

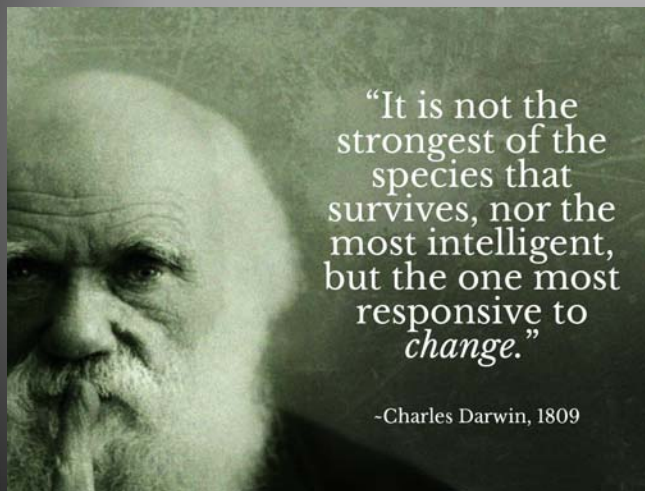
Darwinian Remediation – The Evolution of Remedial Technologies and the Survival of the Fittest

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1

Adapt or Die



2

In the Beginning.....

- Environmental rules & regulations initially developed in the 1970s (Clean Water Act, Clean Air Act, etc.)
- Many hazardous sites identified that required cleanup
- Engineers/Scientists assigned the task



3

The Simplest Solution



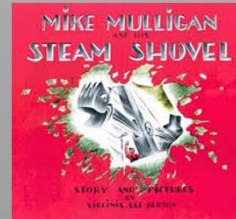
- Soil Excavation
- Still a viable option in source areas
- Problem – does not eliminate contamination, only risk



4

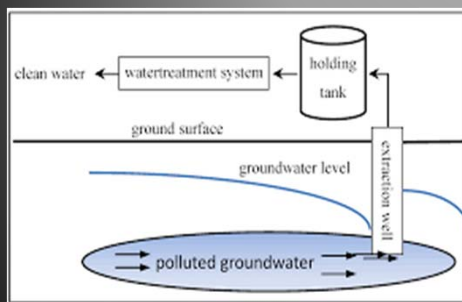
Soil Excavation – Moderation is the Key

Only excavate those soils that are significantly impacted and continuing to act as a source for impacting groundwater and/or vapor intrusion.



5

“But We Have All This Impacted Groundwater!”



▶ Pump-and-treat (P&T) – install pumping wells, remove the impacted groundwater, treat it to remove the chemicals, and discharge it.

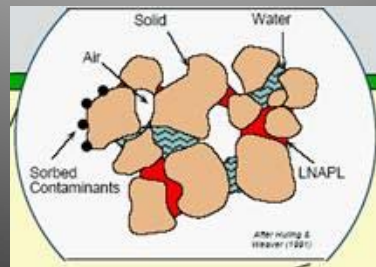
▶ Clean water will replace the impacted water and the site will be cleaned up – right?

6

Groundwater Pump-and-Treat

Seemed like a simple, straightforward solution, but.....

P&T always becomes “diffusion limited”

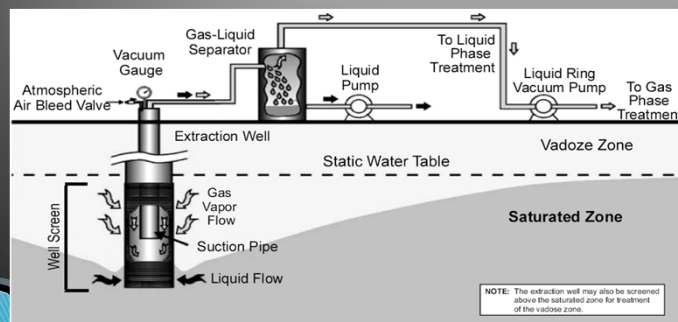


7

“So We’re Pumping All This Water and the Site Isn’t Cleaning Up – Now What?”

