CARUS REMEDIATION TECHNOLOGIES

Excavation and In Situ Technologies:

drivers for the choice

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My background

•**1993-1994**

Milan Engineers University: First Remediation Dissertation

•**1995-1999**

Dames & Moore / URS: Project Manager

•**1999-2002**

GTI / Fluor Daniel / The IT Group: Project Leader

•**2002-2008**

ERM: Principal Consultant

•**2008 - .....**

CARUS Remediation: EMEA Technical Manager

Agenda

- A bit of history
- Criteria for the selection
- Major technologies Pros/Cons
- Latest Remediation Strategies
- Three examples

A Bit of History

Remediation technology evolution has been pretty similar in most countries. As a consequence of country specific sensitivity to soil and groundwater quality issues (mainly driven by industrial presence), the beginning of the evolutive process started in different years (USA, Netherlands, Belgium, UK, few Italian Regions, ….).

At the beginning contamination was detected due to impact of drinking water resources. Law limits were drinking water standards.

No specific technologies are known (locally), authorities had no experience, question to the hydrogeologists (Universities) and …

A Bit of History

.. the hydrogeologists answer:

Darcy A.K.A.

Pump and Treat (P&T)

Someone thought that after 1-2 pore volumes pumping the contamination would have been removed !! (What about Kow?)

And soil?

A Bit of History

.. Soil was just disposed off in case of visual impact: yellow soil from Chromium plating facilities, oil and soil in refineries.

Then science and technologies developed to find out solutions for the more critical issues such as

- Free floating hydrocarbons (LNAPL)
- Petroleum hydrocarbons in the Vadose
- Dissolved Hydrocarbons (in groundwater)

A Bit of History

At the end of the 80s the remediation technologies were: Air Sparging, Soil Vapor Extraction / Bioventing, skimming systems (air driven, electrical, active, passive…), solidification/stabilisation (from the nuclear industry).

Vacuum was the big new issue of the 90's (the equipment decade) with Multi Phase Extraction (MPE), Vacuum Enhanced Vapor Exctraction, Bioslurping, …

Also in the 90s MNA, Biostimulation, bioaugmentation first for aerobic processes and then anaerobic when chlorinated started to be more popular contaminants.

A Bit of History

At the end of the 90s we started to use more chemicals for In Situ Chemical Oxidation (Fenton, Permanganates), and after some Zero Valent Iron, sulphites (bi, thio) for In Situ Chemical Reduction). Finally come treatment trains.

Along this short story also Chemicals of Concerns, threshold limits (form mg/l to µg/l), analytical methods, risk assessment approach and emerging contaminants changed.

Moving towards In Situ

We started to work with visible (oil) dirty soil and free phase and to protect drinking water resourced with hydrodinamic containment (P&T/Hydraulic barriers).

Over time it became apparent that it was no possible to dig below a refinery or very deep, that it was no possible to dig groundwater and that P&T was a never ending (and sometimes expensive) treatment with severe performance limitations and high costs (Macckay and Cherry 1989; NRC 1994; USEPA 1999).

A widely held view that has emerged is that groundwater cleanup by P&T is virtually impossible though P&T can be used as a containment technique (Siegrist, Crimi, Simpkin 2011).

Moving towards In Situ

Few numbers form a study based on the cleanup costs for 25000 sites with DNAPL Kavanaugh et al. (2003):

•Range to operate a P&T system 30,000 – 4,000,000 $/year

•Median cost to operate a P&T system ~ 180,000 $/year (average cost to complete an ISCO project is 230,000 $)

•Combined cost for all US sites with P&T 2.7-4 billion $/year

•Assuming 30 years life, interest 5-10%, lifecycle cost for all P&T systems is 50 - 100 billion $.

This was the first driver to find some In Situ solution. After In Situ was widely accepted money and time pushed to find some more effective, more reliable and less expensive solution. And this solution came from engineers → more equipment.



But now we can choose

Now we have available a lot of techniques to remediate impacted soil and groundwater, from the classical AS/SVE to the more sophisticated multicomponent ISCO.

In which way, and why, we can choose the “right” (or less wrong) technology? Which are the drivers of this choice?

MONEY, TIME, effectiveness, environmental and social impacts,

In other words we must consider the overall ……………….



