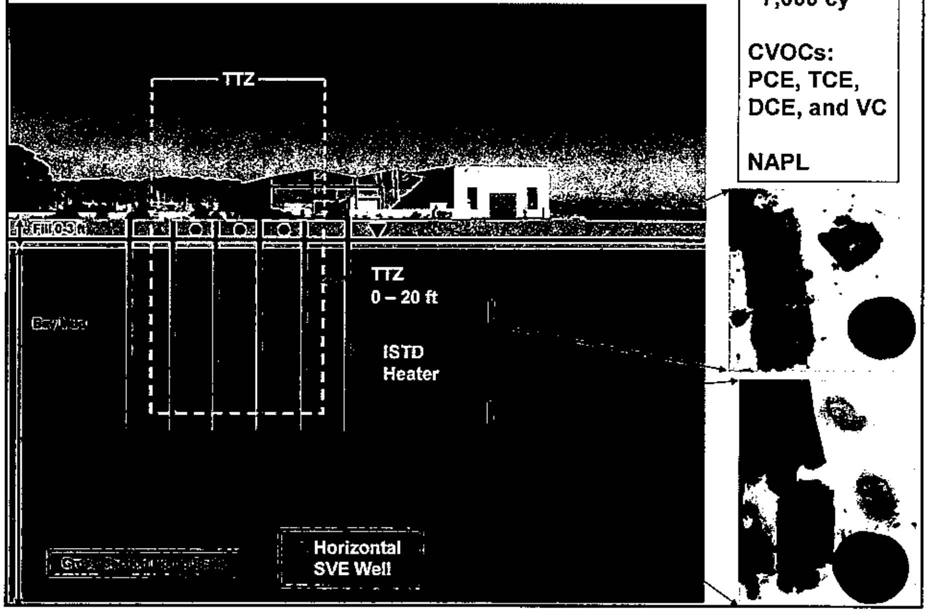
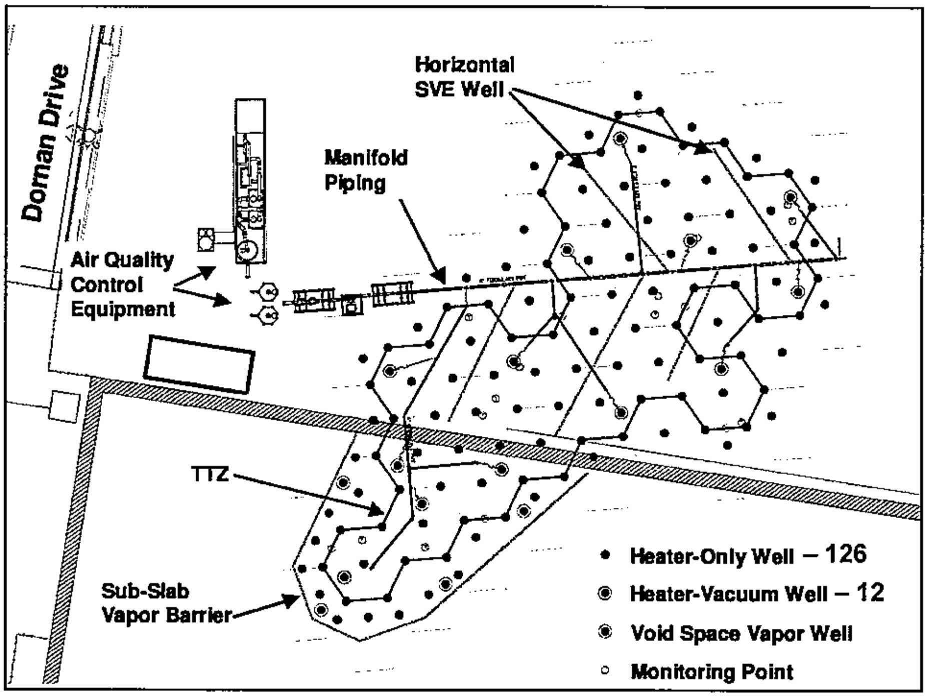
Site Conditions

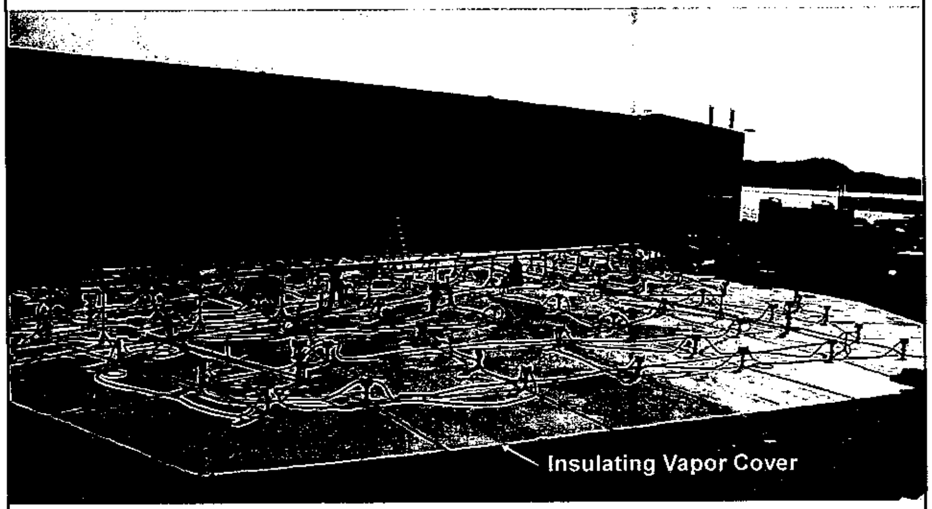
~7,000 cy

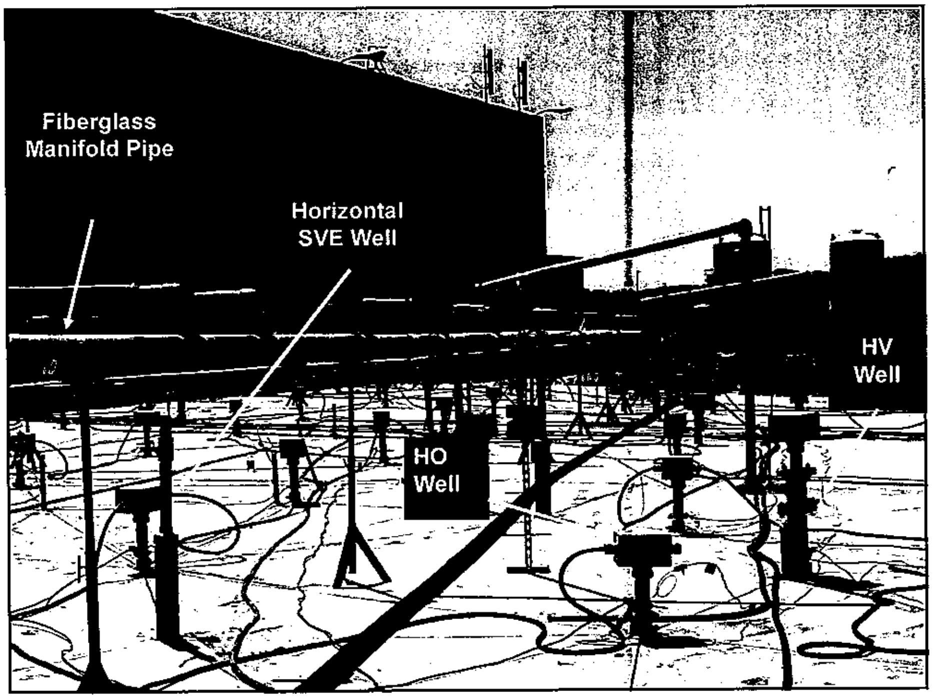
CVOCs:
PCE, TCE,
DCE, and VC

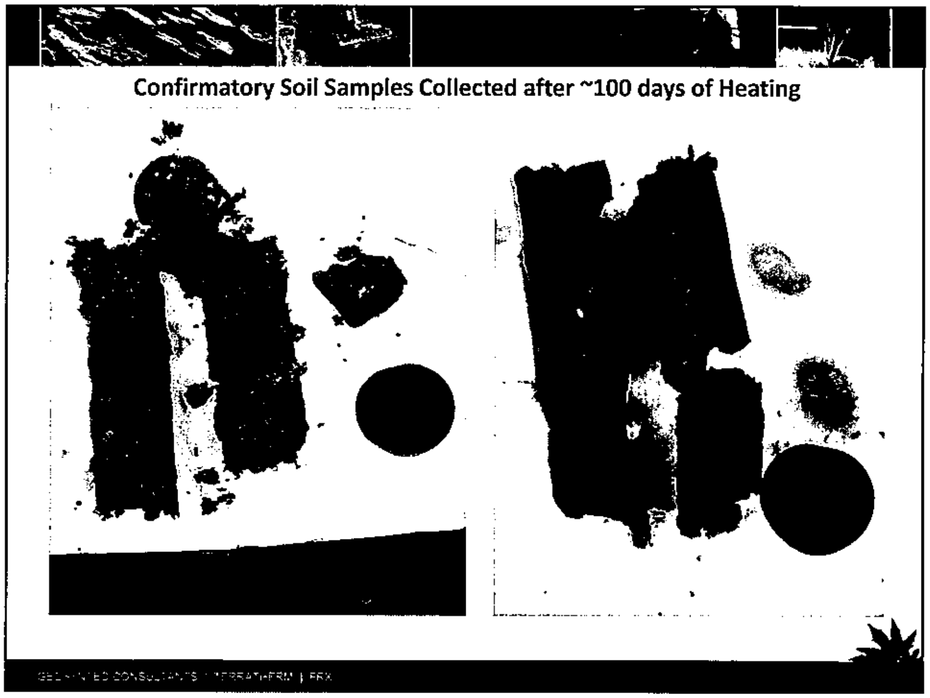
NAPL



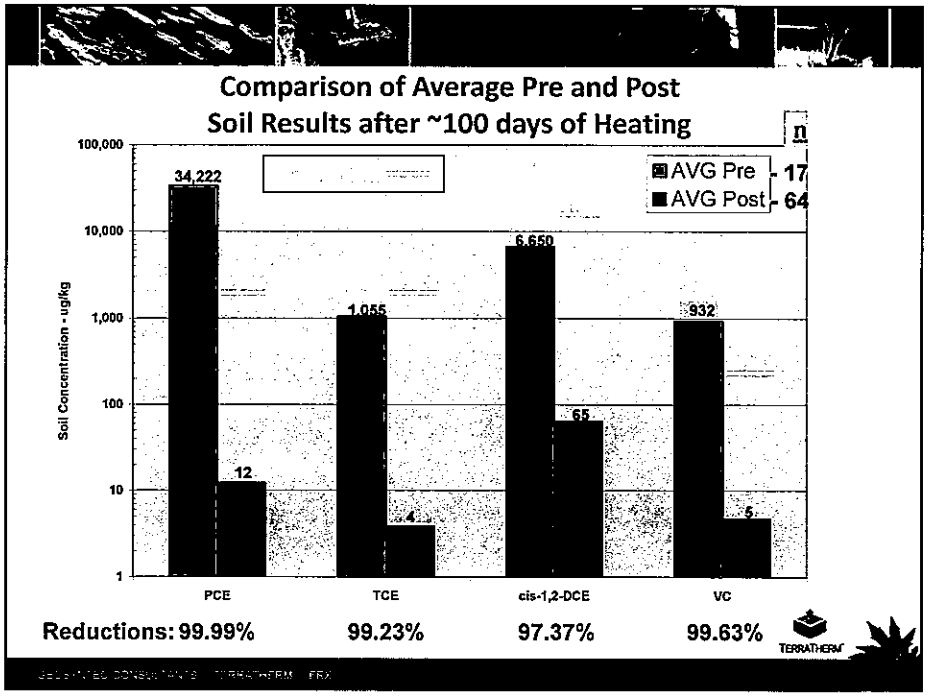



Insulating Vapor Cover


Fiberglass Manifold Pipe
Horizontal SVE Well
HV Well
HO Well



Confirmatory Soil Samples Collected after ~100 days of Heating



Comparison of Average Pre and Post Soil Results after ~100 days of Heating

Reductions: 99.99% 99.23% 97.37% 99.63%

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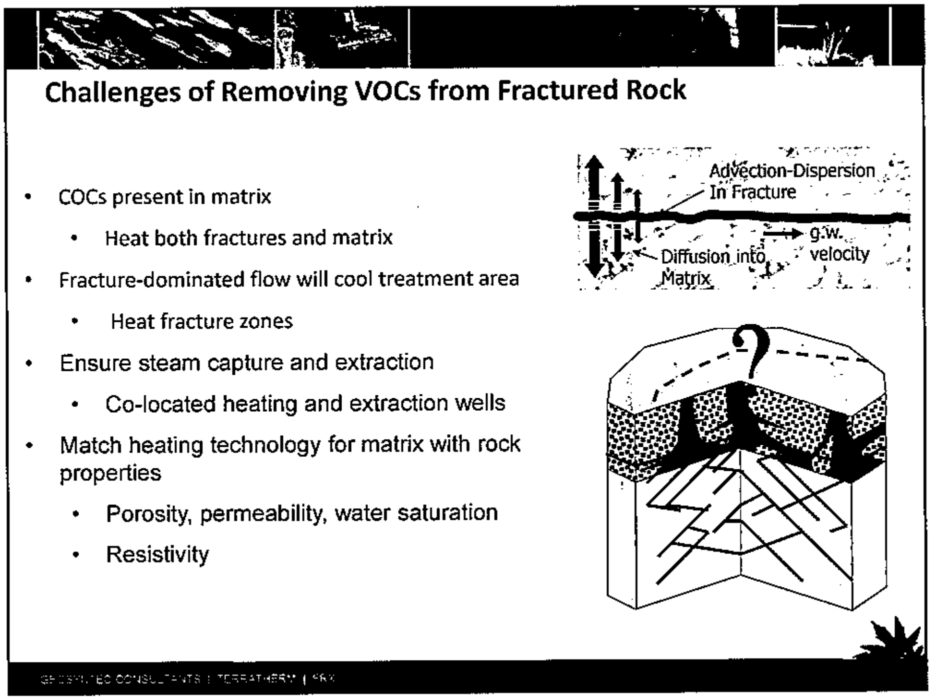
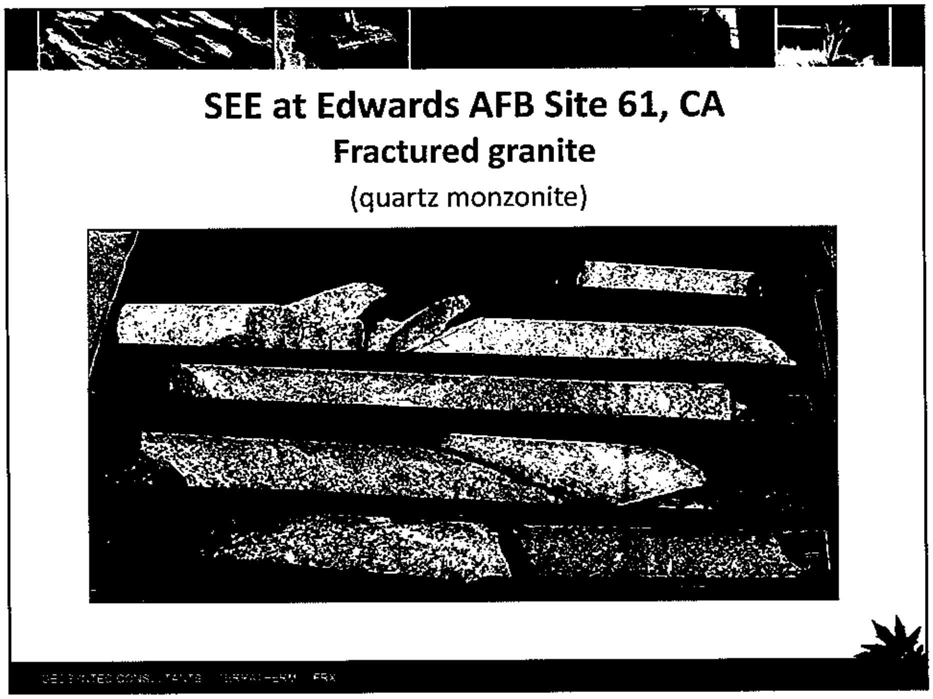


Challenges of Removing VOCs from Fractured Rock

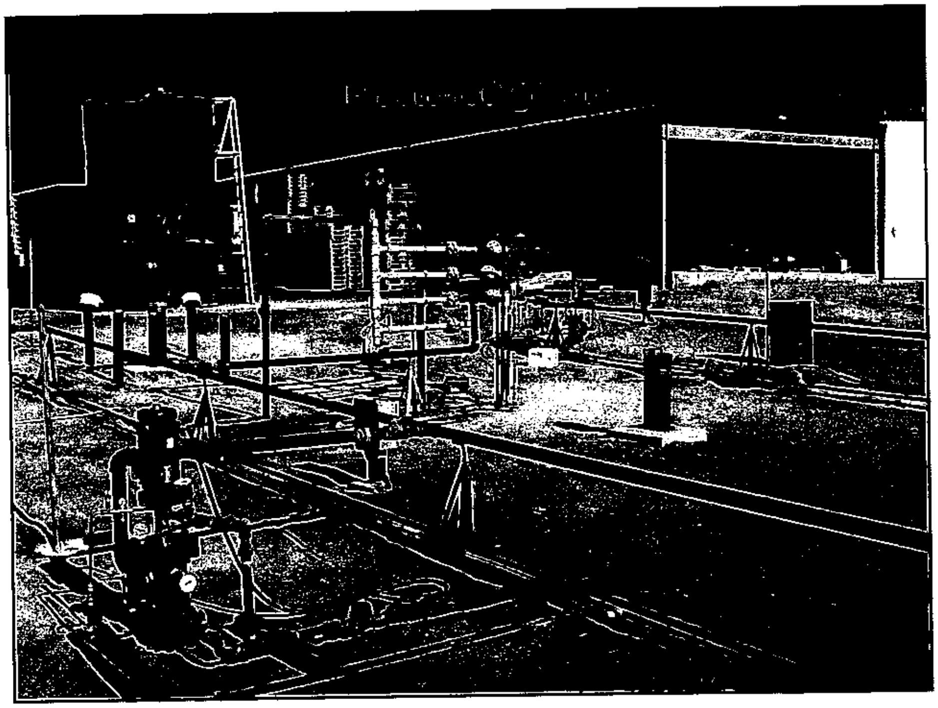
- COCs present in matrix
  - Heat both fractures and matrix
- Fracture-dominated flow will cool treatment area
  - Heat fracture zones
- Ensure steam capture and extraction
  - Co-located heating and extraction wells
- Match heating technology for matrix with rock properties
  - Porosity, permeability, water saturation
  - Resistivity



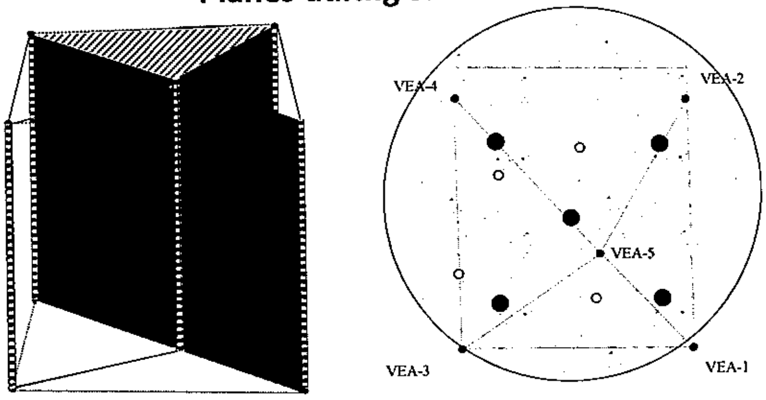
SEE at Edwards AFB Site 61, CA

Fractured granite

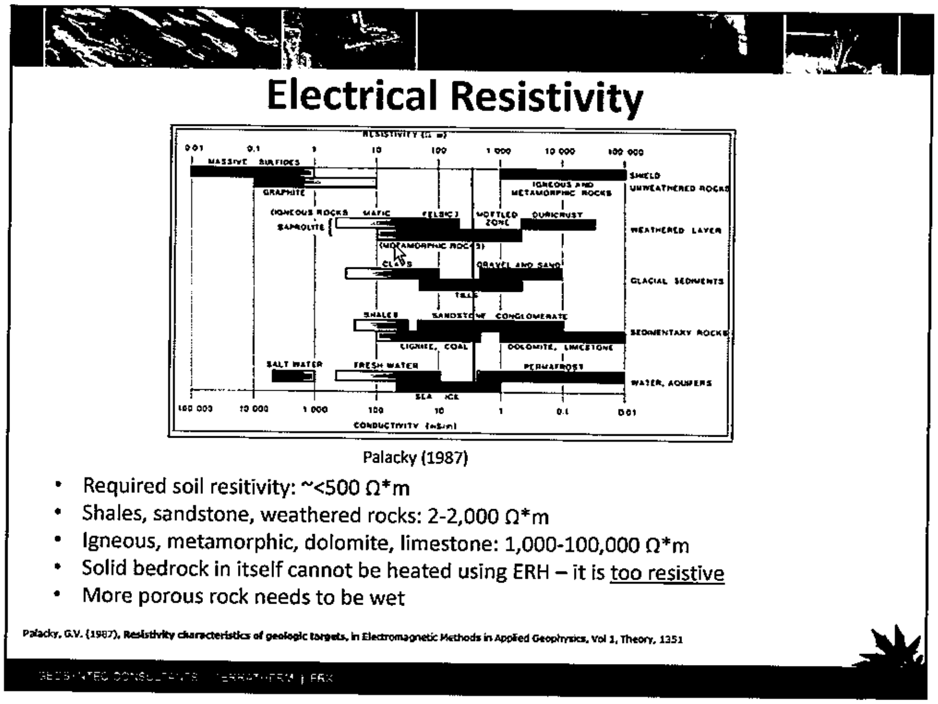
(quartz monzonite)



Edwards AFB Electrical Resistance Tomography (ERT) Data Planes during SEE



⇒ It is difficult to heat fractured rock with steam alone



Electrical Resistivity

Palacky (1987)

- Required soil resitivity: ~<500 Ω*m
- Shales, sandstone, weathered rocks: 2-2,000 Ω*m
- Igneous, metamorphic, dolomite, limestone: 1,000-100,000 Ω*m
- Solid bedrock in itself cannot be heated using ERH – it is <u>too resistive</u>
- More porous rock needs to be wet

Palacky, G.V. (1987), Resistivity characteristics of geologic targets, in Electromagnetic Methods in Applied Geophysics, Vol 1, Theory, 1351

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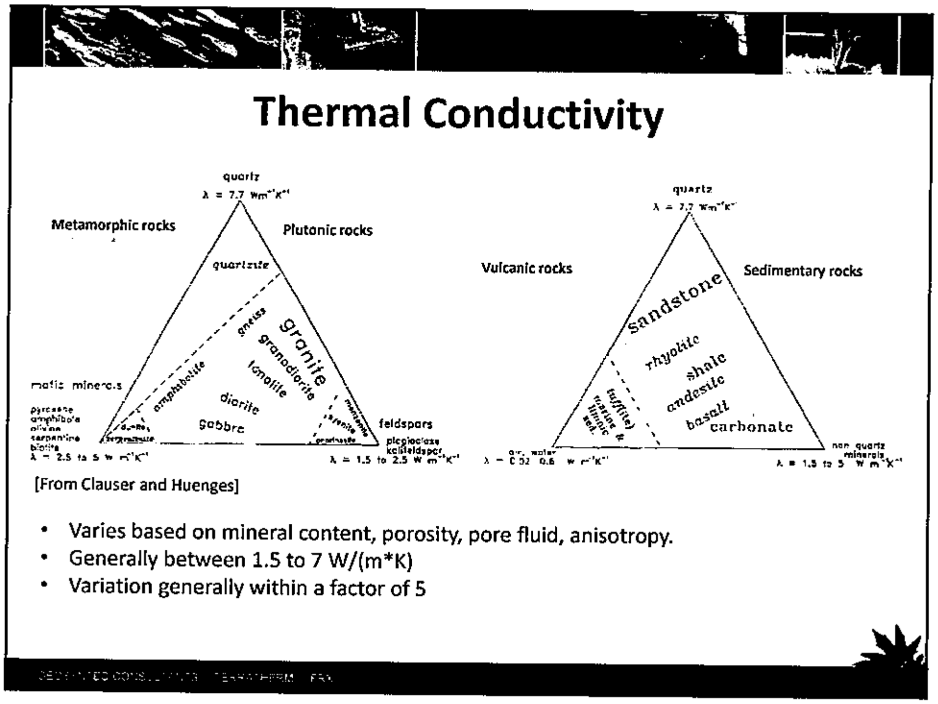

Thermal Conductivity

[From Clauser and Huenges]

- Varies based on mineral content, porosity, pore fluid, anisotropy.
- Generally between 1.5 to 7 W/(m*K)
- Variation generally within a factor of 5

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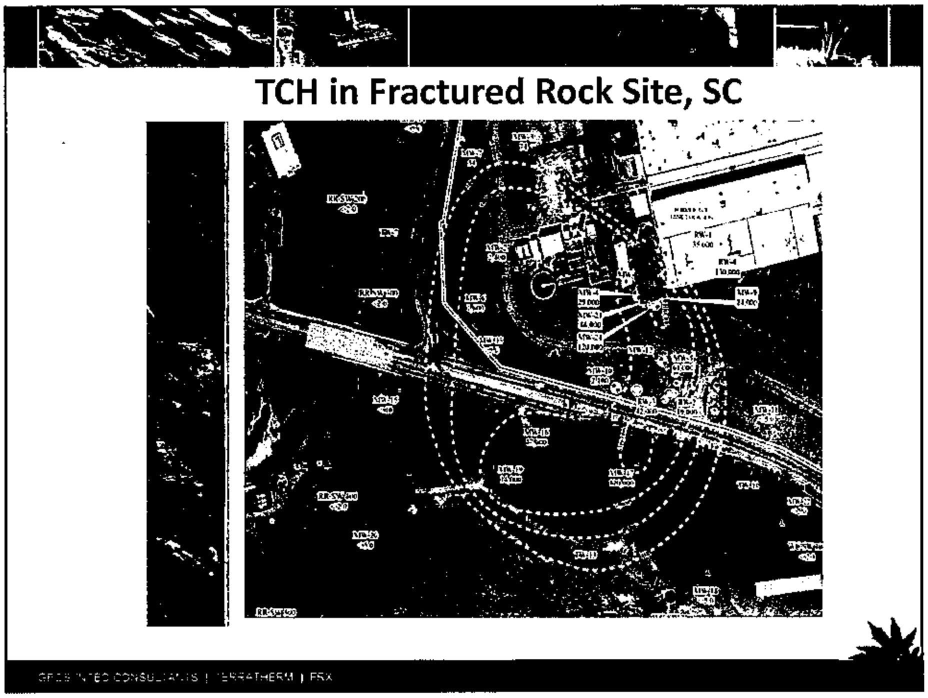

TCH in Fractured Rock Site, SC

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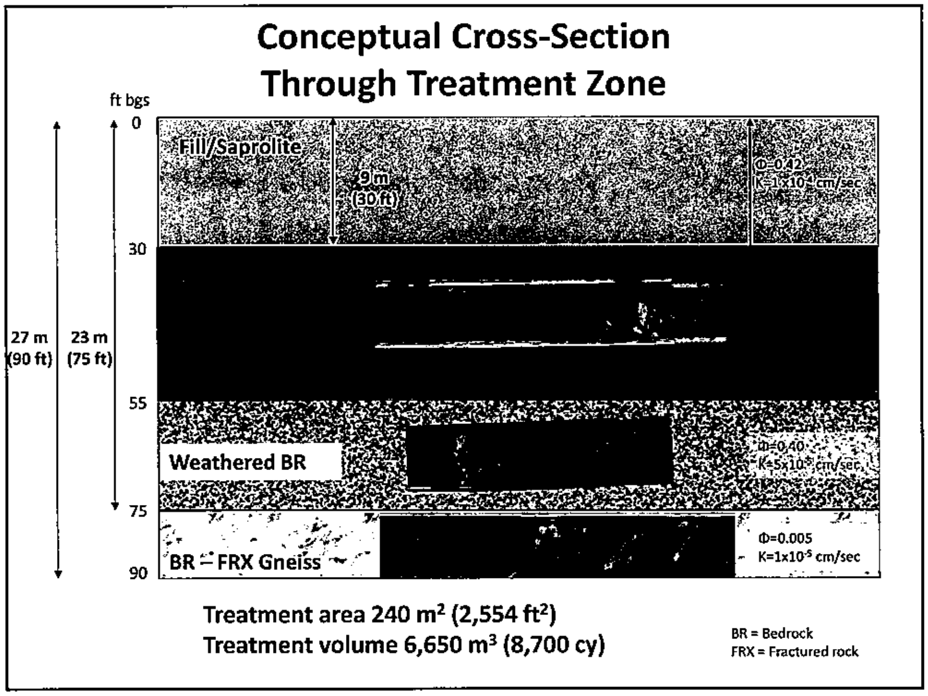
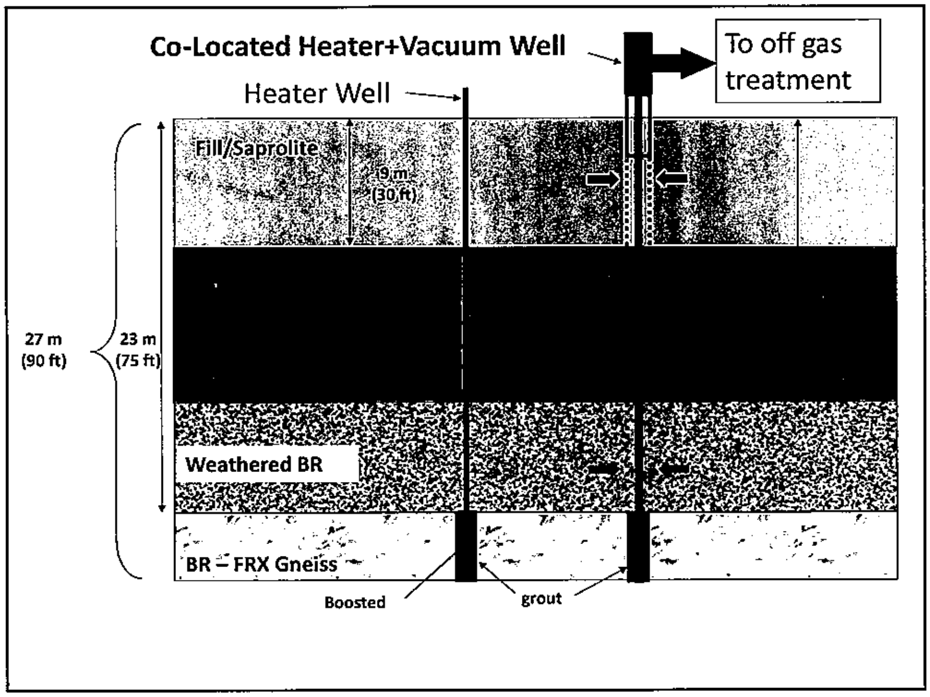
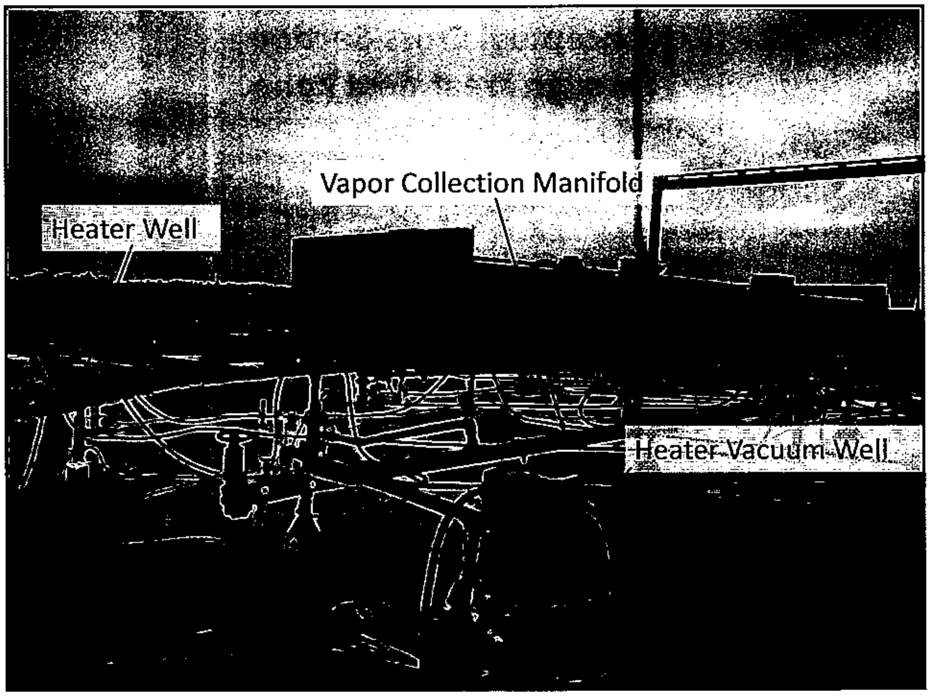