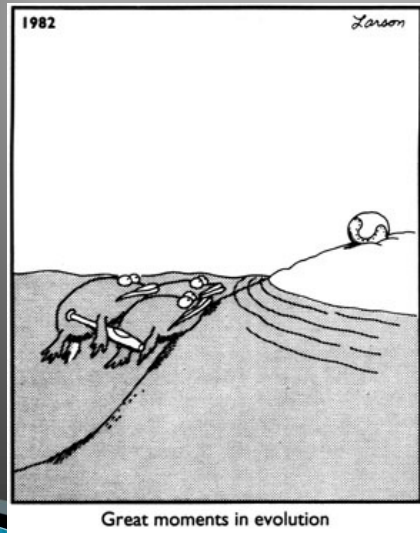


- ▶ Bright idea – removing the water and passing air through the dewatered soil to remove adsorbed material – dual-phase extraction (DPE)



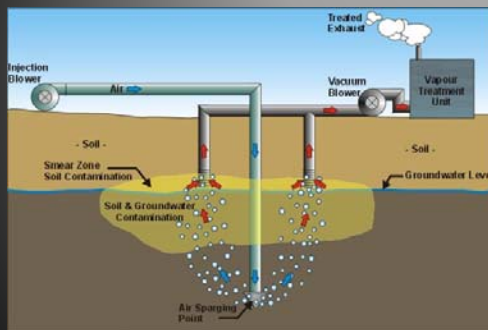
8

We Still Have a Lot of Water to Deal With – There Must Be a Better Way



9

Air Sparging/Soil Vapor Extraction (AS/SVE)



► **Air Sparging** – introducing air below the water table to volatilize contaminants

► **Soil Vapor Extraction (SVE)** – removing the sparged vapors and treating them before discharging to the atmosphere

Does anyone still see a potential issue?

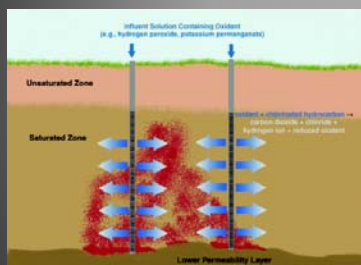
10

MECHANICAL SYSTEMS WILL
ALWAYS BECOME DIFFUSION-
LIMITED!!!



11

What If We Invade and Attack Them in Their Homes?



"It's a contact sport"

- ▶ In-Situ Chemical Oxidation (ISCO)
- ▶ Injection of aggressive chemicals to promote oxidation of contaminants
- ▶ Contact-based approach – injection materials must physically contact contaminants

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“Curse That Diffusion!”

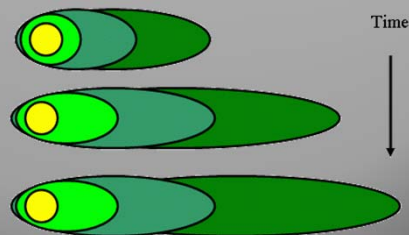
- ▶ ISCO only feasible in high-permeability soils
- ▶ Prone to “channeling” which still creates a diffusion-limited situation



13

And Then Someone Noticed.....

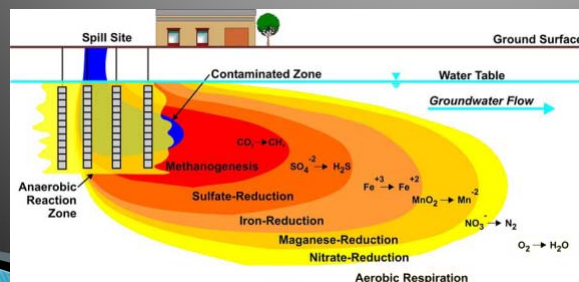
- ▶ Groundwater modeling at a number of sites did not match the actual dimensions of the plumes
- ▶ What could be causing this phenomenon?



14

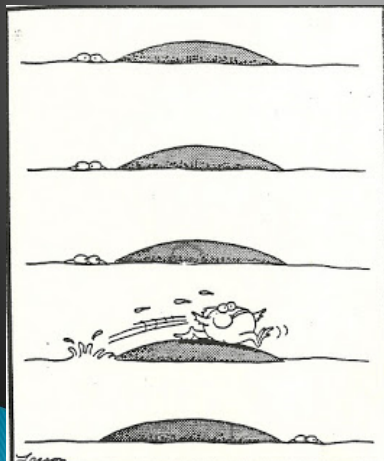
Biodegradation

Naturally occurring in most, if not all, petroleum sites
Eventually, migration = degradation and plume is stable
Remove source and plume will eventually remediate itself



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“But It Takes Too Long for Natural Attenuation to Work – I Don’t Have That Kind of Time”



