APPLICATION OF TIME-RELEASE ELECTRON DONORS AND ELECTRON ACCEPTORS FOR ACCELERATED BIOREMEDIATION

S. Koenigsberg, S. Mullin, and A. Willett
[1] *Regenesis, IO11 Calle Sombra, San Clemente, CA 92673; Phone: (949)366-8000; Fax: (949)366-8090.*

ABSTRACT

There are limited options for cost-effective approaches to remediate soil and groundwater contamination. One technology that has proven its potential involves the use of time-release electron acceptors to accelerate bioattenuation of aerobically degradable compounds and time-release electron donors to accelerate the natural bioattenuation of anaerobically degradable compounds. This technology enjoys its reputation as a sensible strategy for engineering accelerated bioattenuation because it consistently delivers results while 1) minimizing design, capital, and management costs and 2) allowing for the engineering of a low-impact application, invisible-remediation process.

Oxygen Release Compound (ORC®) is proprietary formulation of intercalated magnesium peroxide that slowly releases oxygen for up to a year. This facilitates the aerobic degradation of environmental contaminants including petroleum hydrocarbons, certain chlorinated hydrocarbons, ether oxygenates, and s-triazine herbicides.

Hydrogen Release Compound (HRC®) is a proprietary, food-grade polylactate ester. Upon being deposited into an aquifer, HRC slowly releases lactic acid for one to two years that ferments to hydrogen. Hydrogen donates electrons that drive reductive bioattenuation processes. Compounds degraded by reductive dehalogenation include perchloroethene, trichloroethane, carbon tetrachloride, and their daughter products; pentachlorophenol; and herbicides and pesticides such as dieldrin, dichloropropane, alachlor, and metolachlor. HRC has been used on over 300 sites, which we believe makes it the most widely used electron donor for accelerating bioattenuation.

Key words: HRC, ORC, reductive dechlorination, oxygen, herbicides, pesticides, pentachlorophenol

Application of Time-Release Electron Donors and Electron Acceptors for Accelerated Bioremediation

S. S. Koenigsberg, A. Willett, and S. Mullin
Regenesis, 1011 Calle Sombra, San Clemente, CA 92673, phone: (949) 366-8001, fax: (949) 366-8090, www.regenesis.com

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ORC®
Oxygen Release Compound

A proprietary time release formulation of magnesium peroxide (MgO_2)

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Oxygen Release Compound
Chemistry

- $MgO_2 + H_2O \longrightarrow 1/2\ O_2\uparrow + Mg(OH)_2$
- Extended oxygen release profile (6-12 months)
- $Mg(OH)_2$ – a safe end product
- Mg compounds are insoluble

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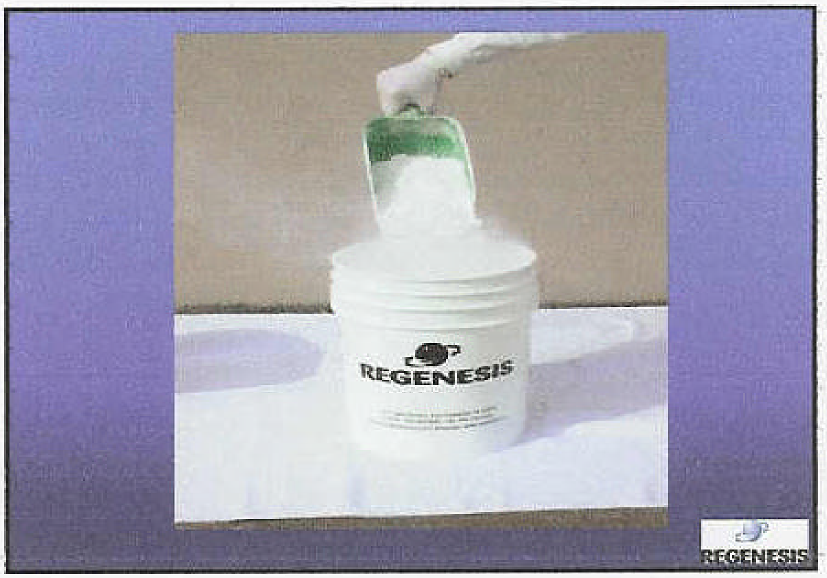
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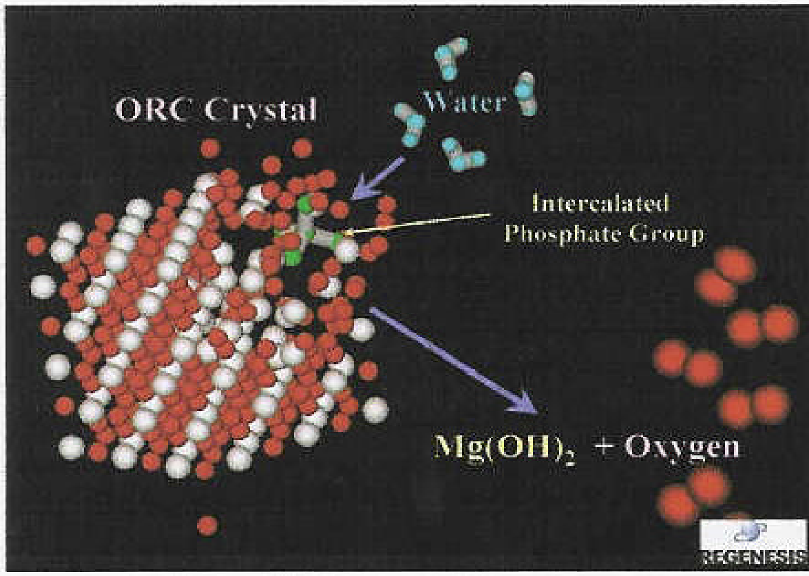
ORC Crystal
Water
Intercalated
Phosphate Group
$Mg(OH)_2$ + Oxygen
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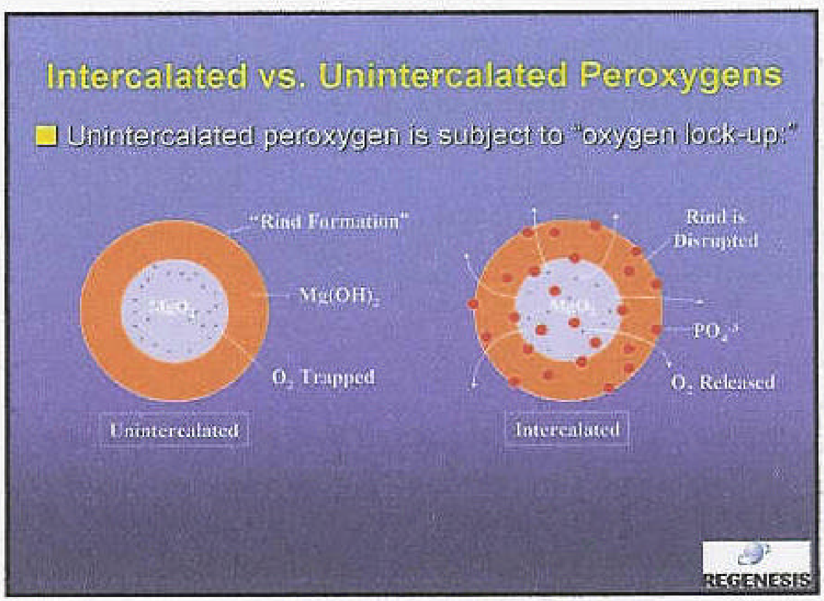
Intercalated vs. Unintercalated Peroxygens
Unintercalated peroxygen is subject to "oxygen lock-up:"
"Rind Formation"
$Mg(OH)_2$
O_2 Trapped
Unintercalated
Rind is
Disrupted
PO_4^{-3}
O_2 Released
Intercalated
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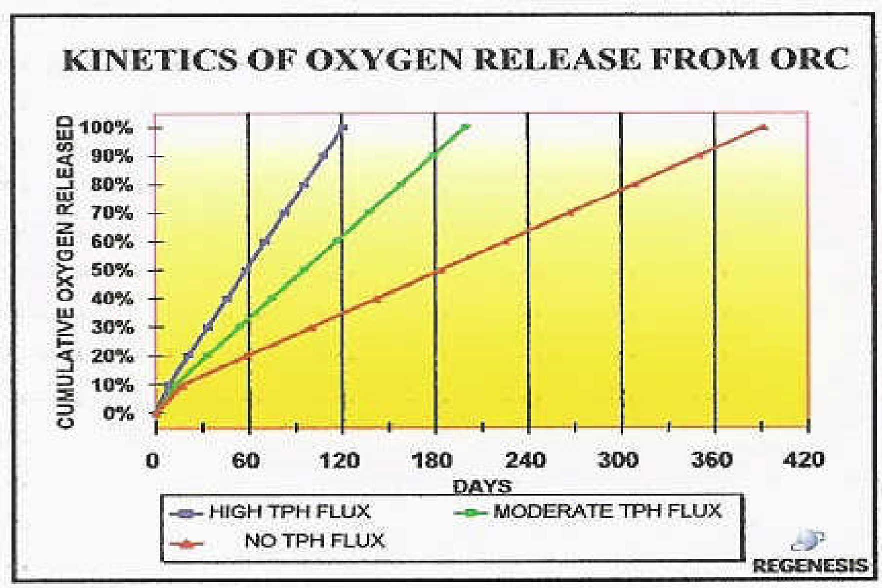
KINETICS OF OXYGEN RELEASE FROM ORC
CUMULATIVE OXYGEN RELEASED
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
0
60
120
180
240
300
360
420
DAYS
HIGH TPH FLUX
MODERATE TPH FLUX
NO TPH FLUX
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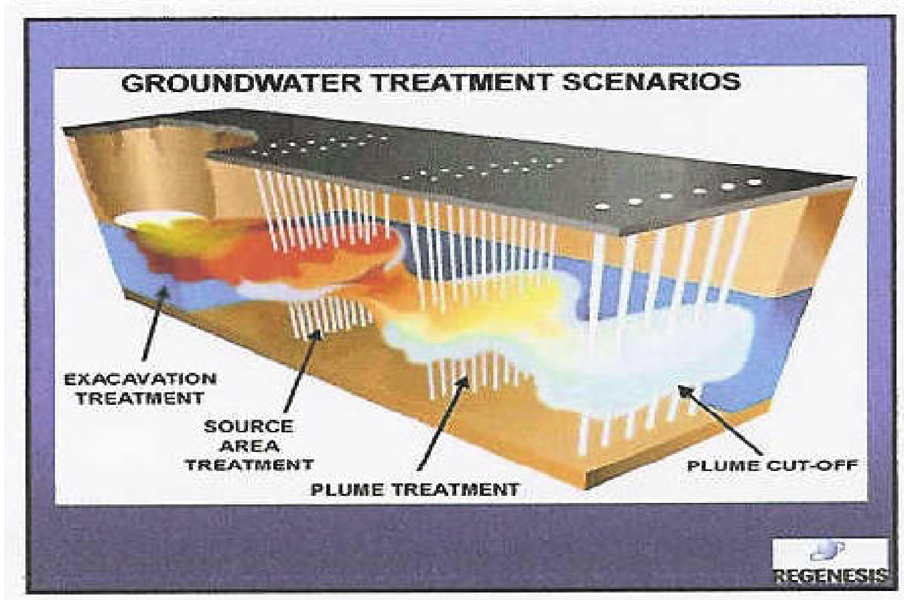
GROUNDWATER TREATMENT SCENARIOS
EXACAVATION TREATMENT
SOURCE AREA TREATMENT
PLUME TREATMENT
PLUME CUT-OFF
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ORC Filter Sock Application
ORC filter socks in 3 sizes
Assembling ORC Socks
Loading a barrier well
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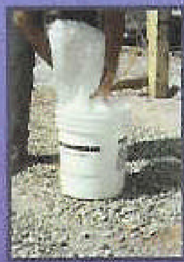
Source Treatment with Slurry Injection Application