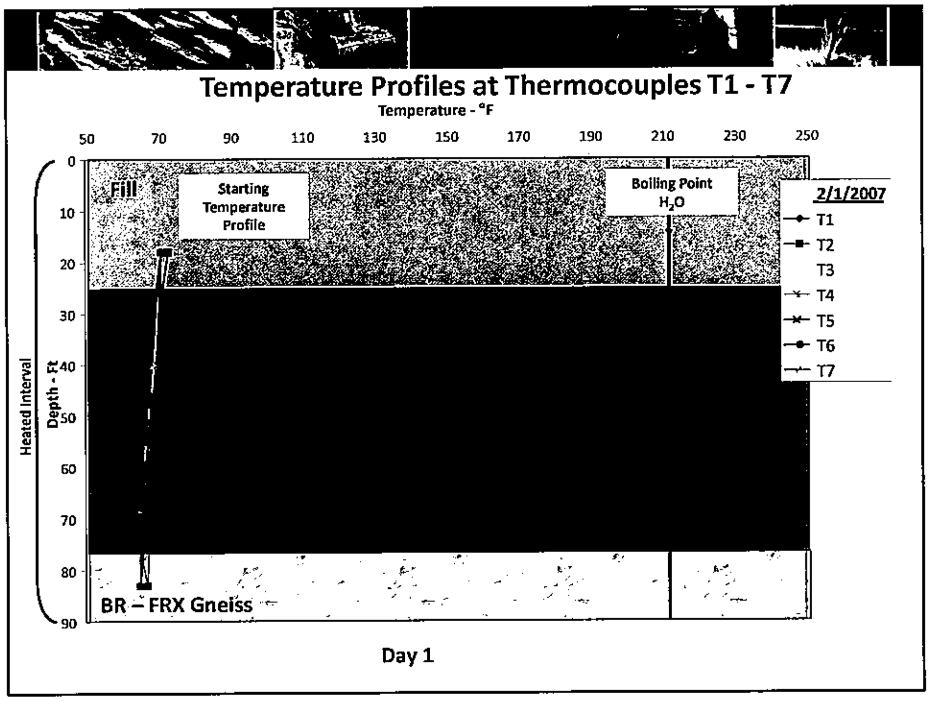
Conceptual Cross-Section Through Treatment Zone

Treatment area 240 m^2 (2,554 ft^2)
Treatment volume 6,650 m^3 (8,700 cy)

BR = Bedrock
FRX = Fractured rock

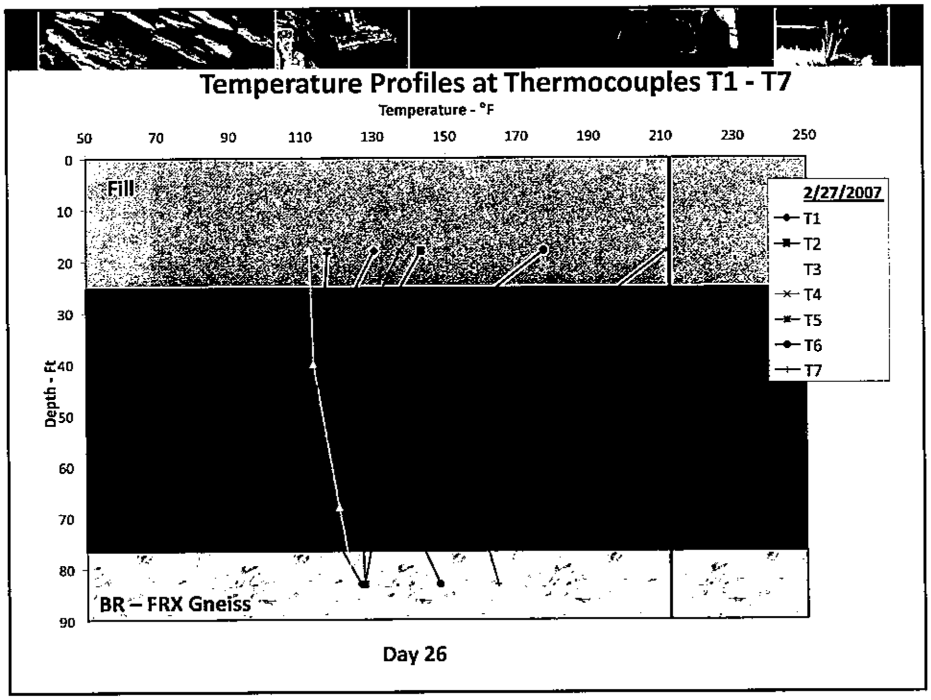

Co-Located Heater+Vacuum Well
To off gas treatment
Heater Well
Fill/Saprolite
9 m
(30 ft)
27 m
(90 ft)
23 m
(75 ft)
Weathered BR
BR – FRX Gneiss
Boosted
grout


Vapor Collection Manifold
Heater Well
Heater-Vacuum Well



Temperature Profiles at Thermocouples T1 - T7

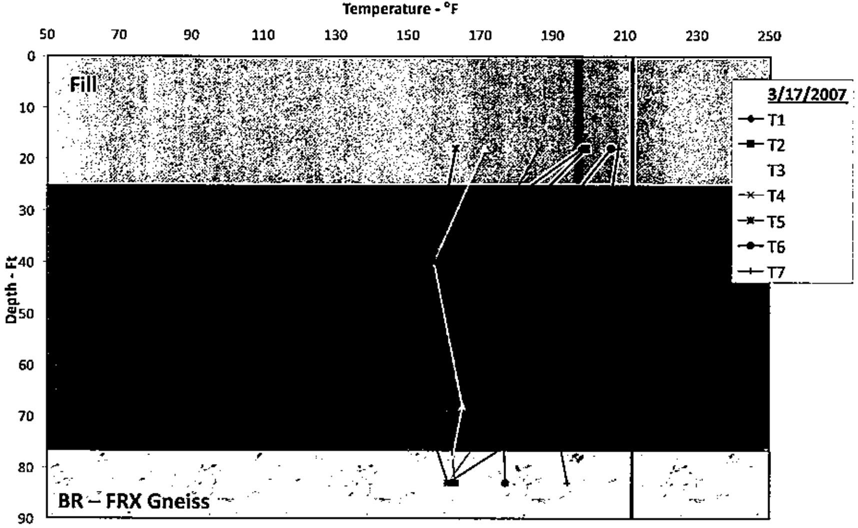
Day 1



Temperature Profiles at Thermocouples T1 - T7

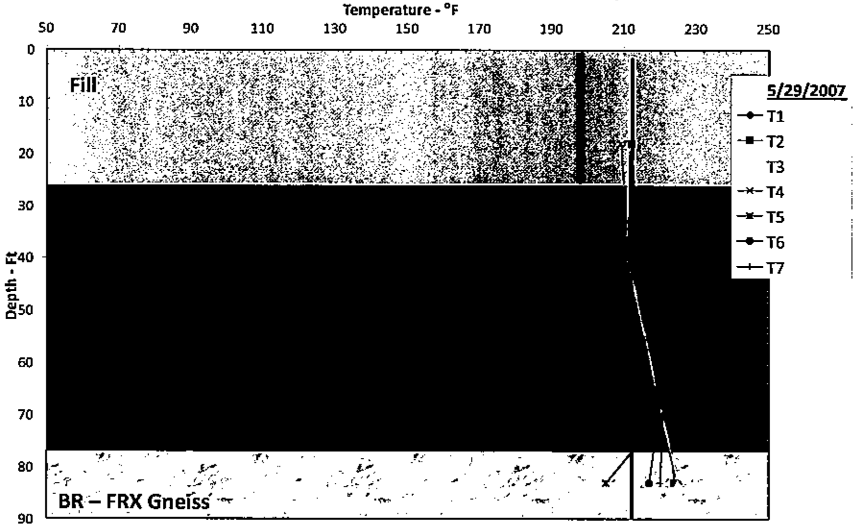
Day 26

Temperature Profiles at Thermocouples T1 - T7



Day 44

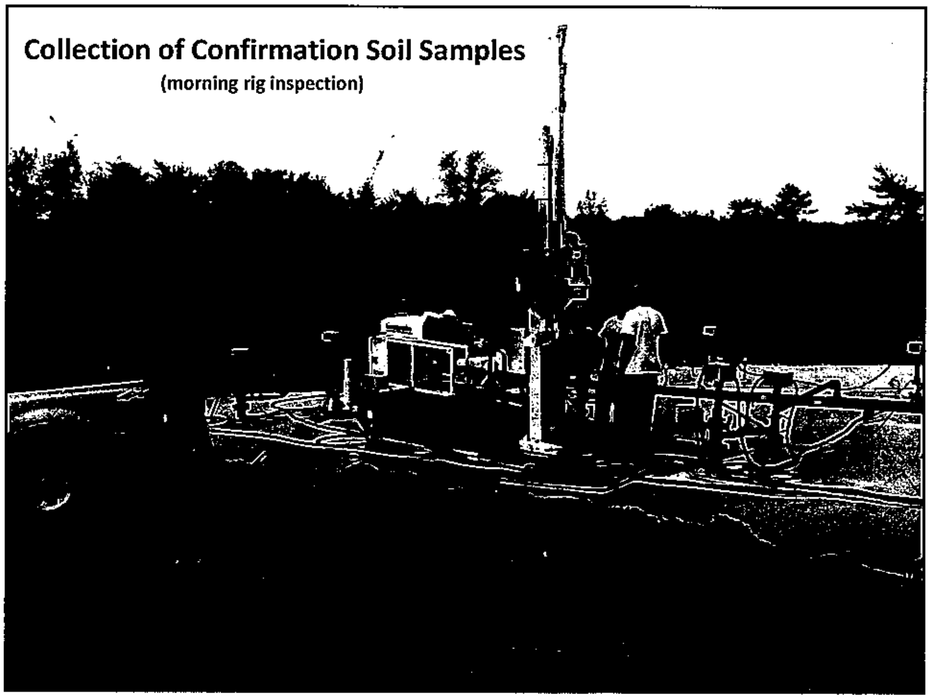
Temperature Profiles at Thermocouples T1 - T7



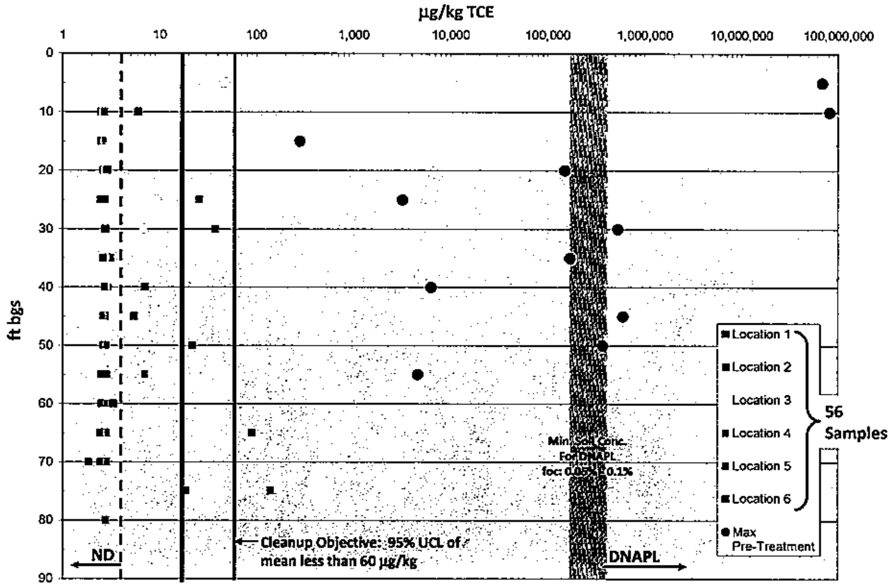
Day 117

Collection of Confirmation Soil Samples

(morning rig inspection)

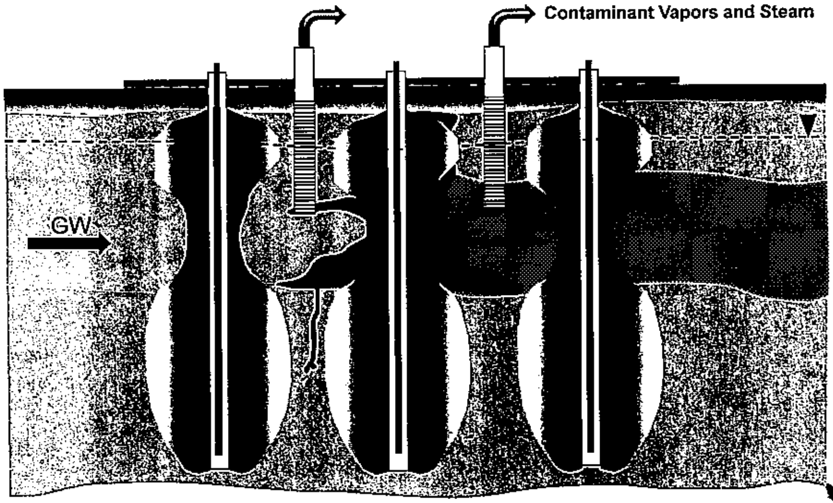


Confirmation Soil Data From TCH Project in SC

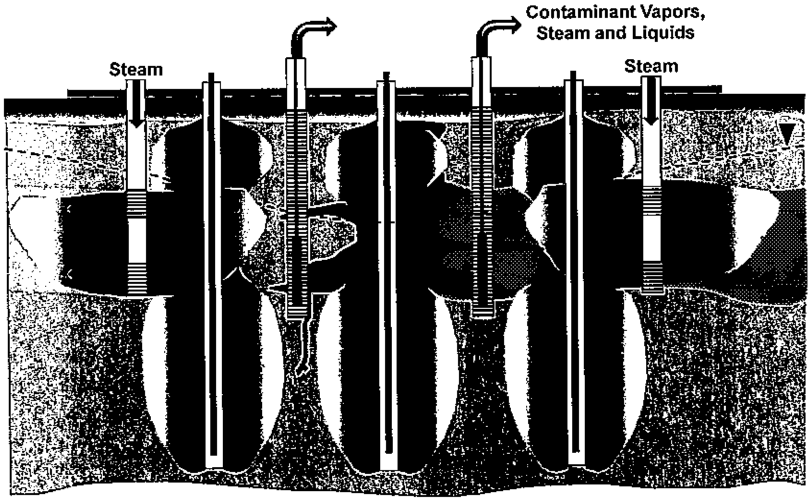


95% UCL of mean TCE conc. = 17 µg/kg

Sometimes One Technology Alone Won't Get the Job Done



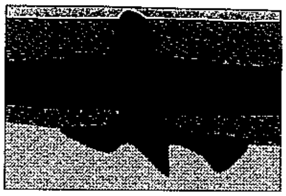
Combine ISTR Technologies to Match Site Conditions

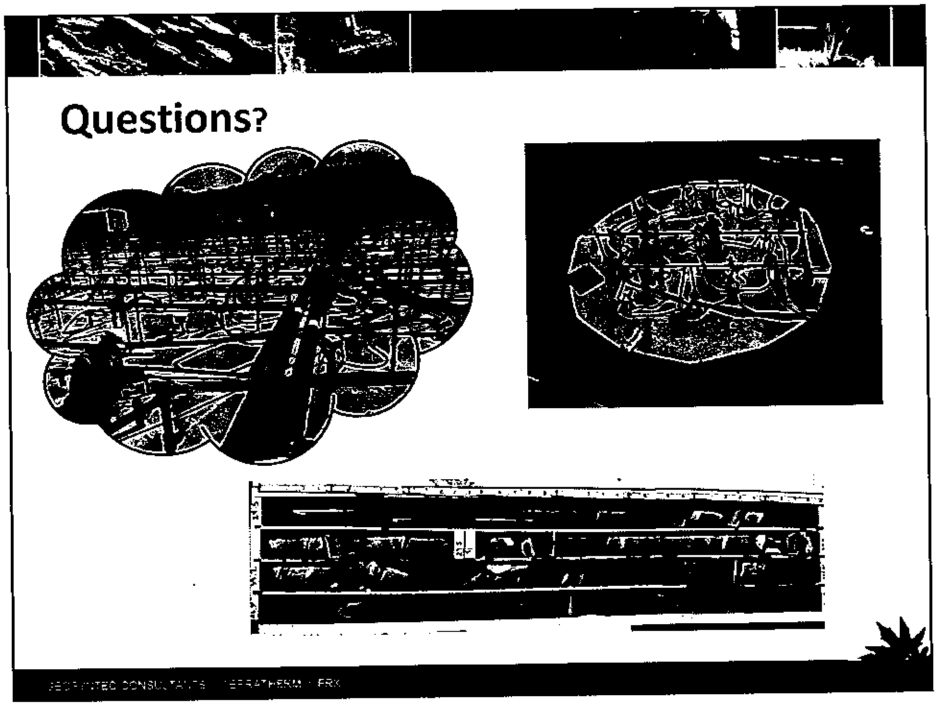


Example TCH-SEE Site

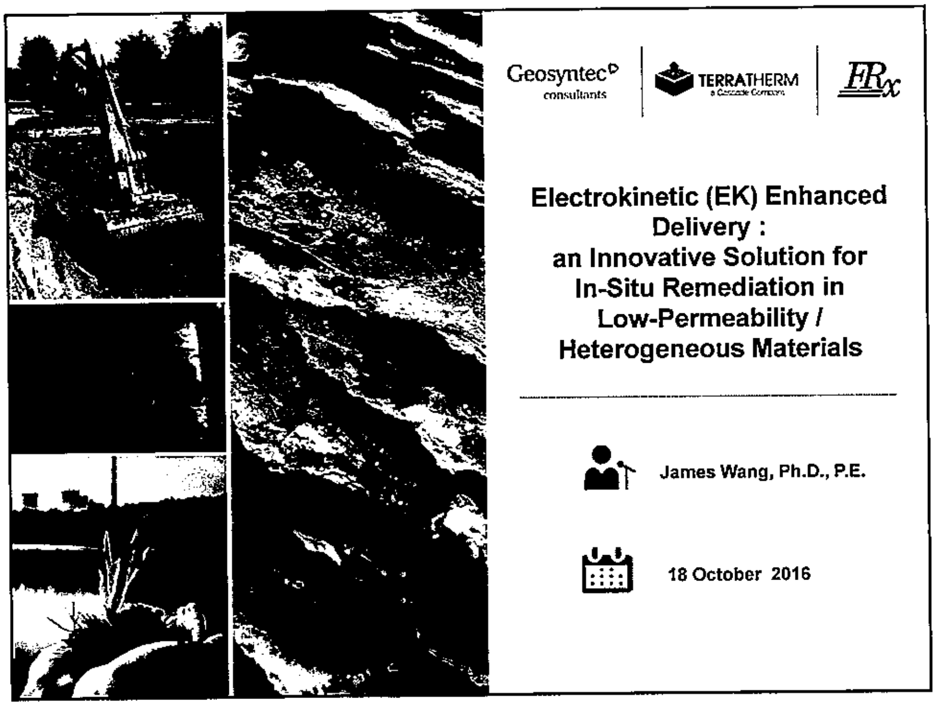
Conclusions

- Select thermal technology based on site conditions
- TCH effective in heating and treating bedrock
- Rocks heat easier than overburden (less heat capacity) – needs to be factored in.
- Use TCH/ERH in combination with SEE when necessary (high groundwater flux)
- ERH may also work in wet porous rock



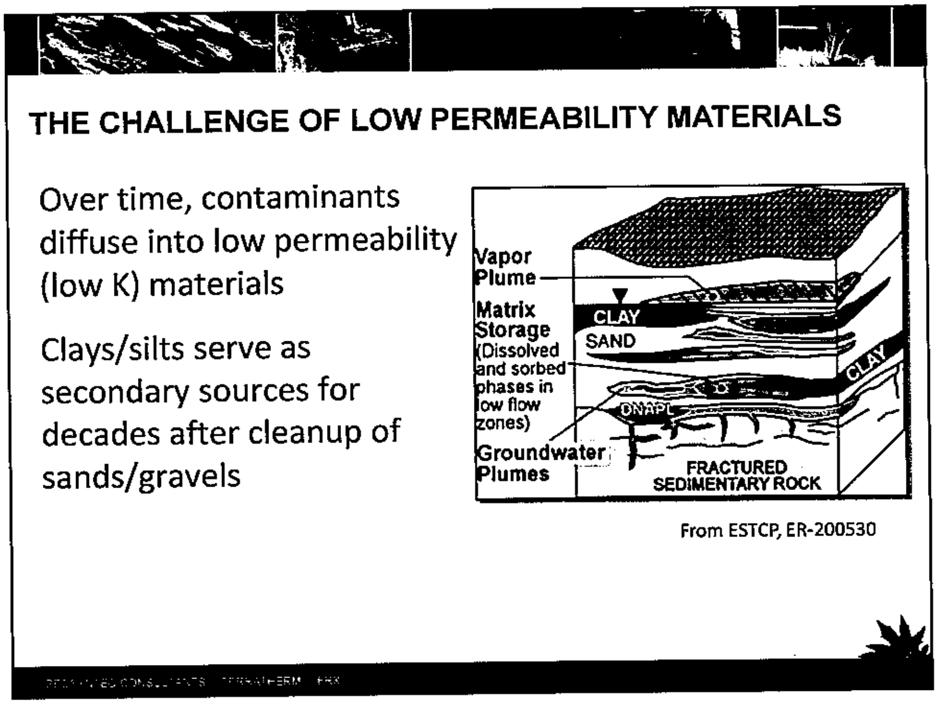
Questions?



Electrokinetic (EK) Enhanced Delivery : an Innovative Solution for In-Situ Remediation in Low-Permeability / Heterogeneous Materials

James Wang, Ph.D., P.E.

18 October 2016

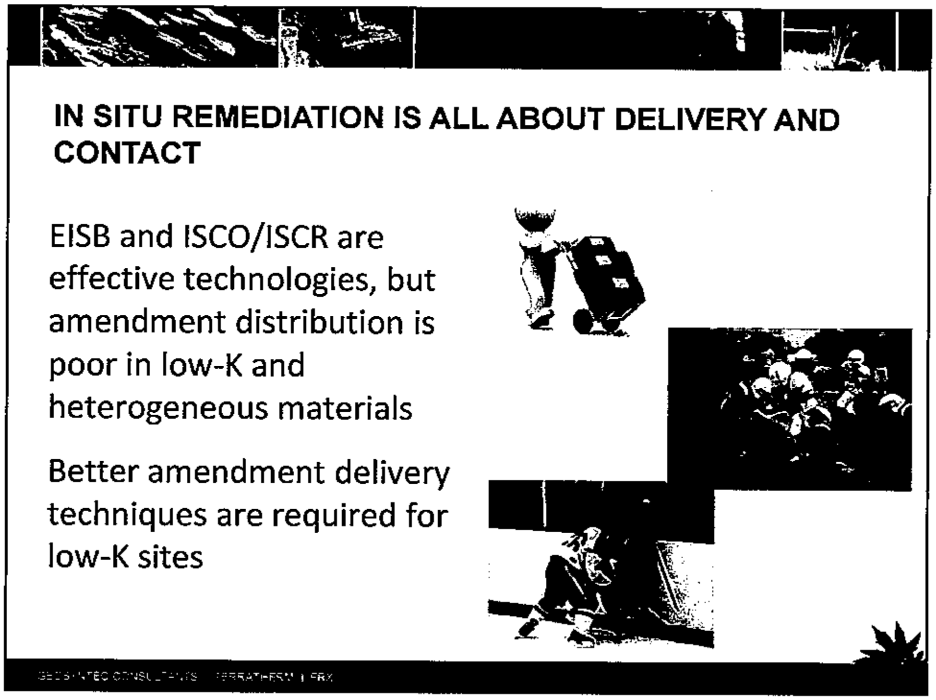


THE CHALLENGE OF LOW PERMEABILITY MATERIALS

Over time, contaminants diffuse into low permeability (low K) materials

Clays/silts serve as secondary sources for decades after cleanup of sands/gravels

From ESTCP, ER-200530

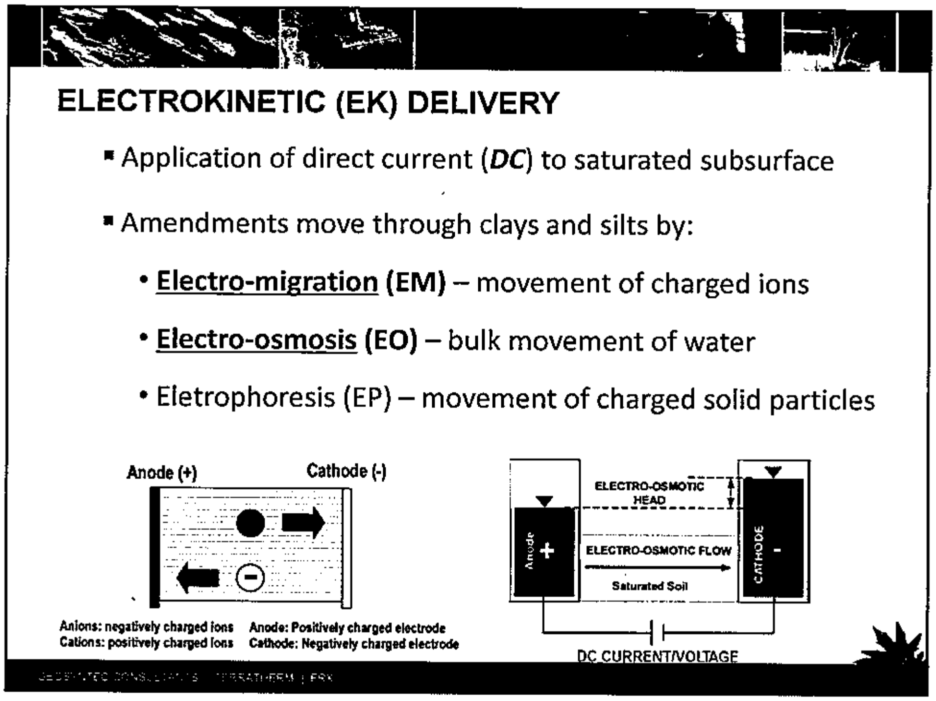


IN SITU REMEDIATION IS ALL ABOUT DELIVERY AND CONTACT

EISB and ISCO/ISCR are effective technologies, but amendment distribution is poor in low-K and heterogeneous materials

Better amendment delivery techniques are required for low-K sites

---



ELECTROKINETIC (EK) DELIVERY

- Application of direct current (*DC*) to saturated subsurface
- Amendments move through clays and silts by:
  - **<u>Electro-migration</u> (EM)** – movement of charged ions
  - **<u>Electro-osmosis</u> (EO)** – bulk movement of water
  - Eletrophoresis (EP) – movement of charged solid particles

Anions: negatively charged ions
Cations: positively charged ions

Anode: Positively charged electrode
Cathode: Negatively charged electrode

Electromigration

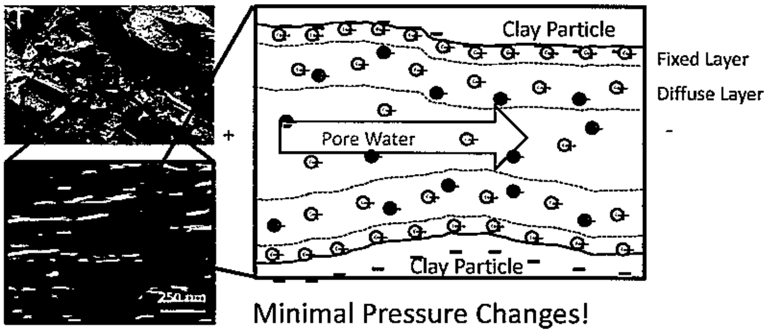
- **Electromigration** is the movement of ions in a fluid due to the applied potential field. Ions are attracted to the electrode of opposite charge
- Electromigration occurs as long as there is a connected water pathway, and the rate is proportional to the gradient of the applied field
  Ion velocities of > 6 inch/day (180 ft/year) are possible

$$J_i = -D_i^* \frac{\partial c_i}{\partial x} - u_i^* c_i \frac{\partial \phi}{\partial x} + q c_i$$

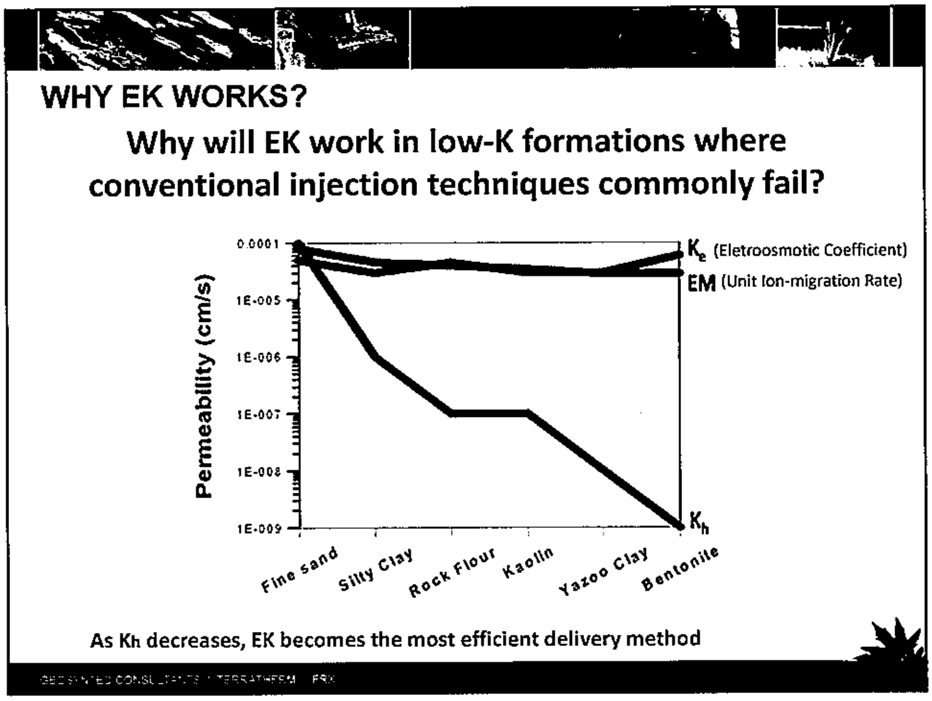
Voltage Gradient (V/cm)

Electroosmosis

Electroosmotic flow is the motion of liquid induced by the applied potential field across a porous material



Minimal Pressure Changes!



WHY EK WORKS?

Why will EK work in low-K formations where conventional injection techniques commonly fail?

As Kh decreases, EK becomes the most efficient delivery method

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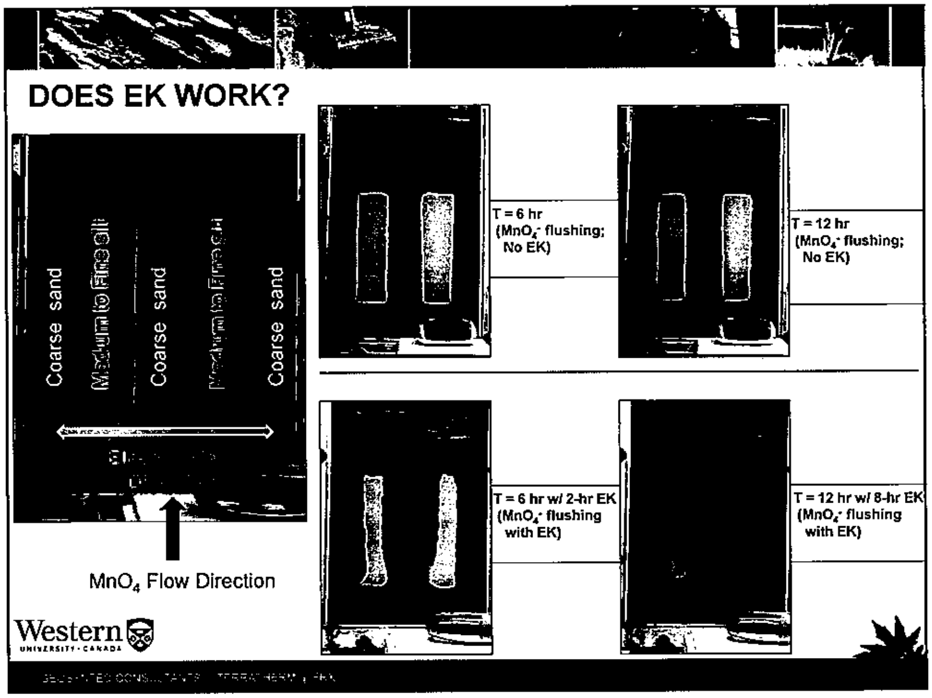

DOES EK WORK?