But now we can choose

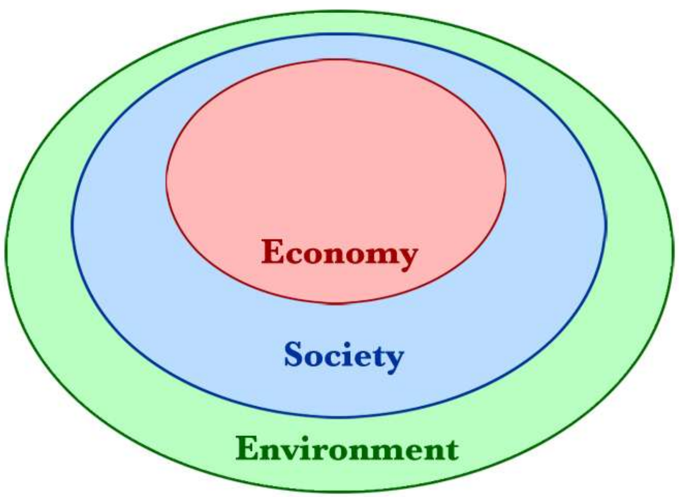
SUSTAINABILITY

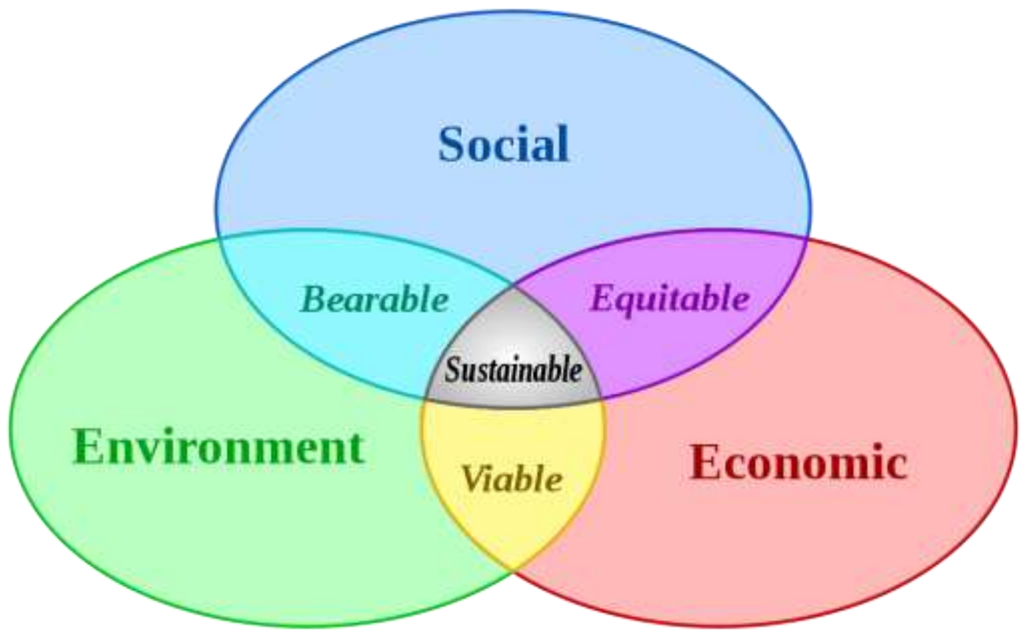
This is a very “fashion” word but includes the main criteria that we have to consider to design a Sustainable Remediation project assuming that all our resources are limited:

- Economic: money and time;
- Environment: effectiveness (contaminants destruction, byproducts, residual contamination, ..)
- Social: residual risk, land use limitation (landfills, NIMBY, ….)

Definition

Sustainable remediation "a remedy or a combination of remedies whose net benefit on human health and the environment is maximized through the judicious use of limited resources." (SURF 2009)





Is that sustainable ? Ex Situ

Dig&Dump

Rapid, no byproducts/residues, no monitoring

Expensive, contamination transfer (no destruction), land use, transport, NIMBY

Dig&Reuse

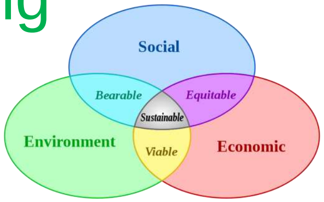
Rapid, no byproducts/residues, no monitoring

Expensive, contamination transfer (no destruction), worse environmental conditions in the reuse site, transport, NIMBY