ORC powder is mixed with water to form a slurry

ORC slurry is poured into the hopper of a Slurry Injection Pump

Direct-push injection of slurry

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Applications by Contaminant

- Petroleum Hydrocarbons
  - BTEX
  - Alkanes (diesel, fuel oil, PAHs)
- MTBE
- Chlorinated Hydrocarbons (DCE and VC)
- Other Aerobically Degradable Compounds
  - Triazine Herbicides (atrazine)
  - Chloroacetamide Pesticides (alachlor, acetochlor, etc.)
  - PCP

Cost Comparison

ORC vs Other Technologies

Site	AS/SVE	ORC	Savings	%Savings
Okalahoma	$158,000	$46,000	$112,000	70%
California	$180,000	$80,000	$100,000	55%
Alabama	$99,000	$26,000	$73,000	74%

ORC vs Monitoring Only

Site	Monitor Only	ORC	Savings	%Savings
Okalahoma	$54,000	$46,000	$8,000	15%
Alabama	$54,000	$26,000	$28,000	52%

*All values were derived independently by the sites' consultant. The costs are full-system costs with the objective of site closure.

ORC has been applied on over 7,500 sites in 50 states & 12 countries

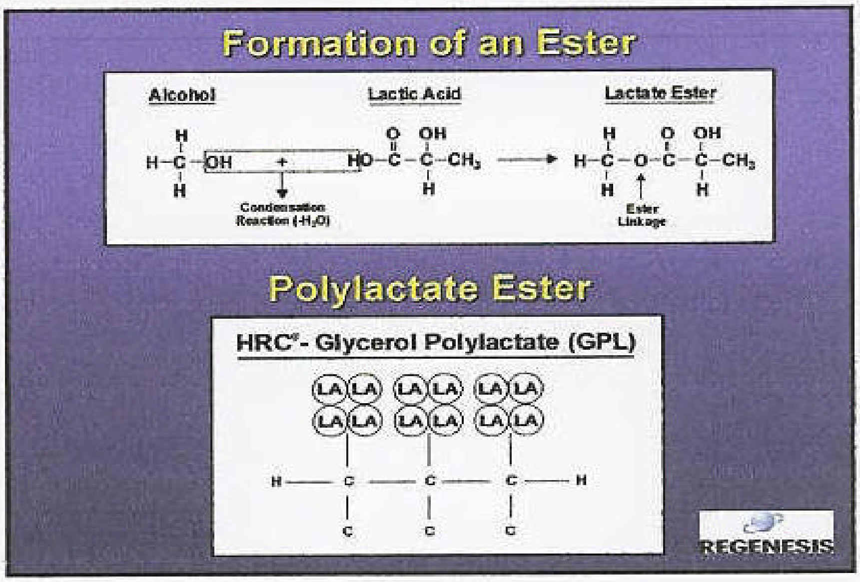
HRC®

Hydrogen Release Compound

A proprietary time release formulation of polylactate ester

Hydrogen Release Compound, HRC™

- HRC is a polylactate ester
- When hydrated, HRC time-releases lactic acid
- HRC accelerates anaerobic bioremediation of CHs such as PCE, TCE, and TCA
  - Microbes metabolize lactic acid to other organic acid intermediates, such as acetic acid
  - **Hydrogen** is released as a by-product
  - This hydrogen facilitates reductive dechlorination of chlorinated hydrocarbons


Formation of an Ester
Alcohol
Lactic Acid
Lactate Ester
Condensation Reaction (-H2O)
Ester Linkage
Polylactate Ester
HRC®- Glycerol Polylactate (GPL)
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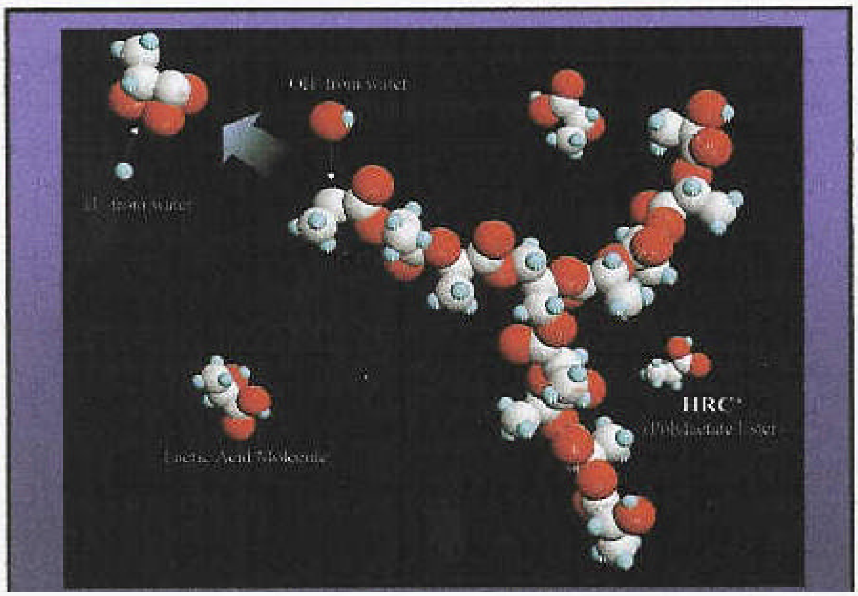
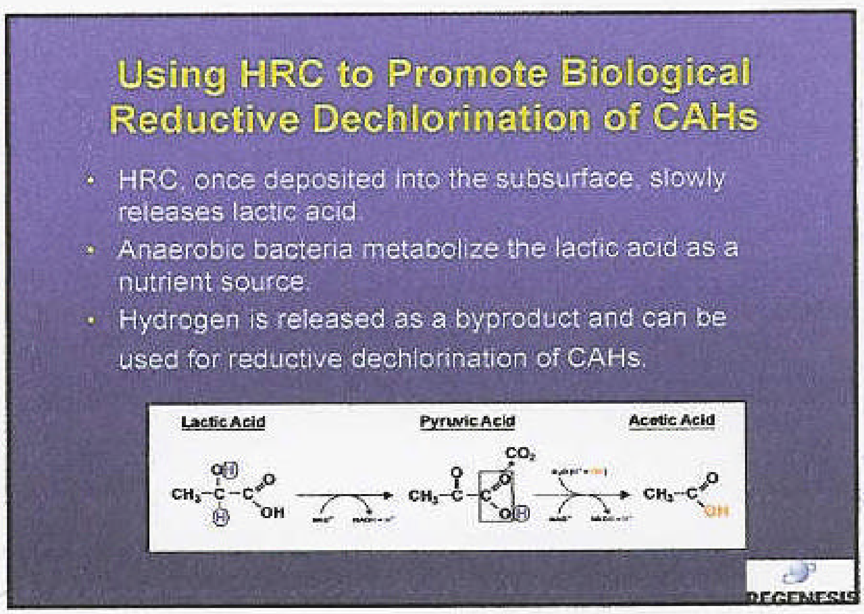