MnO_4 Flow Direction

Western
UNIVERSITY · CANADA

T = 6 hr
(MnO_4^- flushing; No EK)

T = 12 hr
(MnO_4^- flushing; No EK)

T = 6 hr w/ 2-hr EK
(MnO_4^- flushing with EK)

T = 12 hr w/ 8-hr EK
(MnO_4^- flushing with EK)

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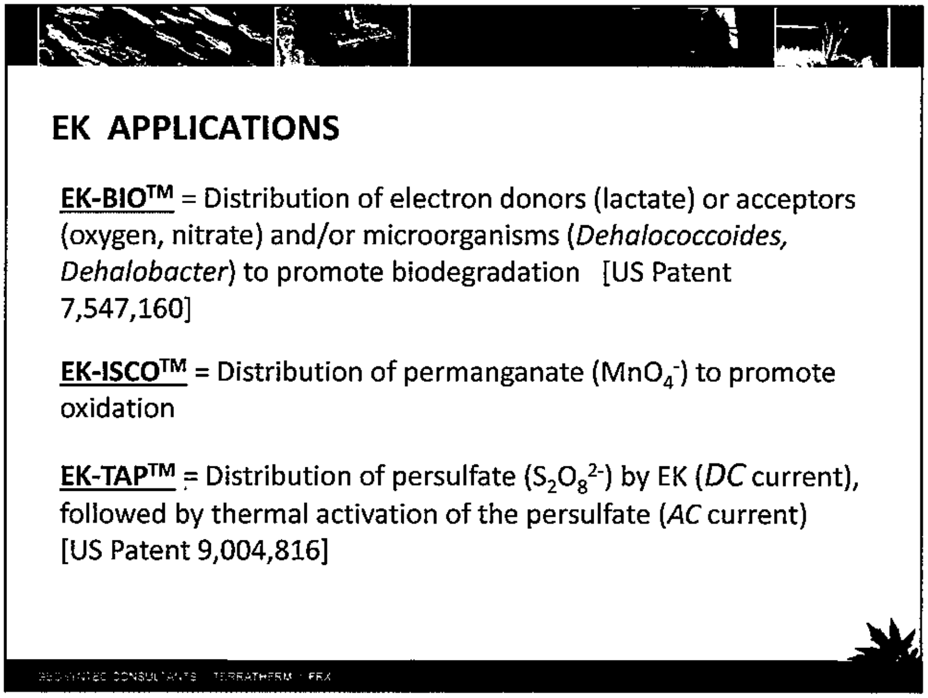
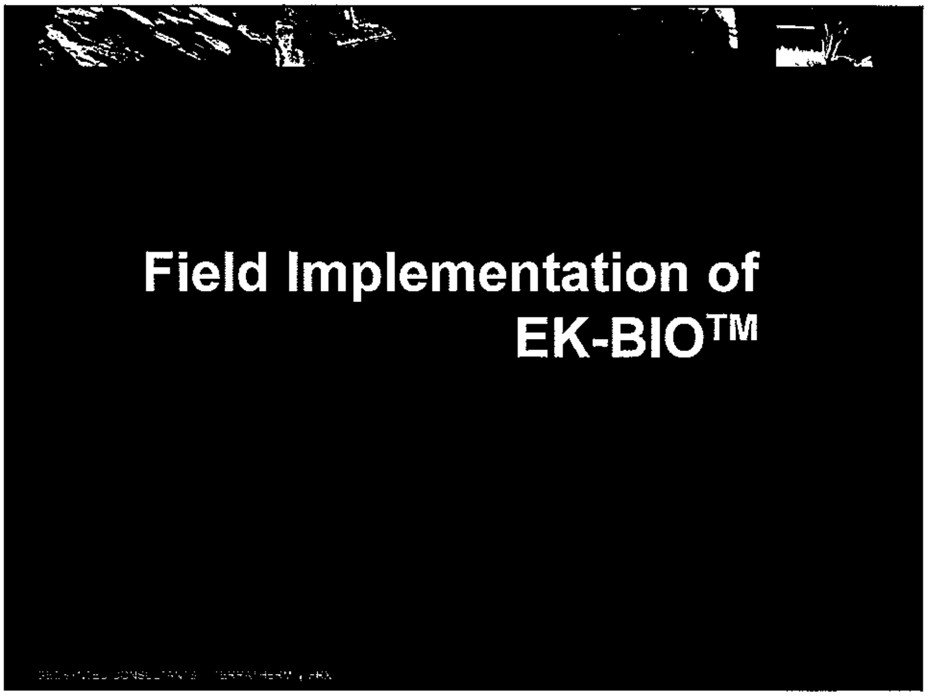


EK APPLICATIONS

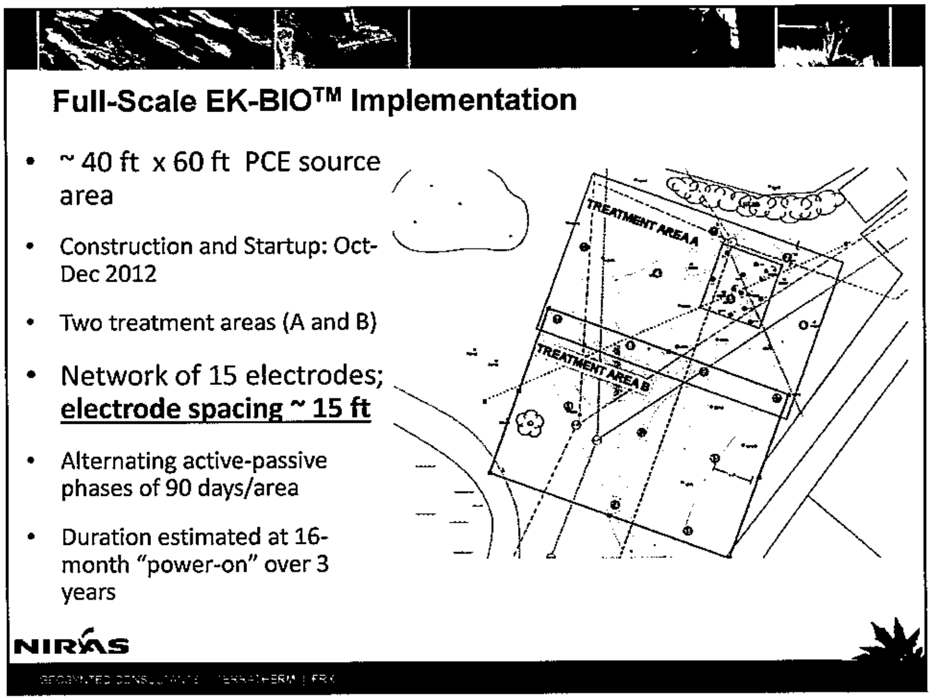
EK-BIO^{TM} = Distribution of electron donors (lactate) or acceptors (oxygen, nitrate) and/or microorganisms (*Dehalococcoides, Dehalobacter*) to promote biodegradation [US Patent 7,547,160]

EK-ISCO^{TM} = Distribution of permanganate (MnO_4^-) to promote oxidation

EK-TAP^{TM} = Distribution of persulfate ($S_2O_8^{2-}$) by EK (*DC* current), followed by thermal activation of the persulfate (*AC* current) [US Patent 9,004,816]



Field Implementation of EK-BIO^{TM}



Full-Scale EK-BIO™ Implementation

- ~ 40 ft x 60 ft PCE source area
- Construction and Startup: Oct-Dec 2012
- Two treatment areas (A and B)
- Network of 15 electrodes; **electrode spacing ~ 15 ft**
- Alternating active-passive phases of 90 days/area
- Duration estimated at 16-month "power-on" over 3 years

NIRAS

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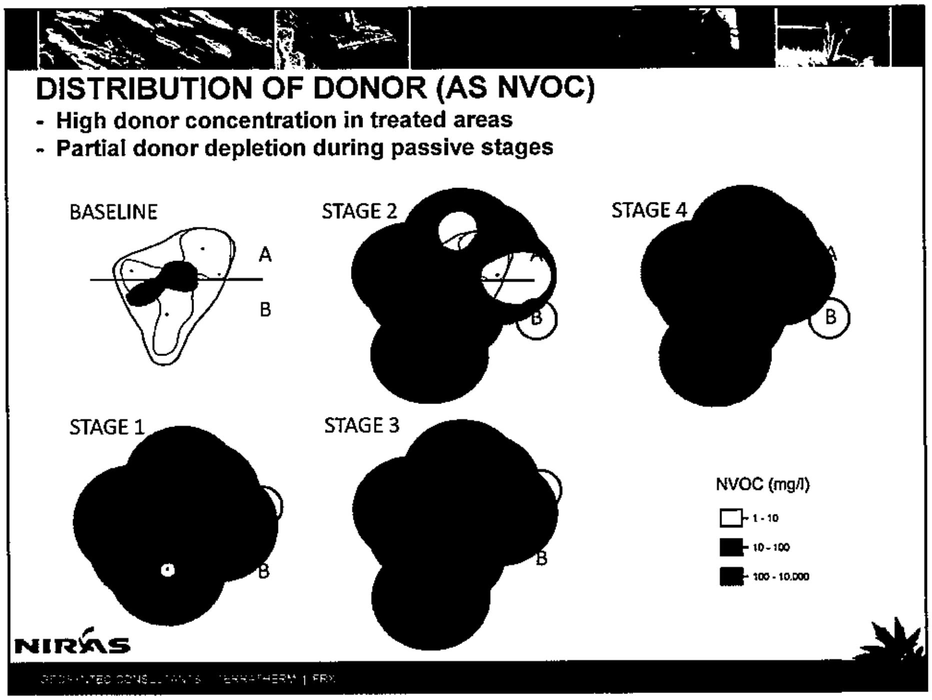

DISTRIBUTION OF DONOR (AS NVOC)

- High donor concentration in treated areas
- Partial donor depletion during passive stages

NVOC (mg/l)

☐ 1 - 10
■ 10 - 100
■ 100 - 10,000

NIRAS

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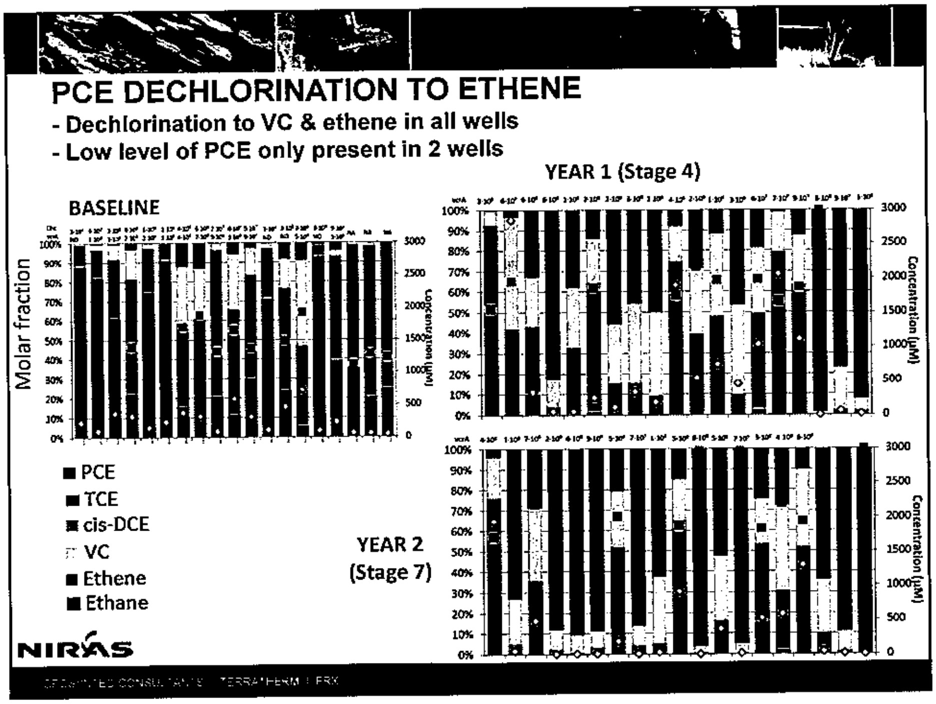

PCE DECHLORINATION TO ETHENE

- Dechlorination to VC & ethene in all wells
- Low level of PCE only present in 2 wells

- ■ PCE
- ■ TCE
- ■ cis-DCE
- ▨ VC
- ■ Ethene
- ■ Ethane

NIRAS

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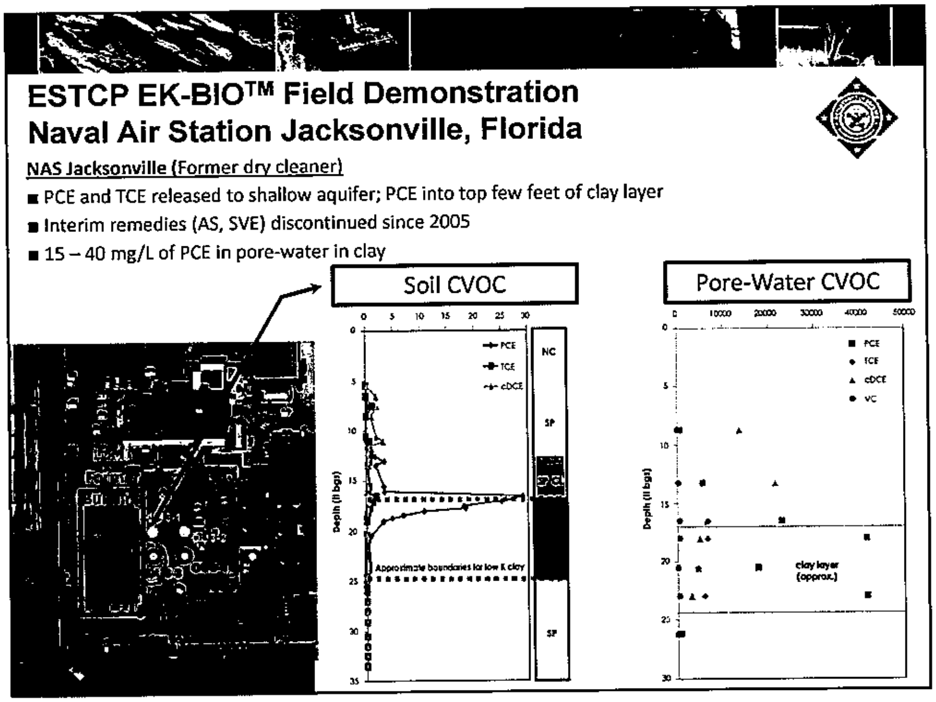
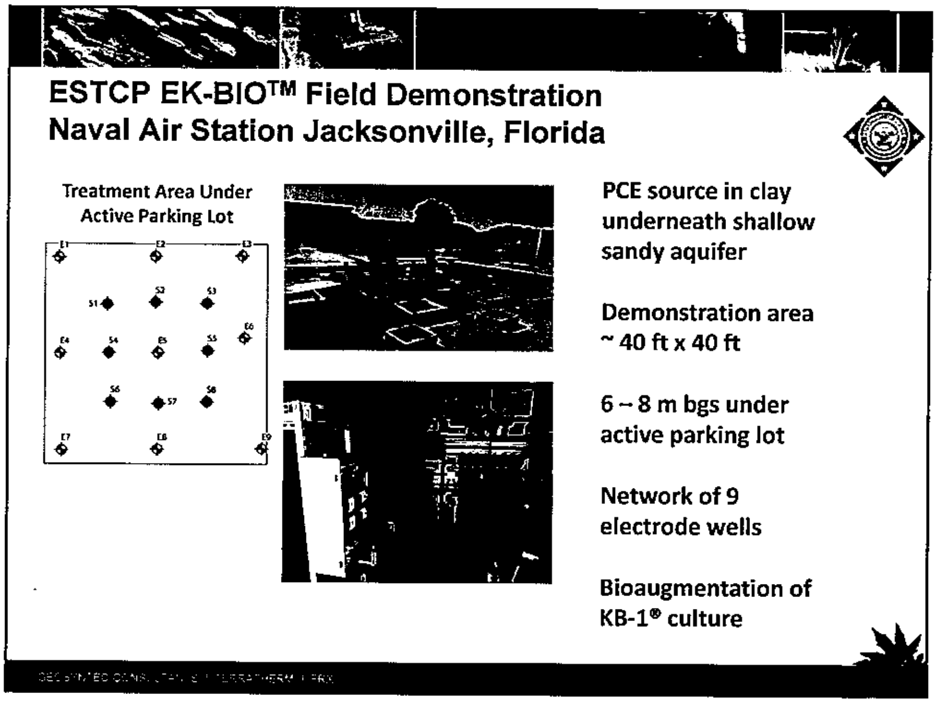


ESTCP EK-BIO™ Field Demonstration Naval Air Station Jacksonville, Florida

NAS Jacksonville (Former dry cleaner)

- ■ PCE and TCE released to shallow aquifer; PCE into top few feet of clay layer
- ■ Interim remedies (AS, SVE) discontinued since 2005
- ■ 15 – 40 mg/L of PCE in pore-water in clay



ESTCP EK-BIO™ Field Demonstration
Naval Air Station Jacksonville, Florida

Treatment Area Under Active Parking Lot

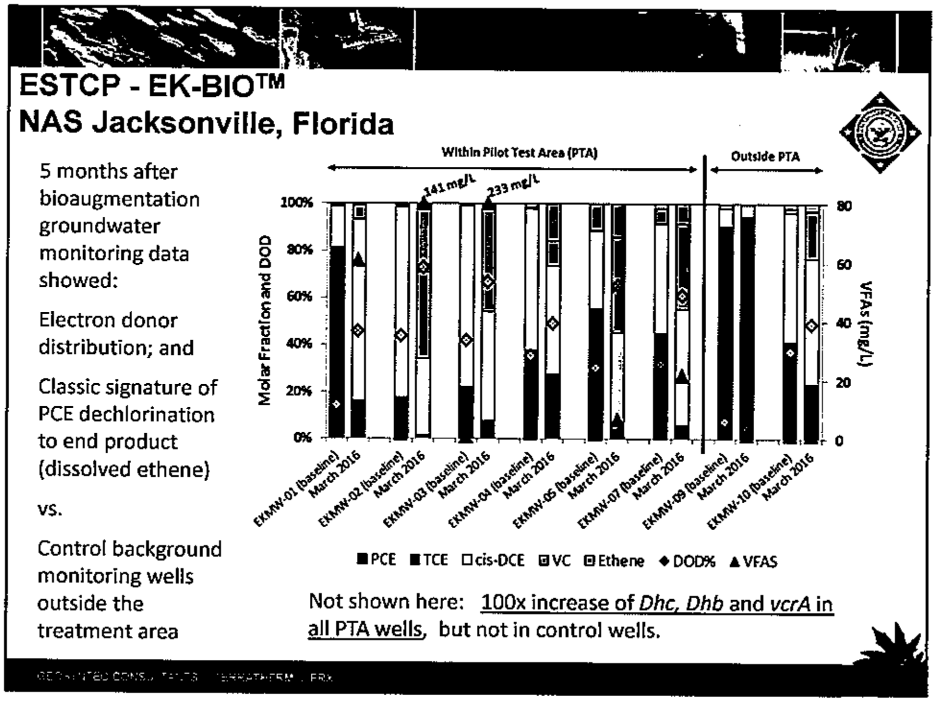
PCE source in clay underneath shallow sandy aquifer

Demonstration area ~ 40 ft x 40 ft

6 – 8 m bgs under active parking lot

Network of 9 electrode wells

Bioaugmentation of KB-1® culture



ESTCP - EK-BIO™
NAS Jacksonville, Florida

5 months after bioaugmentation groundwater monitoring data showed:

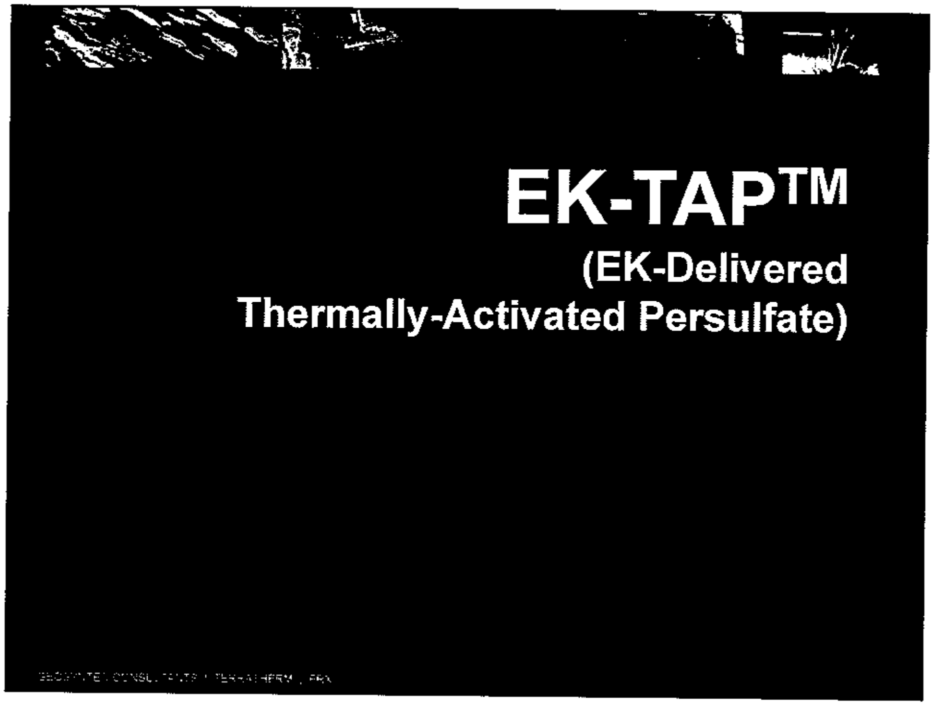
Electron donor distribution; and

Classic signature of PCE dechlorination to end product (dissolved ethene)

vs.

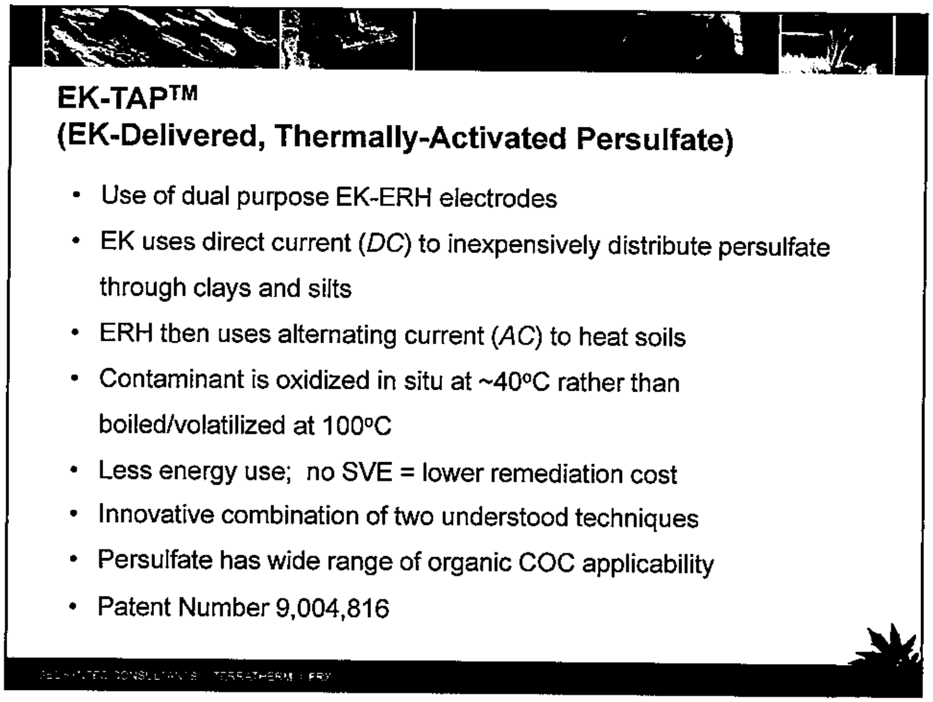
Control background monitoring wells outside the treatment area

Not shown here: <u>100x increase of *Dhc, Dhb* and *vcrA* in all PTA wells</u>, but not in control wells.



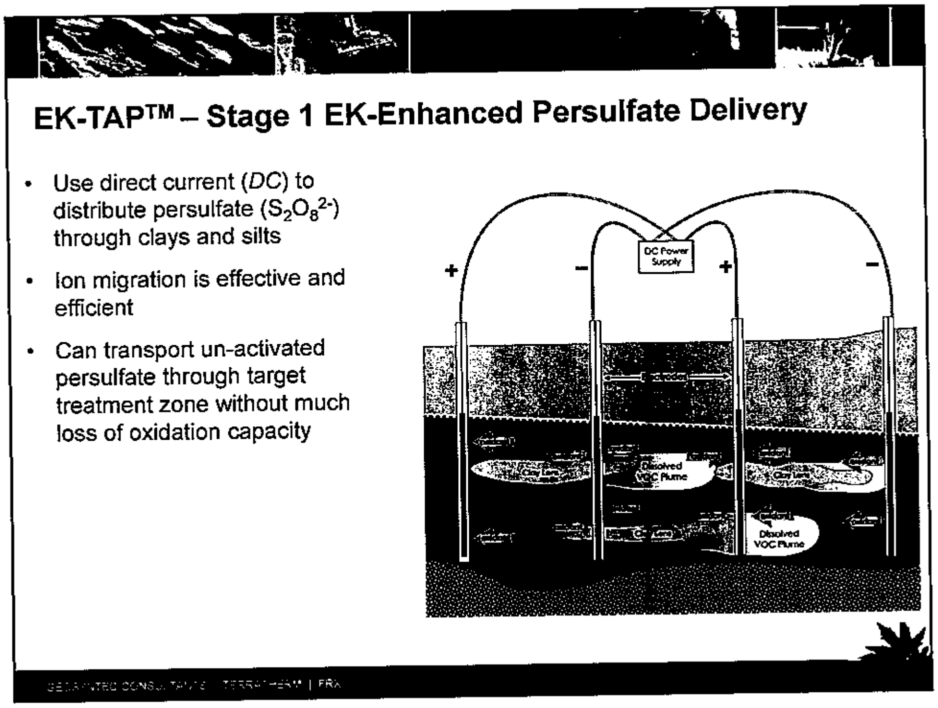
EK-TAP™

(EK-Delivered Thermally-Activated Persulfate)



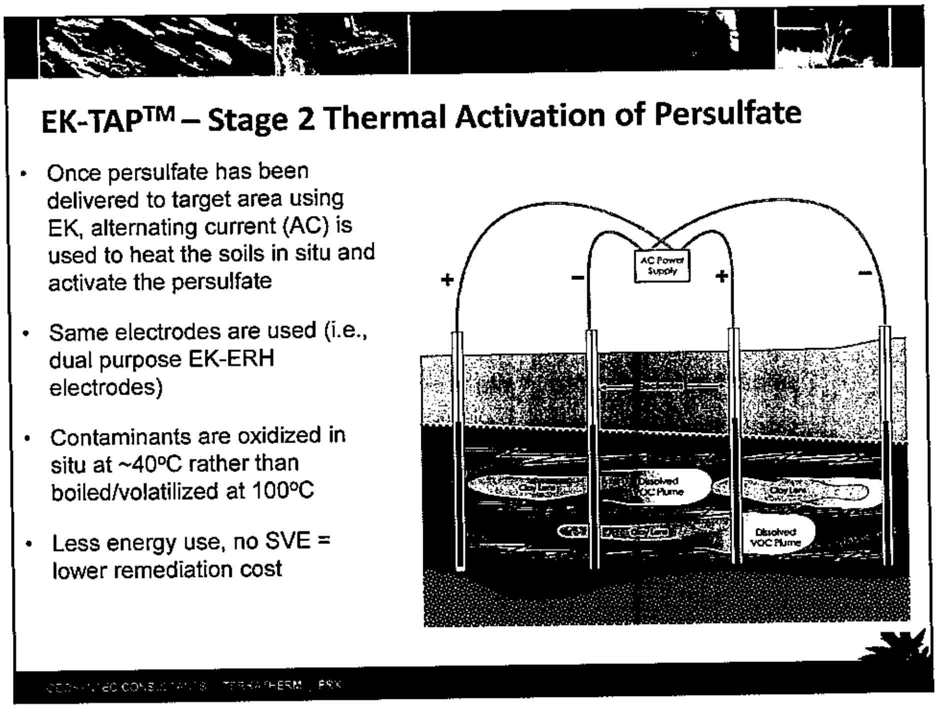
EK-TAP™ (EK-Delivered, Thermally-Activated Persulfate)

- Use of dual purpose EK-ERH electrodes
- EK uses direct current (*DC*) to inexpensively distribute persulfate through clays and silts
- ERH then uses alternating current (*AC*) to heat soils
- Contaminant is oxidized in situ at ~40°C rather than boiled/volatilized at 100°C
- Less energy use; no SVE = lower remediation cost
- Innovative combination of two understood techniques
- Persulfate has wide range of organic COC applicability
- Patent Number 9,004,816



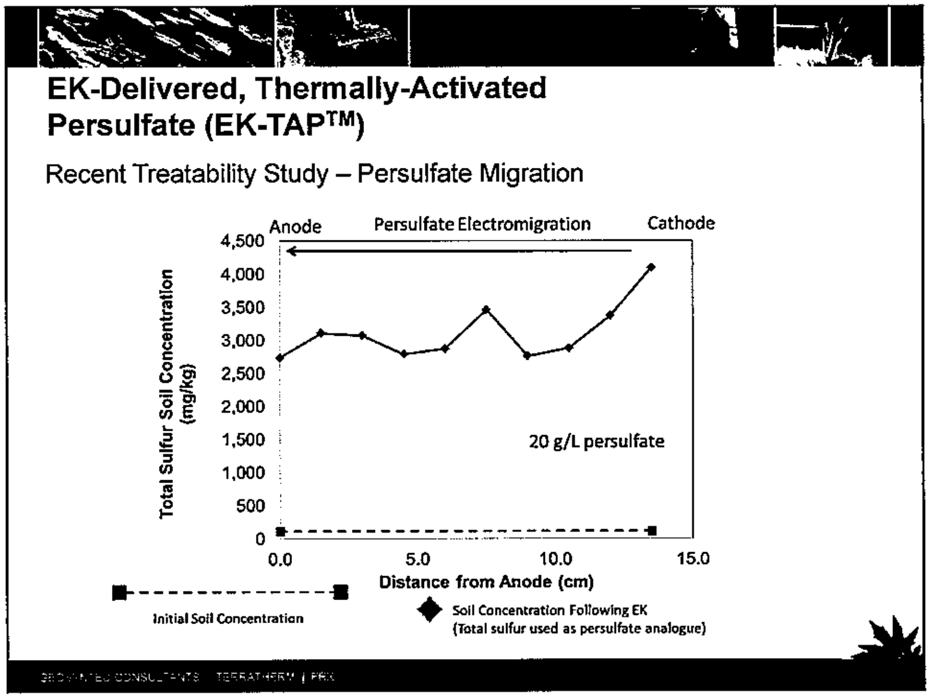
EK-TAP™ – Stage 1 EK-Enhanced Persulfate Delivery

- Use direct current (*DC*) to distribute persulfate ($S_2O_8^{2-}$) through clays and silts
- Ion migration is effective and efficient
- Can transport un-activated persulfate through target treatment zone without much loss of oxidation capacity



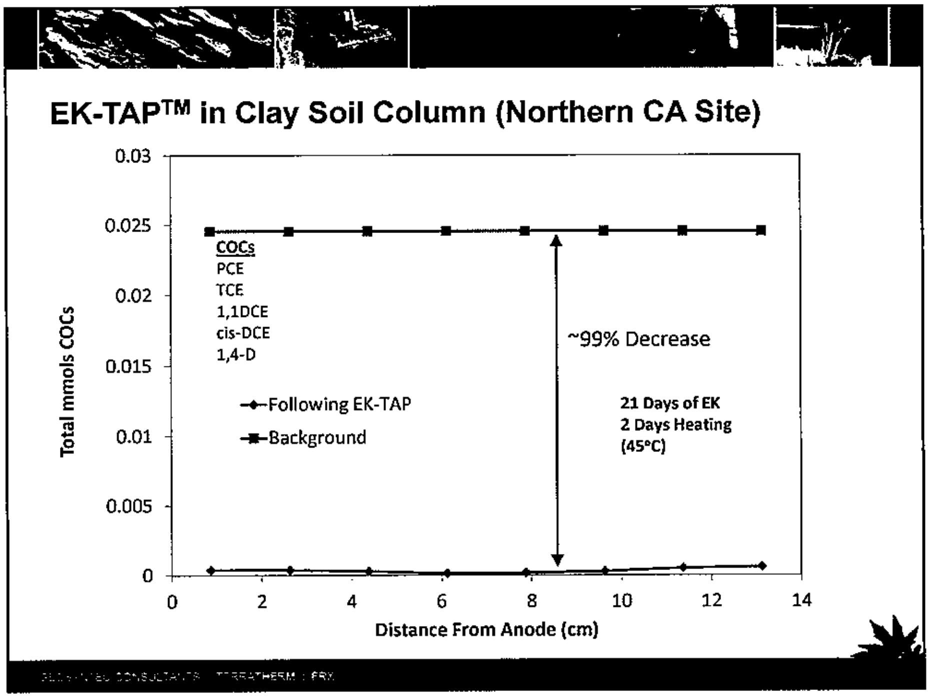
EK-TAP™ – Stage 2 Thermal Activation of Persulfate

