NGWA Workshop
December 6, 2017

The Biogeochemical Toolbox: Enhancing Natural Remedial Processes

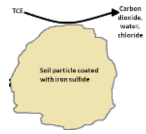
Karen Kinsella
GZA GeoEnvironmental

Proactive By Design.
Our Company Commitment

Helping Nature Heal Herself
Low Impact Technologies

Bioremediation
- Microbial technologies
- Phytotechnologies

Biogeochemical remediation
- Combined remedies
- Leveraging native geochemistry



OVERVIEW
Helping Nature Heal Herself

Chlorinated solvents | Petroleum | Metals

Speed up natural oxidation or reduction by adding **electron acceptors** or **electron donors**

Electron Transfer

Gain electrons: REDUCED

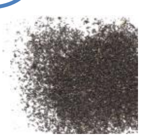
Lose electrons: OXIDIZED

Oxidation/Reduction
REDOX POTENTIAL
Eh, ORP

Electron Transfer

Lose electrons: OXIDIZED

Zero-Valent Iron
Fe^0



Ferric Iron
Fe^{3+}

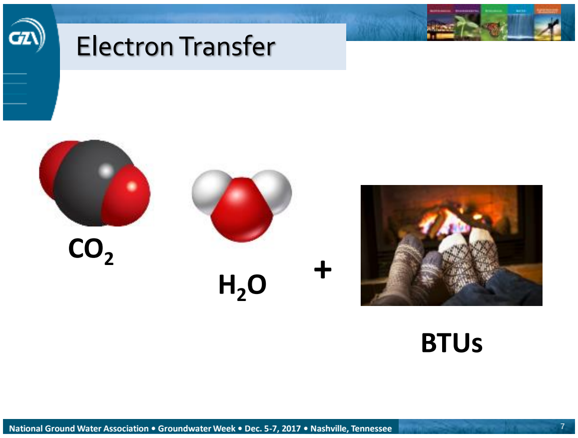
Ferrous Iron
Fe^{2+}

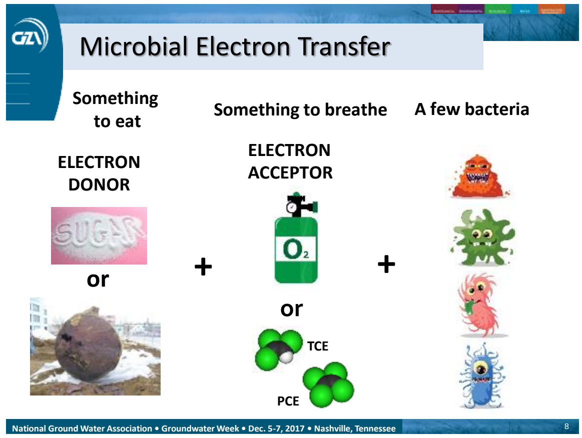
Electron Transfer

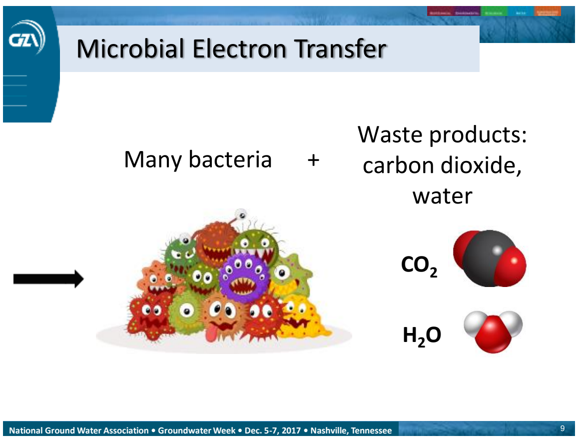
ELECTRON DONOR

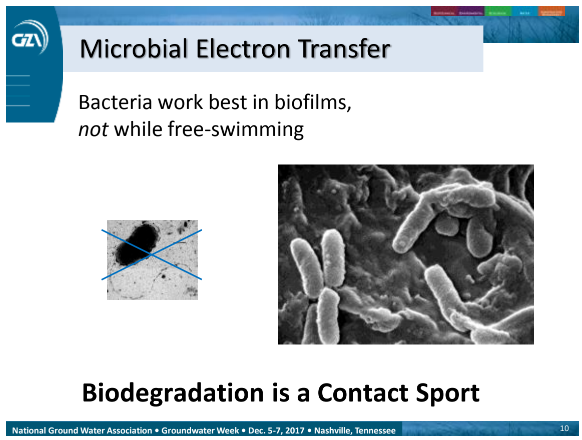
+

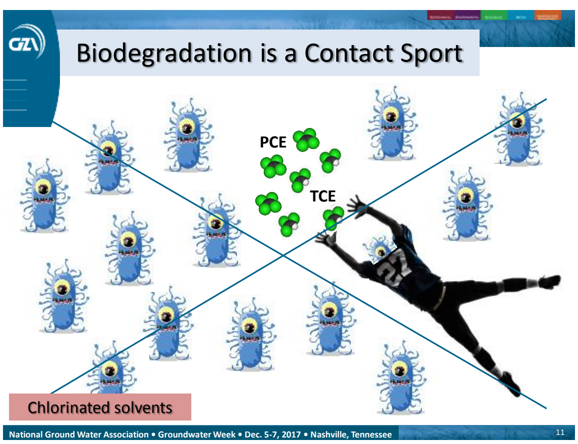
ELECTRON ACCEPTOR

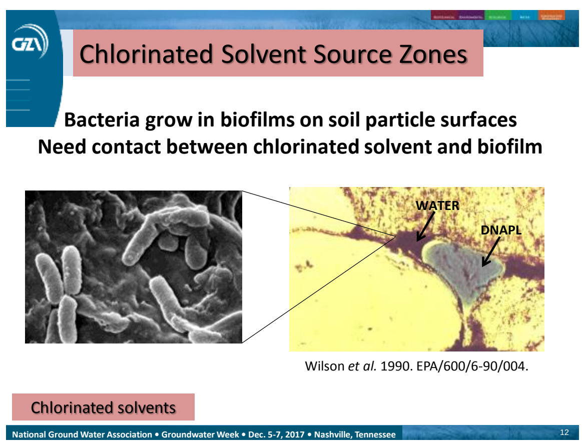

Electron Transfer
CO_2
H_2O
+
BTUs