HRC®


Using HRC to Promote Biological Reductive Dechlorination of CAHs
• HRC, once deposited into the subsurface, slowly releases lactic acid.
• Anaerobic bacteria metabolize the lactic acid as a nutrient source.
• Hydrogen is released as a byproduct and can be used for reductive dechlorination of CAHs.
Lactic Acid
Pyruvic Acid
Acetic Acid
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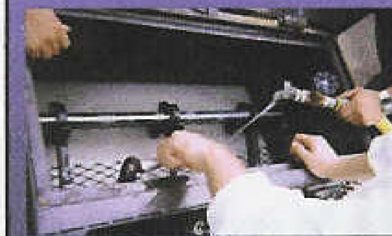
HRC Field Application



HRC is a viscous but injectable substance.

HRC is injected into the aquifer using direct-push technologies.

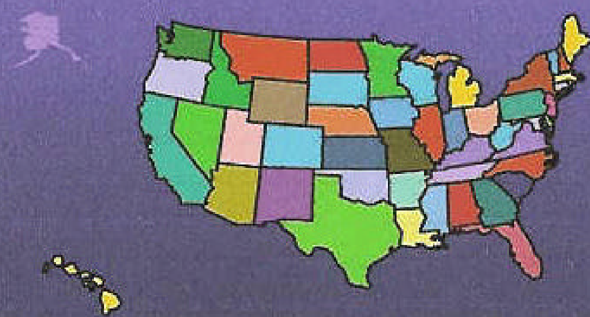
The Benefits of a Persistent, Time-Release Hydrogen Source

- Allows for **passive** chlorinated hydrocarbons (CHs) remediation (**1+ year activity**)
- Cost-Effective
  - **Reduces** capital **costs** in comparison with other technologies
  - Remains in place for continuous hydrogen delivery and continued savings on O&M costs
- Non-invasive, leaves no above-ground disturbance

Applications by Contaminant

- Chlorinated Hydrocarbon Solvents
- Nitroaromatics
- Oxyanions
- Other Anaerobically Degradable Compounds
  - Insecticides
  - Herbicides
  - Fumigants

HRC has been applied on 350 sites in 50 states



75% of all sites treated biologically

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Agriculture Related Contaminants Treatable via ORC and HRC

Chlorinated insecticides:
chlorane, aldrin, dieldrin, heptachlor, lindane (HRC)

Herbicides:
atrazine and other triazine herbicides (ORC), dinoseb (HRC)

Chloroacetamide herbicides:
alachlor, metolachlor,, acetochlor (ORC/HRC)

Fumigants:
di- and tri- chloropropanes, carbon tetrachloride (HRC)

Wood preservatives:
pentachlorophenol (ORC/HRC), copper/chromium/arsenic (HRC)

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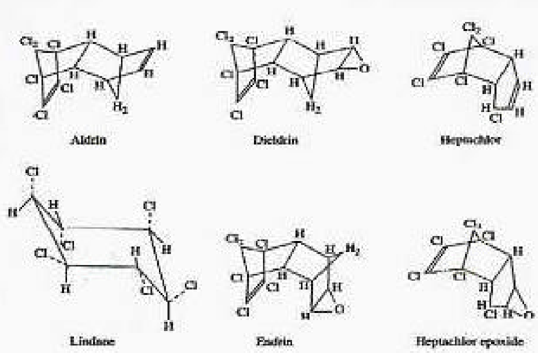
Biodegradation of Chlorinated Insecticides

after: Rittmann and McCarty, Environmental Biotechnology (2001)



Biodegradation of Agriculture Related Chlorinated Contaminants

"Commonly recognized now is that reductive dehalogenation occurs with strongly reducing anaerobic conditions for essentially all chlorinated aromatic and aliphatic compounds."

"Indeed, all of the pesticides.....except heptachlor epoxide, were [rapidly] transformed under anaerobic methanogenic conditions."

From:
Rittmann and McCarty, Environmental Biotechnology (2001)

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Chlordane Biodegradation: Field Application

SITE

- chlordane plume in an aquifer in North Carolina
- an HRC barrier was installed perpendicular to groundwater flow across the 20 feet wide plume (treatment thickness was 5 to 25 feet bgs)

RESULTS:

in-barrier monitoring well:	chlordane decreased from 2090 ppb to 232 ppb (89%) in 23 months
upgradient monitoring well:	minimal chlordane decrease from 617 ppb to 576 ppb

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Biodegradation of Carbon Tetrachloride

- Carbon tetrachloride reductive dechlorination is similar to that for other chlorinated hydrocarbons.
- Laboratory treatability studies for carbon tetrachloride with HRC were successful.