- Once persulfate has been delivered to target area using EK, alternating current (AC) is used to heat the soils in situ and activate the persulfate
- Same electrodes are used (i.e., dual purpose EK-ERH electrodes)
- Contaminants are oxidized in situ at ~40°C rather than boiled/volatilized at 100°C
- Less energy use, no SVE = lower remediation cost



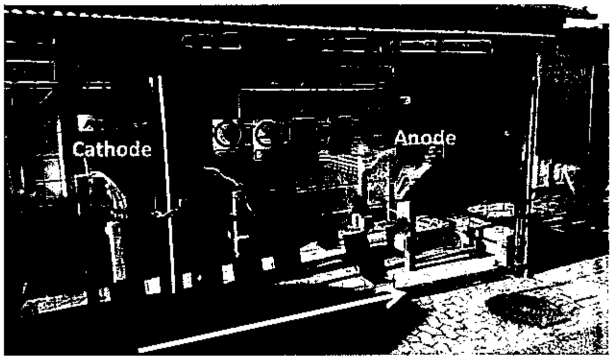
EK-Delivered, Thermally-Activated Persulfate (EK-TAP™)

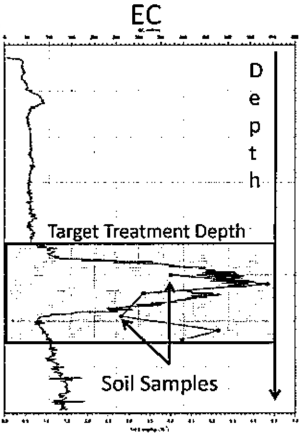
Recent Treatability Study – Persulfate Migration



EK-TAP™ in Clay Soil Column (Northern CA Site)

EK-TAP™ Field Pilot Test (Denmark)

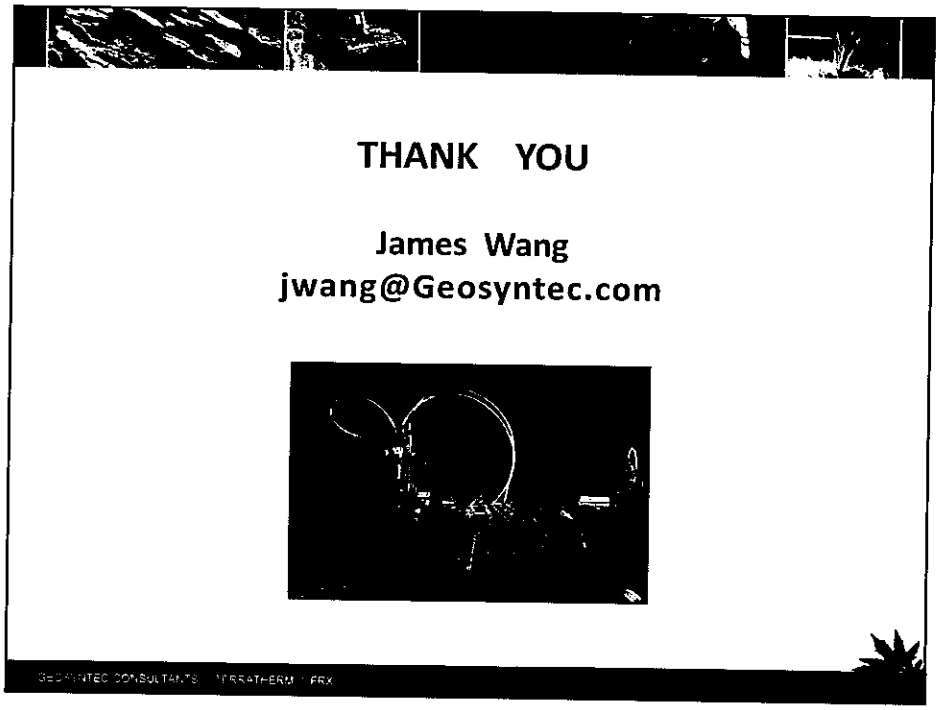




NIRAS Region Hovedstaden ERDC

An Innovative Solution for Low-K / Heterogeneous Sites

- **Many sites with low-K materials → remediation program has been prolonged with escalating remediation costs**
- **EK approach for low-K regions**
  - No high (extreme) pressures → <u>safe</u>, <u>better control</u>, low day-lighting risk
  - Avoid losing the majority of amendments to only a few preferential pathways as commonly seen in hydraulic injection → much more **<u>cost effective</u>**
  - Achieve in-situ treatment; not phase-transfer. Does not lead to 2nd waste stream to capture, treat, and dispose
  - Low energy intensity. May consider solar energy source. Much **<u>lower environmental footprint</u>** compared to thermal remediation



THANK YOU

James Wang
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Environmental Forensics- Utilization of Established and Evolving Techniques

Presented at the AEHS 2016 East Coast Meeting Amherst, MA 2016

R. Paul Philp, School of Geology and
Geophysics, University of Oklahoma,
Norman, OK. 73019.

Presentation Overview

- Introduction
- Methodology - Fractionation-Rayleigh Model-Bulk Isotopes-Isotopes of Individual Compounds
- Integration of GC, GCMS, GCIRMS data
- Applications-Source Discrimination and Remediation
    - Diesel, Gasoline, Motor oil
    - MTBE
    - Chlorinated Solvents
    - PAHs
    - PCBs
    - Benzene
    - Chlorine Isotopes
    - Perchlorate
- Vapor Intrusion Studies
- Fate and Transport Models
- Summary

Introduction

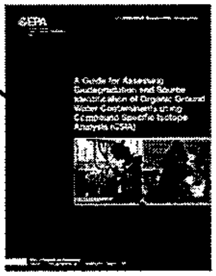
- This course is primarily concerned with certain aspects of environmental forensics and, more specifically, utilization of stable isotopes.
- It is very important to emphasize at the outset that there is a significant difference between the conventional EPA methods and the environmental forensic approach.
- At this time there is no EPA stable isotope method although the approach is widely supported by EPA

CSIA in Contaminant Studies

CSIA is established in ground water contaminant work, with large number of peer-reviewed publications and industry applications.

CSIA applications fairly novel in vadose zone and vapor phase contaminant studies: several peer-reviewed papers to date

More examples of such applications will be given in subsequent sections



A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA)

General Topics to be covered

- What is a stable isotope?
- Where and why use isotopes?
- When do we use isotopes in conjunction with other techniques?
- What type of information can we obtain?
- What type of information is not available? (Age dating)
- Examples

Basic Environmental Forensic Questions

- What is the product?
- Is there more than one source (point of release) and, if so, which one caused the problem?
- How long has it been there?
- Is it degrading?

Utilization of Stable Isotopes

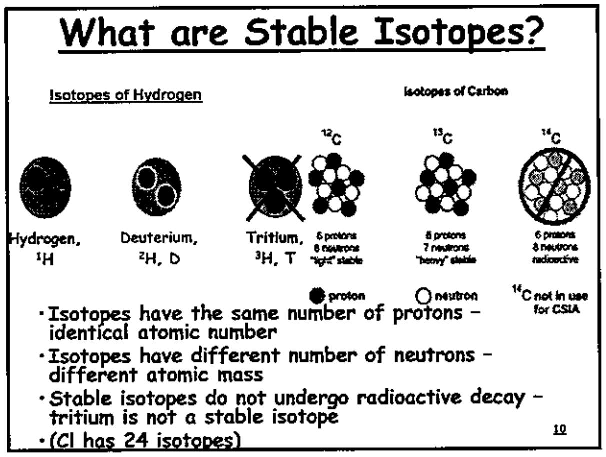
- What is the product? NO
- Is there more than one source and, if so, which one caused the problem? YES
- How long has it been there? NO
- Is it degrading? YES

Applications-Sediments vs. Water

- Basic concepts behind analyzing sediment extracts and water samples are very similar.
- In general changes in isotopic compositions during extraction, diffusion, partitioning in sediments are relatively small and not significant when interpreting natural attenuation data.

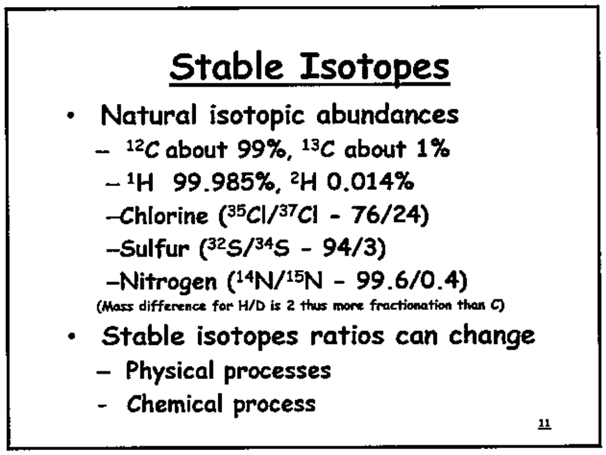
What are Stable Isotopes?

- Carbon exists as two stable isotopes, ^{12}C and ^{13}C which differ in the number of neutrons they contain. ^{12}C has 6 electrons, 6 protons and 6 neutrons; ^{13}C has 7 neutrons.
- ^{1}H has 1 electron and 1 proton and ^{2}H (D-deuterium) has 1 electron, 1 proton and 1 neutron.
- ^{35}Cl has 17 electrons, 17 protons and 18 neutrons; ^{37}Cl has 20 neutrons.



What are Stable Isotopes?

- Isotopes have the same number of protons – identical atomic number
- Isotopes have different number of neutrons – different atomic mass
- Stable isotopes do not undergo radioactive decay – tritium is not a stable isotope
- (Cl has 24 isotopes)

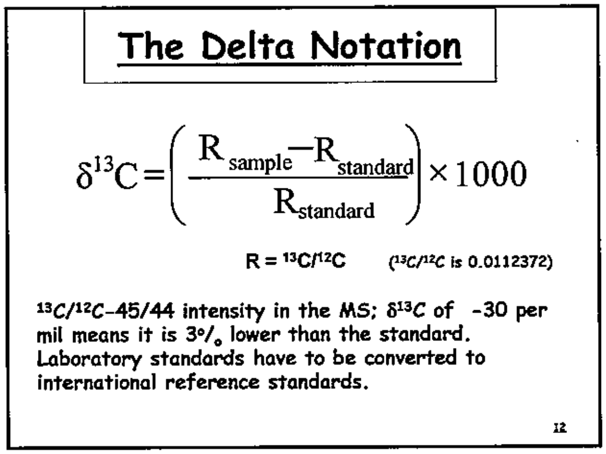


Stable Isotopes

- Natural isotopic abundances
  - ^{12}C about 99%, ^{13}C about 1%
  - ^{1}H 99.985%, ^{2}H 0.014%
  - Chlorine ($^{35}Cl/^{37}Cl$ - 76/24)
  - Sulfur ($^{32}S/^{34}S$ - 94/3)
  - Nitrogen ($^{14}N/^{15}N$ - 99.6/0.4)

(Mass difference for H/D is 2 thus more fractionation than C)

- Stable isotopes ratios can change
  - Physical processes
  - Chemical process



The Delta Notation

$$\delta^{13}C = \left(\frac{R_{sample} - R_{standard}}{R_{standard}} \right) \times 1000$$

$R = {}^{13}C/{}^{12}C$ ($^{13}C/^{12}C$ is 0.0112372)

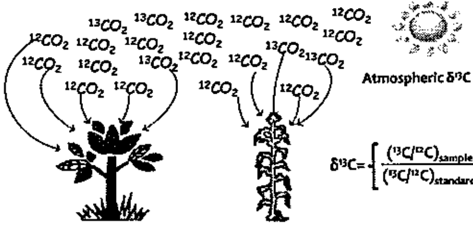
$^{13}C/^{12}C$-45/44 intensity in the MS; $\delta^{13}C$ of -30 per mil means it is 3‰ lower than the standard. Laboratory standards have to be converted to international reference standards.

Stable Isotopes

- Carbon in fossil fuels is derived from atmospheric CO_2. Hydrogen is primarily derived from H_2O. During photosynthesis, fractionation of the two isotopes occurs with preferential assimilation of the lighter isotopes.

Photosynthesis

Carbon isotope fractionation during photosynthesis



Atmospheric $\delta^{13}C \sim -8‰$

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

C_3 plants : >85% of plant species
(all trees, wheat, sugar beat, tobacco, a lot of herbaceous…)

C3 plant $\delta^{13}C \sim -26‰$

C_4 plants : <5% of plant species
(corn, sorghum, millet, sugarcane)

C4 plant $\delta^{13}C \sim -12‰$

$$6{*}CO_2 + 12H_2O \longrightarrow {*}C_6H_{12}O_6 + 6H_2O + 6O_2$$

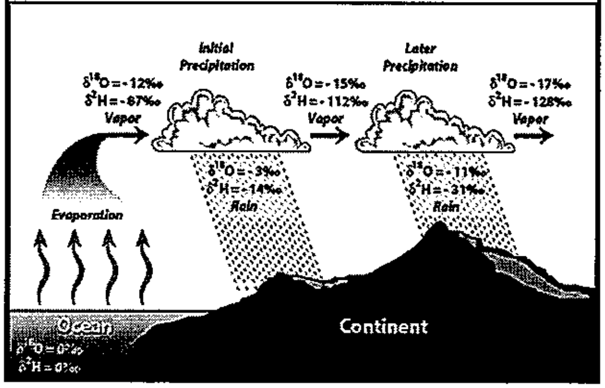
Isotopes and Photosynthesis

- The extent of fractionation during photosynthesis will depend on factors such as: plant type; marine v. terrigenous; C_3 v. C_4 plant types; temperature; sunlight intensity; water depth.
- C_3 Temperate plants; trees; not grasses; 95% plant species-22 to -30; C_4 Grasses; sugar cane; corn; higher temps and sunlight-10 to -14 per mil
- Individual compounds will have a unique isotopic signature reflecting their photosynthetic cycle and/or biochemical cycles.

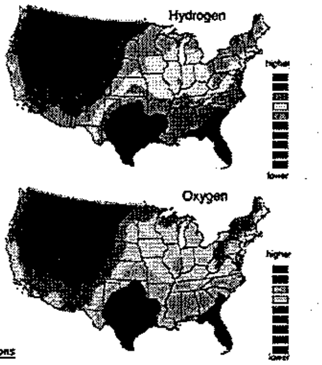
Isotopes of Water

- Evaporation of water from oceans decreases concentration of heavy isotope in the water in the clouds compared to the sea.
- With further evaporation, condensation and precipitation, the deuterium continues to decrease with altitude.
- Ground water reflects this and ultimately so do the plants and higher members of the food chain.
- Reflected in food such as cheese, butter, and milk.

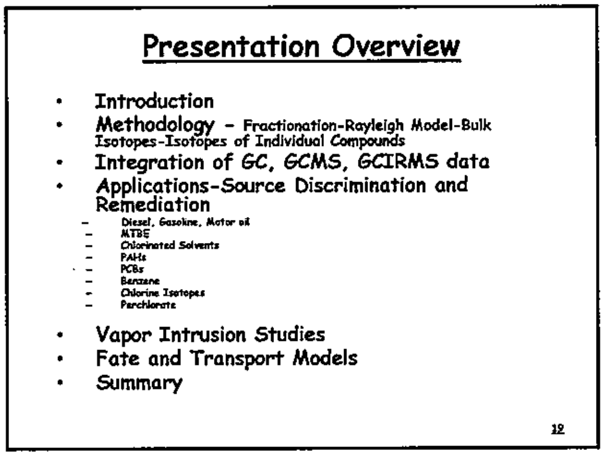
Isotopic Changes in Rainwater



Isotopic Changes in Rainwater



Heavier in coastal regions



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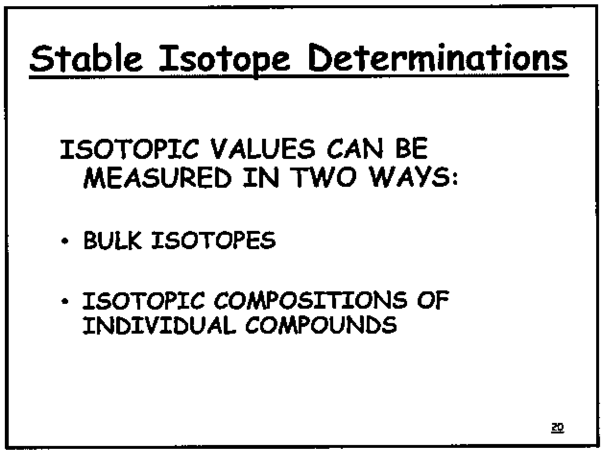
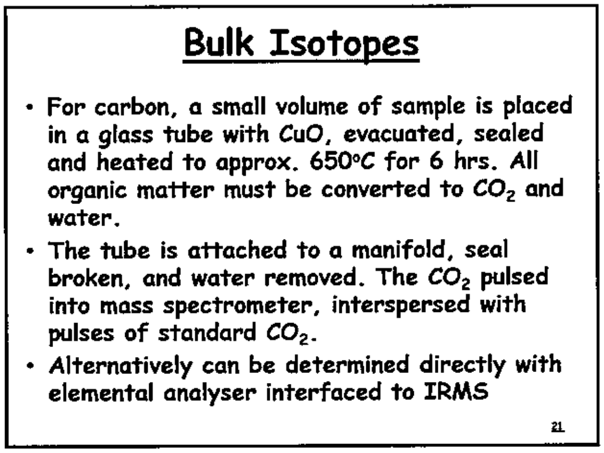


Stable Isotope Determinations

ISOTOPIC VALUES CAN BE MEASURED IN TWO WAYS:

- BULK ISOTOPES
- ISOTOPIC COMPOSITIONS OF INDIVIDUAL COMPOUNDS



Bulk Isotopes

- For carbon, a small volume of sample is placed in a glass tube with CuO, evacuated, sealed and heated to approx. 650°C for 6 hrs. All organic matter must be converted to CO_2 and water.
- The tube is attached to a manifold, seal broken, and water removed. The CO_2 pulsed into mass spectrometer, interspersed with pulses of standard CO_2.
- Alternatively can be determined directly with elemental analyser interfaced to IRMS

Isotopes

- The standard for carbon is a marine carbonate, Pee Dee Belemnite (VPDB), that has a $\delta^{13}C$ value of 0. Virtually every other material that has been measured contains less ^{13}C than the standard and will have a negative $\delta^{13}C$ value. Then one says it is depleted in ^{13}C, is isotopically lighter or has a more negative $\delta^{13}C$ value.

Isotope Standards

Atom	δ	Ratio	Standard	Heavy/Light
Hydrogen	δD	D/H($^2H/^1H$)	SMOW	1.557×10^{-4}
Carbon	$\delta^{13}C$	$^{13}C/^{12}C$	VPDB	1.122×10^{-2}
Nitrogen	$\delta^{15}N$	$^{15}N/^{14}N$	Atmosphere	3.613×10^{-3}
Oxygen	$\delta^{18}O$	$^{18}O/^{16}O$	SMOW, VPDB	2.0052×10^{-3}
Chlorine	$\delta^{37}Cl$	$^{37}Cl/^{35}Cl$	SMOC	~0.31978
Sulfur	$\delta^{34}S$	$^{34}S/^{32}S$	CDT	4.43×10^{-2}

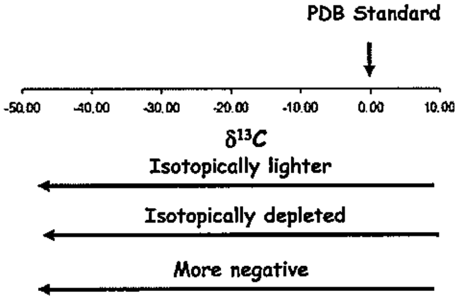
The Delta Notation

$$\delta^{13}C = \left(\frac{R_{sample} - R_{standard}}{R_{standard}} \right) \times 1000$$

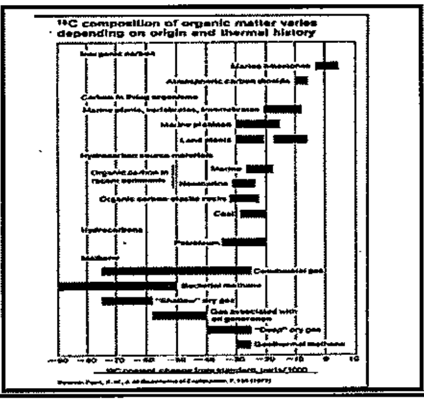
$R = {}^{13}C/{}^{12}C$ (${}^{13}C/{}^{12}C$ is 0.0112372)

$^{13}C/^{12}C$-45/44 intensity in the MS; $\delta^{13}C$ of -30 per mil means it is $3^{\circ}/_{\circ}$ lower than the standard. Laboratory standards have to be converted to international reference standards.

Data Output-Isotope Scale



Variations in Bulk Isotope Values



Stable Isotope Fractionation

- **Preferential partitioning of isotopes between phases or between reaction and product species**
  - Function of difference in masses
- Equilibrium isotope effect
  - One isotope concentrates in one component of a reversible system
- Kinetic isotope effect
  - One isotope reacts more rapidly than other in irreversible system

Equilibrium Isotope Effect

- Evaporation of water in closed container (equilibrium)
  - Lighter isotopes (^1H, ^{16}O) partition to higher energy phase (vapor)

Kinetic Isotope Effect

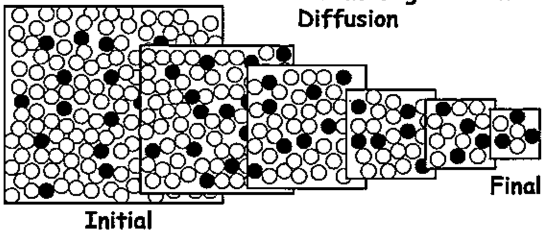
- Hydrocarbon molecules are comprised primarily of ^{12}C-^{12}C bonds; lesser amounts of ^{12}C-^{13}C bonds and even fewer ^{13}C-^{13}C bonds. The kinetic isotope effect can be thought of as the cleavage of the weaker bonds, ^{12}C-^{12}C, which will ultimately lead to an enrichment of the residual substrate.
- Similar effects occur in chlorinated compounds where the ^{12}C-^{35}Cl bonds are preferentially cleaved

Kinetic Isotope Fractionation

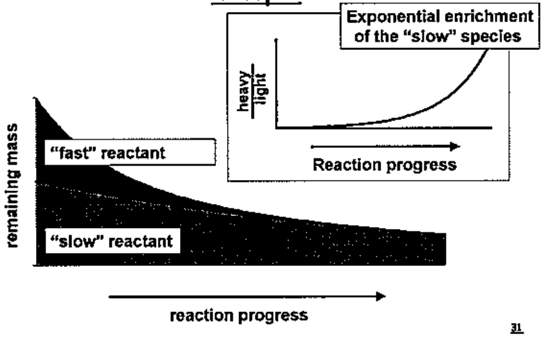
Rate of removal of ○ faster than that of ●

$k_\bullet / k_\circ$ = const.

Biodegradation
Chem. Degradation
Diffusion



Fractionation due to different reaction rates of molecules with "heavy" and "light" isotopes



Data Output

δ notation: $$\delta^{13}C = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000$$

($^{13}C/^{12}C$ is 0.0112372) R = $^{13}C/^{12}C$

Percent MTBE remaining	$\delta^{13}C$	$^{13}C/^{12}C$
100.0	-30.0	0.010900
50.0	-24.5	0.010962
12.5	-13.4	0.011087
1.6	3.3	0.011274

Stable Isotopic Fractionation

Rayleigh Model

The relationship between the isotopic composition of a precursor and product can be followed through the use of the Rayleigh equation. This equation establishes the relationship between the isotopic composition of precursor and product based on the fractionation factor and change in concentration of the substrate.

Stable Isotopic Fractionation
Rayleigh Model

In order to show the relationship between the isotopic ratios of the initial and remaining substrate and the fraction of liquid remaining (F) the following form of the Rayleigh model can be used:

$$(\delta^{13}C_t + 1000)/(\delta^{13}C_{t=0} + 1000) = F^{\alpha-1}$$

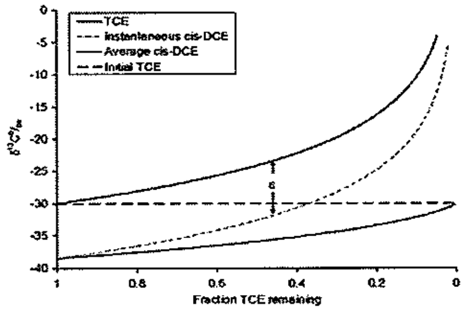
which can be rearranged and simplified to:

$$\delta^{13}C_t = \delta^{13}C_{t=0} + \varepsilon * \ln F \qquad \text{where} \quad \varepsilon = (\alpha - 1) * 1000$$

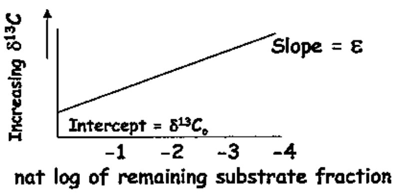
(ε is the enrichment factor and α is the fractionation factor)

(α=R substrate$_t$/R product$_t$)

Stable Isotopic Fractionation

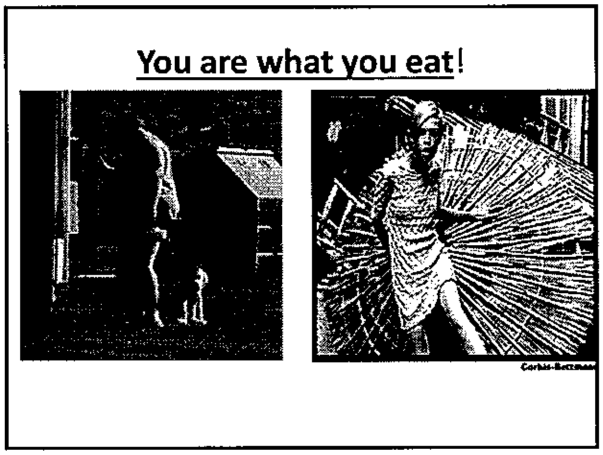


Stable Isotopic Fractionation
Rayleigh Model



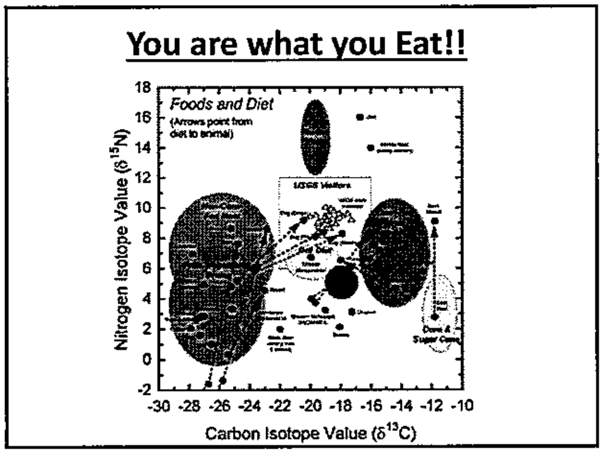
Substrate concentration decreases⟶

$$\delta^{13}C_t = \varepsilon * \ln F + \delta^{13}C_o$$

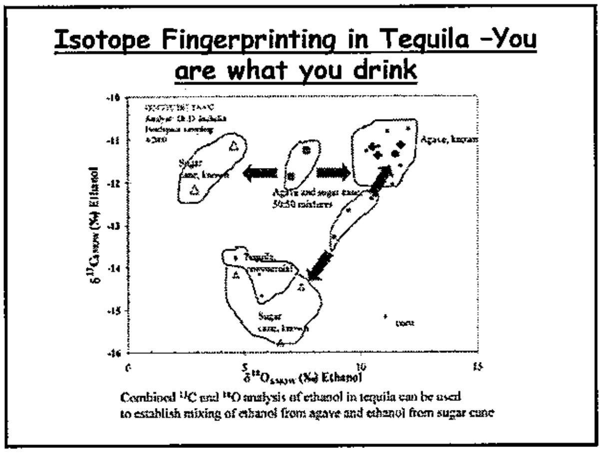


You are what you eat!

Corbis-Bettman

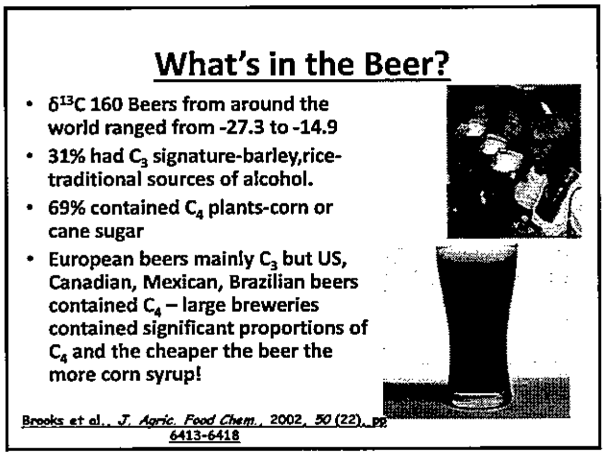


You are what you Eat!!



Isotope Fingerprinting in Tequila –You are what you drink

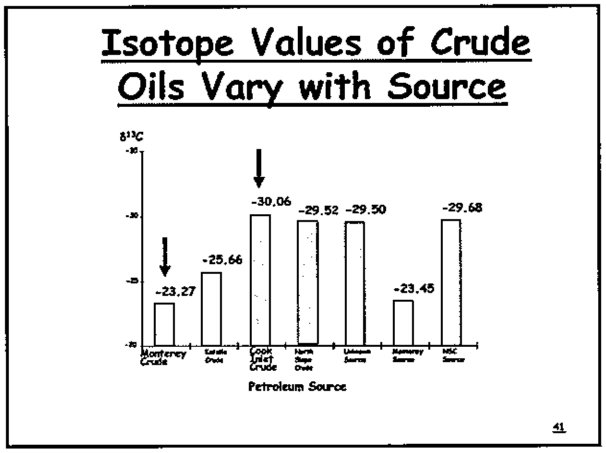
Combined ^{13}C and ^{18}O analysis of ethanol in tequila can be used to establish mixing of ethanol from agave and ethanol from sugar cane



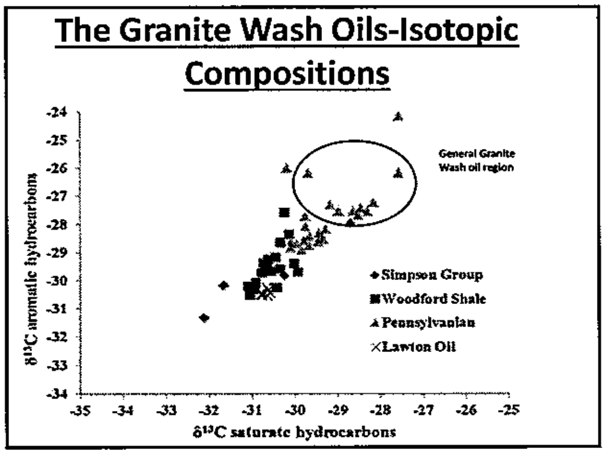
What's in the Beer?

- $\delta^{13}C$ 160 Beers from around the world ranged from -27.3 to -14.9
- 31% had C_3 signature-barley,rice-traditional sources of alcohol.
- 69% contained C_4 plants-corn or cane sugar
- European beers mainly C_3 but US, Canadian, Mexican, Brazilian beers contained C_4 – large breweries contained significant proportions of C_4 and the cheaper the beer the more corn syrup!