National Ground Water Association • Groundwater Week • Dec. 5-7, 2017 • Nashville, Tennessee
7


Microbial Electron Transfer
Something to eat
Something to breathe
A few bacteria
ELECTRON DONOR
ELECTRON ACCEPTOR
or
+
O_2
or
TCE
PCE
+
National Ground Water Association • Groundwater Week • Dec. 5-7, 2017 • Nashville, Tennessee
8


Microbial Electron Transfer
Many bacteria
+
Waste products: carbon dioxide, water
CO_2
H_2O
National Ground Water Association • Groundwater Week • Dec. 5-7, 2017 • Nashville, Tennessee
9


Microbial Electron Transfer
Bacteria work best in biofilms,
not while free-swimming
Biodegradation is a Contact Sport
National Ground Water Association • Groundwater Week • Dec. 5-7, 2017 • Nashville, Tennessee
10


Biodegradation is a Contact Sport
PCE
TCE
Chlorinated solvents
National Ground Water Association • Groundwater Week • Dec. 5-7, 2017 • Nashville, Tennessee
11


Chlorinated Solvent Source Zones
Bacteria grow in biofilms on soil particle surfaces
Need contact between chlorinated solvent and biofilm
WATER
DNAPL
Wilson *et al.* 1990. EPA/600/6-90/004.
Chlorinated solvents
National Ground Water Association • Groundwater Week • Dec. 5-7, 2017 • Nashville, Tennessee
12