Dig&Treat+Reuse (excluded inertisation/stabilisation)

Rapid, no byproducts/residues, no transfer, no monitoring

Expensive, transport, NIMBY (minor)





Is that sustainable ? On Site

Soil Washing (separation only)

No byproducts/residues, no transport, no monitoring

Long time, expensive, contamination transfer (no destruction), land use, water requirement, fill soil (quality/quantity), energy

Soil Washing (with treatment)

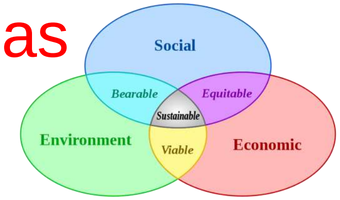
No byproducts/residues, no transport, no monitoring, no fill soil

Long time, expensive, water requirement, energy, chemicals?

Thermal (desorption/incineretion)

No byproducts/residues, no transport, no monitoring, no fill soil

Long time, very expensive, huge fuel requirement, off gas treatment



Is that sustainable ? On Site

Solidifcation/Stabilisation/Inertisation

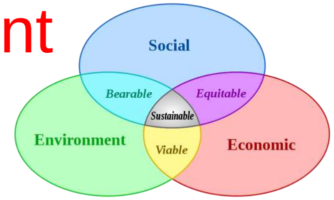
No transport, no fill soil

Long time, can be expensive, stability/duration of the treatment, land use limitations

P&T

Rapid to install (sometimes), no byproducts/residues downgradient (effective migration containment)

Expensive, contamination transfer to shallow receptors, aquifer deployment (overpumping), water treatment systems (O&M, chemicals, carbons,…), monitoring (groundwater and treatment efficiency), never ending, lot of energy (pumps, treatment equipment)



Is that sustainable ? NAPL removal

Dual Pump (water+product)

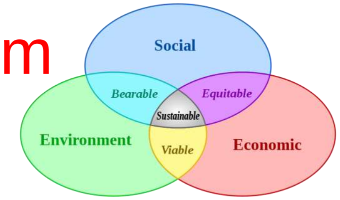
Easy and rapid to install, proven and accepted, containment

Low efficiency due to 2 phases hydrodinamics, Long lasting (for ever?), residual NAPL, see P&T

Multi Phase Extraction (MPE) - Vacuum

High removal efficiency (free product, dissolved, vapors), effective on residual NAPL (capillary forces). bioremediation can be enhanced, proven and accepted

Long lasting (1-3 years), expensive equipment and operation (energy), off gas+water treatment, waste production from treatment, off gas+water monitoring.



Is that sustainable ? NAPL removal

Thermal Enhaced Recovery (LNAPL mainly)

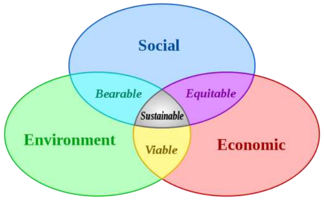
Very effective, rapid results, can be less expensive compared wit "never ending" technologies

Very intensive (lot of energy for few months), some residual NAPL, increased concentrations in GW (increased solubility), bacteria ??

NAPL recovery with skimmers only

Very simple, not expensive, low O&M

Inefficient, long lasting (for ever?), residual NAPL



Is that sustainable ? In Situ

Air Sparging / Biosparging (Aquifer)

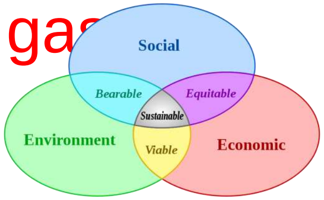
Mass Transfer based on air, simple and easy to install, bioremediation enhanced, proven and accepted

Long lasting (1-3 years), expensive equipment, DNAPL, energy for compressors, off gas production into the soil (SVE required), not suitable for pressurized aquifers, low mass transfer efficiency

Soil Vapor Extraction / Bioventing (Vadose)

Mass transfer based on air, simple and easy to install, bioremediation enhanced proven and accepted

Long lasting (1-3 years), expensive off gas treatment, waste production (condense from KO drums, carbons from off gas treatment), energy for machines, off gas monitoring.