Brooks et al., *J. Agric. Food Chem.*, 2002, *50* (22), pp 6413-6418

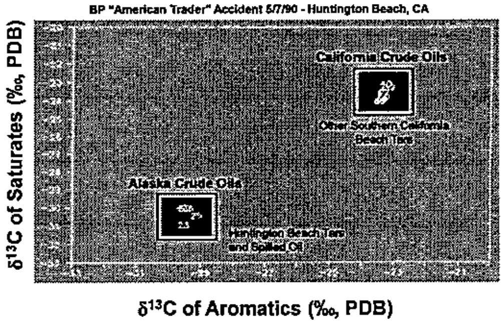


Isotope Values of Crude Oils Vary with Source

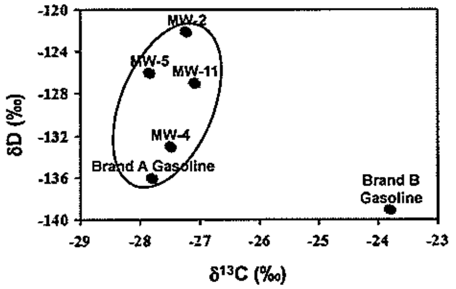


The Granite Wash Oils-Isotopic Compositions

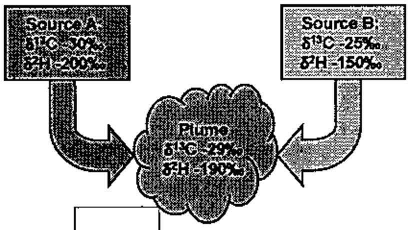
Correlations Using Carbon Isotopes



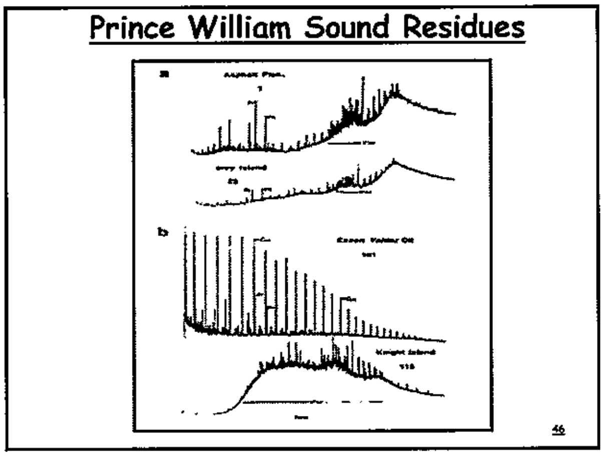
Correlations Using Carbon and Hydrogen Isotopes



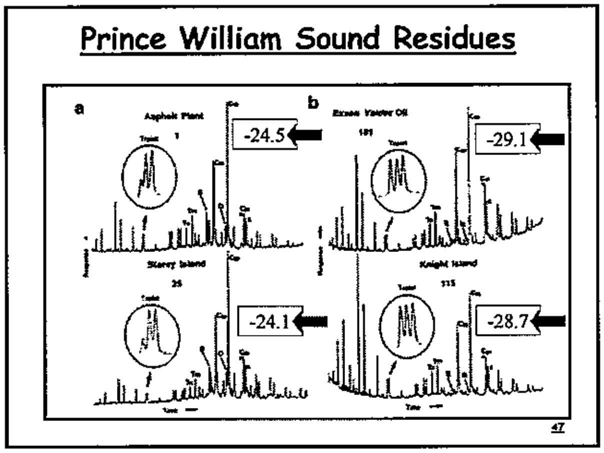
Allocation – 2 Sources



Plume = 80% Source A, 20% Source B



Prince William Sound Residues



Prince William Sound Residues

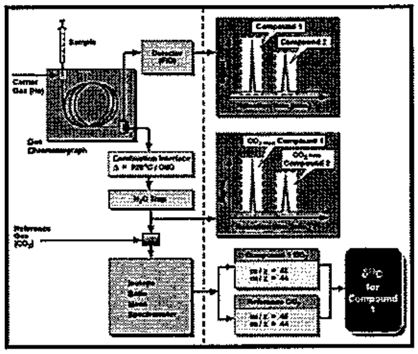
Isotopic Values of Individual Compounds

- Bulk numbers represent an average of the isotopic values of all the individual compounds in the sample
- The combination of gas chromatography with isotope ratio mass spectrometry (GCIRMS) permits us to determine isotopic compositions of individual compounds in complex mixtures, so far routine for C and H.
- Methods now being developed for Cl

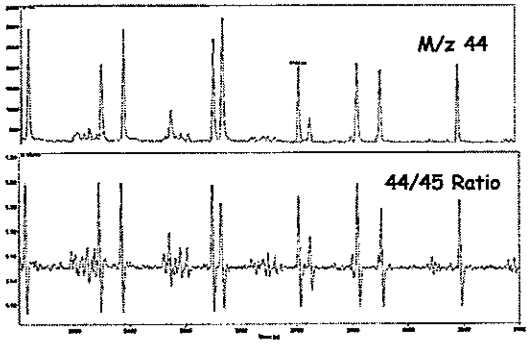
On-Line Determination

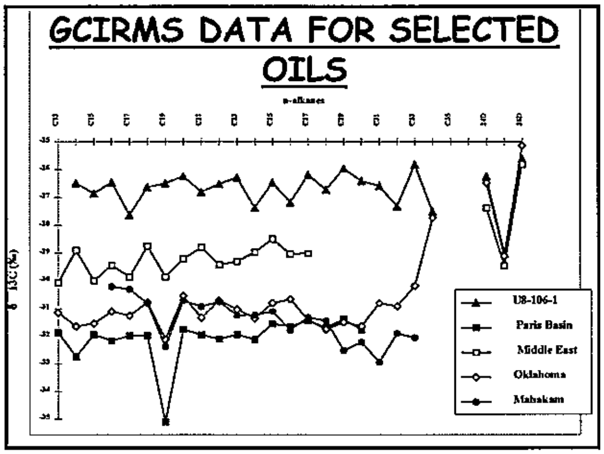
- For carbon, combustion interface converts everything to CO_2 and water; water removed; CO_2 enters the IRMS system.
- For hydrogen the sample is pyrolysed to produce ^1H and ^2H which enter IRMS, and carbon deposited on the tube
- Cl will be discussed below
- Important no GC resolution lost during combustion process

GCIRMS System

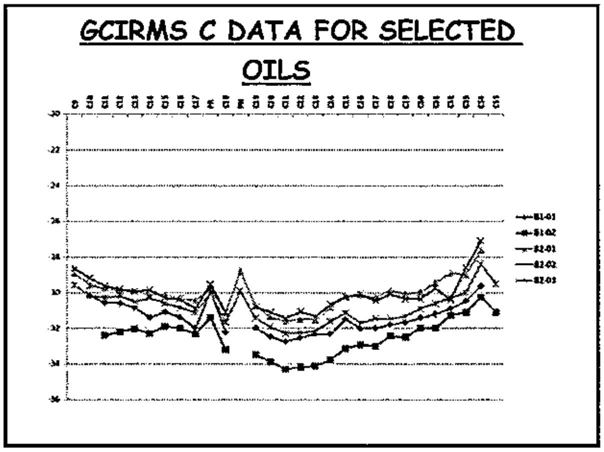


Output from GCIRMS

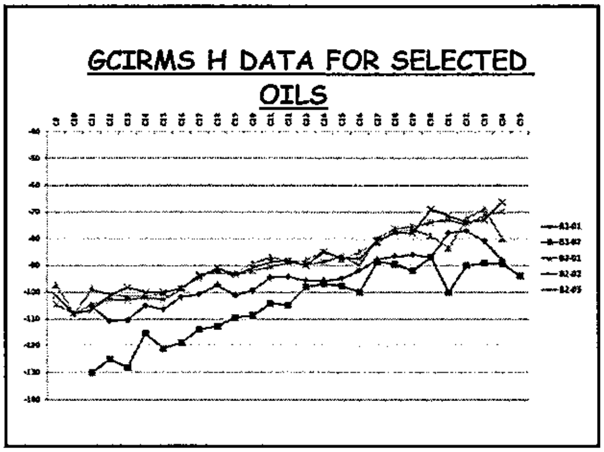




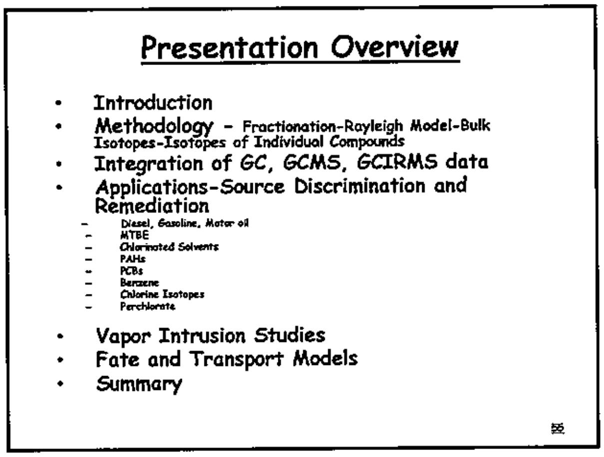
GCIRMS DATA FOR SELECTED OILS



GCIRMS C DATA FOR SELECTED OILS



GCIRMS H DATA FOR SELECTED OILS



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- Integration of GC, GCMS, GCIRMS data
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  - Diesel, Gasoline, Motor oil
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  - PCBs
  - Benzene
  - Chlorine Isotopes
  - Perchlorate
- Vapor Intrusion Studies
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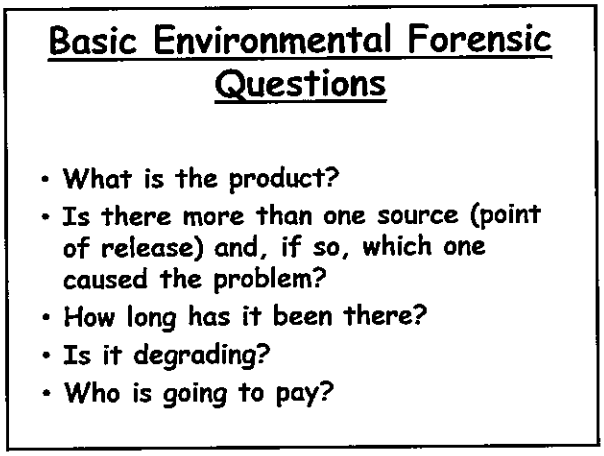
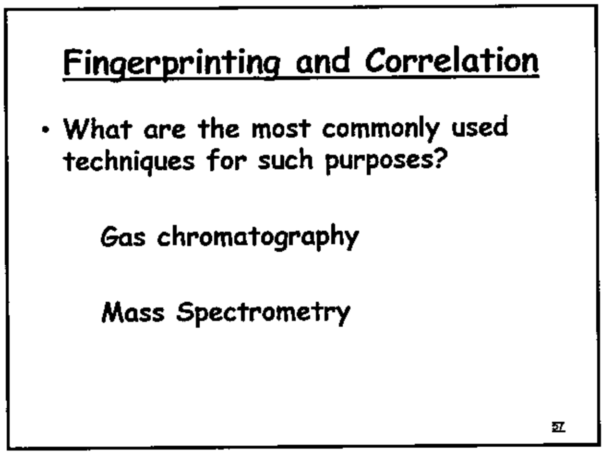


Basic Environmental Forensic Questions

- What is the product?
- Is there more than one source (point of release) and, if so, which one caused the problem?
- How long has it been there?
- Is it degrading?
- Who is going to pay?

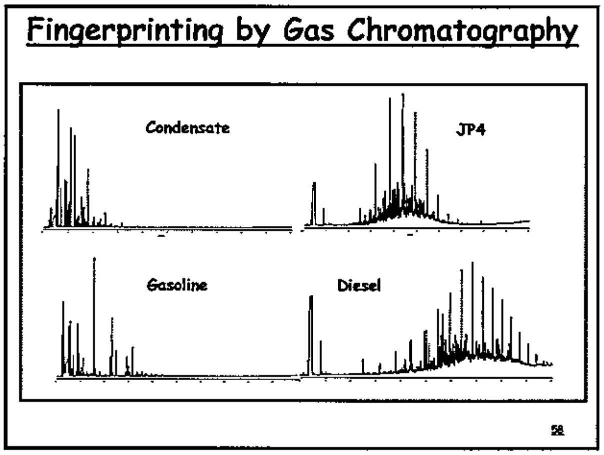


Fingerprinting and Correlation

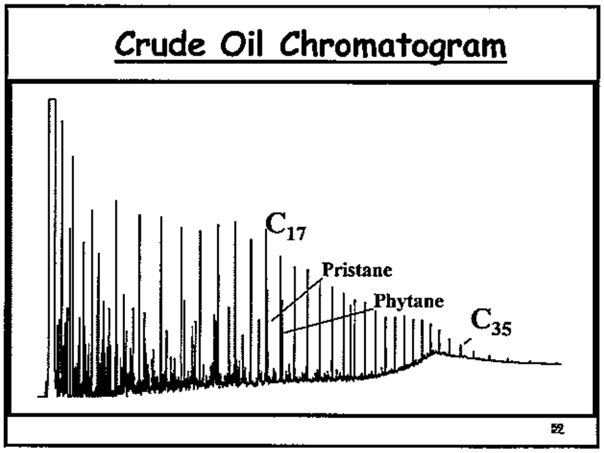
- What are the most commonly used techniques for such purposes?

Gas chromatography

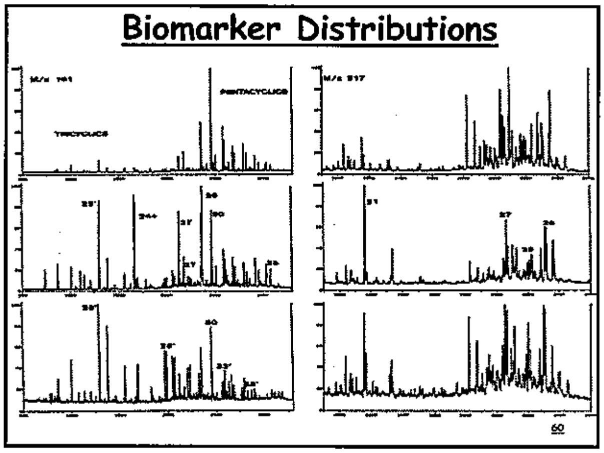
Mass Spectrometry



Fingerprinting by Gas Chromatography



Crude Oil Chromatogram

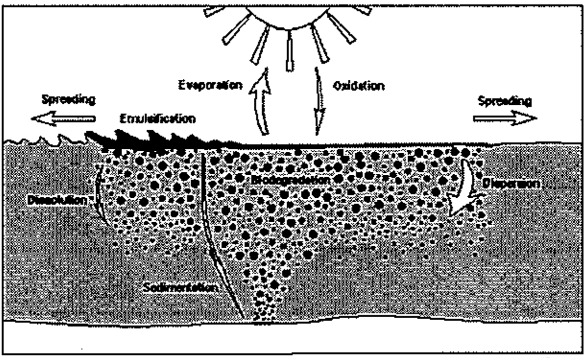


Biomarker Distributions

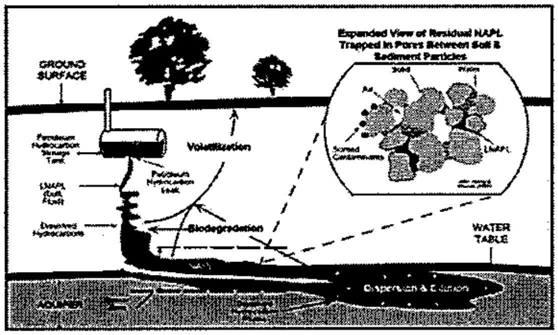
Hydrocarbon Spills and Weathering

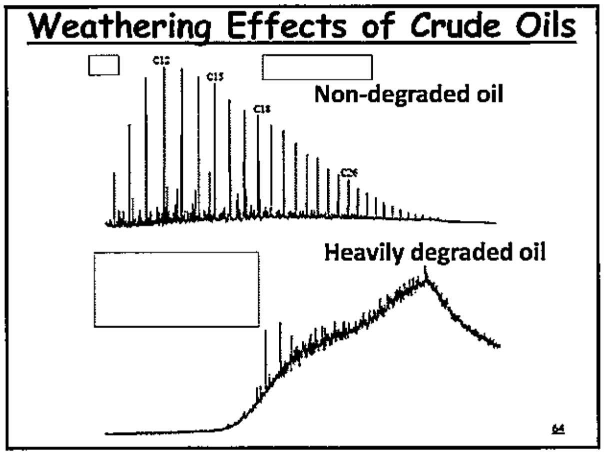
- Major effects of weathering from a geochemical perspective are :
  - Evaporation
  - Water washing
  - Biodegradation

Processes acting on Spilled Oils

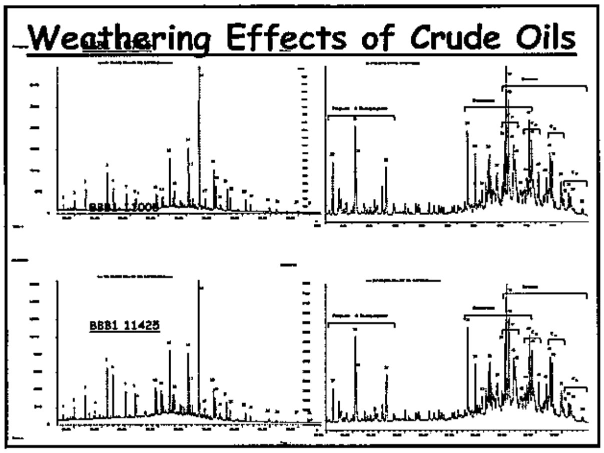


Processes acting on below-ground spills

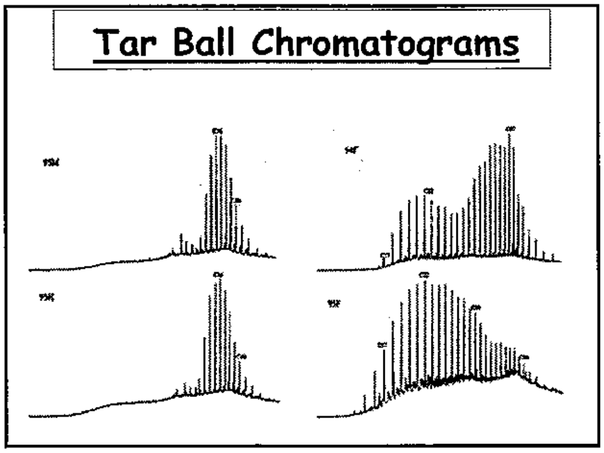




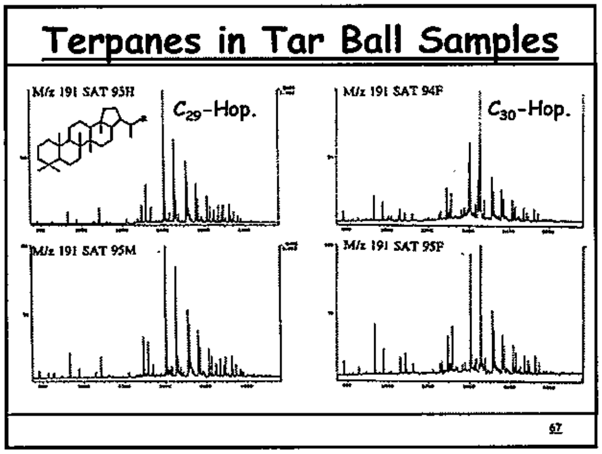
Weathering Effects of Crude Oils



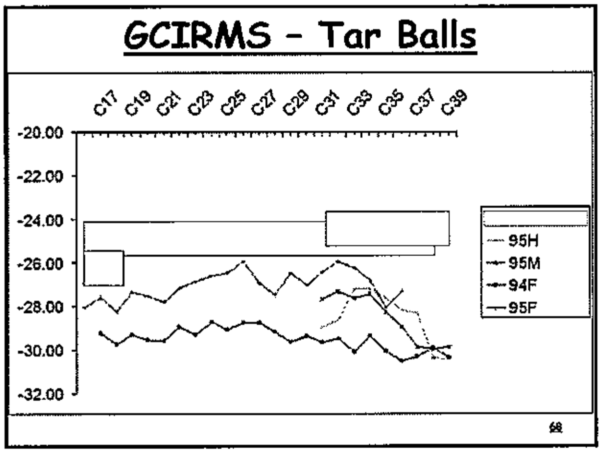
Weathering Effects of Crude Oils



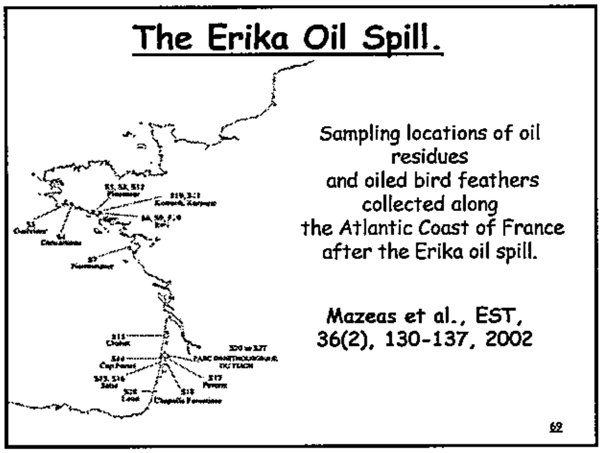
Tar Ball Chromatograms



Terpanes in Tar Ball Samples



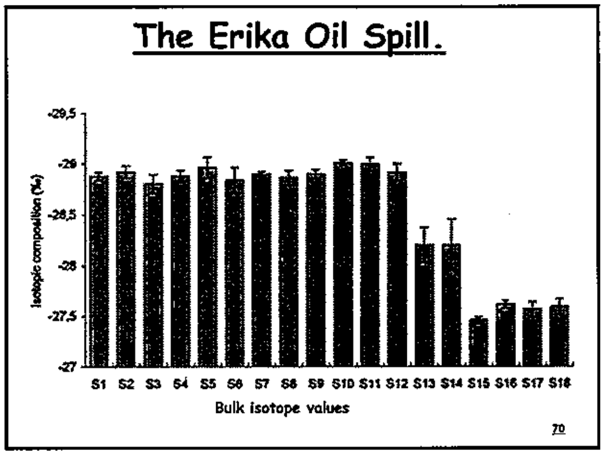
GCIRMS - Tar Balls



The Erika Oil Spill.

Sampling locations of oil residues
and oiled bird feathers
collected along
the Atlantic Coast of France
after the Erika oil spill.

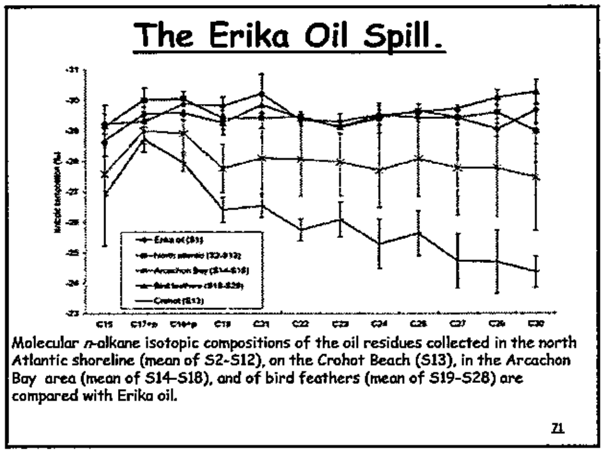
Mazeas et al., EST, 36(2), 130-137, 2002



The Erika Oil Spill.

Bulk isotope values

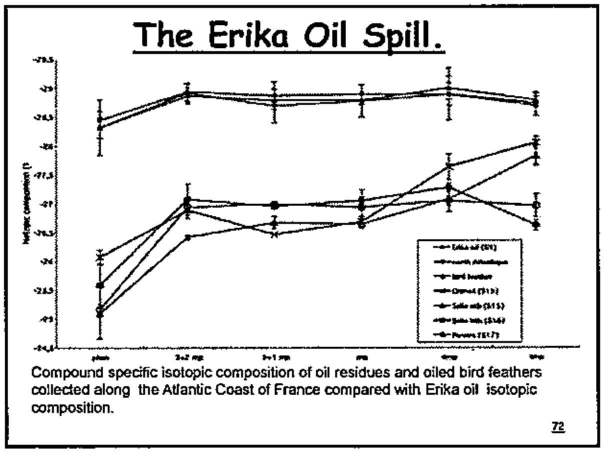
70



The Erika Oil Spill.

Molecular *n*-alkane isotopic compositions of the oil residues collected in the north Atlantic shoreline (mean of S2-S12), on the Crohot Beach (S13), in the Arcachon Bay area (mean of S14-S18), and of bird feathers (mean of S19-S28) are compared with Erika oil.

71



The Erika Oil Spill.

Compound specific isotopic composition of oil residues and oiled bird feathers collected along the Atlantic Coast of France compared with Erika oil isotopic composition.

72

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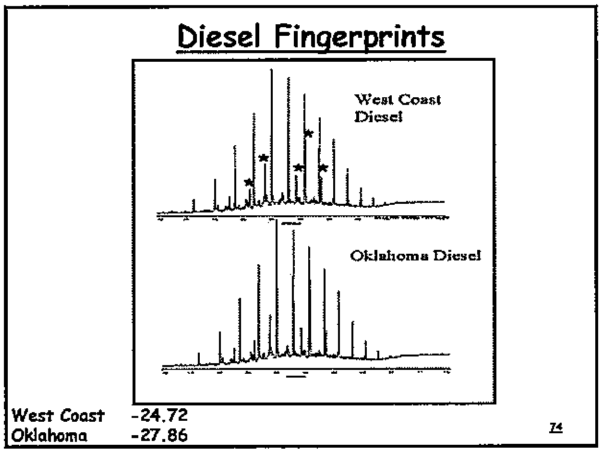
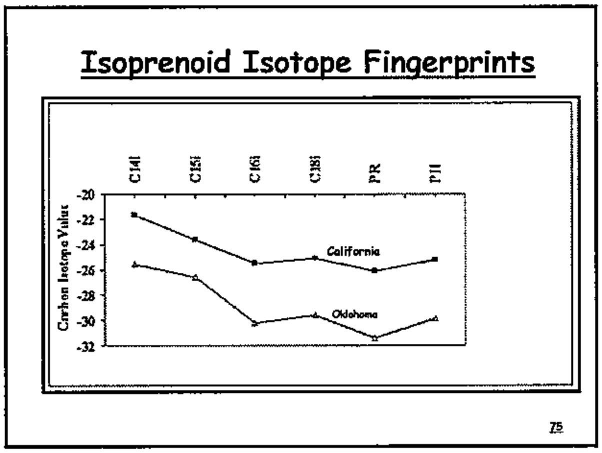
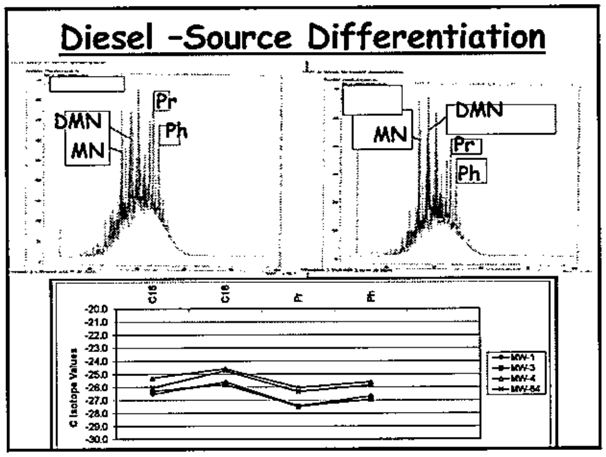


Diesel Fingerprints

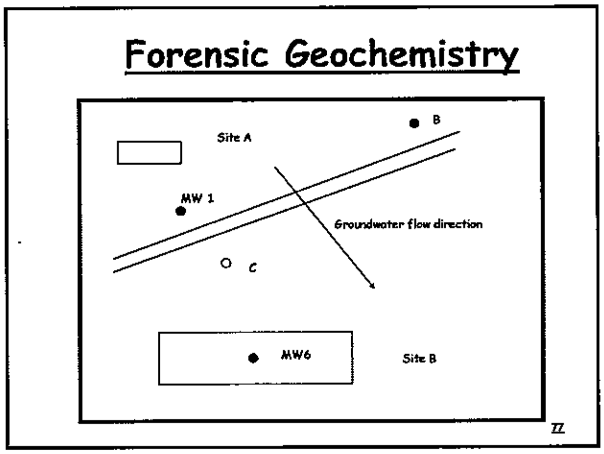
West Coast	-24.72
Oklahoma	-27.86



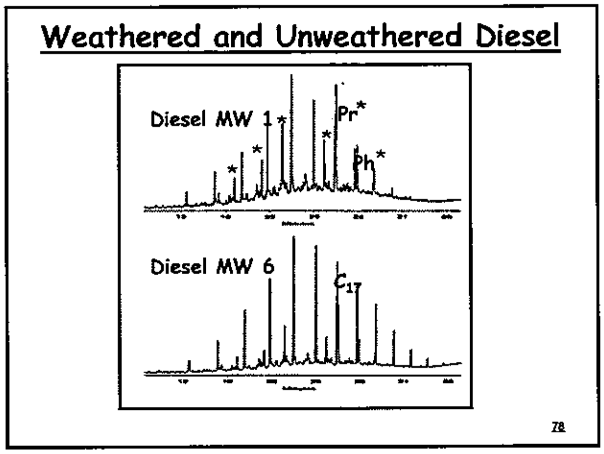
Isoprenoid Isotope Fingerprints



Diesel -Source Differentiation

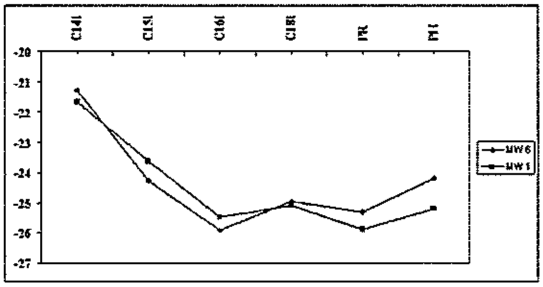


Forensic Geochemistry

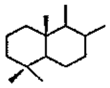


Weathered and Unweathered Diesel

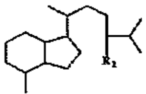
Carbon Isotope Values for Isoprenoids



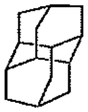
Diesel Correlations



Sesquiterpanes(123)



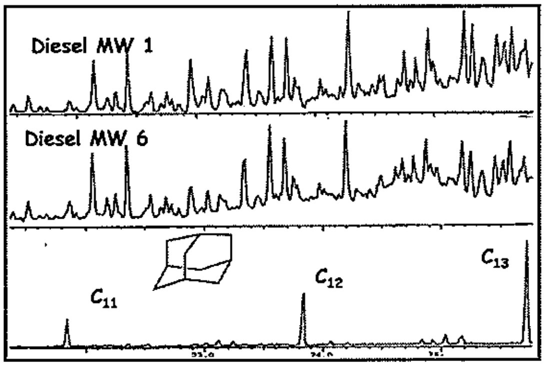
Degraded steranes (110;124)



Diamantane (135)

Adamantane (187)

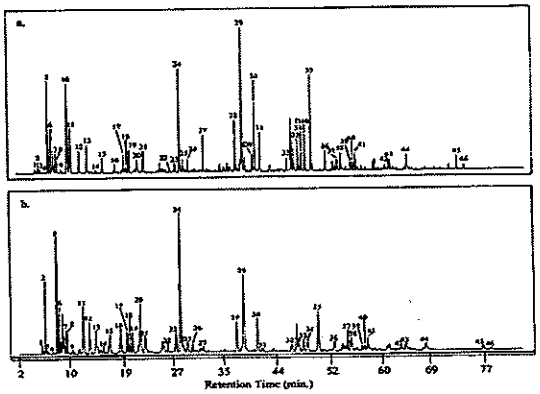
Adamantanes in Diesel Fuels



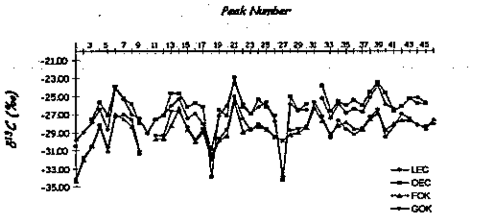
Gasolines

- Gasolines from different sources often have very similar chromatograms, making it difficult to distinguish such samples. Gasolines are also devoid of biomarkers, further limiting correlation possibilities.
- One solution here is to use GCIRMS for both the hydrocarbons and additives.