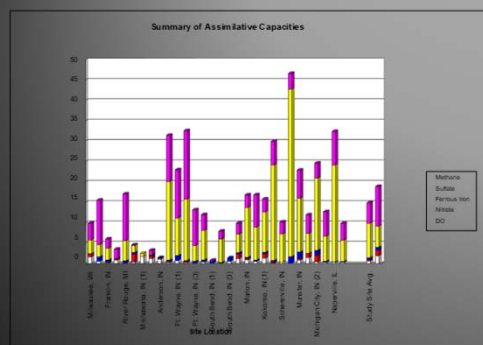
“In the long history of humankind, those who learned to collaborate and improvise most efficiently have prevailed” – Charles Darwin

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- ▶ Adding oxygen (aerobic) or chemicals/bacteria (anaerobic) to accelerate degradation
- ▶ Not diffusion limited because bacteria are mobile



Natural (Unenhanced) Petroleum
Biodegradation is Typically Anaerobic –
Much Slower for Petroleum than Aerobic

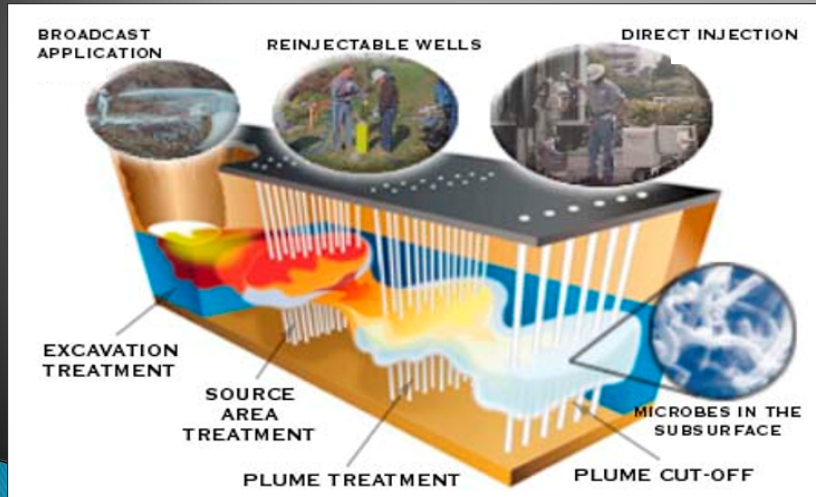


- ▶ Most of natural attenuation is methane (purple) & sulfate (yellow) reduction

Figure 2. Summary of Assimilative Capacity

9

In-Situ Enhanced Bioremediation Application Options



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Aerobic Biodegradation (Oxygen Addition)

Primarily applicable to Petroleum Hydrocarbons
Can also be effective for Vinyl Chloride

Case History O-9



Surgical Site Closure – 30 Sites in Indiana Receive Closure using ORC®

CASE SUMMARY

Surgical Site Closure

"Surgical Site Closure" is an innovative remedial strategy designed to intelligently integrate natural attenuation, risk-based cleanup goals and focused source removal/treatment to cost-effectively remediate contaminated areas. This approach is best applied at sites where released materials are amenable to biodegradation and where long-term, natural attenuation-type strategies are not suitable for reasons of property transfer or potential off-site liability. This strategy was performed at 30 sites in Indiana for a major oil company.

Service Stations/Bulk Storage Terminals – Indiana

From 1998-2008, a total of 30 service station/bulk storage terminal sites were targeted for Surgical Site Closure in Indiana. The subsurface matrix consisted of unconsolidated sediments ranging from low-permeability silty clays with sand stringers to sand and



Figure 1. Site Closures in IN



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Aerobic Bio Case History Summary

- ▶ 30 Sites (1998 – 2008)
- ▶ 30 of 30 (100%) rec'd NFA (last one 4/08)
- ▶ Average time to closure: 3 years
- ▶ Average cost to closure: \$70,000

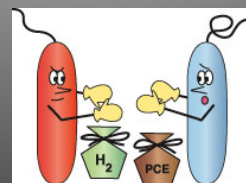


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Chlorinated Hydrocarbon Degradation



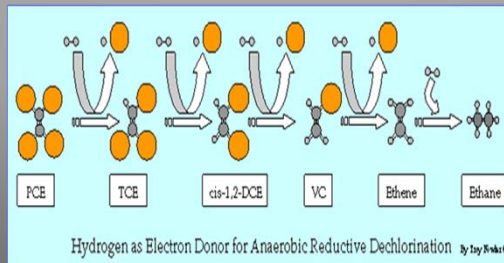
- ▶ Occurs under **anaerobic** conditions
- ▶ Most Midwestern sites have **aerobic** conditions