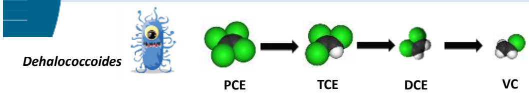
Source Zone Bioremediation

Residual chlorinated solvent: continuous supply of electron acceptor

Dehalococcoides **prefers to breathe more chlorinated**
Daughter products can accumulate in source zones

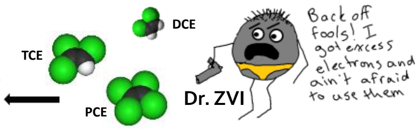
Chlorinated solvents

In-Situ Biological and Chemical Reduction: ISBR (biotic) and ISCR (abiotic)



Combined ISBR (biotic reduction) and ISCR (abiotic reduction)
minimizes daughter product accumulation and balances pH

Short-lived chloroacetylenes & acetylene; very little VC



Chlorinated solvents

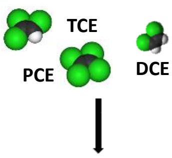
Abiotic Degradation: ISCR on Soil Minerals

ELECTRON DONORS

Iron sulfides and hydroxides, sorbed Fe^{2+}, green rust, magnetite

MAGNETITE: most magnetic mineral; measure soil *Magnetic Susceptibility* to semi-quantify

ELECTRON ACCEPTORS



Short-lived chloroacetylenes and acetylene

Very little VC

Chlorinated solvents

Synergistic Biotic/Abiotic Solution

Kinetics
Biotic: more chlorinated degrade faster
Abiotic: variable degradation rate

Balanced pH
Biotic lowers pH
Abiotic raises pH

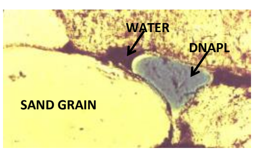
Hydrogen
Fuel for microbial dechlorination

Chlorinated solvents

Biotic/Abiotic Synergy continued

Biotic reduction in dissolved phase only

Abiotic not limited by dissolution and desorption



Wilson *et al.* 1990. EPA/600/6-90/004.

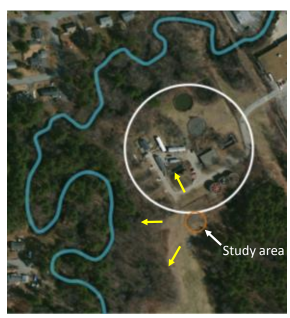
Abiotic reduction can occur within NAPL
Slower process, but ZVI lasts longer

Chlorinated solvents

Case Study: Biotic/Abiotic Synergy - Combined Biotic/Abiotic Dechlorination at a Former Wastewater Treatment Facility

Chlorinated VOCs in source area groundwater include:

Tetrachloroethene (PCE)
Trichloroethene (TCE)
1,1,2,2-Tetrachloroethane
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Carbon tetrachloride



Chlorinated solvents

Combined Biotic/Abiotic Dechlorination

Former WWTF: three degradation mechanisms:

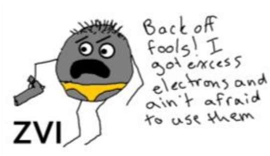
1) Abiotic I
2) Abiotic II
3) Biological