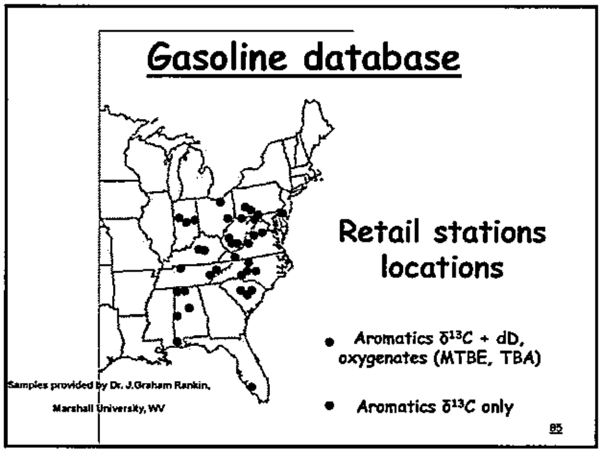
Comparison of Gasolines by GC



Carbon Isotopic Composition of Gasolines from Oklahoma (FOK, GOK) and the East Coast (LEC, OEC)



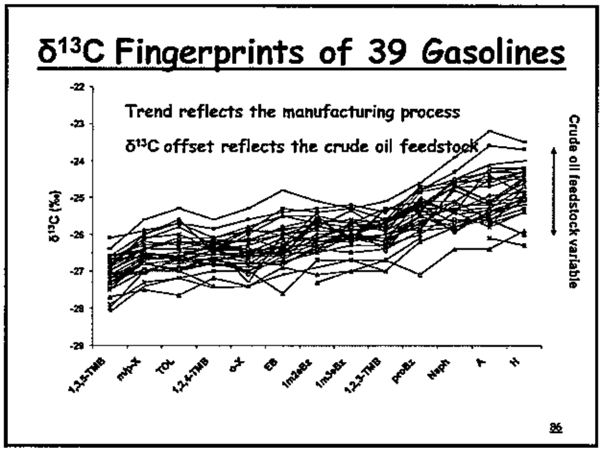
This figure shows the carbon isotopic fingerprint of gasolines sampled from Oklahoma and from the East Coast and demonstrates that these gasolines are significantly different in terms of isotopic composition and can be discriminated from each other on this basis. The peak numbers are identified in the section above.



Gasoline database

Retail stations locations

- Aromatics $\delta^{13}C$ + dD, oxygenates (MTBE, TBA)
- Aromatics $\delta^{13}C$ only



$\delta^{13}C$ Fingerprints of 39 Gasolines

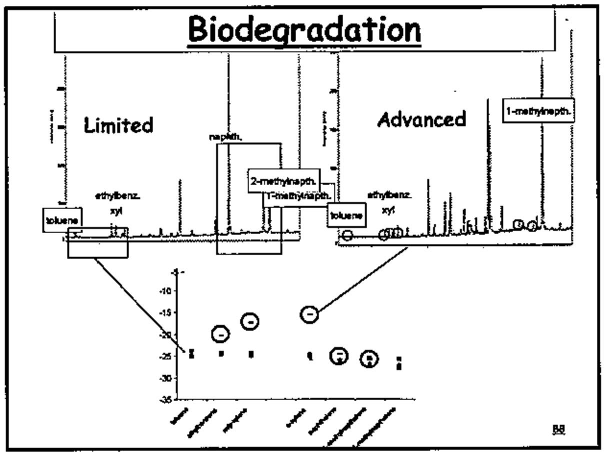
Trend reflects the manufacturing process

$\delta^{13}C$ offset reflects the crude oil feedstock

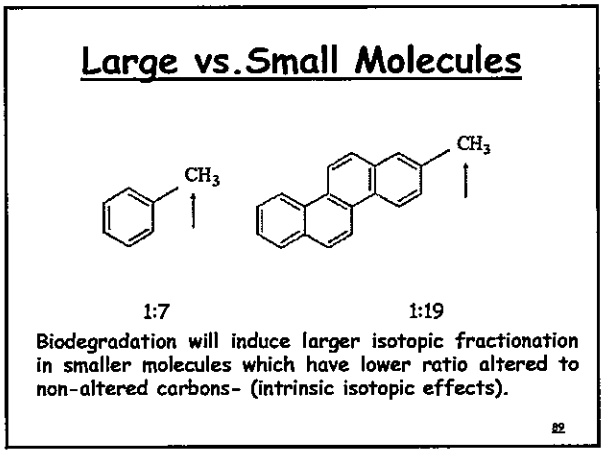
Crude oil feedstock variable

When are Two Fingerprints Different?

- Factors causing differences:
  - Source
  - Precision and Accuracy
  - Fresh samples vs. Environmental samples
  - Weathering and biodegradation



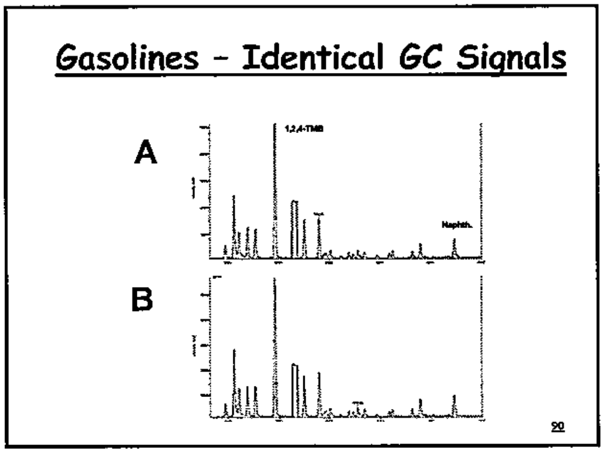
Biodegradation



Large vs.Small Molecules

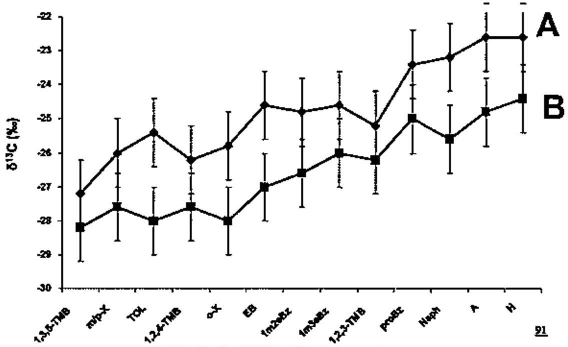
1:7 1:19

Biodegradation will induce larger isotopic fractionation in smaller molecules which have lower ratio altered to non-altered carbons- (intrinsic isotopic effects).



Gasolines - Identical GC Signals

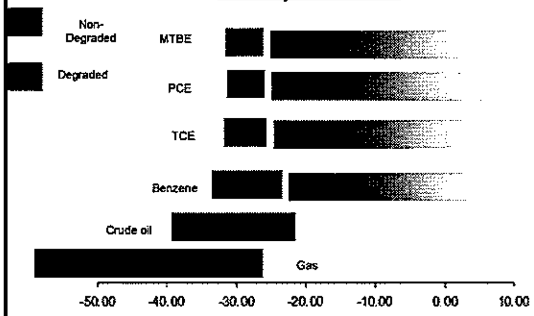
Gasolines - Different δ13C Fingerprints



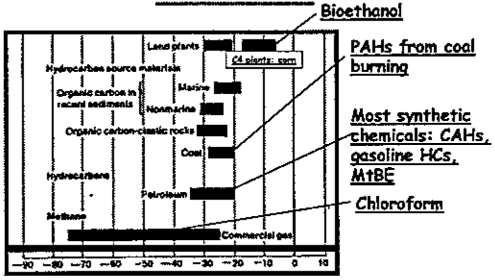
Source Discrimination- Ground-water Problems

- Source discrimination
  - Stable isotopes provide a tool that can be used to discriminate source of common ground water and sediment contaminants.
  - Particularly valuable for single component contaminants
  - Volatile compound source signatures may be affected by "weathering"
  - Relatively narrow range of signatures

Non-degraded v. Degraded Components

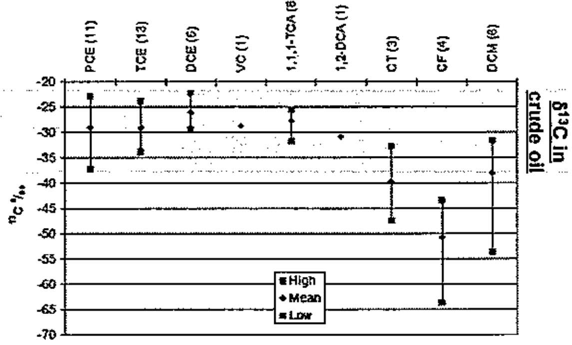


The Isotopes in Manufactured Chemicals are Inherited from Synthetic Feedstocks



Carbon isotope Ratios

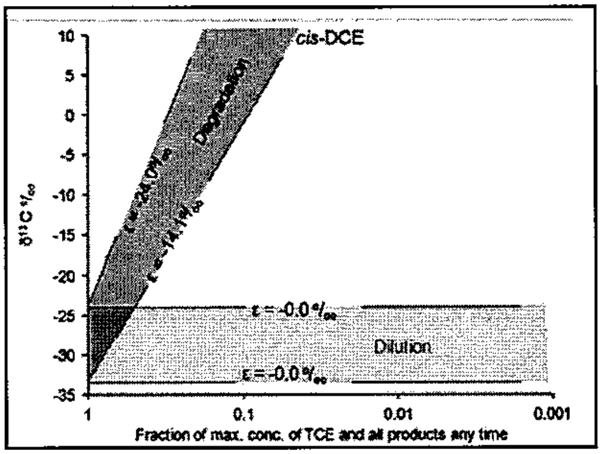
C Isotope Ratios of Misc. CAHs



after USEPA 2006

Remediation Studies

- How can isotopes assist in remediation studies?
- Provide independent verification that attenuation is taking place
- Provide estimates of extent of attenuation
- Distinguish mechanisms of degradation
- Distinguish non-degradative processes that may be taking place



Isotopes in Remediation Studies

- Provide independent verification that attenuation is taking place
- Basically looking for isotopic enrichment such that the substrate is isotopically enriched relative to the original source material
- Enrichment magnitude should exceed that of abiotic (physical) processes
- Ranges of source signatures established for most common contaminants

Isotopes in Remediation Studies

- Provide independent verification that attenuation is taking place
- Ideally 2D or even 3D isotope monitoring will provide more reliable evidence for attenuation
- Mechanism specific since one isotope may be enriched, but little change in the others depending on mechanism.

Remediation - Summary

- Provide estimates of extent of attenuation
- Conservative estimates of the extent of degradation can be obtained from the Rayleigh equation
- Information can also be incorporated into flow transport models

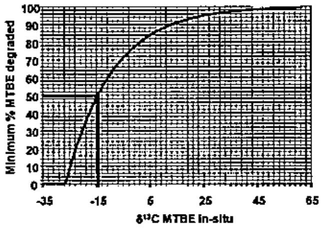
Use of CSIA data to determine the progress of in-situ degradation (anaerobic)

Simplified Rayleigh equation: $\delta^{13}C_{insitu} = \delta^{13}C_{initial} + \varepsilon * \ln F$

Mixing with less degraded MTBE will lower the degradation estimate

Calculation is made using a conservative value of $\delta^{13}C_{initial}$

This is a conservative approach



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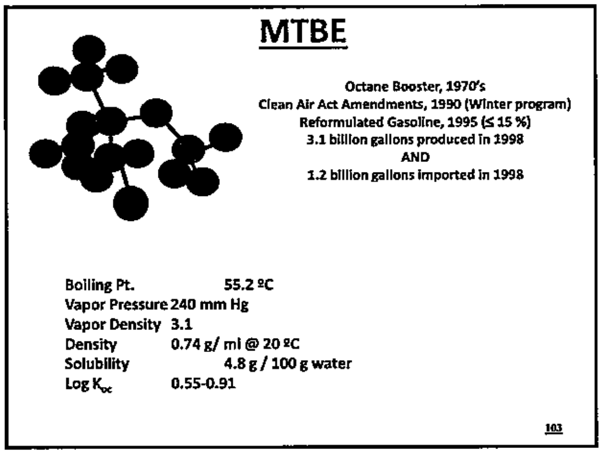
  - PAHs
  - PCBs
  - Benzene
  - Chlorine Isotopes
  - Perchlorate
- Vapor Intrusion Studies
- Fate and Transport Models
- Summary



MTBE

Octane Booster, 1970's
Clean Air Act Amendments, 1990 (Winter program)
Reformulated Gasoline, 1995 (≤ 15 %)
3.1 billion gallons produced in 1998
AND
1.2 billion gallons imported in 1998

Boiling Pt.	55.2 °C
Vapor Pressure	240 mm Hg
Vapor Density	3.1
Density	0.74 g/ ml @ 20 °C
Solubility	4.8 g / 100 g water
Log K_{oc}	0.55-0.91

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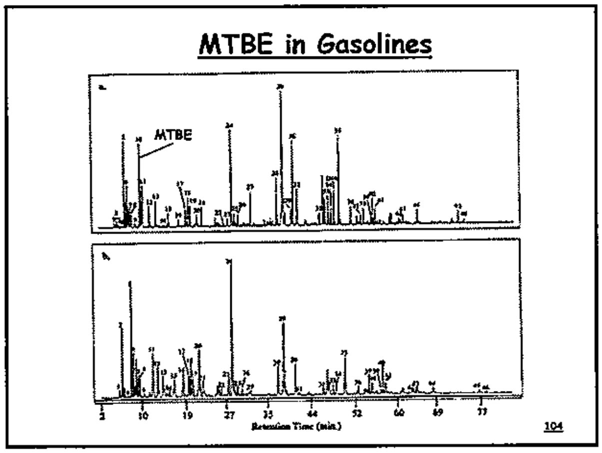

MTBE in Gasolines

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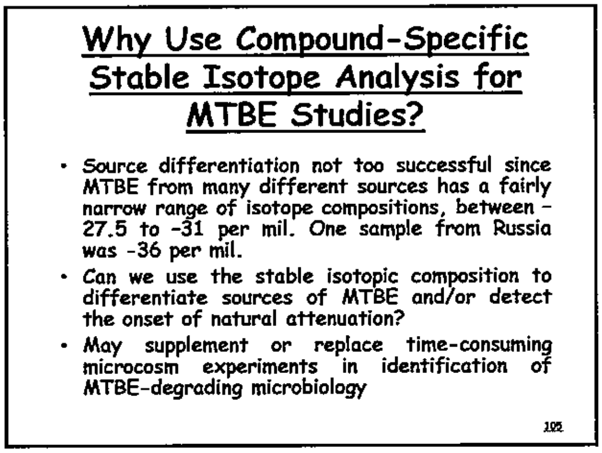

Why Use Compound-Specific Stable Isotope Analysis for MTBE Studies?

- Source differentiation not too successful since MTBE from many different sources has a fairly narrow range of isotope compositions, between -27.5 to -31 per mil. One sample from Russia was -36 per mil.
- Can we use the stable isotopic composition to differentiate sources of MTBE and/or detect the onset of natural attenuation?
- May supplement or replace time-consuming microcosm experiments in identification of MTBE-degrading microbiology

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Routine PT- GCIRMS Quantitation Limits

$\delta^{13}C$ MTBE	$\delta^{13}C$ TBA	δD MTBE	δD TBA
1 ppb	20/30ppb	10/20ppb	NA

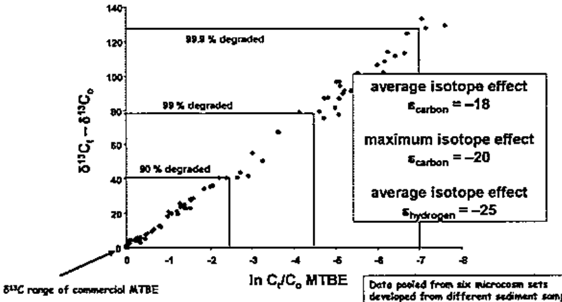
Data Interpretation

Qualitative - if MTBE composition is "heavier" than the reference commercial MTBE, degradation may be inferred

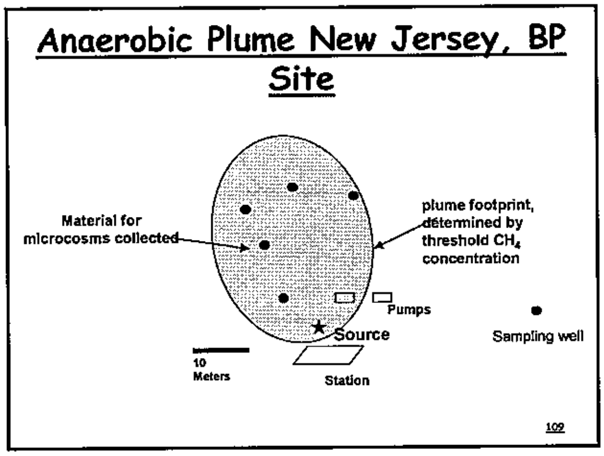
Composition range of undegraded MTBE:

Carbon: -33 to -27.5 permil $\delta^{13}C$
Hydrogen: -125 to -80 permil δD

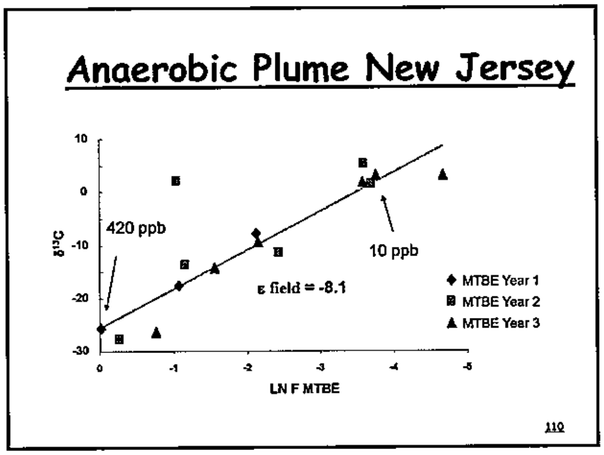
ISOTOPE FRACTIONATION in MICROCOSMS



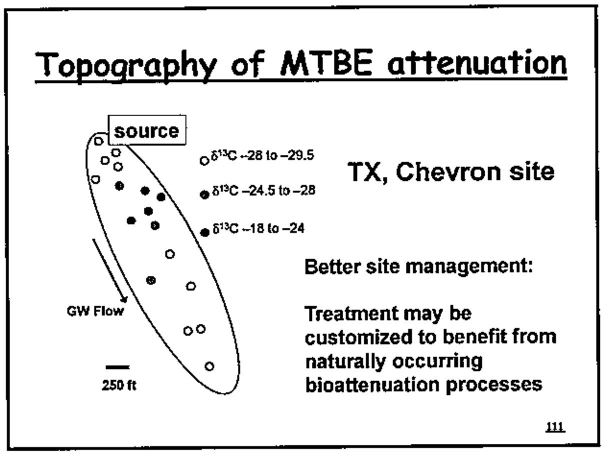
Data pooled from six microcosm sets developed from different sediment samples (misc. gas station sites). -20 SR and methanogenic microcosms are included.



Anaerobic Plume New Jersey, BP Site



Anaerobic Plume New Jersey



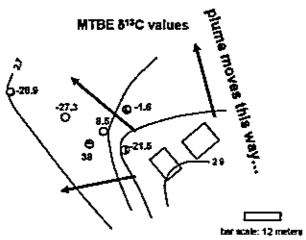
Topography of MTBE attenuation

TX, Chevron site

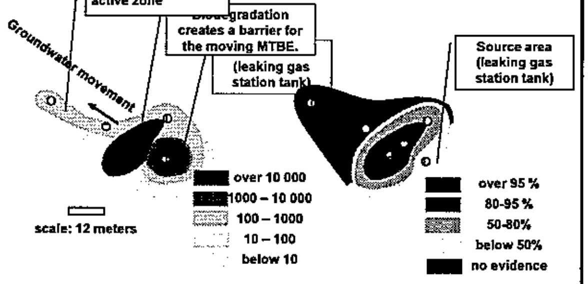
Better site management:

Treatment may be customized to benefit from naturally occurring bioattenuation processes

Dana Point, Orange County, CA



Gas s range County, CA, USA



This part of the plume represents MTBE avoiding the active zone

gradation creates a barrier for the moving MTBE.

(leaking gas station tank)

Source area (leaking gas station tank)

MTBE concentrations (μg/L)

conservative extent of MTBE biodegradation calculated from CSIA data

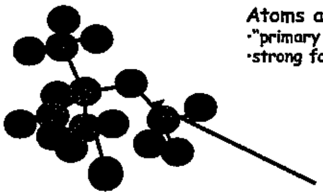
MTBE Degradation Experiments

- Kuder et al., (2005) first used C and H isotope data from both microcosm and field data to demonstrate anaerobic degradation of MTBE.
- Showed similar enrichment factors for both C and H.
- Common degradation pathway at several sites
- First step is cleavage of $O\text{-}CH_3$ bond.

Kuder et al., 2005

Isotope Effects Reflect Reaction Mechanisms

Strong isotope fractionation affects atoms of the reacting bond



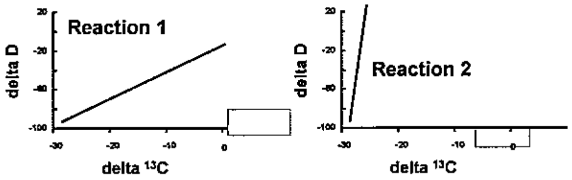
Atoms at the reacting bond:
- *"primary effects"*
- *strong for $^{13}C/^{12}C$*

Bond cleavage

Remaining atoms:
- "secondary effects"
- negligible for $^{13}C/^{12}C$

Isotopic Fractionation During MTBE - TBA Conversion

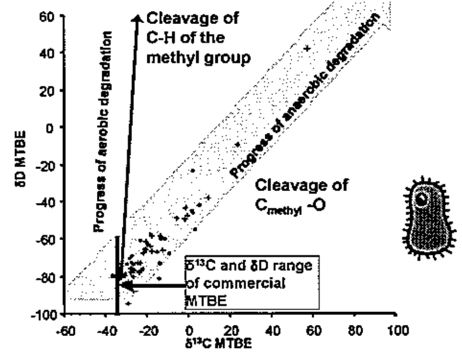
- **Reaction 1:** Ether bond hydrolysis: primary isotopic effect on carbon, secondary effect of hydrogen
- **Reaction 2:** Terminal methyl group oxidation: primary isotopic effect both on carbon and hydrogen



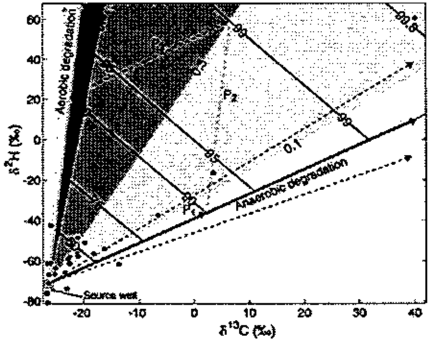
Overview of Isotope Effects in MTBE Degradation Studies

Culture	ε_C ‰	ε_H ‰	reference
Aerobic microcosm enrichment	-1.64 to -1.97± 0.05	Not analyzed	Hunkeler et al. 2001
Aerobic cometabolic enrichment	-1.52 ± 0.06	Not analyzed	Hunkeler et al. 2001
Aerobic microcosm; PM1	-2.0 ±0.1 to -2.4 ± 0.3	-33 ± 5 to -36 ± 6	Gray et al., 2002
Aerobic microcosm; VAFB	-1.4 to -1.8 ± 0.1	-29 ± 4 to -66 ± 3	Gray et al., 2002
Methanogenic microcosm	-9.2 ± 5.0	Not analyzed	Kolhatkar et al., 2002
Methanogenic enrichment microcosm	-13 ±1.1	-16 ± 5	Kuder et al., 2005
Methanogenic enrichment microcosm	-15.6 ± 4.1, -14.6 ± 5.2	Not analyzed	Somsamak et al., 2005
Methanogenic microcosm	-15.1 ± 3.3	-20.5 ± 5.5	Kuder et al., unpublished
Methanogenic microcosm	-12.5, -12.0	Not analyzed	Kuder et al., unpublished
Mixed medium anaerobic (SR and CH4)	-17	Not analyzed	Kuder et al., unpublished

Discrimination of Aerobic vs. Anaerobic Degradation by 2D CSIA



2D-Isotope Analyses of MTBE at Industrial Site



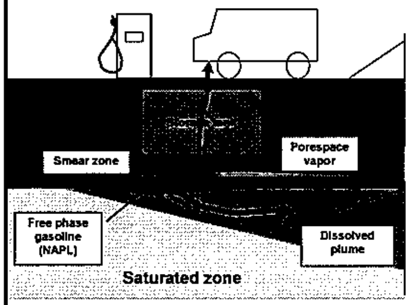
after van Breukelen; Env. Sci. Tech.,41,4004, 2007

Isotope Effects in Non-Degradative MTBE Attenuation

Do physical attenuation processes result in measurable isotope fractionation?

If so, does it interfere with CSIA-based biodegradation assessment?

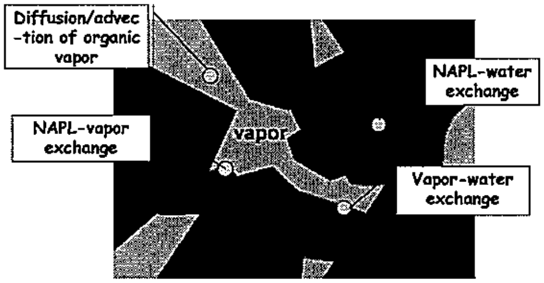
Volatile Contaminants – Processes affecting MTBE Mass Distribution



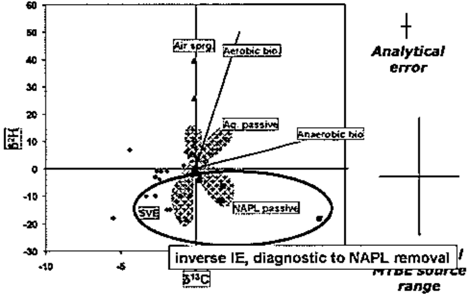
Changes of the source's isotope signal might affect interpretation of CSIA data from the dissolved plume.

Abiotic changes of isotope composition might mimic or obscure biodegradation signal in the dissolved plume.

Vadose Zone Physical Attenuation- Complex Interactions



2D-CSIA of Different Volatilization Processes



inverse IE, diagnostic to NAPL removal

Shaded area represent 95% mass removal benchmark

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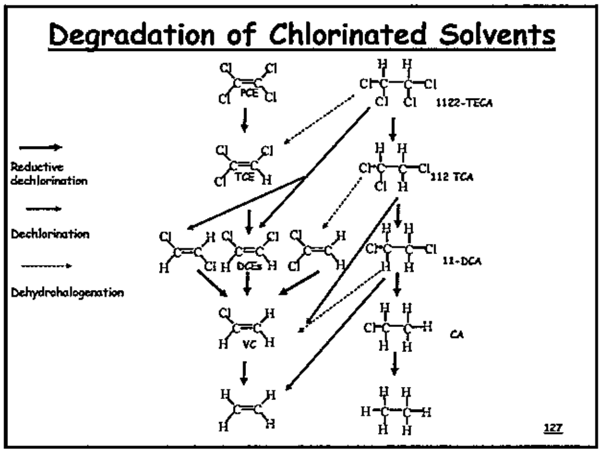
Detection Limits for Chlorinated Solvents

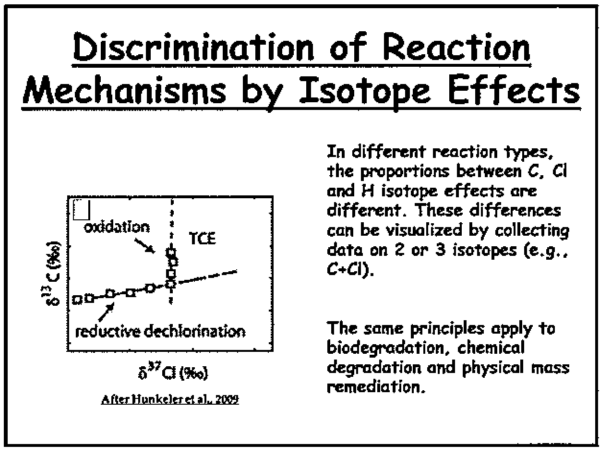
- C and Cl Isotopes
  - TCE, PCE AND cis-DCE 1ug/L
  - VC 2ug/L
- H Isotopes
  - TCE 20-30ug/L
  - Cis-DCE 5-10ug/L
  - VC 10-20ug/L

$\delta^{13}C$ Values for TCE from Several Manufacturers

Numerical key	Manufacturer	$\delta^{13}C$	Off-line precision
1	Dow	−31.90	0.05
1A	Dow	−29.84	0.07
2	ICI	−31.32	0.03
3	PPG	−27.80	0.01
3A	PPG	−31.68	0.17
4	Aldrich	−33.49	0.08
5	Holt et al. (1997)	−27.18	0.1
6	A	−31.53	0.01
7	B	−27.90	0.08
8	C	−29.93	0.18



Degradation of Chlorinated Solvents

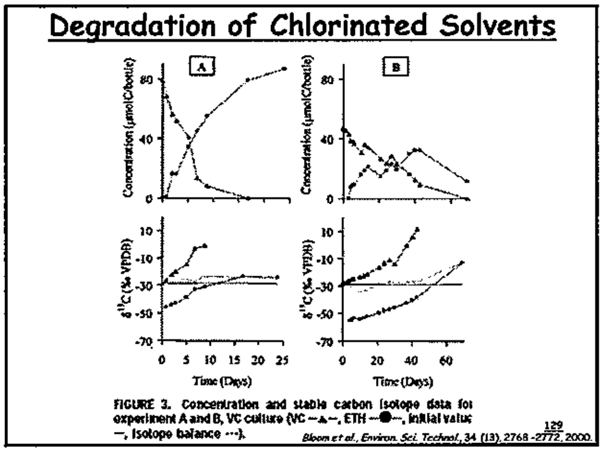


Discrimination of Reaction Mechanisms by Isotope Effects

After Hunkeler et al., 2009

In different reaction types, the proportions between C, Cl and H isotope effects are different. These differences can be visualized by collecting data on 2 or 3 isotopes (e.g., C+Cl).

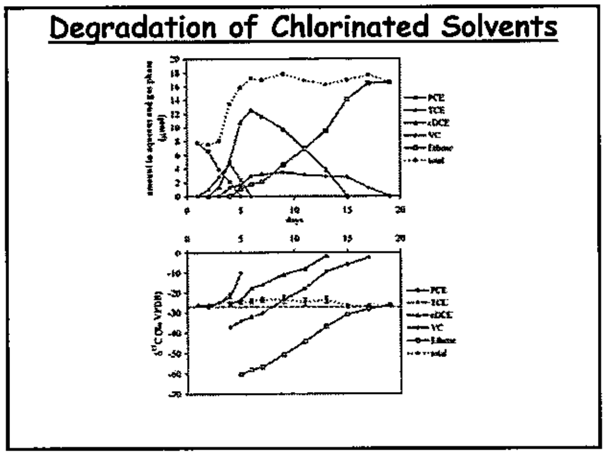
The same principles apply to biodegradation, chemical degradation and physical mass remediation.



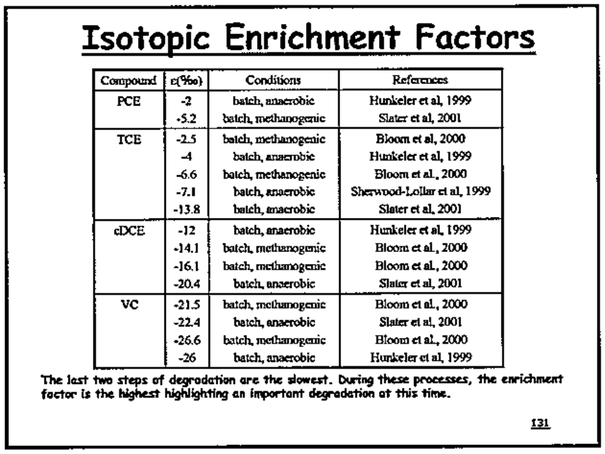
Degradation of Chlorinated Solvents

FIGURE 3. Concentration and stable carbon isotope data for experiment A and B, VC culture (VC –▲–, ETH –●–, initial value —, isotope balance ···).

Bloom et al., Environ. Sci. Technol., 34 (13), 2768 -2772, 2000.