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Anaerobic Biodegradation (also known as Enhanced Reductive Dechlorination, or ERD)

Introduction of
substrates/bacteria
into the water-
bearing zone to
create an anaerobic
environment and
provide electron
donors (hydrogen)



Beware
of
Dog



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Case History – Manufacturing Facility – Northern Indiana

Problem

- Dissolved Plume emanating from former AST area
- ISCO approach proposed initially – difficult to inject and more costly

Solution

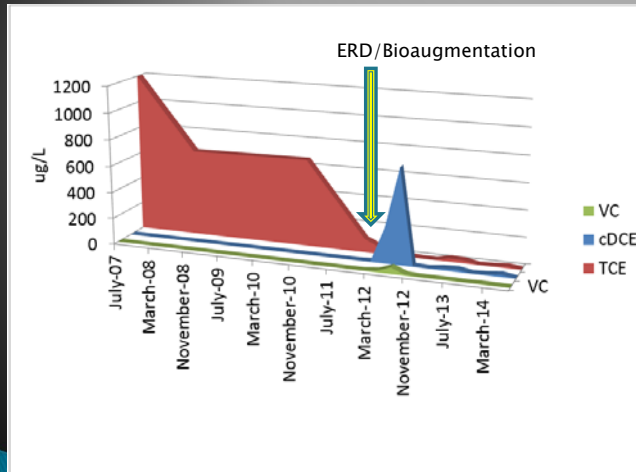
- IDEM–mandated ERD pilot test followed by full scale injection of electron donor and bioaugmentation substrate



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Case History – Manufacturing Facility – Northern Indiana

MW-4 (Source Area Well) – Pilot



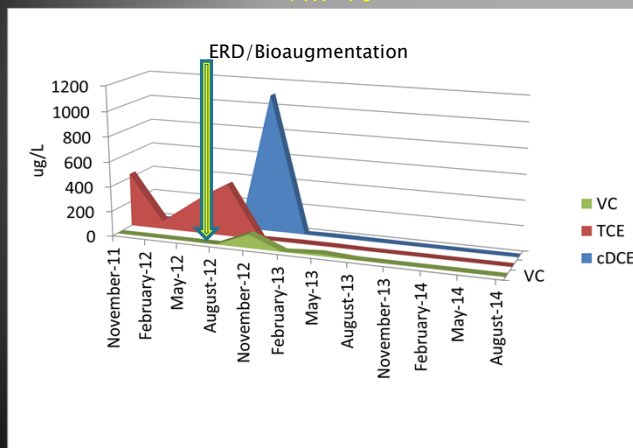
Site Details

- ▶ 13,000 square foot injection area
- ▶ TCE 40–600 ppb
- ▶ Geology: Fine-medium sand; DTW 15–20' bgs
- ▶ Products: 3DMe, BDI-Plus

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Case History – Manufacturing Facility – Northern Indiana

MW-16



Site Details

- ▶ 13,000 square foot injection area
- ▶ TCE 40–600 ppb
- ▶ Geology: Fine-medium sand; DTW 15–20' bgs
- ▶ Products: 3DMe, BDI-Plus

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Manufacturing Facility – Northern Indiana

Results

- Pilot study demonstrated to regulatory agency that ERD would work quickly and effectively
- Full-scale injection resulted in dramatic reductions within 6 months of the ERD treatment. Continued reductions with time
- After 3 years of monitoring, all wells achieved target cleanup levels
- Closure received Feb. 2016 (3 ¼ years after full-scale injection)

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Success!



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ERD Performance Review – 8 Sites

Details

- 8 Sites (4 Industrial, 4 Dry Cleaners)
 - Reviewed Total of 36 Performance Monitoring Wells Within Treatment Areas
- Chlorinated Solvent Average Starting Concentrations of Performance Wells
 - PCE Avg. = 2.7 mg/L
 - TCE Avg. = ~0.6 mg/L
 - Cis-DCE Avg. = 0.9 mg/L
 - VC Avg. = 0.2 mg/L
- Variable Geology (Sand – 4 sites; Sand Lenses – 4 sites)
- Risk-Based Closure Goals (Com/Ind)



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ERD Performance Review – 8 Sites