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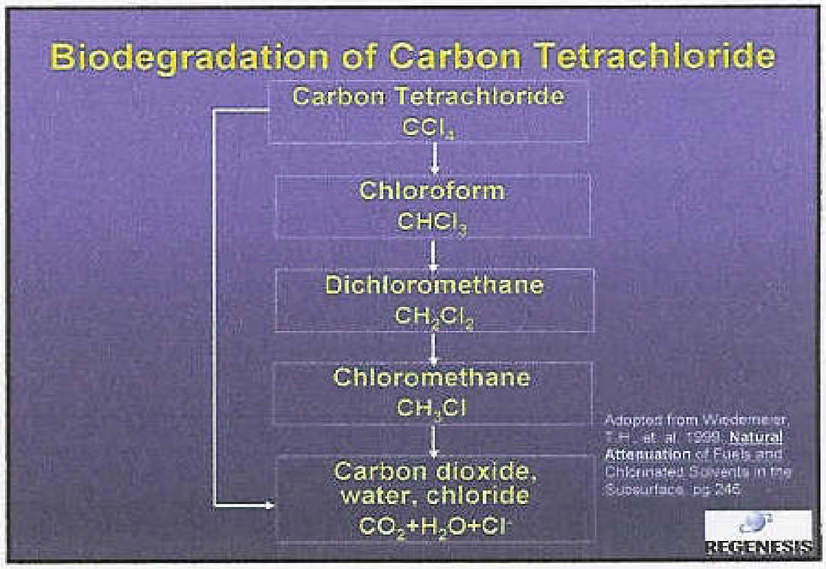
Biodegradation of Carbon Tetrachloride
Carbon Tetrachloride
CCl_4
Chloroform
$CHCl_3$
Dichloromethane
CH_2Cl_2
Chloromethane
CH_3Cl
Carbon dioxide, water, chloride
$CO_2+H_2O+Cl^-$
Adopted from Wiedemeier, T.H., et. al. 1999. Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface. pg 246
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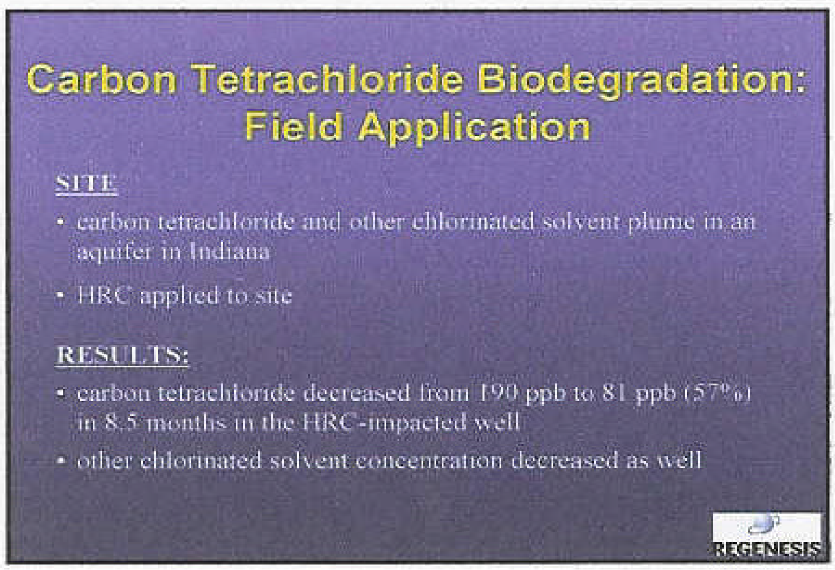
Carbon Tetrachloride Biodegradation: Field Application
SITE
• carbon tetrachloride and other chlorinated solvent plume in an aquifer in Indiana
• HRC applied to site
RESULTS:
• carbon tetrachloride decreased from 190 ppb to 81 ppb (57%) in 8.5 months in the HRC-impacted well
• other chlorinated solvent concentration decreased as well
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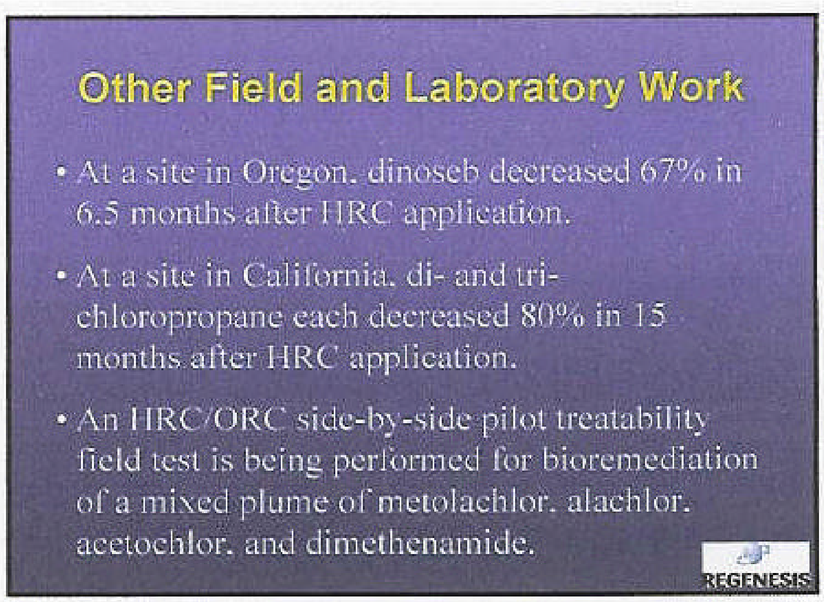
Other Field and Laboratory Work
• At a site in Oregon, dinoseb decreased 67% in 6.5 months after HRC application.
• At a site in California, di- and tri-chloropropane each decreased 80% in 15 months after HRC application.
• An HRC/ORC side-by-side pilot treatability field test is being performed for bioremediation of a mixed plume of metolachlor, alachlor, acetochlor, and dimethenamide.
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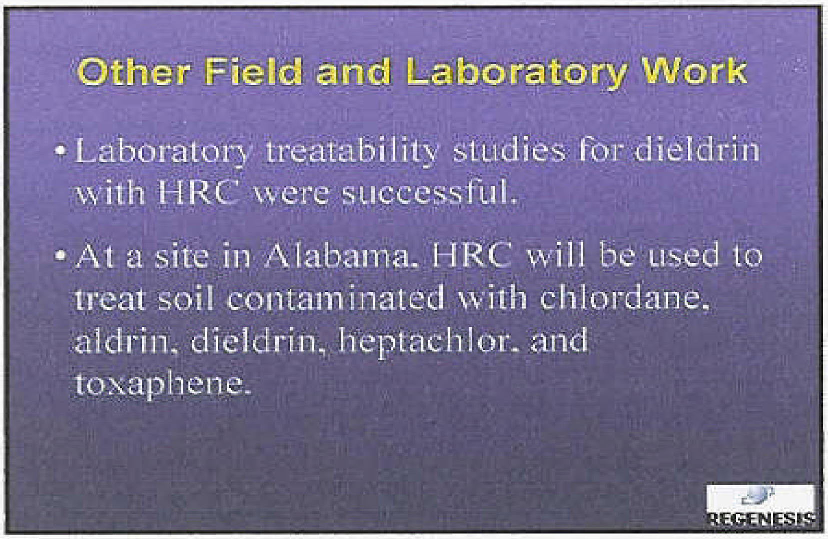
Other Field and Laboratory Work
• Laboratory treatability studies for dieldrin with HRC were successful.
• At a site in Alabama, HRC will be used to treat soil contaminated with chlordane, aldrin, dieldrin, heptachlor, and toxaphene.
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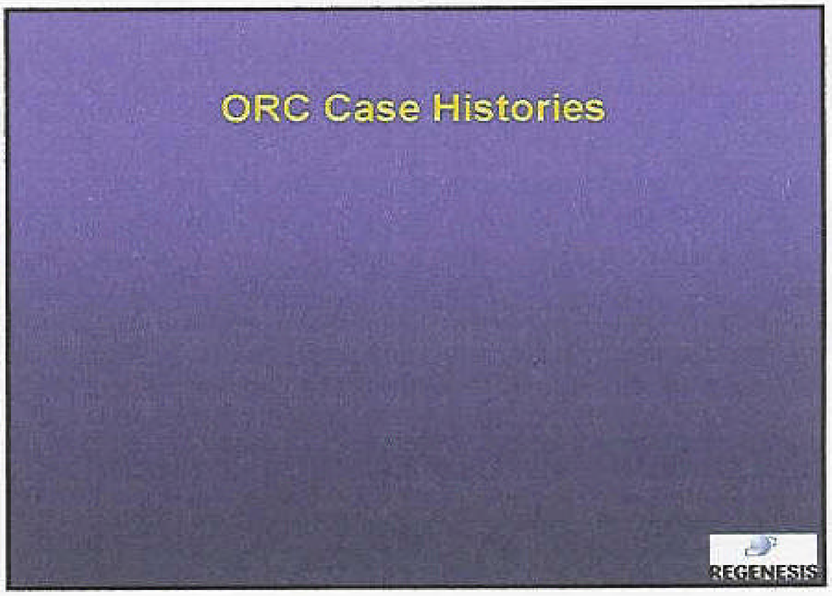
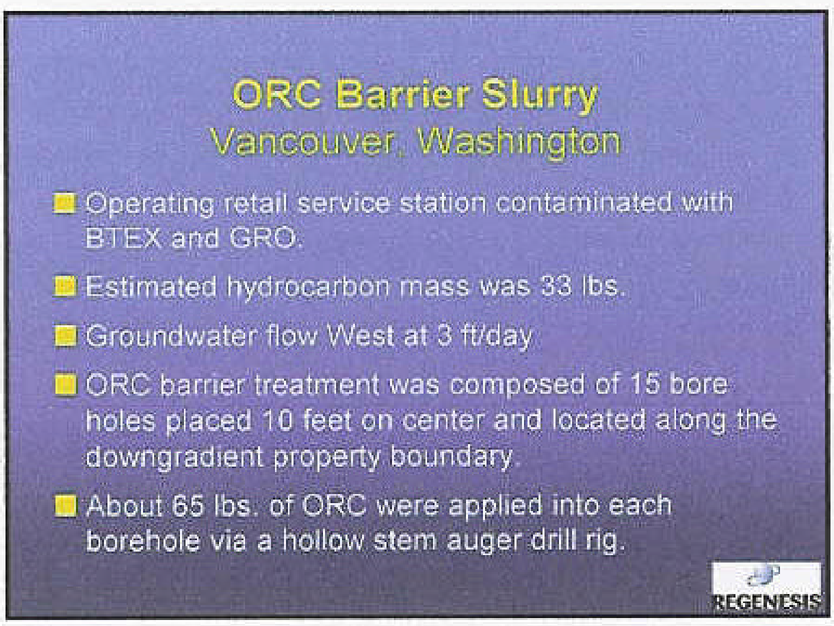
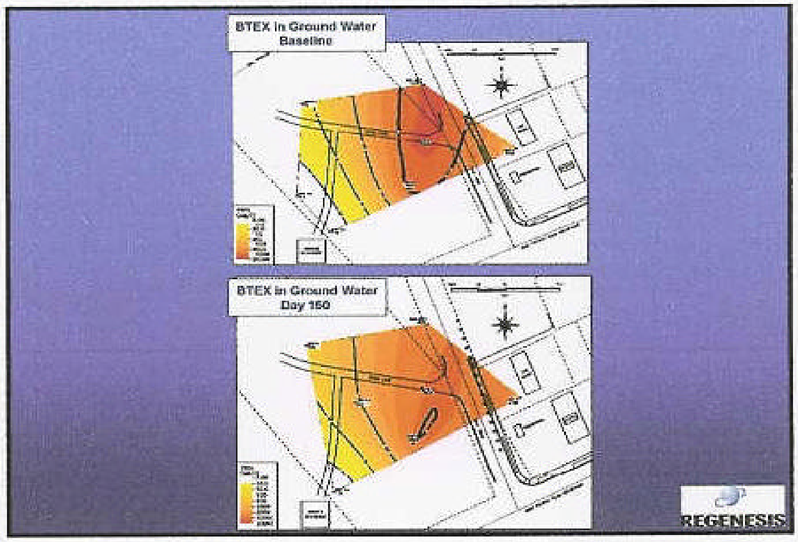