Chlorinated solvents

Combined Biotic/Abiotic Dechlorination

Abiotic I

ELECTRON DONOR



ELECTRON ACCEPTOR

TCE

Chlorinated solvents

Combined Biotic/Abiotic Dechlorination

Abiotic II

ELECTRON DONOR

ORGANIC CARBON

ELECTRON ACCEPTOR

SULFATE

SULFATE-REDUCING BACTERIA

MICROBIALLY-GENERATED SULFIDE

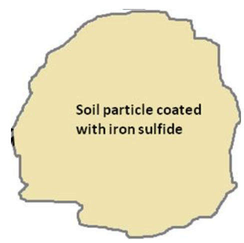
Chlorinated solvents

Abiotic II Degradation

SULFIDE from SULFATE-REDUCING BACTERIA

+

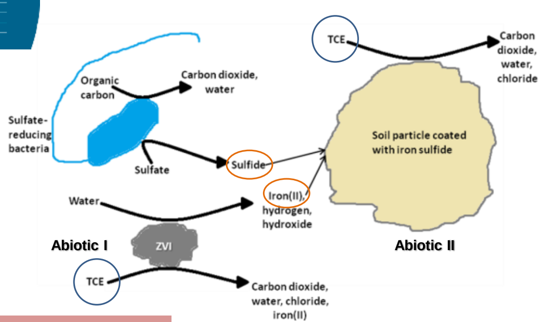
DIVALENT (FERROUS) IRON from ZVI that donated electrons to PCE & TCE



Reactive ferrous sulfide coatings on soil particles

Chlorinated solvents

Biogeochemical Synergy



Chlorinated solvents

Abiotic Remediation

1st post injection sampling round (1 month):

Abiotic I — TCE ↓, Iron ↑

2nd post injection sampling round (3 months):

Abiotic II — TCE ↓↑, Iron ↓, Sulfate ↓

4th post injection sampling round (9 months):

Abiotic/Biotic — TCE ↓↓, Iron ↓, Sulfate ↑

Chlorinated solvents

Combined Biotic/Abiotic Dechlorination

Well ID	GZ-802US	ZVI			
Post-pilot	Baseline	1 month	3 months	9 months	20 months
PCE (µg/L)	400	400	300	200	70
TCE (µg/L)	384,000	196,000	264,000	51,400	7,000
cis -DCE (µg/L)	113,000	103,000	148,000	67,600	17,400
VC (µg/L)	<100	<100	<100	<100	6
Iron (mg/L)	7.65	557	29.3	15.4	1.6
Sulfate (mg/L)	12.1	34.0	9.0	65.0	31.6
pH	5.9	7.1	6.3	6.3	6.3
ORP (mV)	-25	79	-3	-5	19

Combined Biotic/Abiotic Dechlorination

Well ID	GZ-802US		FeS		
Post-pilot	Baseline	1 month	3 months	9 months	20 months
PCE (µg/L)	400	400	300	200	70
TCE (µg/L)	384,000	196,000	264,000	51,400	7,000
cis -DCE (µg/L)	113,000	103,000	148,000	67,600	17,400
VC (µg/L)	<100	<100	<100	<100	6
Iron (mg/L)	7.65	557	29.3	15.4	1.6
Sulfate (mg/L)	12.1	34.0	9.0	65.0	31.6
pH	5.9	7.1	6.3	6.3	6.3
ORP (mV)	-25	79	-3	-5	19

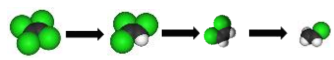
Combined Biotic/Abiotic Dechlorination

Well ID	GZ-802US			FeS/Bio	
Post-pilot	Baseline	1 month	3 months	9 months	20 months
PCE (µg/L)	400	400	300	200	70
TCE (µg/L)	384,000	196,000	264,000	51,400	7,000
cis -DCE (µg/L)	113,000	103,000	148,000	67,600	17,400
VC (µg/L)	<100	<100	<100	<100	6
Iron (mg/L)	7.65	557	29.3	15.4	1.6
Sulfate (mg/L)	12.1	34.0	9.0	65.0	31.6
pH	5.9	7.1	6.3	6.3	6.3
ORP (mV)	-25	79	-3	-5	19

Combined Biotic/Abiotic Dechlorination

Well ID	GZ-802US				Bio
Post-pilot	Baseline	1 month	3 months	9 months	20 months
PCE (µg/L)	400	400	300	200	70
TCE (µg/L)	384,000	196,000	264,000	51,400	7,000
cis -DCE (µg/L)	113,000	103,000	148,000	67,600	17,400
VC (µg/L)	<100	<100	<100	<100	6
Iron (mg/L)	7.65	557	29.3	15.4	1.6
Sulfate (mg/L)	12.1	34.0	9.0	65.0	31.6
pH	5.9	7.1	6.3	6.3	6.3
ORP (mV)	-25	79	-3	-5	19