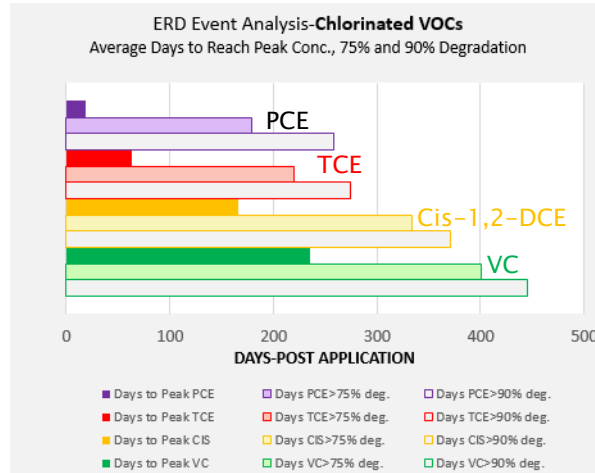
Details

- Grid arrays – ranging from 10 ft spacing to 20' x 50'
- Projects with >1 year of Data
- Injection Areas: 1,000 to 66,000 sq. ft.
- 3DMe Injected: 1,300 to 48,000 gallons–solution 10%–25%.
- BDI Plus Injected: 18 to 170 Liters
- Focused Supplemental Injections
 - Average 30% of initial injection



30

Question #1 – How Long Does ERD Take? ERD Performance Review – 8 Sites

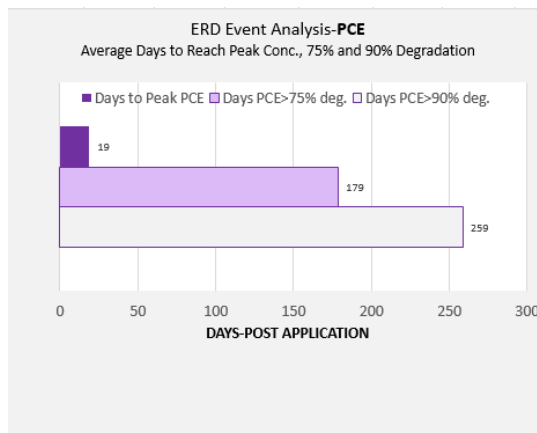


Explanation of Parameters

- **Peak PCE/TCE/CIS/VC** = Days after application when maximum (peak) concentration was detected
- **75% Reduction** = days after application when 75% concentration reduction metric was reached (from maximum)
- **90% Reduction** = days when 90% reduction metric was reached (from maximum)

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Question #1 – How Long Does ERD Take? ERD Performance Review – 8 Sites

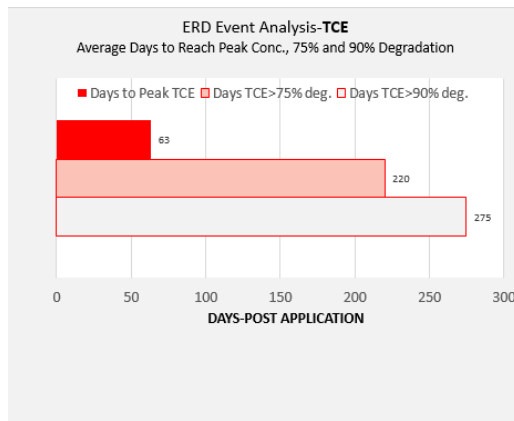


PCE

- PCE Elimination 180 to 260 days on average
- 160 to 240 days from peak

32

Question #1 – How Long Does ERD Take? ERD Performance Review – 8 Sites

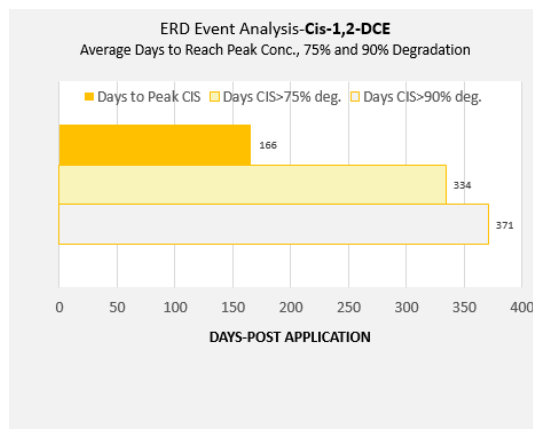


TCE

- TCE Elimination 220 to 275 days on average
- 160 to 210 days after peak (max. conc.)