ORC Case Histories
REGENESIS


ORC Barrier Slurry
Vancouver, Washington
Operating retail service station contaminated with BTEX and GRO.
Estimated hydrocarbon mass was 33 lbs.
Groundwater flow West at 3 ft/day
ORC barrier treatment was composed of 15 bore holes placed 10 feet on center and located along the downgradient property boundary.
About 65 lbs. of ORC were applied into each borehole via a hollow stem auger drill rig.
REGENESIS



ORC Barrier Slurry

Vancouver, Washington

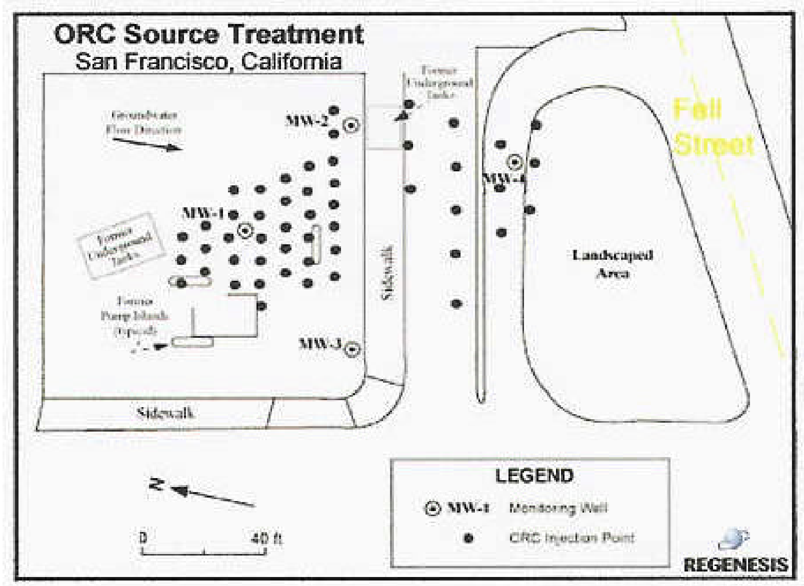
Conclusion

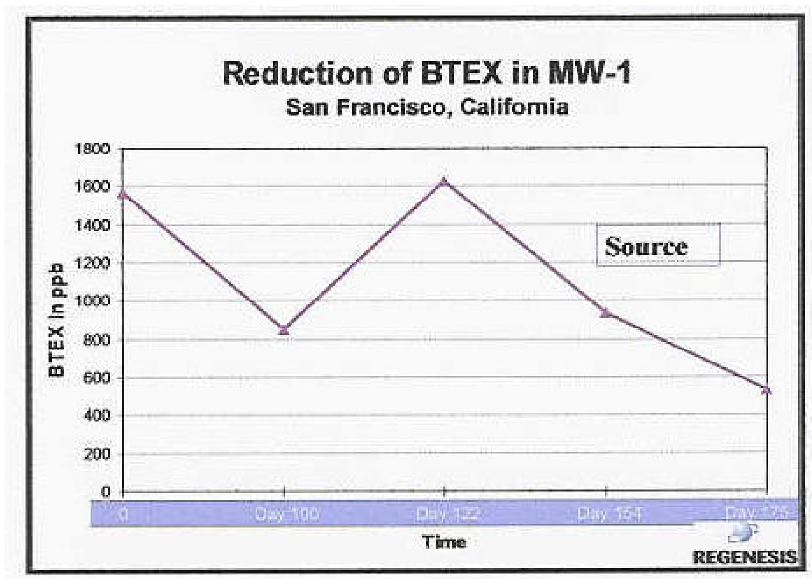
- There was an overall mass reduction of 43% for BTEX, 71% for benzene, and 62% for GRO in five months.
- Actionable BTEX level in the sentinel well at the leading edge of the plume (MW-11) was reduced 95%.
- The client's total cost was $40,000. This represented a savings of $210,000 versus alternative designs.

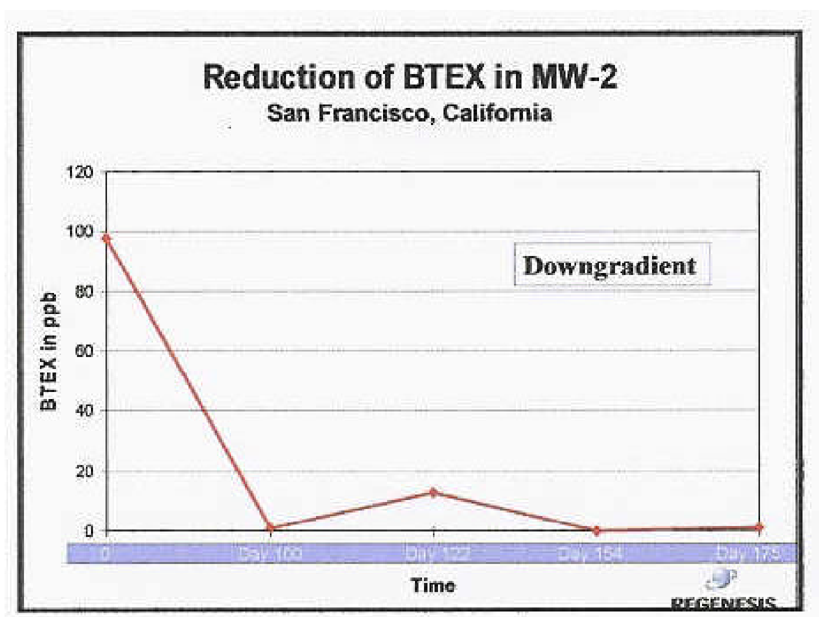
ORC Injection Array Treatment

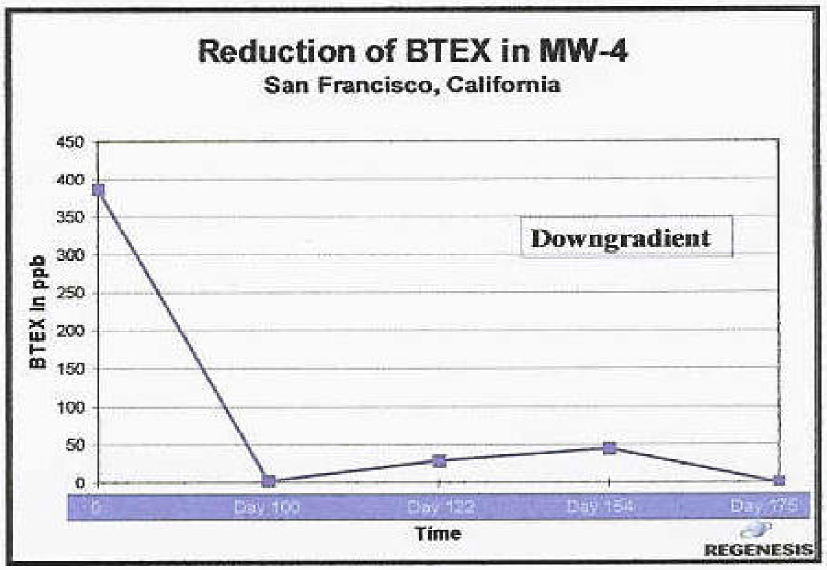
San Francisco, California

- Downtown real estate construction site had groundwater contamination of BTEX
- Groundwater flow South up to 0.15 m/day
- Aquifer consists of silt and sandy silt
- Approximately 2,500 lbs. of ORC slurry were injected into 50 push points for treatment using a cone penetrometer rig due to extremely tight "bay muds."


ORC Source Treatment
San Francisco, California
MW-2
MW-1
MW-3
MW-4
Sidewalk
Sidewalk
Fell
Street
Landscaped
Area
LEGEND
MW-4 Monitoring Well
ORC Injection Point
N
0
40 ft
REGENESIS


Reduction of BTEX in MW-1
San Francisco, California
BTEX in ppb
1800
1600
1400
1200
1000
800
600
400
200
0
Source
0
Day 100
Day 122
Day 154
Day 175
Time
REGENESIS


Reduction of BTEX in MW-2
San Francisco, California
BTEX in ppb
120
100
80
60
40
20
0
Downgradient
0
Day 100
Day 122
Day 154
Day 175
Time
REGENESIS



ORC Injection Array Treatment
San Francisco, California
Conclusion

After five months:

- BTEX decreased 66% in MW-1 (source area)
- BTEX decreased 100% in the both wells immediately downgradient of ORC injection
- Regulators recognized:ORC significantly reduced the contaminant source mass and granted a "no further action required"
- The client's cost of product and application cost was approx. $25,000. This represented a savings of $150,000 versus alternative designs.