Is that sustainable ? In Situ

Multi Phase Extraction (MPE) – Vacuum (Aquifer+Vadose)

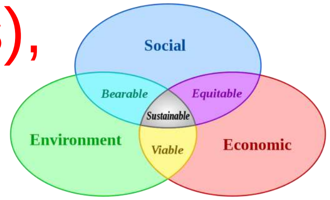
High removal efficiency (free product, dissolved, vapors), effective on residual NAPL (capillary forces). bioremediation can be enhanced, proven and accepted

Long lasting (1-3 years), expensive equipment and operation (energy), off gas+water treatment, waste production from treatment, off gas+water monitoring.

Phytoremediation (Aquifer+Vadose)

Natural process, low cost (usually), can destroy contaminants, accepted

Depth and climate restrictions, long lasting (many years), possible waste production (old plants with accumulated contaminants).



Is that sustainable ? In Situ

Aerobic Biostimulation (Equipment)

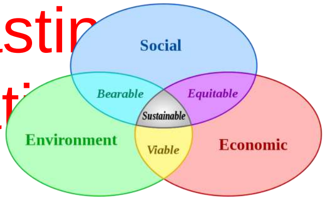
Proven, effective on low to medium concentrations, low cost, presence of autoctonous bacteria, accepted

Long lasting (1-3 years), not very effective with NAPL or high concentrations (toxicity), low Oxygen transfer efficiency for groundwater

Aerobic Biostimulation (Chemicals)

Proven, effective on low to medium concentrations, presence of autoctonous bacteria, accepted

For residual contamination or plume control, high cost depending on contaminants mass (concentration or extent), long lastin
3 years), not very effective with NAPL or high concentrat
(toxicity)

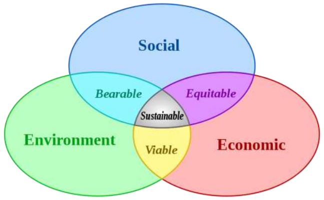


Is that sustainable ? In Situ

Anerobic Biostimulation/Reductive Dechlorination

Proven, effective on low to medium concentrations, low cost, accepted, possibility to use food grade substrates

Long lasting (1-3 years), not very effective with NAPL or high concentrations (toxicity), more complex design and monitoring, byproducts (DCE+VC hang-up), right bacteria strains must be present

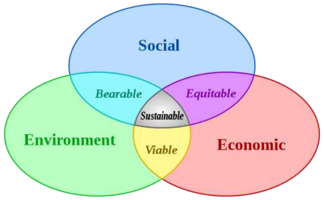


Is that sustainable ? In Situ

MNA Monitored Natural Attenuation (Aquifer+Vadose)

Natural process, very low cost, can destroy contaminants, compatible with other technologies, accepted ?

Dilution is not Solution, long lasting (many years), monitoring can be expensive on the long term, byproducts?, temporary land use limitation (until concentrations decreases), rarely accptable without source treatment