33

Question #1 – How Long Does ERD Take? ERD Performance Review – 8 Sites

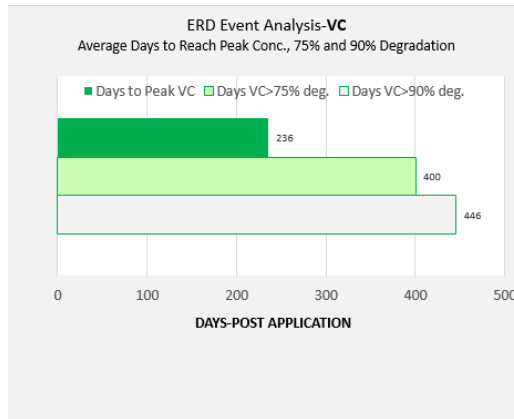


Cis-DCE

- Cis-DCE Elimination 330 to 370 days on average
- 170 to 200 days after peak

34

Question #1 – How Long Does ERD Take? ERD Performance Review – 8 Sites

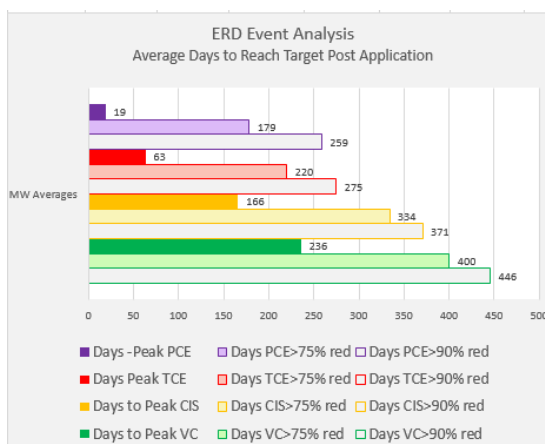


VC

- VC Elimination 400 to 405 days on average
- 170 to 210 days after peak
- Complete ERD – Once you've eliminated VC you are done!!

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Question #1 – How Long Does ERD Take? ERD Performance Review – 8 Sites



Summary of Observations

- Each constituent degraded approximately 6 months after peak – strikingly consistent on average
- Looking at PCE timeframes will give you early indication of likelihood for success
- Use Proactive Monitoring. Spot any “dogs” early, then respond quickly!!

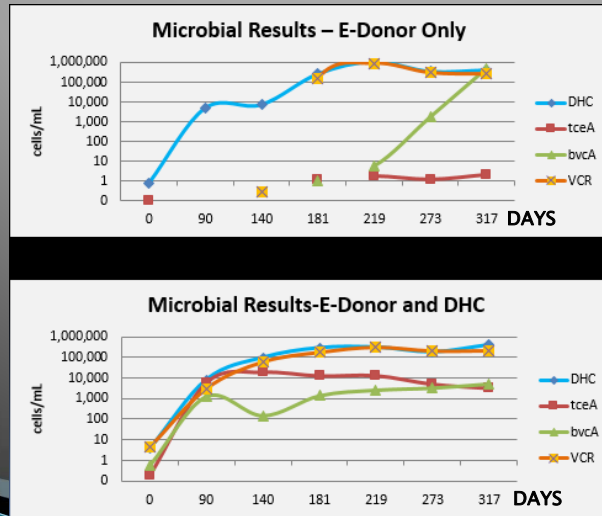
36

Key to Success: Co-application of Donor and DHC at Outset-Why?

Pilot test—two areas—
NW IN Site:

- 1-E-Donor Only
- 1-E-Donor + DHC

- DHC populations is similar for two cells over time
- Functional genes *tceA*, *bvcA* and VCR populations much more robust early on
- Note >6 month lag time for these in E-Donor only cell!

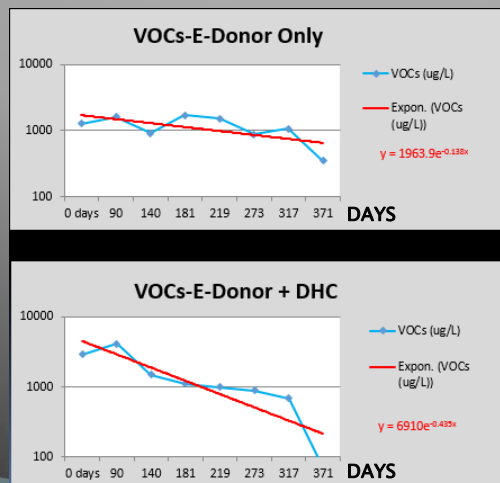


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Co-application of Donor and DHC at Outset-Why?