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Quantifying Enhanced Natural Attenuation

(1) $\frac{dC}{dt} = -kC$ Reduction of concentration with time

Upon integration

(2) $C = C_o e^{-kt}$

where C = final Concentration

C_o = initial Concentration

k = rate constant

t = time

(3) $k = \ln\left(\frac{C_o}{C}\right) / t$

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Rates
ORC Source Treatment (BTEX)
Dexter, Michigan
Bohan and Schlett, "Enhanced Natural Bioremediation Using a Time Release Oxygen Compound,"- Battelle 1997.
• ORC was installed at a convenience store site in MI. undergoing a renovation.
• Contamination levels before and after ORC application in sentinel well MW 2 were recorded.
• 3,052 lbs. of ORC were applied via 54 points.
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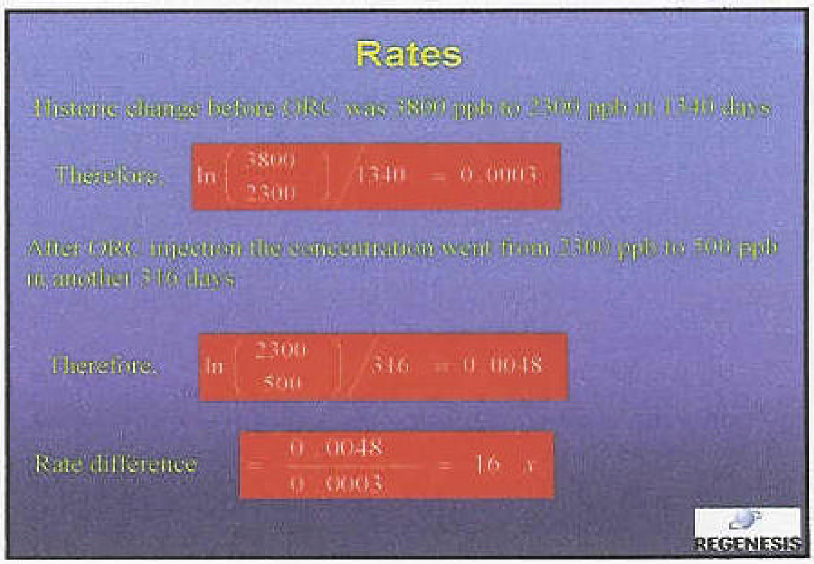
Rates
Historic change before ORC was 3800 ppb to 2300 ppb in 1340 days
Therefore, $\ln\left(\frac{3800}{2300}\right)/1340 = 0.0003$
After ORC injection the concentration went from 2300 ppb to 500 ppb in another 316 days
Therefore, $\ln\left(\frac{2300}{500}\right)/316 = 0.0048$
Rate difference $= \frac{0.0048}{0.0003} = 16\ x$
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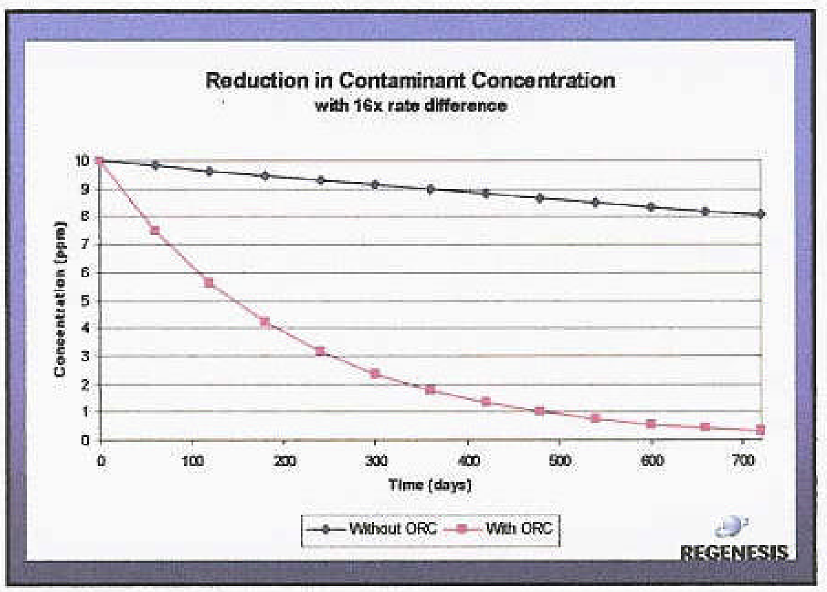
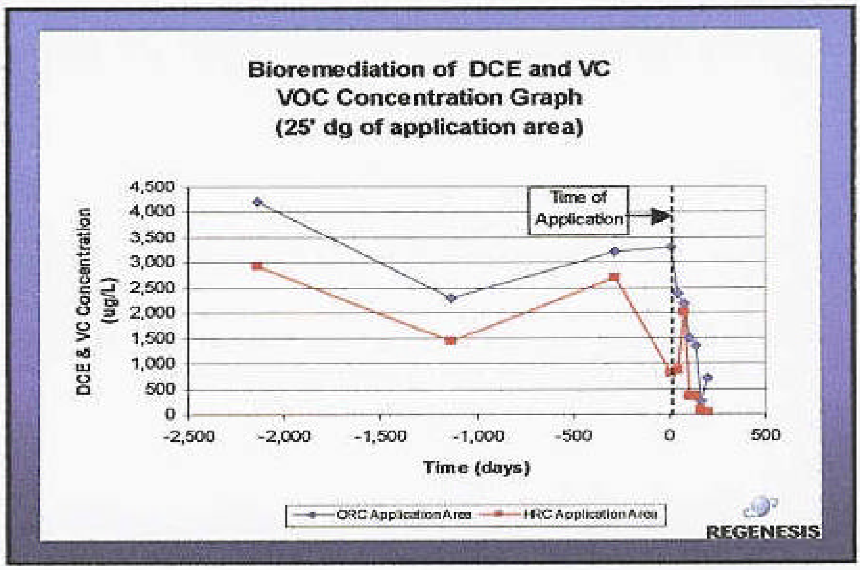

Reduction in Contaminant Concentration
with 16x rate difference
Concentration (ppm)
10
9
8
7
6
5
4
3
2
1
0
0
100
200
300
400
500
600
700
Time (days)
Without ORC
With ORC
REGENESIS



Conclusions

- ORC has been shown over the last several years to be a highly effective management tool at sites contaminated with several classes of aerobically degradable compounds.
- The technology works optimally when used on properly characterized sites and where the primary objective is to accelerate natural attenuation. Quantifying this statement we usually see at least an order of magnitude of rate improvement. MCL's can be achieved as a function of starting concentrations, rates and the time available to meet those goals.

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Conclusions

- Other collateral benefits accompany the use of simple push-point deposition of the material and these include the virtual elimination of design and capital costs. O&M essentially consists of making one or more re-applications if necessary.
- Additional benefits include ease of application and management and the fact that the treatment operates silently below ground, which has particular import at active sites.