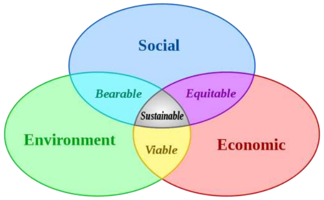


Is that sustainable ? In Situ

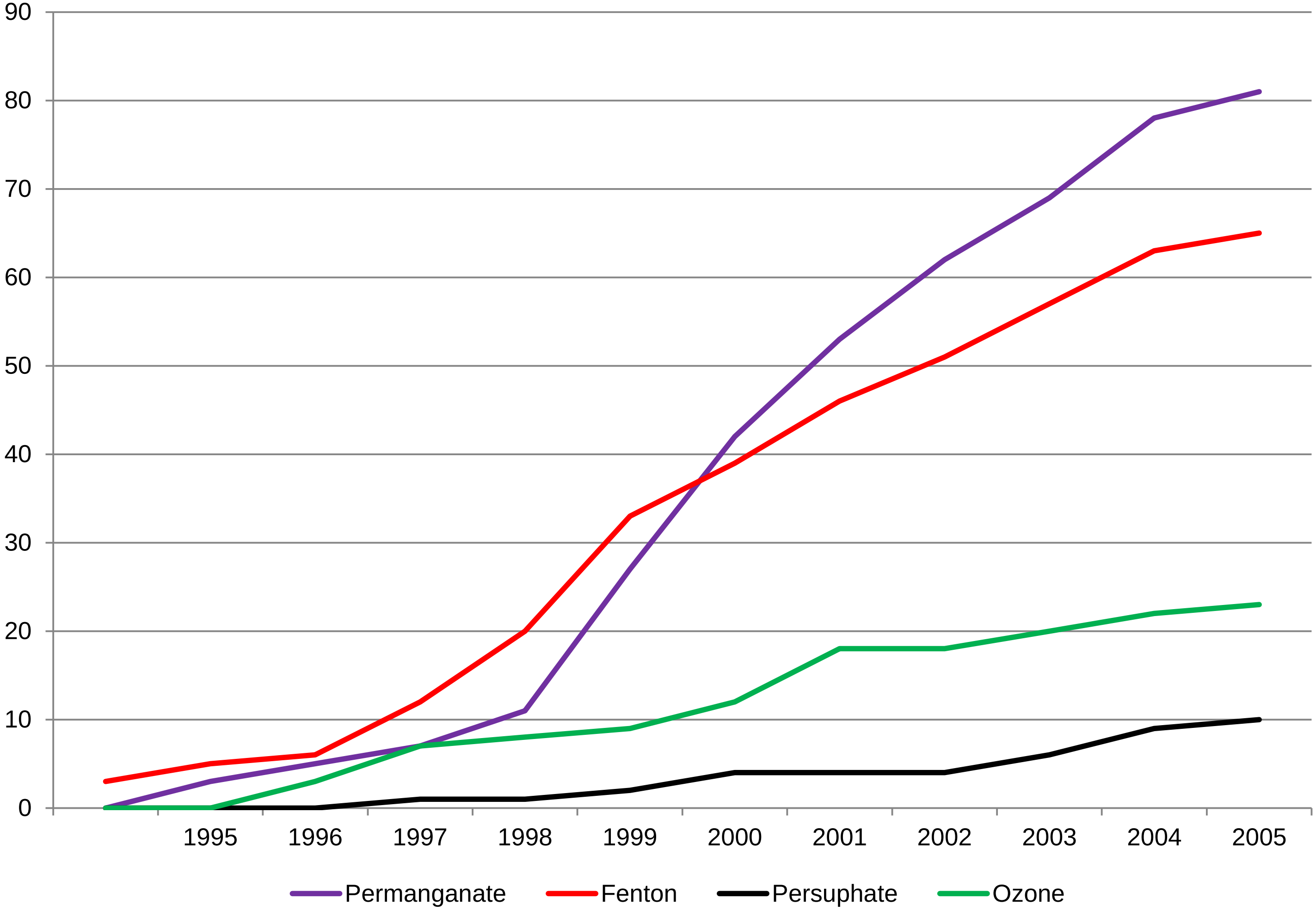
ISCO/ISCR

Rapid, proven, effective on a wide range of contaminants and concentrations, moderate cost for source areas (average 200.000 $ per site), complete destruction is possible, sometimes compatible with bioremediation

Accurate design and source areas identification needed, use of chemicals (do we prefer VC or some Permanganate in our groundwater?), low permeability issues, parassite reactions (NOD), rebound

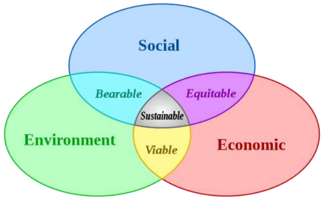


Is that sustainable ? In Situ



US ISCO sites

Krembs, 2008

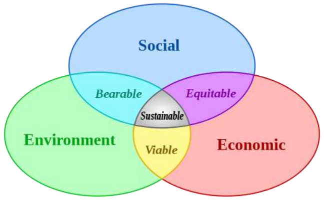


Is that sustainable ? In Situ

Electrochemical/Electrophysiscal processes

Can be effective also on recalcitrant compounds, enhances mobility/contact, cost can be reasonable

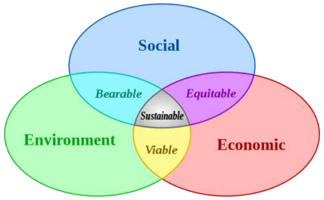
Immature, depth limitations (electrodes installation), long lasting



Is that sustainable ?