Biological Reductive Dechlorination



PCE TCE DCE VC

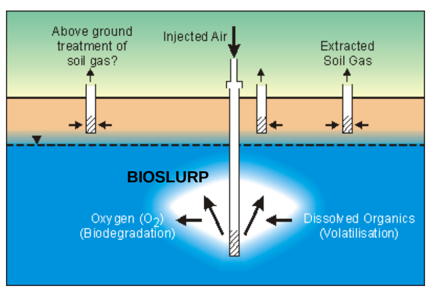
Petroleum Bioremediation

Aerobic or facultative aerobic
Breathe oxygen or nitrate
Eat gasoline, diesel, fuel oil

Anaerobic
Sulfate-reducing bacteria
Breathe sulfate
Eat gasoline, diesel, fuel oil

Petroleum

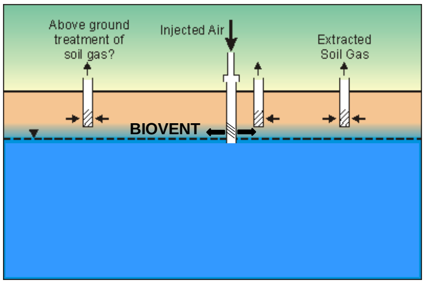
Aerobic Petroleum Bioremediation



http://www.clw.csiro.au/

Petroleum

Aerobic Petroleum Bioremediation



Petroleum

Case Study: Biovent/Soil Vapor Extraction (SVE)

#2 Fuel Oil LUST

10 years of pump and treat plus four surfactant injections

Installation of SVE system to biovent soil in the vadose zone

Implement groundwater monitoring program to confirm limited migration during biodegradation

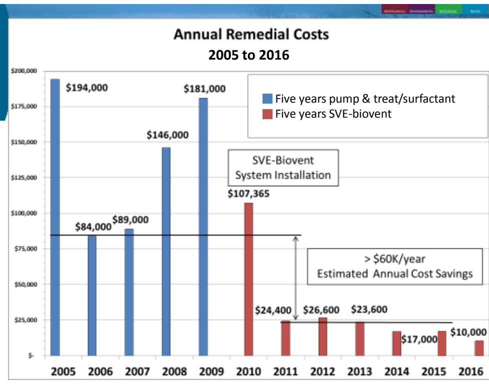
Petroleum

SVE System

Note size of GAC canister: most of fuel oil is biologically degraded

(GAC = granular activated carbon)

Petroleum



Petroleum

Petroleum Bioremediation

Aerobic or facultative aerobic
Breathe oxygen or nitrate
Eat gasoline, diesel, fuel oil

Anaerobic
Sulfate-reducing bacteria
Breathe sulfate
Eat gasoline, diesel, fuel oil

Petroleum

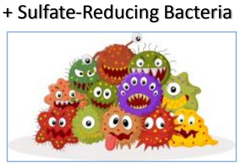
Anaerobic Petroleum Bioremediation: Sulfate

Organic Carbon
ELECTRON DONOR
(GASOLINE or FUEL OIL)

\+

Sulfate
ELECTRON ACCEPTOR
(GYPSUM or EPSOM SALT)

\+ Sulfate-Reducing Bacteria



→ Carbon Dioxide + Water + Sulfide

Petroleum

Anaerobic Petroleum Bioremediation: Sulfate

Remove LUST

Mix gypsum into backfill

Petroleum

Anaerobic Petroleum Bioremediation: Sulfate

Petroleum

Contingency: install perforated injection piping

Metals: Reducing Mobility

Keeping lead out of groundwater: ideal soil pH between 6.5 and 8.5
low pH - add lime

Best Management Practices at Shooting Ranges
(EPA-902-B-01-001, Revised June 2005)

Metals

Hexavalent Chromium

Oxidized chromium is water soluble (hexavalent chromium)

Reduced chromium has poor water solubility (trivalent chromium)