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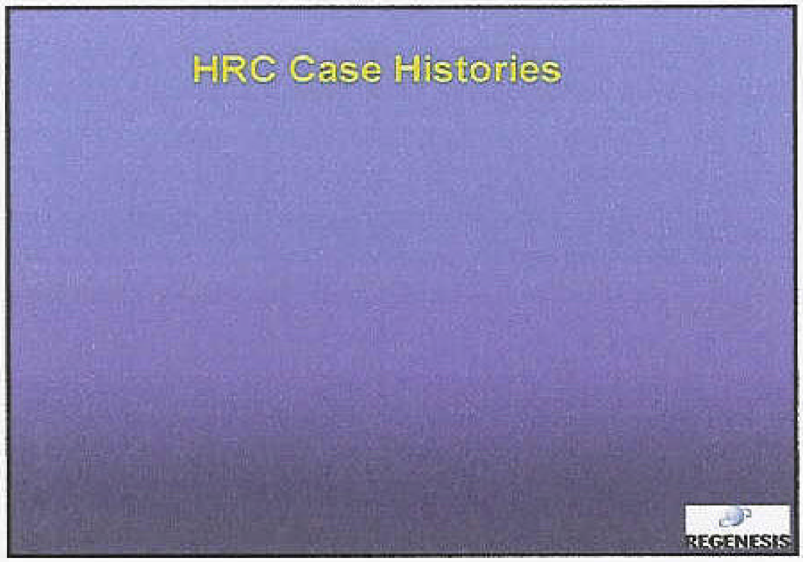
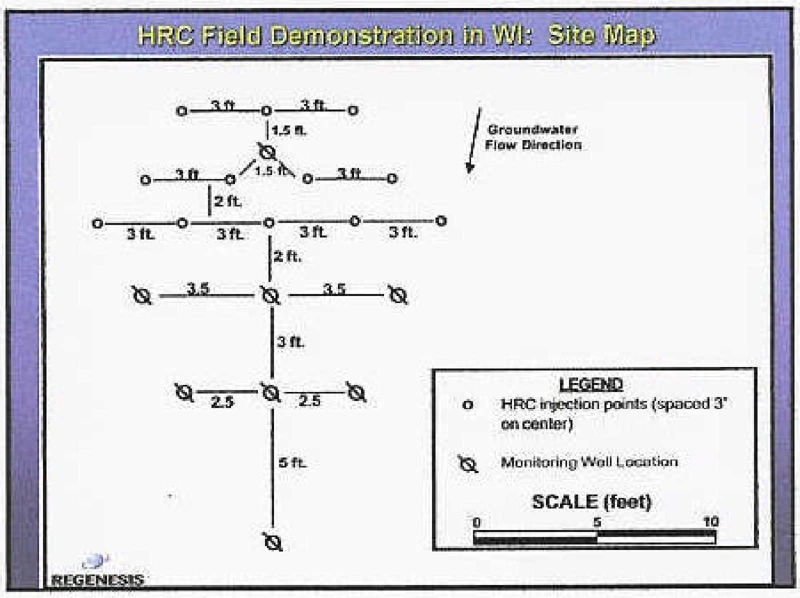
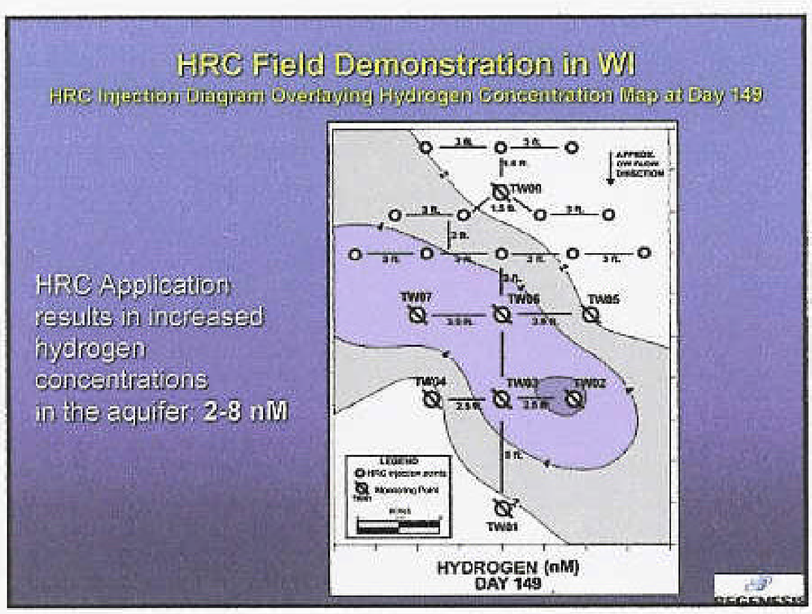
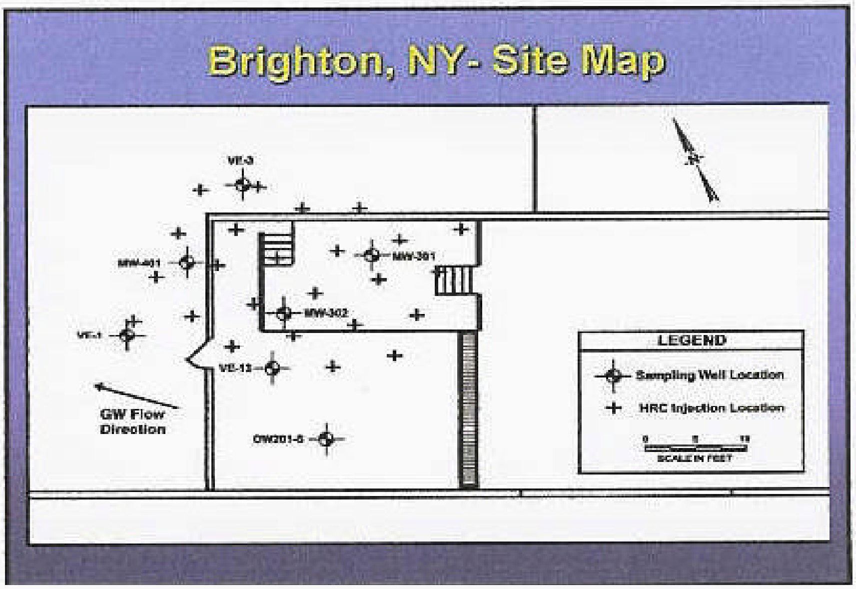
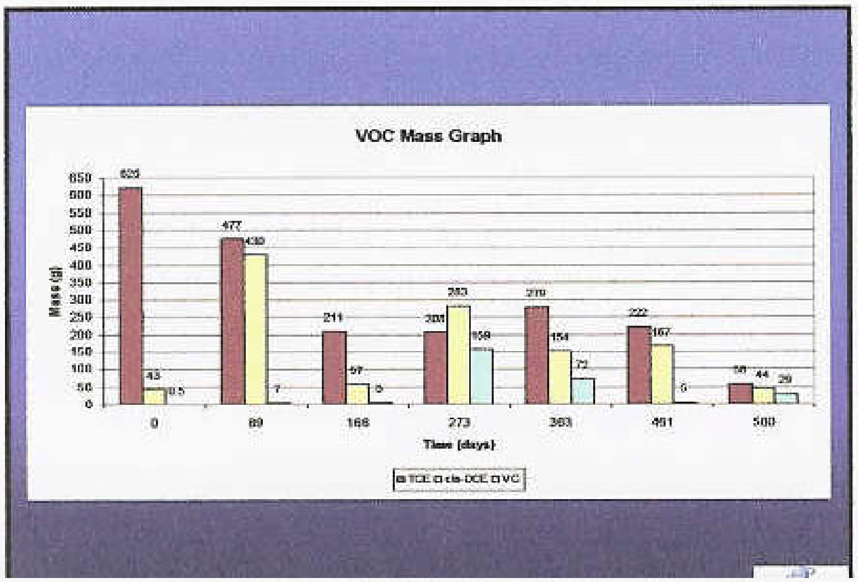

HRC Case Histories
REGENESIS


HRC Field Demonstration in WI: Site Map
3 ft.
1.5 ft.
2 ft.
3.5
5 ft.
2.5
Groundwater
Flow Direction
LEGEND
HRC injection points (spaced 3' on center)
Monitoring Well Location
SCALE (feet)
0
5
10
REGENESIS

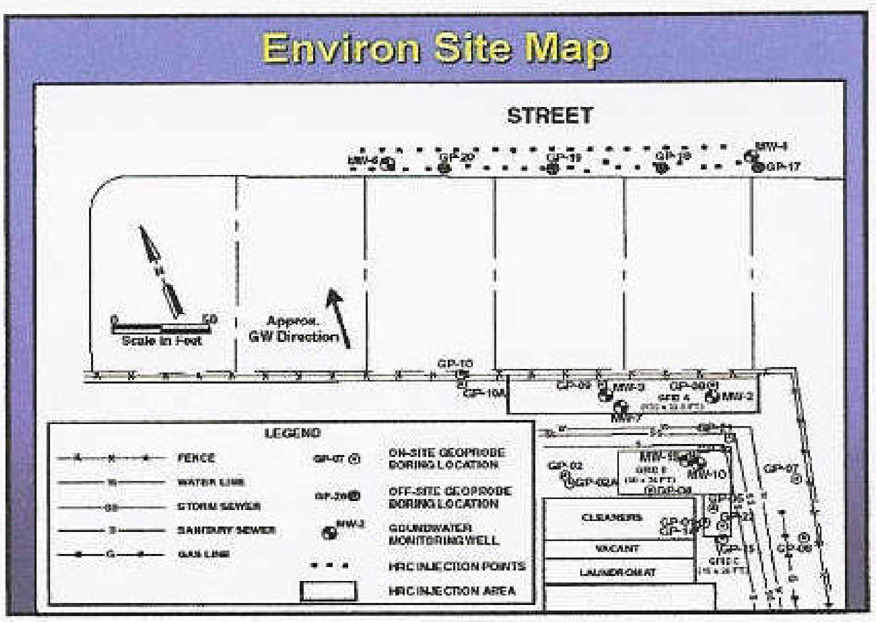

HRC Field Demonstration in WI
HRC Injection Diagram Overlaying Hydrogen Concentration Map at Day 149
HRC Application
results in increased
hydrogen
concentrations
in the aquifer: 2-8 nM
TW00
TW07
TW06
TW05
TW04
TW03
TW02
TW01
LEGEND
HYDROGEN (nM)
DAY 149