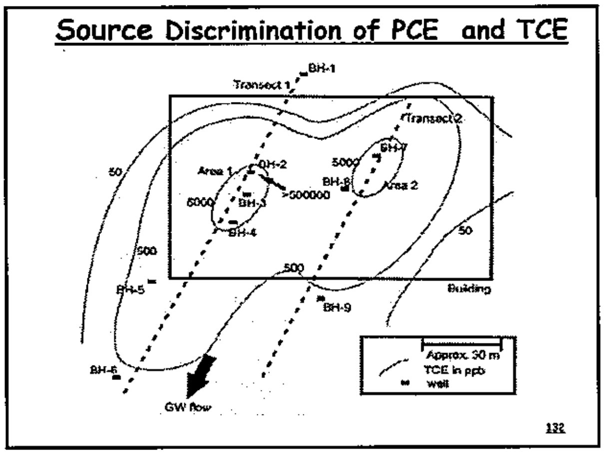
Degradation of Chlorinated Solvents



Isotopic Enrichment Factors

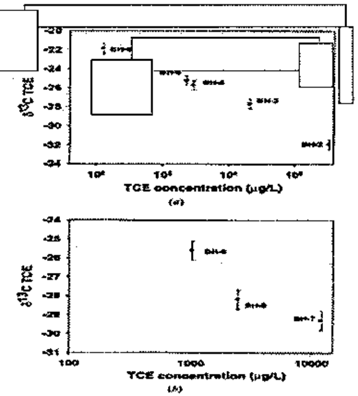
Compound	ε(‰)	Conditions	References
PCE	-2	batch, anaerobic	Hunkeler et al, 1999
	-5.2	batch, methanogenic	Slater et al, 2001
TCE	-2.5	batch, methanogenic	Bloom et al, 2000
	-4	batch, anaerobic	Hunkeler et al, 1999
	-6.6	batch, methanogenic	Bloom et al., 2000
	-7.1	batch, anaerobic	Sherwood-Lollar et al, 1999
	-13.8	batch, anaerobic	Slater et al, 2001
cDCE	-12	batch, anaerobic	Hunkeler et al, 1999
	-14.1	batch, methanogenic	Bloom et al., 2000
	-16.1	batch, methanogenic	Bloom et al., 2000
	-20.4	batch, anaerobic	Slater et al, 2001
VC	-21.5	batch, methanogenic	Bloom et al., 2000
	-22.4	batch, anaerobic	Slater et al, 2001
	-26.6	batch, methanogenic	Bloom et al., 2000
	-26	batch, anaerobic	Hunkeler et al, 1999

The last two steps of degradation are the slowest. During these processes, the enrichment factor is the highest highlighting an important degradation at this time.



Source Discrimination of PCE and TCE

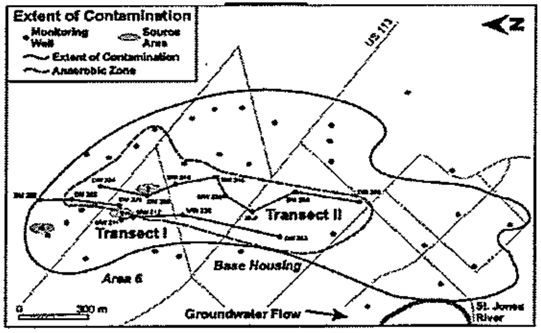
Source Discrimination of PCE and TCE



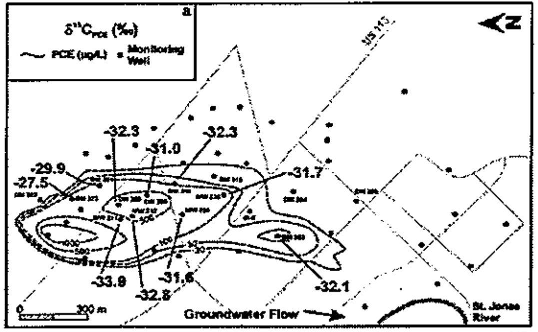
Reductive Dechlorination of PCEs

- Sherwood Lollar et al., EST 2001,35,261-269-first showed that during anaerobic reductive dechlorination of chlorinated hydrocarbons,isotopic enrichment of PCE and TCE was observed at Area 6 Dover AFB.

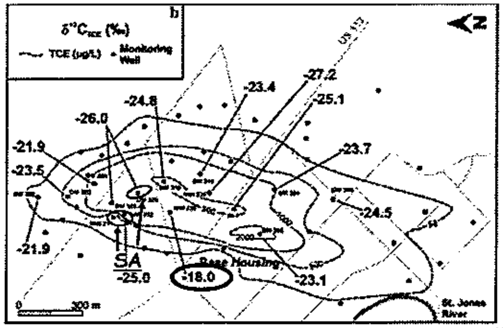
Reductive Dechlorination of PCEs



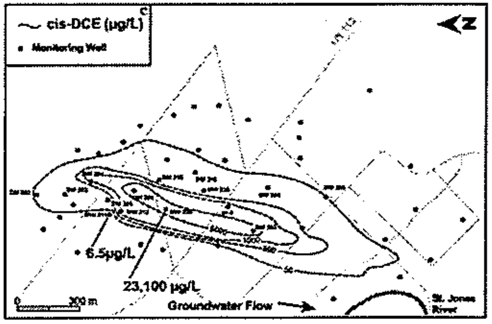
Reductive Dechlorination of PCEs

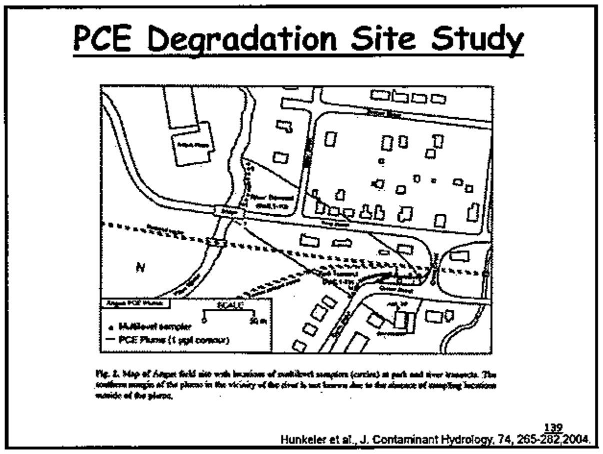


Reductive Dechlorination of PCEs



Reductive Dechlorination of PCEs

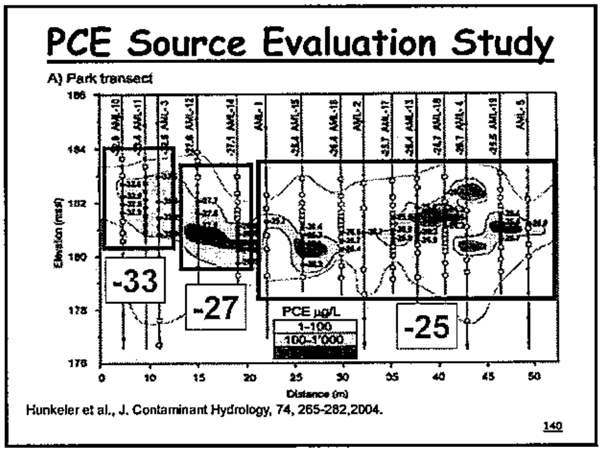




PCE Degradation Site Study

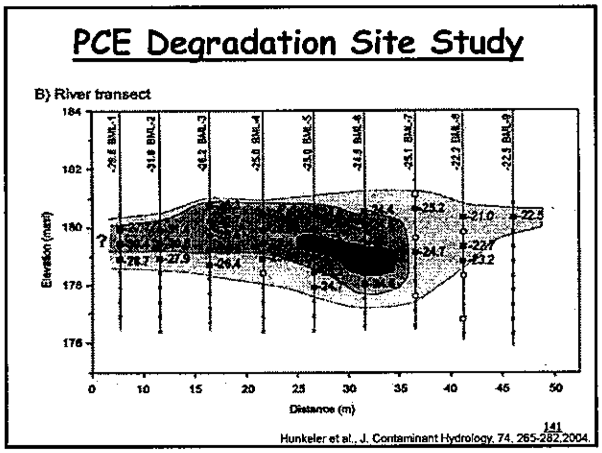
Fig. 2. Map of [illegible] field site with locations of multilevel samplers (circles) at park and river transects. The southern margin of the plume in the vicinity of the river is not known due to the absence of sampling locations outside of the plume.

Hunkeler et al., J. Contaminant Hydrology, 74, 265-282,2004.



PCE Source Evaluation Study

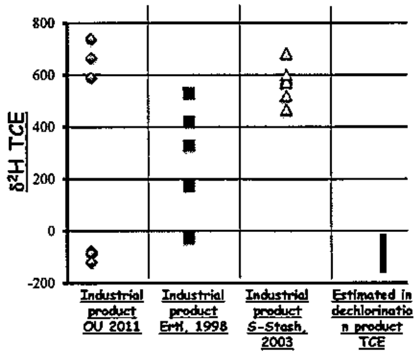
Hunkeler et al., J. Contaminant Hydrology, 74, 265-282,2004.



PCE Degradation Site Study

Hunkeler et al., J. Contaminant Hydrology, 74, 265-282,2004.

H Isotope Ratios of Manufactured TCE



Abiotic and Microbial Transformation of PCE and TCE

Microbial processes are most rapid transformation of PCE and TCE in the field and should be exploited for this purpose where appropriate.

Abiotic processes can contribute to transformation of PCE and TCE where significantly higher mass loadings of reactive minerals are generated in situ as part of a remediation technology or where the activity of dechlorinating bacteria is low.

Abiotic processes can also play a significant role in cases where complete microbial degradation of PCE or TCE to ethene does not occur.

Under these conditions, although slow, abiotic processes may still contribute to the complete transformation of PCE and TCE to benign products at contaminated sites.

Biogenic vs. Abiogenic Degradation

PCE	ε
FeS ph 7 – abiotic	-30.2 +/- 4.3
FeS pH 8 – abiotic	-29.54 +/- 0.83
BB1 – biological	-1.39 +/- 0.21
Sm – biological	-1.33 +/- 0.13

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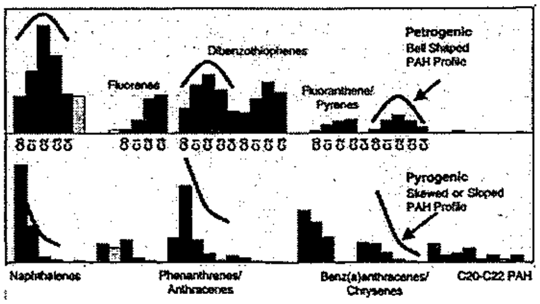
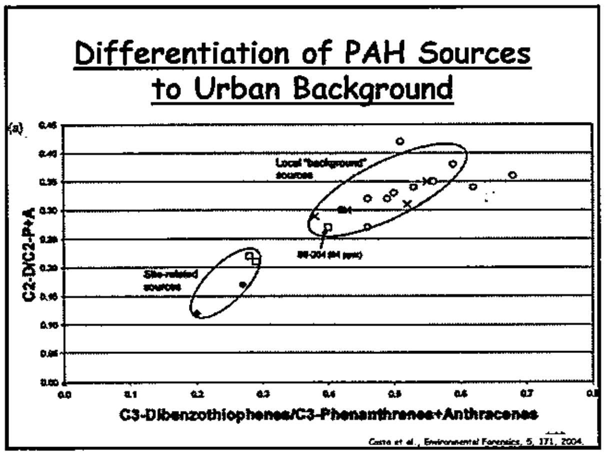
Sources of PAHs to Urban Background

- Natural background
  - Pre-existing and naturally produced
- Atmospheric fallout
  - Transportation, heating systems, power generation, industries
- Fill
  - Building materials
  - Debris, ash, trash
- Spills and sprays

Are the isotope ratios different for different sources? Can they be sorted out?

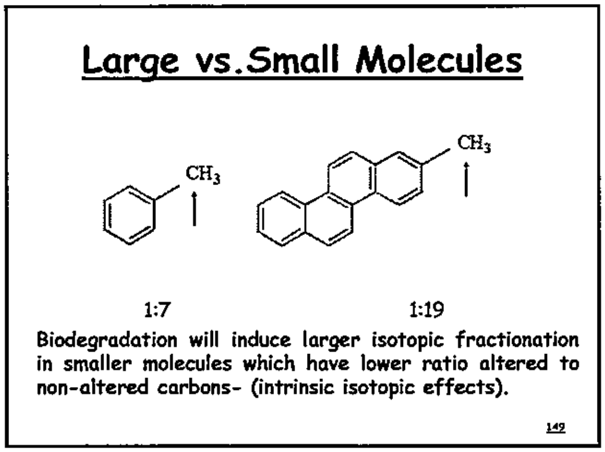
Petrogenic vs. Pyrogenic





Differentiation of PAH Sources to Urban Background

Costa et al., Environmental Forensics, 5, 171, 2004.



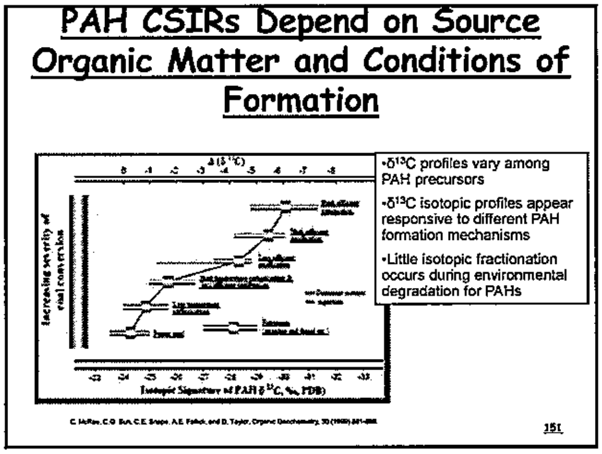
Large vs.Small Molecules

1:7 1:19

Biodegradation will induce larger isotopic fractionation in smaller molecules which have lower ratio altered to non-altered carbons- (intrinsic isotopic effects).

PAHs and Stable Isotopes

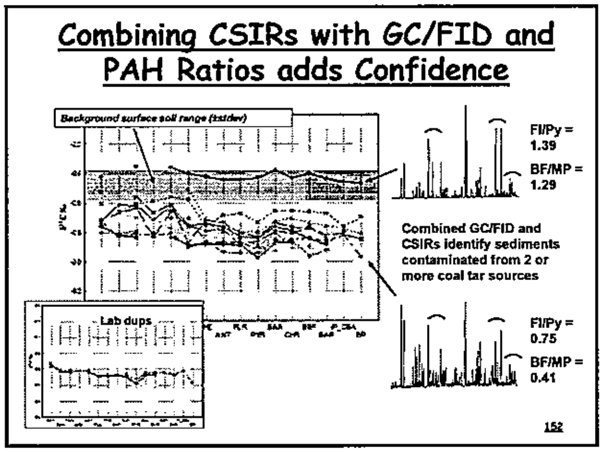
- Current interest is centered around whether carbon isotopes can be used to discriminate PAHs derived from former manufactured gas plant (MGP) wastes versus those from general urban background aromatics
- Urban backgrounds have a fairly narrow range and small differences may be related to source differences



PAH CSIRs Depend on Source Organic Matter and Conditions of Formation

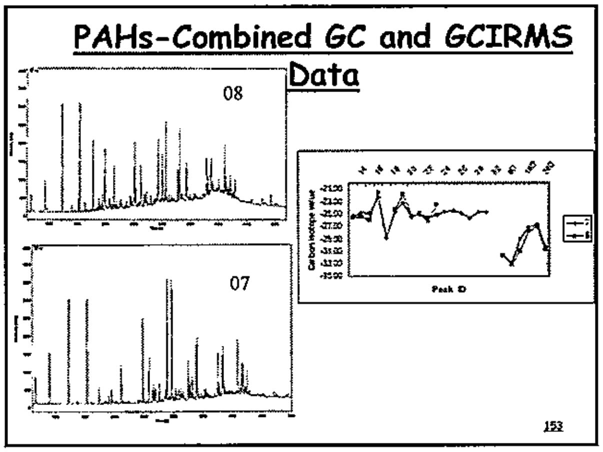
- δ¹³C profiles vary among PAH precursors
- δ¹³C isotopic profiles appear responsive to different PAH formation mechanisms
- Little isotopic fractionation occurs during environmental degradation for PAHs

C. McRae, C.G. Sun, C.E. Snape, A.E. Fallick, and D. Taylor, Organic Geochemistry, 30 (1999) 881-889.



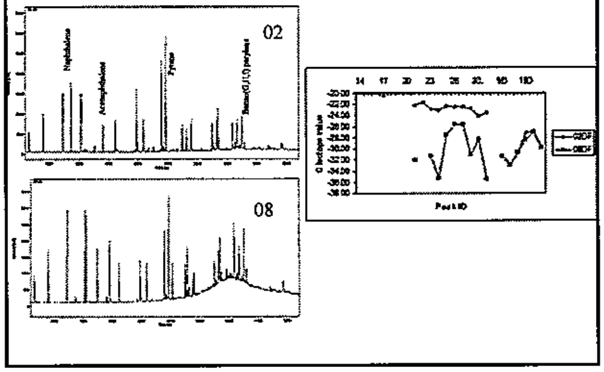
Combining CSIRs with GC/FID and PAH Ratios adds Confidence

Combined GC/FID and CSIRs identify sediments contaminated from 2 or more coal tar sources

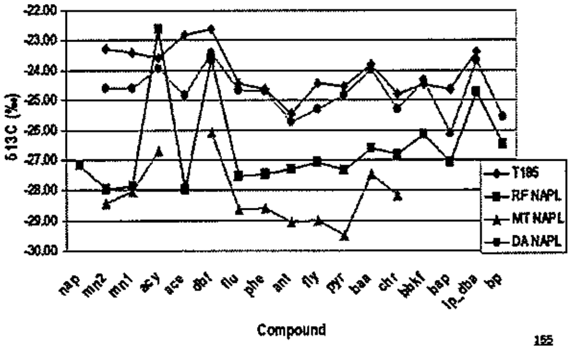


PAHs-Combined GC and GCIRMS Data

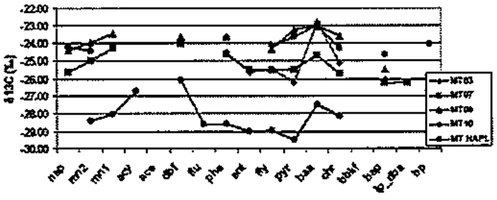
PAHs-Combined GC and GCIRMS Data



CSIRs of NAPL Samples



PAH Fingerprints and Isotopes Show No MGP Contribution to Background



MT03, MT07, MT09, MT10 – background soil samples from town

MT NAPL – tar from MGP site in town

	TPAH (ug/kg)	Fl/Py
MT03	2,510	1.177
MT07	11,100	1.136
MT09	3,880	1.194
MT10	6,940	1.208
MT NAPL		0.64

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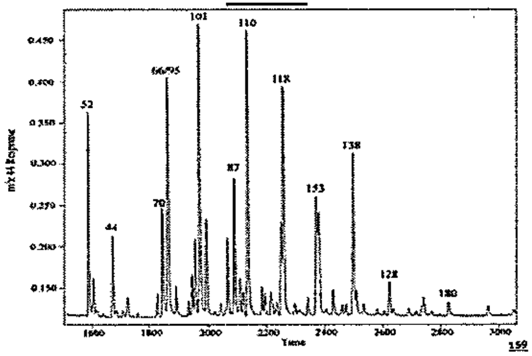
PCB Applications

- Drenzek and other (EST, 35, 3310-3313, 2001) used GCIRMS to show that in laboratory reductive dechlorination no carbon isotopic fractionation occurred.
- However 3 batches of Aroclor 1268 showed a intrinsic trend of ^{13}C depletion with increasing chlorine content.
- Hence a combination of this information will provide information on mechanisms by which these compounds are formed.

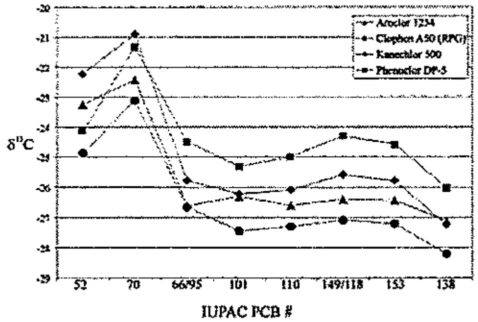
M/z 44 Chromatogram for Aroclor 1245



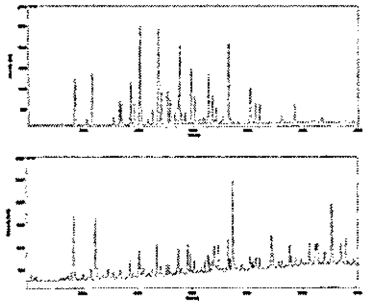
PCBs

- Study by Yanik et al., *OG*, 239-253, 34, 2003 showed that different Aroclors may be isotopically different and thus useful for source discrimination although there is some slight enrichment from degradation.

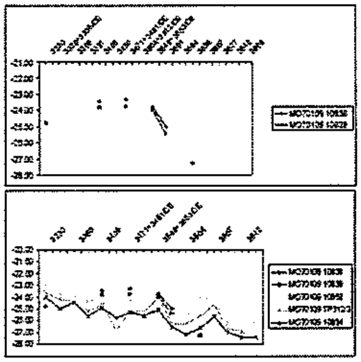
Variations in Isotopic Composition of Various Congeners



PCB Contamination



PCB Contamination



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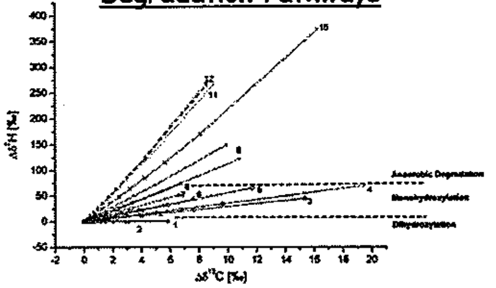
Benzene Sources

- Source differences

	$\delta^{13}C$	δ^2H
Aldrich	-27.92	-27.9
Baker	-26.10	-69.2
BDH I	-24.93	-94.4
BDH II	-27.90	-74.6

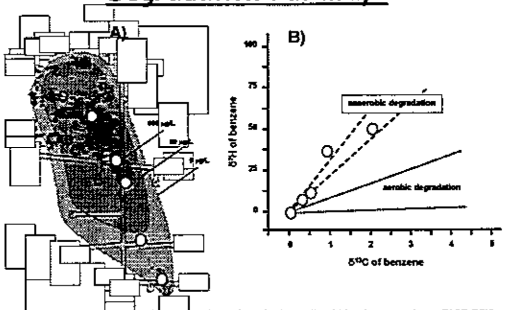
Hunkler et al., EST, 35,3462-3467, 2001

2D-CSIA Discrimination of Benzene Degradation Pathways



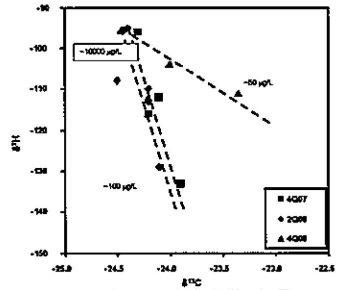
1) R. opacus B-4, 2) P. putida ML2, 3) Burkholderia sp. (17),
4) C. necator ATCC 17697, 5) A. denitrificans strain BC (aerobic),
6) R. pickettii PKO1, 7) Acinetobacter sp. (17),
8) A. denitrificans strain BC (chlorate-reducing), 9) Nitrate-reducing mixed culture (18),
10) Sulfate-reducing mixed culture (18), 11) Methanogenic mixed culture (18),
12) Sulfate-reducing mixed culture

2D-CSIA Discrimination of Benzene Degradation Pathways



Application of CSIA at an industrial site. A) Locations of monitoring wells within a benzene plume; B) 2D-CSIA of benzene from the five monitoring wells. Note that net fractionation is larger for hydrogen than for carbon by a factor of ~20. This is consistent with anaerobic degradation in the core of the plume, but not consistent with aerobic degradation. At this site, the extent of isotope fractionation accounts for 50-60% of benzene mass removal in the distal monitoring well. The apparent attenuation trend of benzene concentration is larger (see the "Caveat" below).

2D-CSIA Discrimination of Benzene Degradation Pathways



2D-CSIA plot of data from a benzene site in California. Three quarterly sample sets are shown. Note the inverse H fractionation, similar to the trends observed for volatilization of MTBE from NAPL phase. The difference between 4Q08 vs. the two other sets may represent relatively less prominent volatilization in 4Q08.

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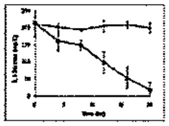
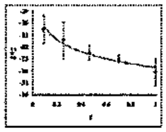
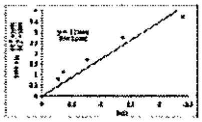
1,4-Dioxane

- 1,4-Dioxane used as a stabilizer for chlorinated solvents and an ingredient in personal care products and printer inks.
- Probable carcinogen.
- Highly water soluble and spreads more extensively than the chlorinated solvents.
- Can be degraded in advance water treatment methods.
- Degrades relatively slowly *in-situ*

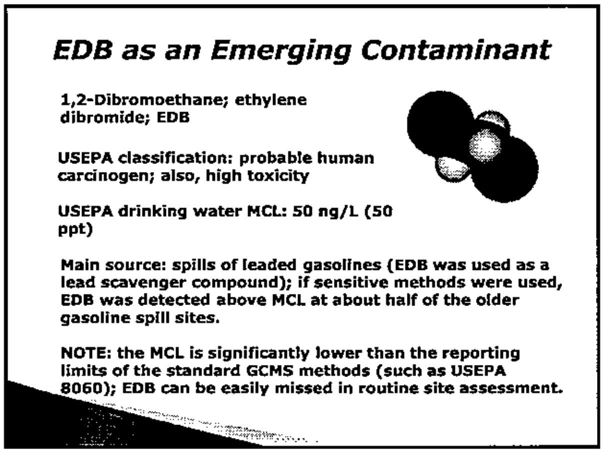
1,4-Dioxane







Laboratory studies show that Pseudonocardia dioxanivorans CB1190 will degrade 1,4-dioxane aerobically. However so far exeperiments done on pure compounds and not yet applied to ground water samples.
(Pornwongthong et al., 2011)



EDB as an Emerging Contaminant

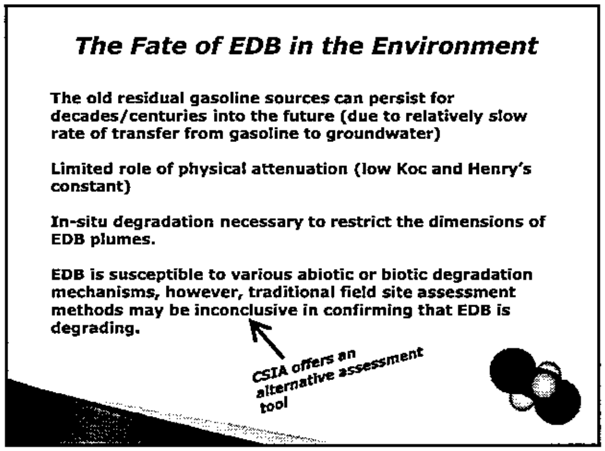
1,2-Dibromoethane; ethylene dibromide; EDB

USEPA classification: probable human carcinogen; also, high toxicity

USEPA drinking water MCL: 50 ng/L (50 ppt)

Main source: spills of leaded gasolines (EDB was used as a lead scavenger compound); if sensitive methods were used, EDB was detected above MCL at about half of the older gasoline spill sites.

NOTE: the MCL is significantly lower than the reporting limits of the standard GCMS methods (such as USEPA 8060); EDB can be easily missed in routine site assessment.



The Fate of EDB in the Environment

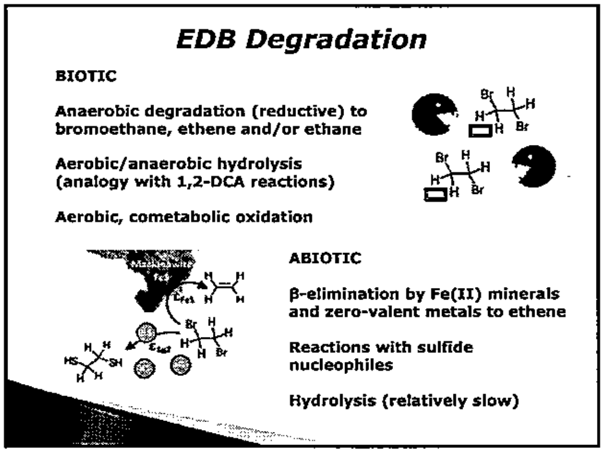
The old residual gasoline sources can persist for decades/centuries into the future (due to relatively slow rate of transfer from gasoline to groundwater)

Limited role of physical attenuation (low Koc and Henry's constant)

In-situ degradation necessary to restrict the dimensions of EDB plumes.

EDB is susceptible to various abiotic or biotic degradation mechanisms, however, traditional field site assessment methods may be inconclusive in confirming that EDB is degrading.

CSIA offers an alternative assessment tool



EDB Degradation

BIOTIC

Anaerobic degradation (reductive) to bromoethane, ethene and/or ethane

Aerobic/anaerobic hydrolysis (analogy with 1,2-DCA reactions)

Aerobic, cometabolic oxidation

ABIOTIC

β-elimination by Fe(II) minerals and zero-valent metals to ethene

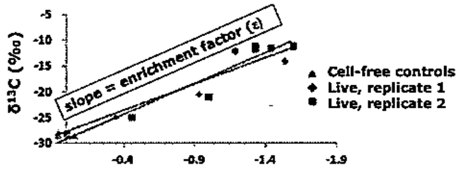
Reactions with sulfide nucleophiles

Hydrolysis (relatively slow)

Isotope Effects in Aerobic (Cometabolic) Biodegradation

Microcosms, *Mycobacterium spaghni* grown with ethane

Enrichment factors (ε) in two replicates: −12±3 and −10±5‰, respectively (−11±2‰ for the pooled data).



Rayleigh-type plot: isotope ratios vs. log of the concentration decrease

Conclusions: Implications for the Use of CSIA in EDB Attenuation Assessment

Significant C isotope effects were observed in all degradation pathways studied to date.

So far, the few biodegrading organisms examined exhibited no significant dampening of the isotope effect (e.g., via commitment to catalysis)

Good perspective for the assessment of degradation of EDB by CSIA methods (if degradation were occurring at the site, the isotope enrichments should be readily detectable)

Unlike in most traditional CSIA work, abiotic pathways must be considered as viable mechanisms leading to isotope fractionation

With C-CSIA data alone, differentiation of alternative degradation mechanisms may be difficult. Awaiting progress in Br-CSIA to permit dual C-Br isotope approach

What can be done with Chlorine Isotopes?

- First the stable isotopes are-^{35}Cl (75.77%) and ^{37}Cl (24.23%).
- Standard-SMOW but some disagreement re. absolute ratio of these isotopes in the OW

(SMOW-Standard Mean Ocean Water; OW Ocean Water)

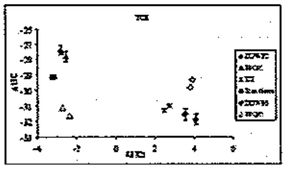
Problems that can be investigated

- As with carbon and hydrogen the two problems that, potentially, can be investigated with chlorine are:
  - Source
  - Natural Attenuation

Chlorine Isotopes

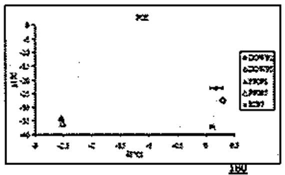
- Heraty et al., (OG., 30, 793-799, 1999) first showed that both chlorine and carbon were enriched in laboratory microbial degradation experiments of dichloromethane (DCM).
- Determination of the kinetic fractionation factors for microbial degradation could be important in distinguishing microbial from abiogenic degradation processes.

Source Differentiation with C and Cl Isotopes

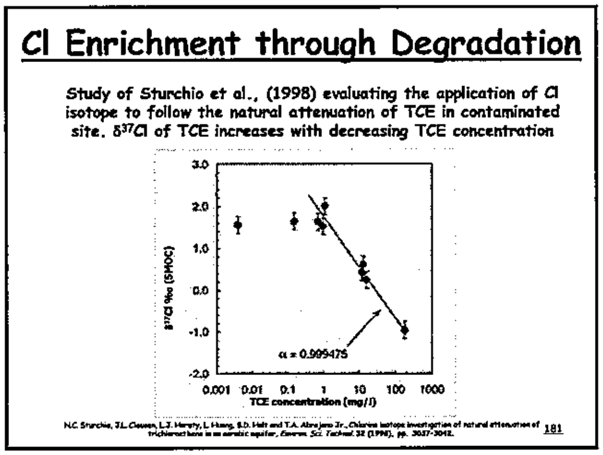


Each compound from each manufacturer show a specific isotopic composition on C and Cl. The variations between years are due to changes in the isotopic composition of products used in the synthesis of PCE and TCE.

The idea was to conduct this kind of survey study with TCE and PCE coming from different manufacturers (DOW, PPG, ICI)...