Answer = Results!

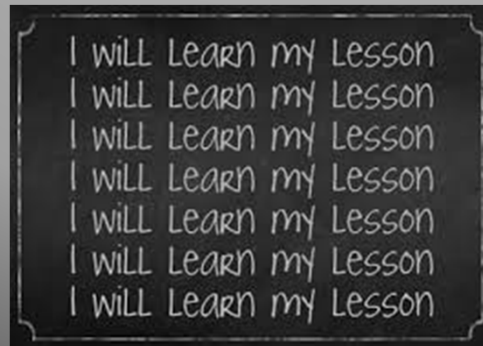
- Faster Degradation Rates
- ~3X VOC degradation rate increase over 1 year



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Lessons Learned

- ▶ Well Defined CSM is KEY
- ▶ Good Data = Good Design = Good Application
- ▶ Bioaugmentation is almost always beneficial
- ▶ ERD happens quickly
- ▶ Be **aggressive** with supplemental injections. If needed go early.



The Formula: Donor + DHC + Distribution = Success!

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Liquid Activated Carbon (LAC) – A New Enhancement to Biodegradation



PetroFIX
Remediation Fluid

40

LAC – A Promising New Approach

- ▶ Captures and biodegrades a wide range of contaminants
- ▶ Distributes widely under low injection pressures
- ▶ Stops contaminant migration
- ▶ Addresses back-diffusion
- ▶ Promotes long-term biodegradation as well as continued capture



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A Brief Case History

- ▶ Former petroleum bulk plant site in northern Indiana
- ▶ Historical releases from both ASTs and USTs
- ▶ Previous remedial attempts (2005–2009) using AS/SVE
- ▶ Widespread, high-level dissolved-phase impacts (10,000 – 50,000 ppb total petroleum VOCs)
- ▶ High-permeability aquifer



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Liquid AC Pilot Test

- ▶ Performed around 1 well with approx. 30,000 ppb total petroleum VOCs
- ▶ 2,000 lbs. PetroFix injected into 12 points
- ▶ Results:
 - 1 mo. – ND for VOCs
 - 3 mo./6 mo. – 99.99% removal maintained despite continued impact from upgradient
 - Microbial activity confirmed to be increasing



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Remedial Plan



- ▶ Liquid AC (PetroFix, mfg. by RegenesiS) barriers in multiple areas (6 total)
- ▶ 1,600 – 6,000 lbs. of PetroFix per area
- ▶ ISCO/Enhanced Bio in one area
- ▶ Injected uniformly from 17–25 feet
- ▶ Injection completed April 2019

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Preliminary Results (2 months post-injection)

Total VOC Concentration (ppb)

	<u>Pre-Inj.</u>	<u>Post-Inj.</u>
PMW-29	15,700	115
PMW-30	4,100	ND
PMW-31	2,000	300
PMW-32	5,700	ND
PMW-34	6,800	70
PMW-35	30,000	10

PMW-37* 41,400 20,100

*PersulfOx/ORC-A injection area

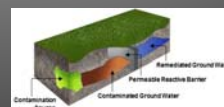
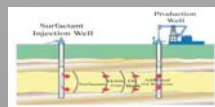
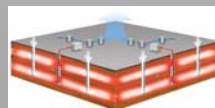
Only one PetroFix area (PMW-25) where no significant reductions occurred (yet)



45

Other (Expensive) Technologies

- ▶ Steam-enhanced extraction
- ▶ Surfactant injection/Extraction
- ▶ Thermal Desorption
- ▶ Permeable Reactive Barriers ("containment only in most cases")



46

Vapor Intrusion (VI) Issues



- ▶ Of primary concern for chlorinated solvents (or free-phase petroleum)
- ▶ VI has become the driver at many sites
- ▶ In general, vapor mitigation is **NOT** remediation

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Vapor Mitigation

Includes both passive and active systems

PASSIVE

- ▶ Sealing
- ▶ Vapor barriers (pre- and post-construction)
- ▶ Passive venting

ACTIVE

- ▶ Sub-slab depressurization
- ▶ Building overpressurization



Sub-slab depressurization system

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And On Top of All That...