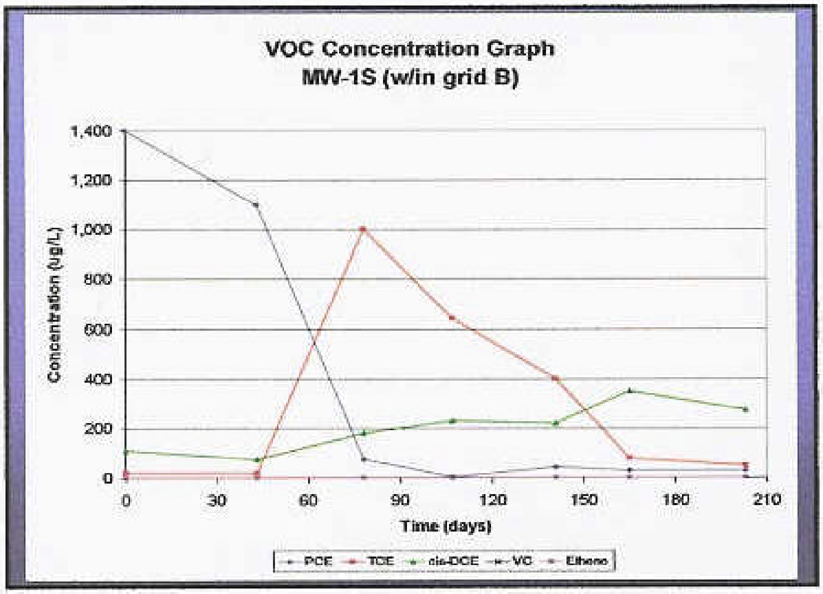
Brighton, NY- Site Map
MW-401
MW-301
MW-302
VE-1
VE-13
OW201-5
GW Flow Direction
LEGEND
Sampling Well Location
HRC Injection Location
SCALE IN FEET



VOC Mass Graph
650
600
550
500
450
400
350
300
250
200
150
100
50
0
Mass (g)
477
430
7
211
222
167
44
0
273
500
Time (days)
TCE cis-DCE VC



Environ Site Map
STREET
MW-8
GP-17
Scale in Feet
Approx. GW Direction
GP-10
GP-10A
MW-3
MW-2
MW-7
MW-10
GP-07
GP-06
CLEANERS
VACANT
LAUNDROMAT
LEGEND
FENCE
WATER LINE
STORM SEWER
SANITARY SEWER
GAS LINE
ON-SITE GEOPROBE BORING LOCATION
OFF-SITE GEOPROBE BORING LOCATION
GOUNDWATER MONITORING WELL
HRC INJECTION POINTS
HRC INJECTION AREA

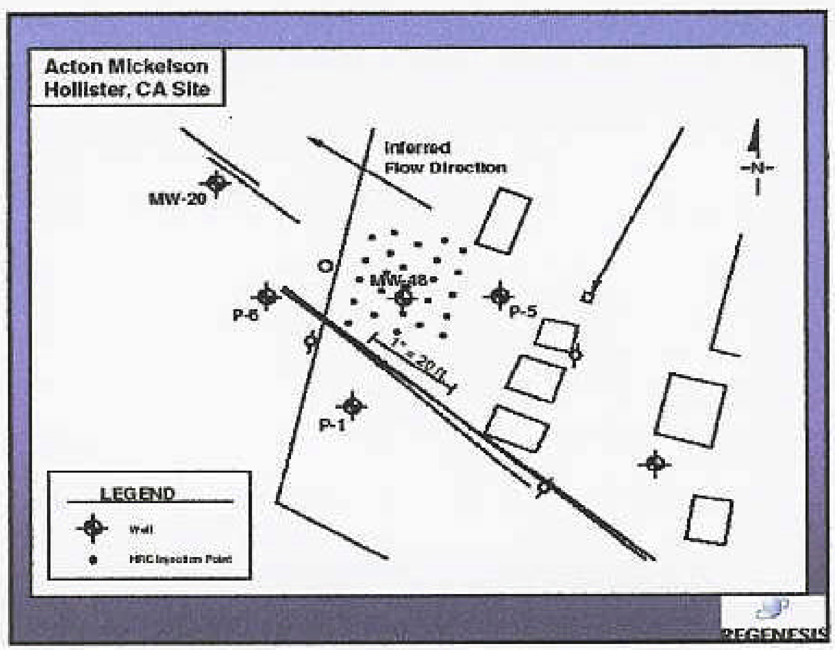


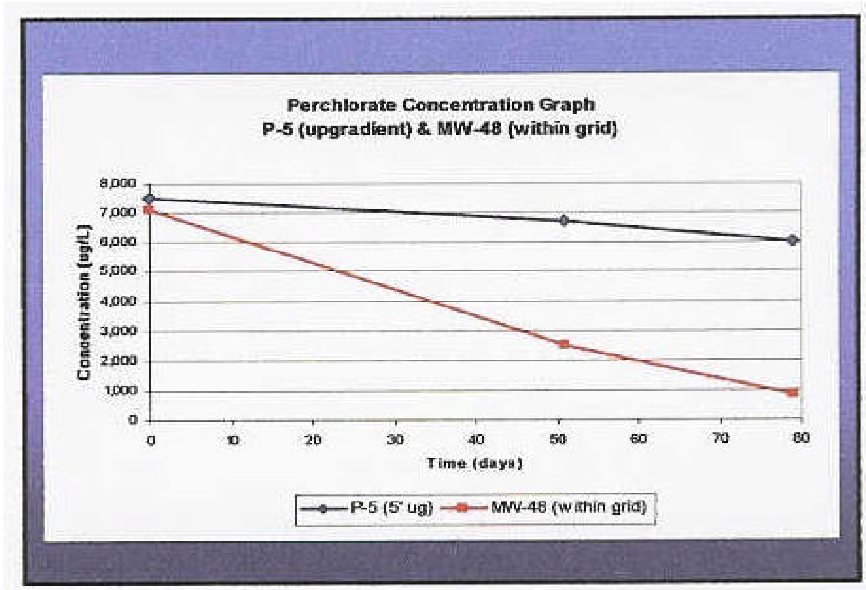
Whittaker Ordnance Facility - Hollister, CA

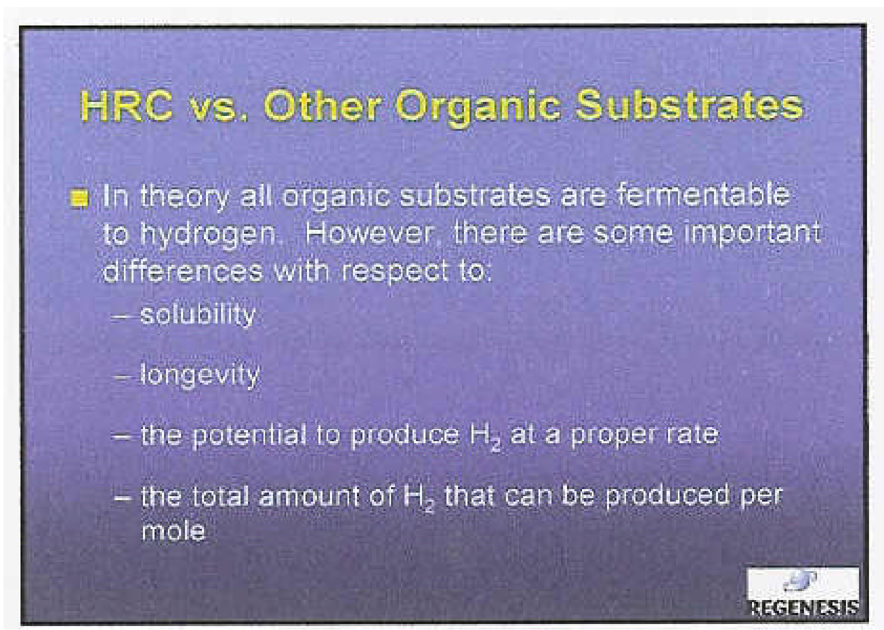
Site Characteristics and Application

- HRC pilot test at an Ordnance Facility
- Aquifer consists of medium to fine silty sand
- Application thickness = 15 ft, GW velocity = 26 ft/yr
- Contaminated with TCE, TCA, Perchlorate at levels of approximately 4,500 ug/L; Chrome 6 and Fr-113 at levels of approximately 220-300 ug/L
- 660 lb of HRC injected into aquifer via direct push, points spaced 5' on center

REGENESIS




Perchlorate Concentration Graph
P-5 (upgradient) & MW-48 (within grid)
Concentration (ug/L)
8,000
7,000
6,000
5,000
4,000
3,000
2,000
1,000
0
0
10
20
30
40
50
60
70
80
Time (days)
P-5 (5' ug)
MW-48 (within grid)


HRC vs. Other Organic Substrates
In theory all organic substrates are fermentable to hydrogen. However, there are some important differences with respect to:
– solubility
– longevity
– the potential to produce H_2 at a proper rate
– the total amount of H_2 that can be produced per mole
REGENESIS