Metals

Chromium Biological Immobilization

ELECTRON DONOR

Molasses Drip

+

ELECTRON ACCEPTOR

Oxidized, water soluble, hexavalent chromium

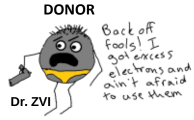
Trivalent chromium precipitates out as chromium and mixed chromium-iron oxides and hydroxides

Metals

Hexavalent Chromium Abiotic Immobilization: Zero-Valent Iron (ZVI) Permeable Reactive Barrier

ELECTRON ACCEPTOR

ELECTRON DONOR



Trivalent chromium precipitates out as chromium and mixed chromium-iron oxides and hydroxides

ITRC Permeable Reactive Barrier Technology Update (2011)
http://www.itrcweb.org/

Metals

Copper: Keeping it Out of Surface Water

Copper – Low Surface Water Protection Criteria
Based on EPA Aquatic Life Criteria (ALC)
Typical Surface Water ALC:
Chronic 5 ppb
Acute 14 ppb

Metals

Case Study: Former Industrial Facility Hexavalent Chromium and Copper

Sandy silt with sand lenses
Seasonal variations in groundwater elevation +/- 5 feet
Up to 800 ppm chromium and 2 ppm copper in groundwater

Metals

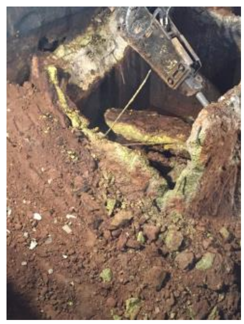
Case Study: Former Industrial Facility Hexavalent Chromium and Copper

Unlined Cr(VI) tank

Metals

Case Study: Former Industrial Facility Hexavalent Chromium and Copper

Unlined chrome tank removed



Metals

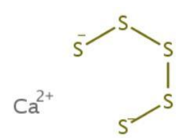
Case Study: Former Industrial Facility Hexavalent Chromium and Copper

Backfilling and injection pipe installation

Metals

Case Study: Former Industrial Facility Hexavalent Chromium and Copper

Calcium polysulfide injected
Donates electrons to hexavalent chromium
Reduced to insoluble trivalent chromium



Metals

Case Study: Former Industrial Facility Hexavalent Chromium and Copper

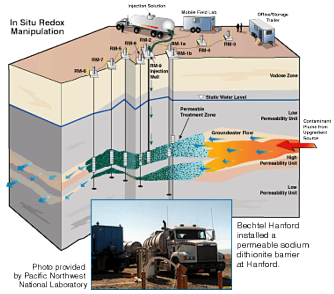
Calcium polysulfide injected
Donates electrons to hexavalent chromium
Reduced to insoluble trivalent chromium

Sulfide byproduct combines with copper, lowering its solubility and reducing copper mobility

Groundwater concentrations in source area rebounded after excavation, but with calcium polysulfide treatment:
Hexavalent chromium lowered from 42,800 to <10 µg/L
Copper lowered from 3,230 to 328 µg/L

Metals

Case Study, Hexavalent Chromium: Redox Manipulation Pacific Northwest National Laboratory – Hanford, Washington

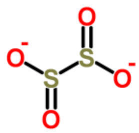


Metals

http://infohouse.p2ric.org/ref/14/0_initiatives/init/summer00/hanford.htm
http://www.wmsym.org/archives/2000/pdf/18/18-4.pdf

Hanford: Permeable Sodium Dithionite Barrier

Dithionite donates electrons to native iron in soil



Fe^{3+}

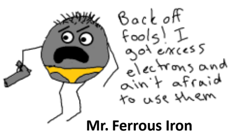
ELECTRON DONOR

ELECTRON ACCEPTOR

Metals

Hanford: Permeable Sodium Dithionite Barrier

Reduced iron donates electrons to Cr(VI)



Mr. Ferrous Iron

Cr(VI) is reduced to less-soluble Cr(III)