- Dig&Dump — no (but for a very small amount of soil ….)
- Pump&Treat — never (this is not remediation – with one exception)
- Natural attenuation — yes (but dilution is NOT solution..)
- Bioremediation — yes but not always effective (hot spots!!)
- Chemical O/R — yes but accurate design is mandatory
- SVE, AS, Vacuum — yes but only of impact is reasonable

  (fuel, footprints, equipment, steel,)



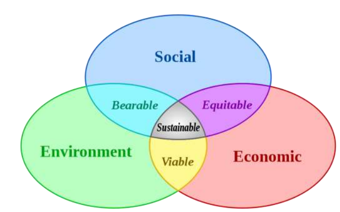


A Bit of History again - Strategies

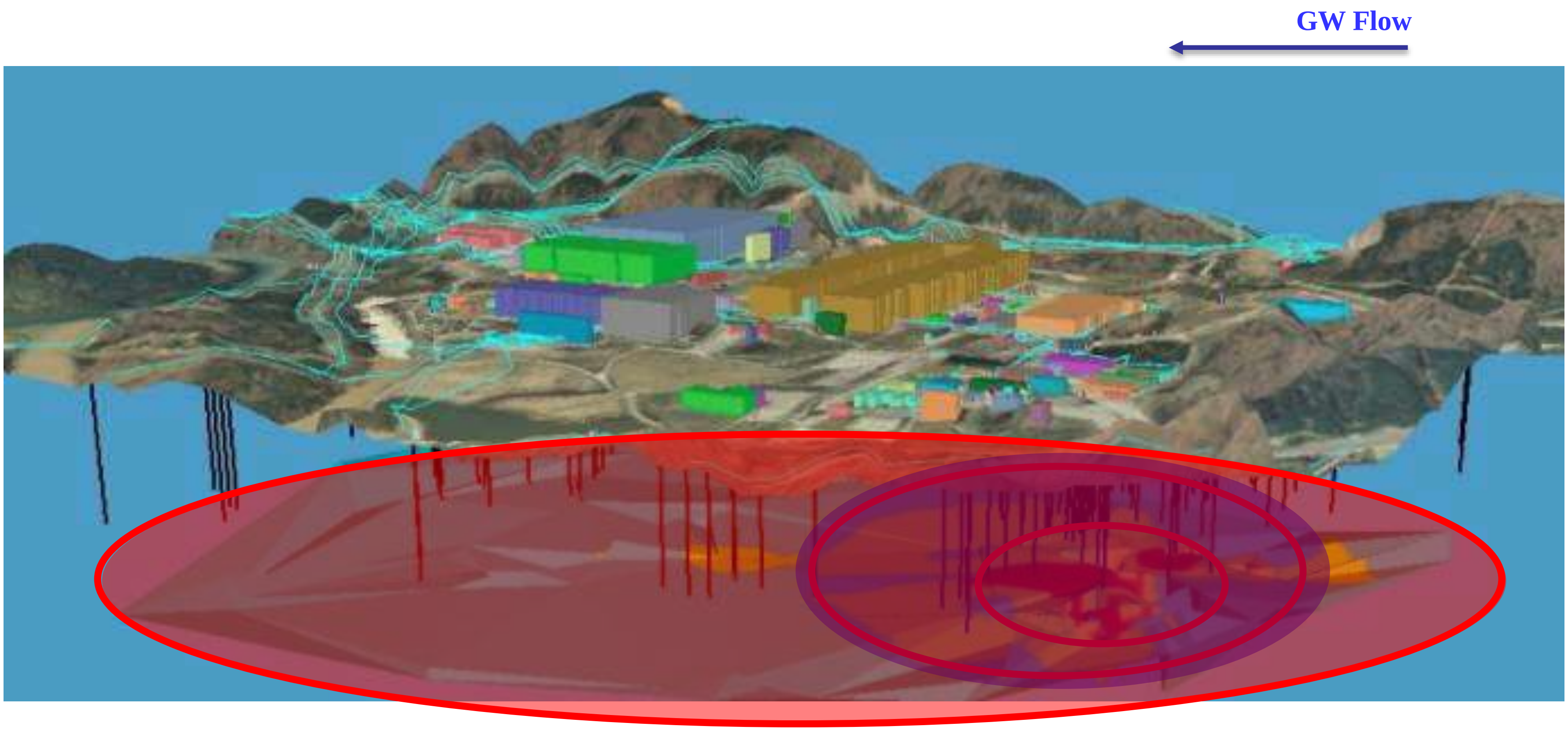
"Early strategies based on containment (P&T). Then attention was addressed to source areas remediation and in most of sites we were selecting one specific technology "*(1 site 1 technology)*.