“The Proverbial Dirt-Eating Kid”

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Protect Your Liability, But Don't Be a Victim of Pointless Remediation

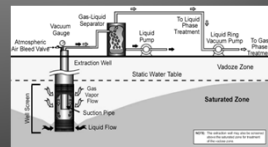
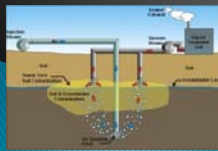
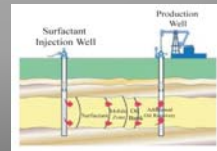
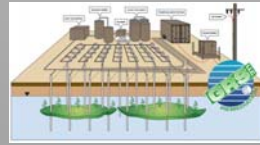


“We are not here to clean up the environment, we are here to close sites”



50

“So How Do I Know What’s Best for My Site?”



51

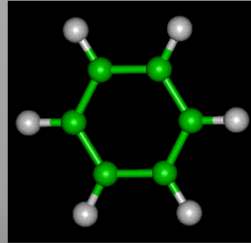
1. Identify Your True Risks and Manage Them Accordingly



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2. Understand the Physical Properties of the Chemical(s) to be Remediated

- ▶ VOCs (BTEX/MTBE; PCE; TCE, etc.) are volatile, mobile, and biodegradable
- ▶ Most PAHs are adsorptive, non-volatile, and relatively immobile
- ▶ Metals and PCBs are very highly adsorptive with very low mobility



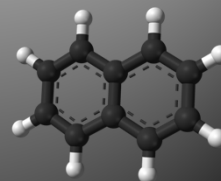
Benzene



PCE



PCB



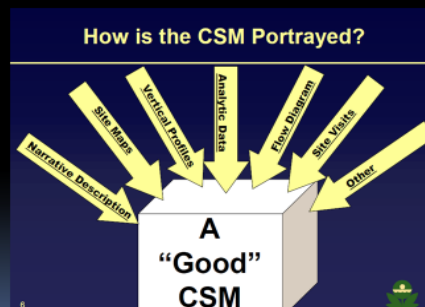
Naphthalene

53

3. Develop an Accurate CSM

Key to Success – Designing to A Well Defined Conceptual Site Model

- Geology/Hydrogeology
- Nature & Extent of Soil/GW Impacts
- Limitations
 - Depth of impacts
 - Buildings/utilities
 - Operations
- Remedial Goals



*http://www.epa.gov/osw/hazard/correctiveaction/pdfs/workshop/csm_slides.pdf

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4. Know The Benefits & Limitations of Various Remedial Technologies

Soil Excavation – still good for focused source removal

P&T/DPE – only really useful for free product recovery or capture/containment

AS/SVE – only for volatile compounds in permeable formations and if plume too large for an injection approach



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Know The Benefits & Limitations of Remedial Technologies

ISCO – primarily for rapid mass removal in source areas

Enhanced Bio – often a viable option if applied properly

Liquid Activated Carbon/Enhanced Bio – a promising new approach



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Know The Benefits & Limitations of Remedial Technologies

Other Approaches

- Steam-enhanced extraction
- Surfactant-enhanced extraction
- Thermal desorption

Very costly – handle with care!!!

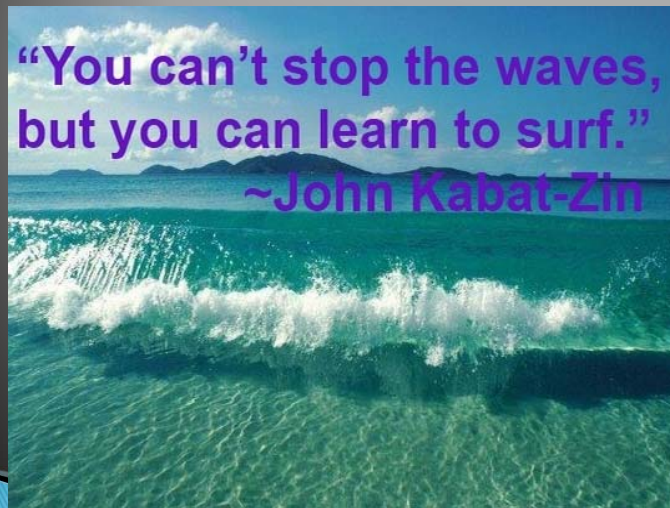
Permeable reactive barriers – containment only



57

Contaminated Sites Will Happen – Deal With Them Cost-Effectively

**“You can’t stop the waves,
but you can learn to surf.”**
~John Kabat-Zin



58

5. Always Choose a Trusted, Experienced Partner



"I am not apt to follow blindly the lead of other men" – Charles Darwin



THINK OUTSIDE THE BOX