Metals

Hanford: Permeable Sodium Dithionite Barrier

Chromium plume stays out of salmon spawning beds

Metals

Adding Amendments to Enhance Natural Attenuation

Excavator

Disc harrow

Chlorinated solvents

Petroleum

Metals

Adding Amendments to Enhance Natural Attenuation: In-Situ Soil Blending

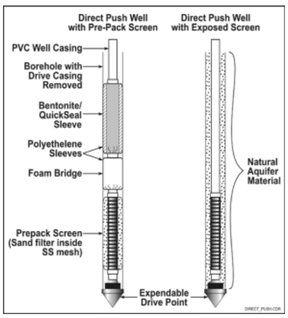
Geo-Con rig: drill platform on Manitowoc crane
(Engineering News-Record 2007)

Redox Tech Soil Blender

Chlorinated solvents | Petroleum | Metals

Adding Amendments to Enhance Natural Attenuation: Additive Injection

Adding Amendments to Enhance Natural Attenuation: Additive Injection

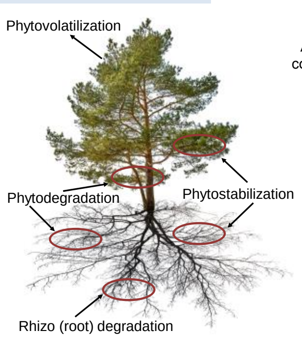


Permanent injection wells
(*Best Practices for Injection and Distribution of Amendments*, NAVFAC 2013)

Adding Amendments to Enhance Natural Attenuation: Additive Injection

Buried perforated injection piping

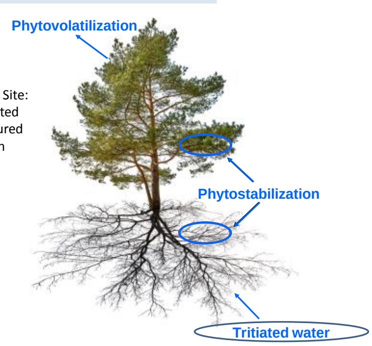
Phytotechnologies



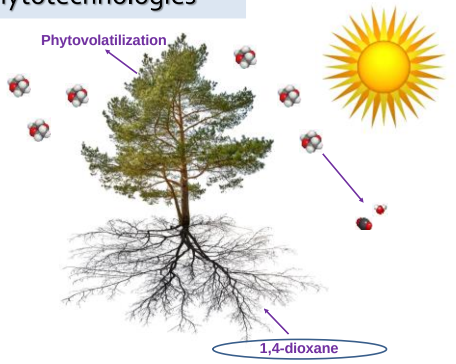
And hydraulic control: Nature's pump & treat system

Phytotechnologies

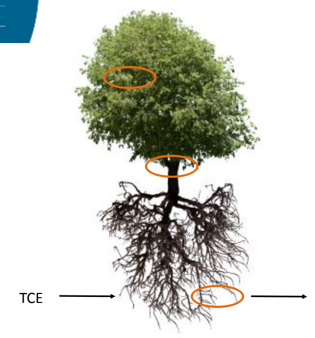
DoE Savannah River Site: Tritium-contaminated groundwater captured in 2.7 million gallon pond and used to irrigate pine trees, minimizing tritium transport to river



Phytotechnologies



Phytotechnologies



Natural bacteria that live inside poplar tree tissues and can degrade chlorinated solvents

Doty *et al*. 2017
Environmental Science & Technology
51(17): 10050-10058.

SUMMARY

Manipulate ELECTRONS to keep pollutants out of groundwater

Clip art used under license from Shutterstock.com

Questions?

National Ground Water Association – www.ngwa.org

U.S. Environmental Protection Agency (EPA) – clu-in.org

U.S. Department of Defense, with EPA & DoE – www.serdp-estcp.org

Air Force Center for Engineering and the Environment – www.usaf.com/orgs/environmental.htm

Naval Facilities Engineering Command – www.navfac.navy.mil

Interstate Technology and Regulatory Council – www.itrcweb.org

Karen.Kinsella@gza.com – 860-573-9787