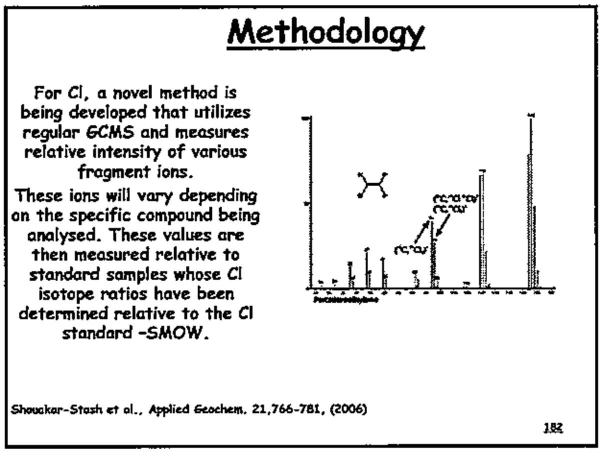
From Beneteau et al., 1999; Warmerdarm et al., 1995



Cl Enrichment through Degradation

Study of Sturchio et al., (1998) evaluating the application of Cl isotope to follow the natural attenuation of TCE in contaminated site. $\delta^{37}Cl$ of TCE increases with decreasing TCE concentration

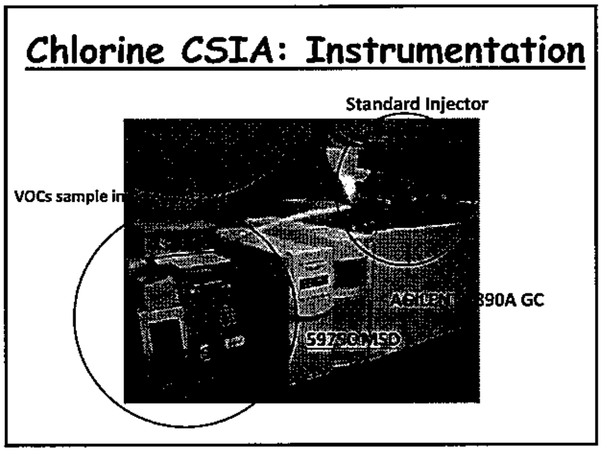
N.C. Sturchio, J.L. Clausen, L.J. Heraty, L. Huang, B.D. Holt and T.A. Abrajano Jr., Chlorine isotope investigation of natural attenuation of trichloroethene in an aerobic aquifer, *Environ. Sci. Technol.* 32 (1998), pp. 3037-3042.



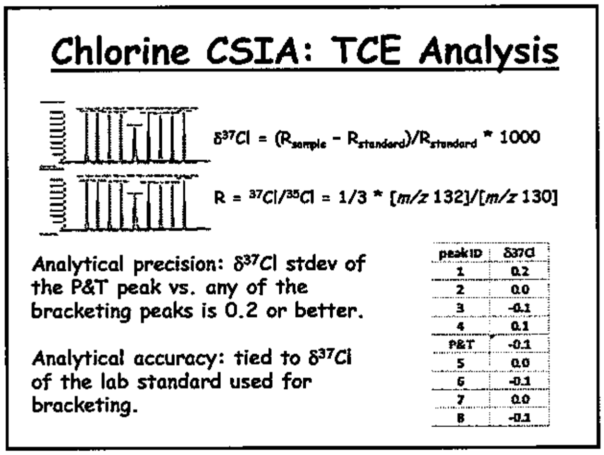
Methodology

For Cl, a novel method is being developed that utilizes regular GCMS and measures relative intensity of various fragment ions.
These ions will vary depending on the specific compound being analysed. These values are then measured relative to standard samples whose Cl isotope ratios have been determined relative to the Cl standard -SMOW.

Shouakar-Stash et al., Applied Geochem. 21,766-781, (2006)



Chlorine CSIA: Instrumentation



Chlorine CSIA: TCE Analysis

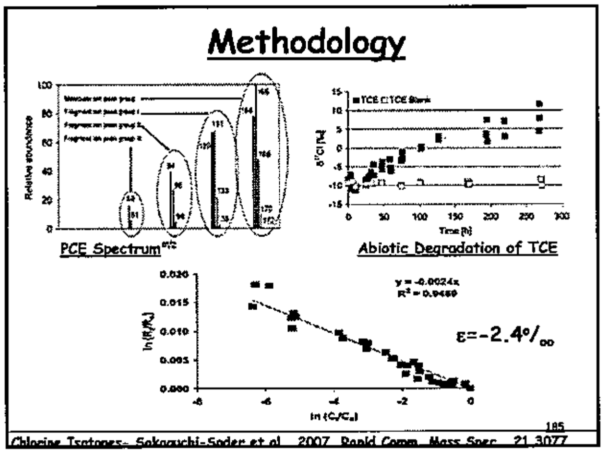
$\delta^{37}Cl = (R_{sample} - R_{standard})/R_{standard} * 1000$

$R = {}^{37}Cl/{}^{35}Cl = 1/3 * [m/z\ 132]/[m/z\ 130]$

Analytical precision: $\delta^{37}Cl$ stdev of the P&T peak vs. any of the bracketing peaks is 0.2 or better.

Analytical accuracy: tied to $\delta^{37}Cl$ of the lab standard used for bracketing.

peak ID	δ37Cl
1	0.2
2	0.0
3	-0.1
4	0.1
P&T	-0.1
5	0.0
6	-0.1
7	0.0
8	-0.1



Methodology

PCE Spectrum$^{m/z}$

Abiotic Degradation of TCE

ε=-2.4°/oo

Chlorine Isotopes- Sakaguchi-Soder et al 2007 Rapid Comm. Mass Spec. 21 3077

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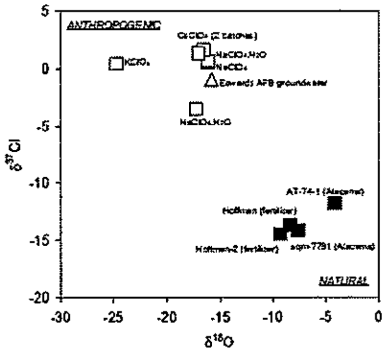
Perchlorate

Perchlorate taints water in 22 states. The main sources of this contamination are users of perchlorate salts: military bases, aerospace installations, and defense contractors that build rockets-such as the Massachusetts Military Reservation on Cape Cod or Lockheed Propulsion in Redlands, Calif., which manufactured rockets. A small amount of perchlorate pollution in the U.S. is believed to have stemmed from a sodium nitrate fertilizer made in Chile.
Since 1992, EPA has recommended safe levels ranging from 4 to 18 ppb
Perchlorate can cause adverse effects by blocking the uptake of iodine by the thyroid

Perchlorate Problems

- Source-source variability must be characterized first; natural (fertilizer) *vs.* anthropogenic (oxidant)?
- Natural Attenuation (microbial degradation has large (~15‰) KIE for Cl)

Are Perchlorate Sources Isotopically Distinct?



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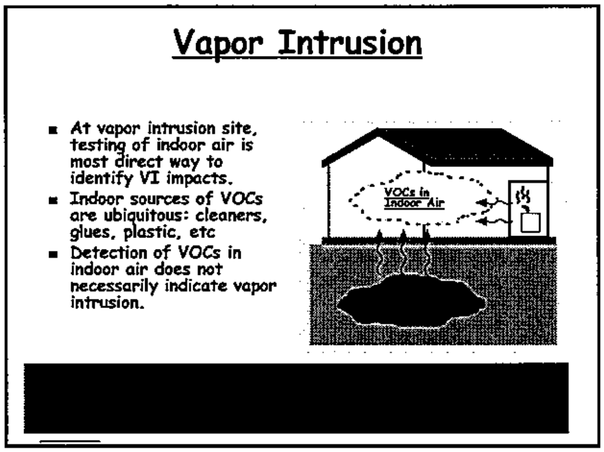
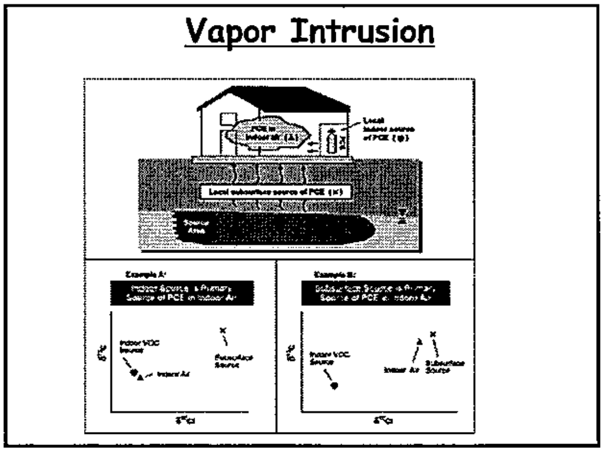


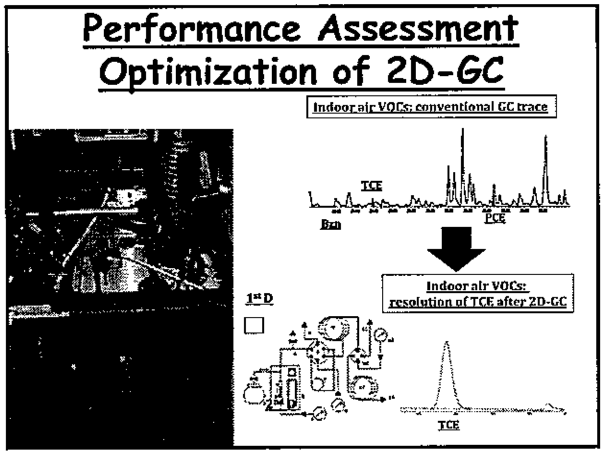
Vapor Intrusion

- At vapor intrusion site, testing of indoor air is most direct way to identify VI impacts.
- Indoor sources of VOCs are ubiquitous: cleaners, glues, plastic, etc
- Detection of VOCs in indoor air does not necessarily indicate vapor intrusion.

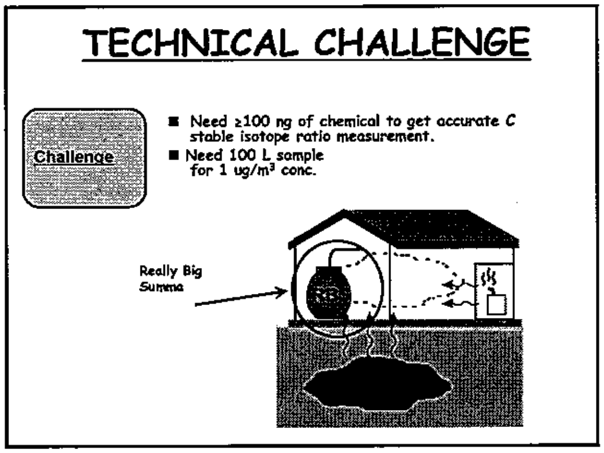
[redacted]



Vapor Intrusion



Performance Assessment Optimization of 2D-GC



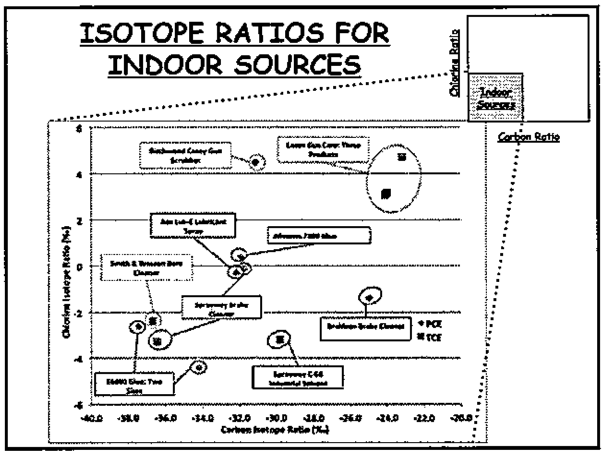
TECHNICAL CHALLENGE

Challenge

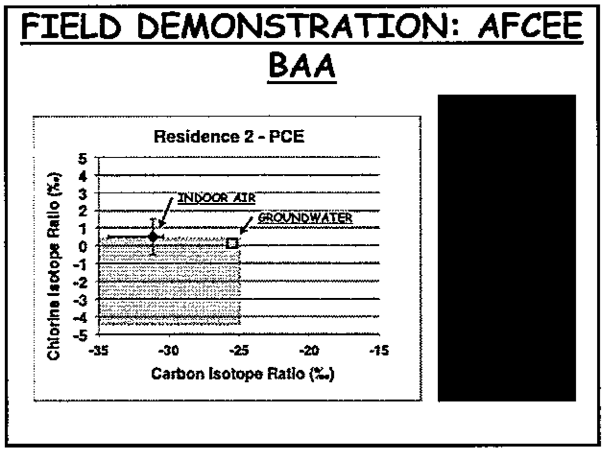
- Need ≥100 ng of chemical to get accurate C stable isotope ratio measurement.
- Need 100 L sample for 1 ug/m³ conc.

Vapor Intrusion

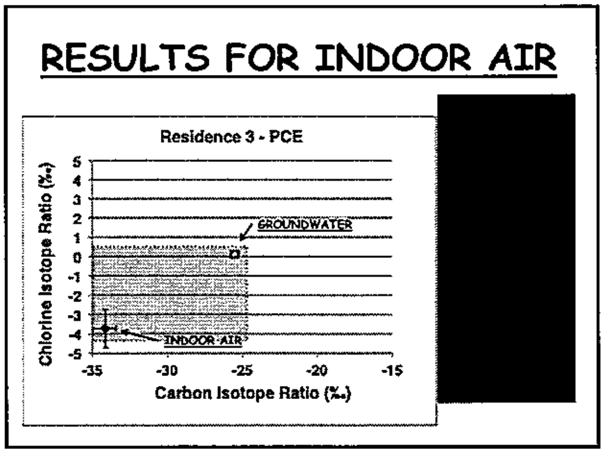
ISOTOPE RATIOS FOR INDOOR SOURCES

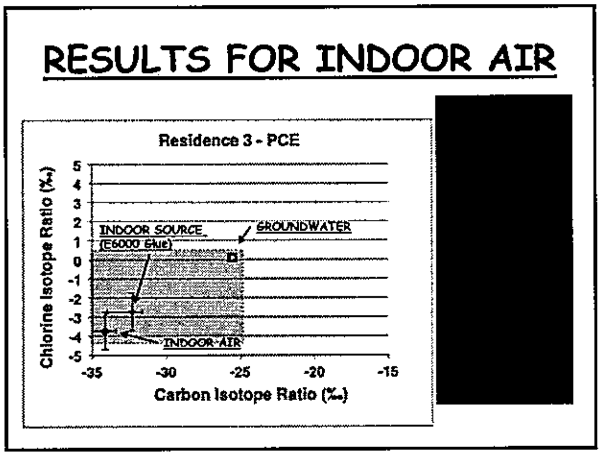


FIELD DEMONSTRATION: AFCEE BAA

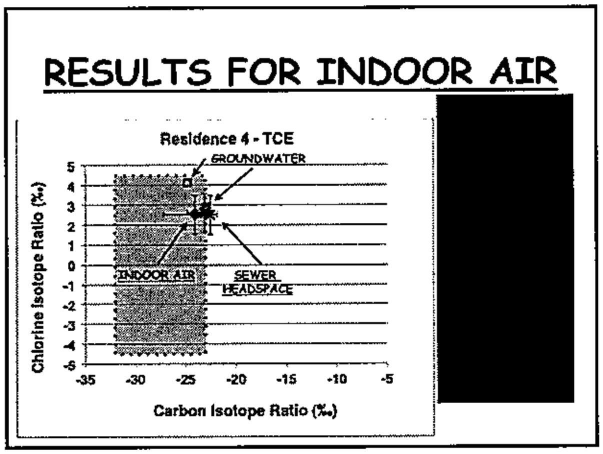


RESULTS FOR INDOOR AIR

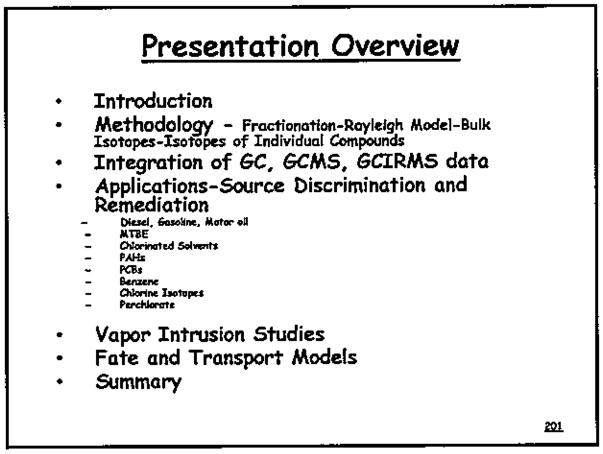




RESULTS FOR INDOOR AIR



RESULTS FOR INDOOR AIR



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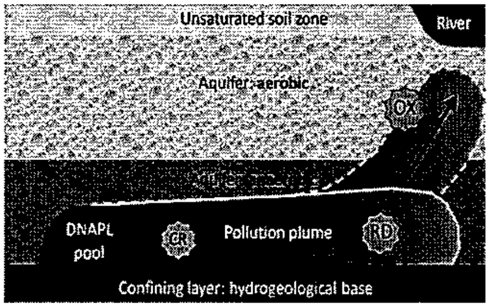
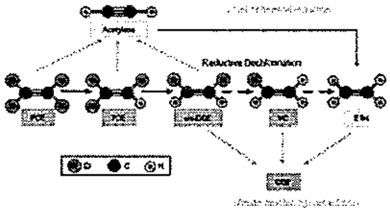
Reactive Transport Model (RTM) Incorporating Isotope Fractionation

- Success and acceptance of MNA depends on strong conceptual site model (CSM) documenting attenuation processes and contaminant mass removal using multiple lines of evidence
- For many sites, decreasing mass, the presence of intermediate degradation products, low oxygen concentrations, and favorable geochemical indicators (e.g., nitrate, sulfate, alkalinity etc.) are sufficient to support selection of a full or partial MNA remedy.
- In the absence of some or all of these lines of evidence, MNA remedies can be difficult to implement.
- CSIA provides strong evidence to support MNA assessment and strengthen CSMs.

Potential Degradation Pathways for Chlorinated Ethenes

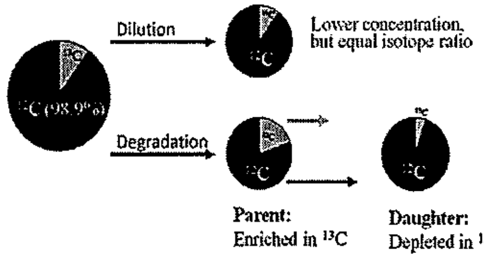


Degradation Pathways of Chlorinated Ethenes



Primary degradation processes in a reaction network for chlorinated ethene degradation. Anaerobic degradation pathway is dominant for most sites with MNA remedies. Each pathway needs to be quantified.

Dilution vs. Dispersion for Chlorinated Ethenes



Technology Description Reactive Transport Modeling of Isotope Fractionation

- RTMs permit simulation of complex reaction networks together with isotopic fractionation and accounting for physical processes such as hydrodynamic dispersion, diffusion, and sorption.
- Identification of prevalent degradation pathways
- More accurate assessment of parent contaminant
- Quantitative assessment of net degradation/accumulation of dechlorination intermediates

RTM Model and Software Platforms

- RTM model and software platforms used to develop modeling tools for CSIA interpretation include:
- PHREEQC - A one dimensional (1D) geochemical transport model developed by the US Geological Survey (USGS).
- PHAST - A three dimensional (3D) groundwater flow and transport model capable of simulating the same set of reactions as PHREEQC. PHAST couples PHREEQC to the groundwater flow and solute transport model HST3D.
- PHT3D - A three dimensional (3D) groundwater flow and transport model capable of simulating the same set of reactions as PHREEQC. PHT3D couples PHREEQC to the groundwater flow model MODFLOW and the solute transport model MT3DMS.
- Python - A general purpose scripting language available for free download. Algorithms written in Python scripts have been developed for this project to visualize output from modeling programs.

Key Parameters for RTMs

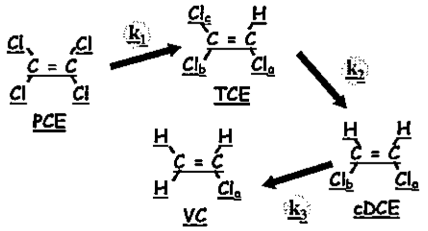
Conceptual Info	- Site history - Key contaminants - Base map	- A good conceptual site model - Source identity and history
Hydrogeologic Data	- Hydraulic conductivity at several locations - Effective porosity - Configuration of the transmissive zone (layers, location of any no-flow boundaries) - Confined vs. unconfined conditions	- Any recharge/discharge zones - Recharge rates to transmissive zone - Hydraulic gradient information - Location, pumping rate of any major wells
Transport Data	- Bulk density of soil in aquifer matrix - Total porosity of soils in aquifer matrix - Fraction organic carbon in aquifer matrix - Partition coefficients	- Estimates of longitudinal and transverse dispersivity - Diffusion coefficient estimates - Tortuosity or effective diffusion coefficients - General ranges of expected degradation coefficients
Reactive Data	- Reaction rates (k) for various CEs under different biogeochemical conditions	- Isotope fractionation factors (α)
Contaminant Data	- Decay chain for the contaminants of interest - Parent compound concentration at multiple locations and multiple times - Daughter compound concentration at multiple locations and multiple times	- Carbon isotope (13C) data at multiple locations (probably 10 or more) for at least one sampling event. - Chlorine isotope (Cl) data at multiple locations (probably 10 or more) for at least one sampling event. - Hydrogen isotope data (optional)

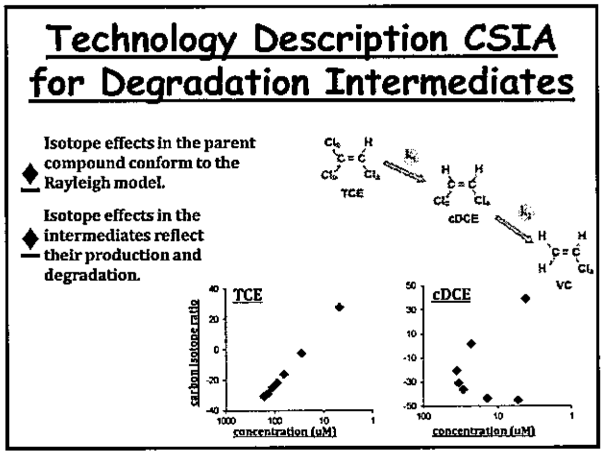
Technology Description Reactive Transport Modeling of Isotope Fractionation

- A standard reactive transport model predicts concentrations of a contaminant degrading in a hydrogeologic transport network
- To predict isotope ratios, ^{13}C and ^{12}C are modeled as separate species
- $^{13}C/^{12}C$ is obtained from absolute concentrations of the isotopic species integrated at specific XYZ coordinates
- The ^{13}C and ^{12}C kinetic degradation constants are determined by calibration of the model (best fit to the calibration data)

Technology Description Sequential Dechlorination

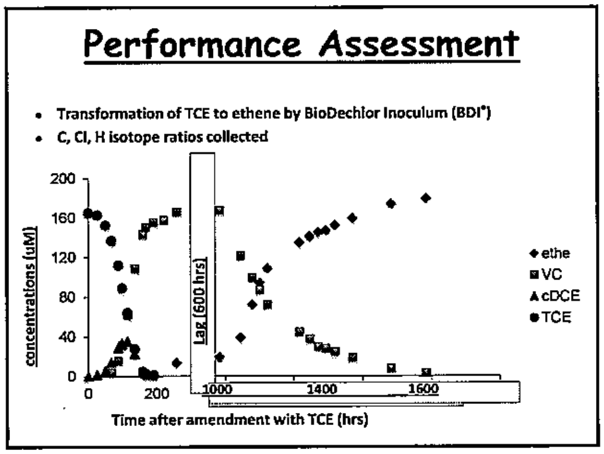
Net isotope effects of intermediates reflect their production and degradation.





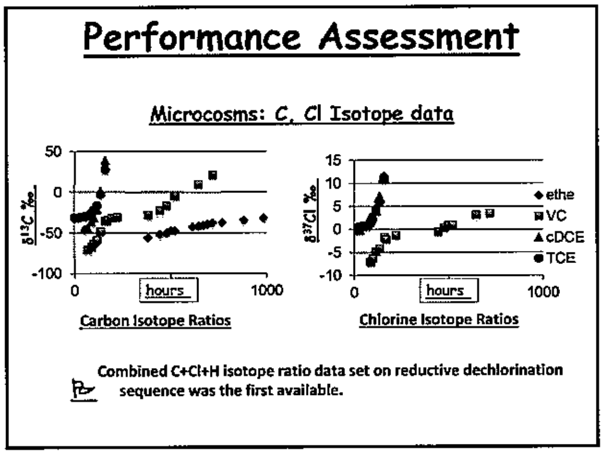
Technology Description CSIA for Degradation Intermediates

- Isotope effects in the parent compound conform to the Rayleigh model.
- Isotope effects in the intermediates reflect their production and degradation.



Performance Assessment

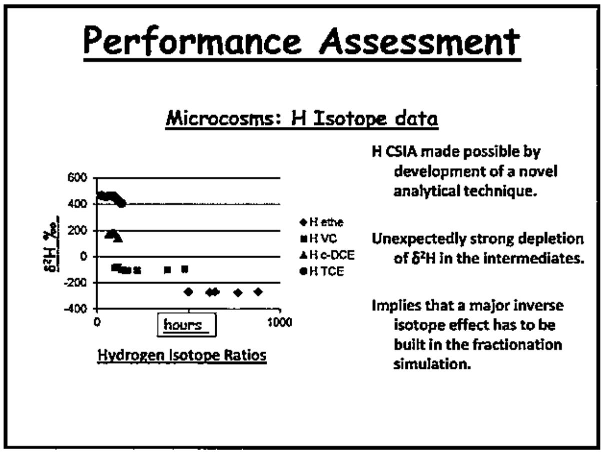
- Transformation of TCE to ethene by BioDechlor Inoculum (BDI®)
- C, Cl, H isotope ratios collected



Performance Assessment

Microcosms: C, Cl Isotope data

Combined C+Cl+H isotope ratio data set on reductive dechlorination sequence was the first available.

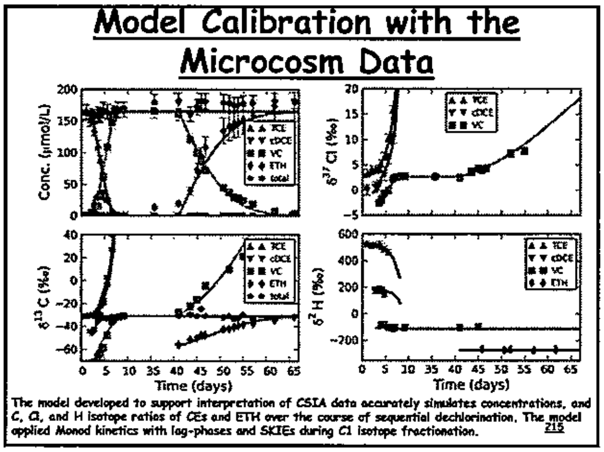


Performance Assessment

Microcosms: H Isotope data

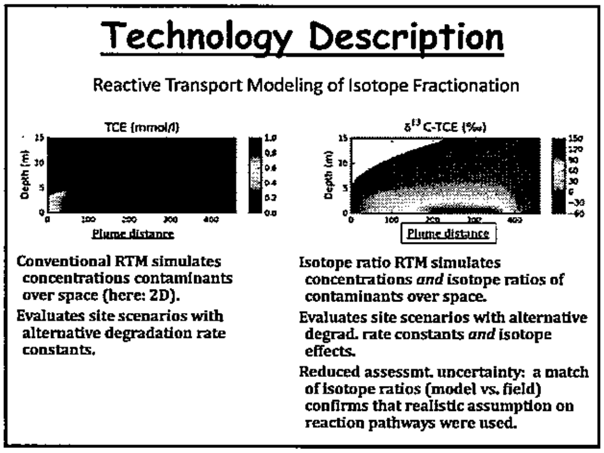
Hydrogen Isotope Ratios

- H CSIA made possible by development of a novel analytical technique.
- Unexpectedly strong depletion of δ^2H in the intermediates.
- Implies that a major inverse isotope effect has to be built in the fractionation simulation.



Model Calibration with the Microcosm Data

The model developed to support interpretation of CSIA data accurately simulates concentrations, and C, Cl, and H isotope ratios of CEs and ETH over the course of sequential dechlorination. The model applied Monod kinetics with lag-phases and SKIEs during Cl isotope fractionation. 215



Technology Description

Reactive Transport Modeling of Isotope Fractionation

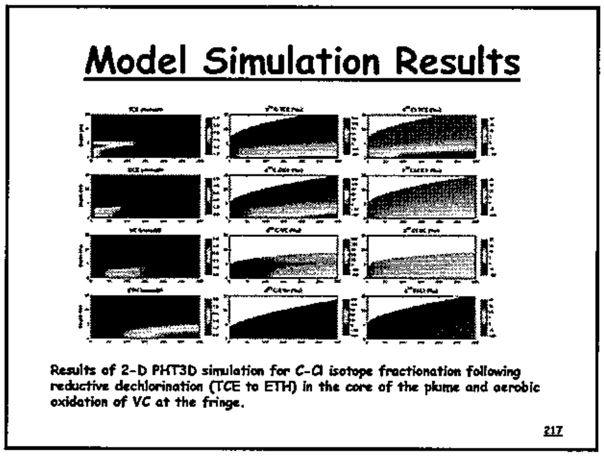
Conventional RTM simulates concentrations contaminants over space (here: 2D).

Evaluates site scenarios with alternative degradation rate constants.

Isotope ratio RTM simulates concentrations *and* isotope ratios of contaminants over space.

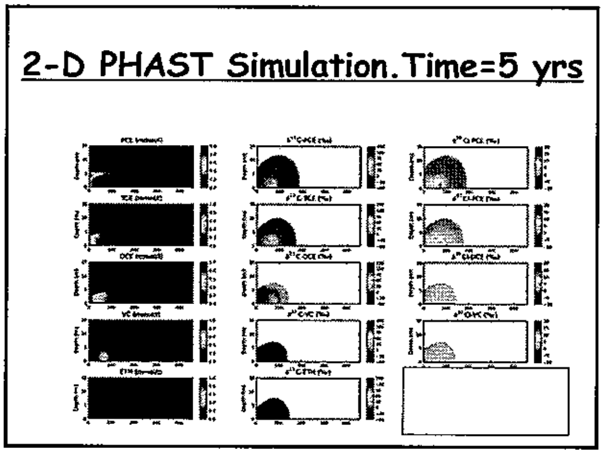
Evaluates site scenarios with alternative degrad. rate constants *and* isotope effects.

Reduced assessmt. uncertainty: a match of isotope ratios (model vs. field) confirms that realistic assumption on reaction pathways were used.

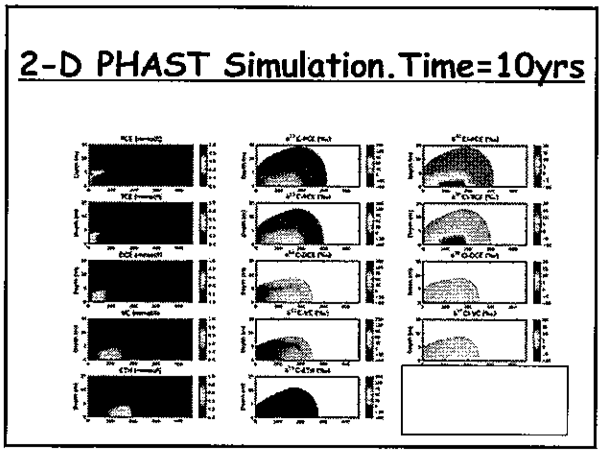


Model Simulation Results

Results of 2-D PHT3D simulation for C-Cl isotope fractionation following reductive dechlorination (TCE to ETH) in the core of the plume and aerobic oxidation of VC at the fringe.

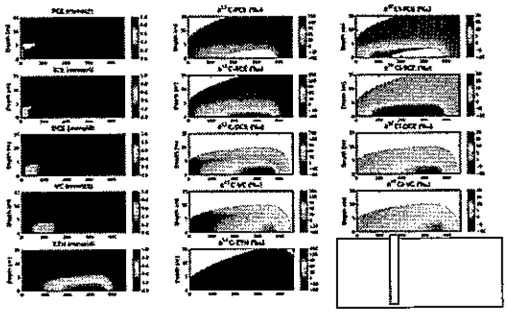


2-D PHAST Simulation.Time=5 yrs



2-D PHAST Simulation.Time=10yrs

2-D PHAST Simulation.Time=20 yrs



SUMMARY

- Stable isotopes provide a powerful complimentary tool for the correlation of spilled products in the environment with suspected sources.
- Can be used to evaluate onset of natural attenuation and extent of degradation.
- Isotopes can play a valuable role in remediation studies in furthering the understanding of degradation mechanisms.
- Can distinguish biogenic, abiogenic mechanisms from non-degradative processes causing concentration changes.

SUMMARY

- GC and GCMS already widely used techniques in forensic geochemistry
- For refined products, or those not containing biomarkers, need an alternative approach
- Stable isotopes (C,H, and Cl) of individual compounds are, and will continue to develop as, extremely important tools for forensic studies