"Currently, remediation of areas with source zones is increasingly viewed as best accomplished by combining remedies simultaneously or sequentially for different zones of contamination" (NRC, 2005).

Sustainable remediation is "a remedy or a combination of remedies whose net benefit on human health and the environment is maximized through the judicious use of limited resources." (SURF 2009)



Technology Selection

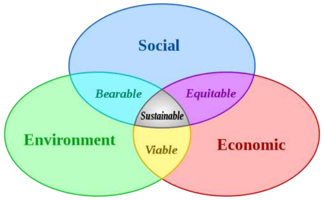


Dissolved Plume Area 10% Mass	Core Plume Area 10% Mass	Source Area 80% Mass
75% Plume Size	20% Plume Size	5% Plume Size
Bioremediation, Natural Attenuation, ISCO-ISCR (speed only)	ISCO - ISCR, BioRemediation,	Physical, Thermal, ISCO - ISCR

Treatment Trains – Three Cases of Species

ISCO with RemOx L Permanganate ISCO Reagent and Reductive dechlorination with CAP18 for a site in The Netherlands

EZVI: Combined Zero Valent Iron (ZVI) with CAP18 in two sites in the USA





CARUS REMEDIATION TECHNOLOGIES

RemOx L ISCO In Situ Chemical Oxidation

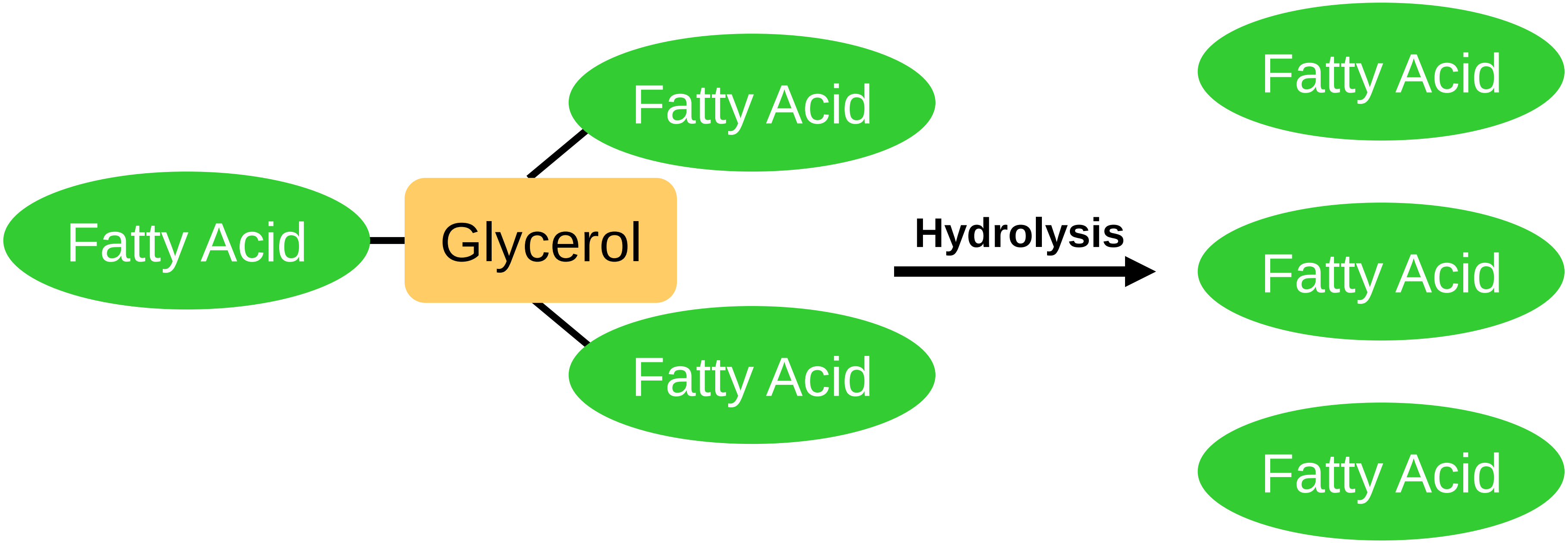
and CAP 18 Biotic Reductive Dechlorination

What is RemOx L

RemOx L is a Sodium Permanganate 40% solution designed for groundwater remediation with the lowest trace metals content in the market.

What is CAP 18

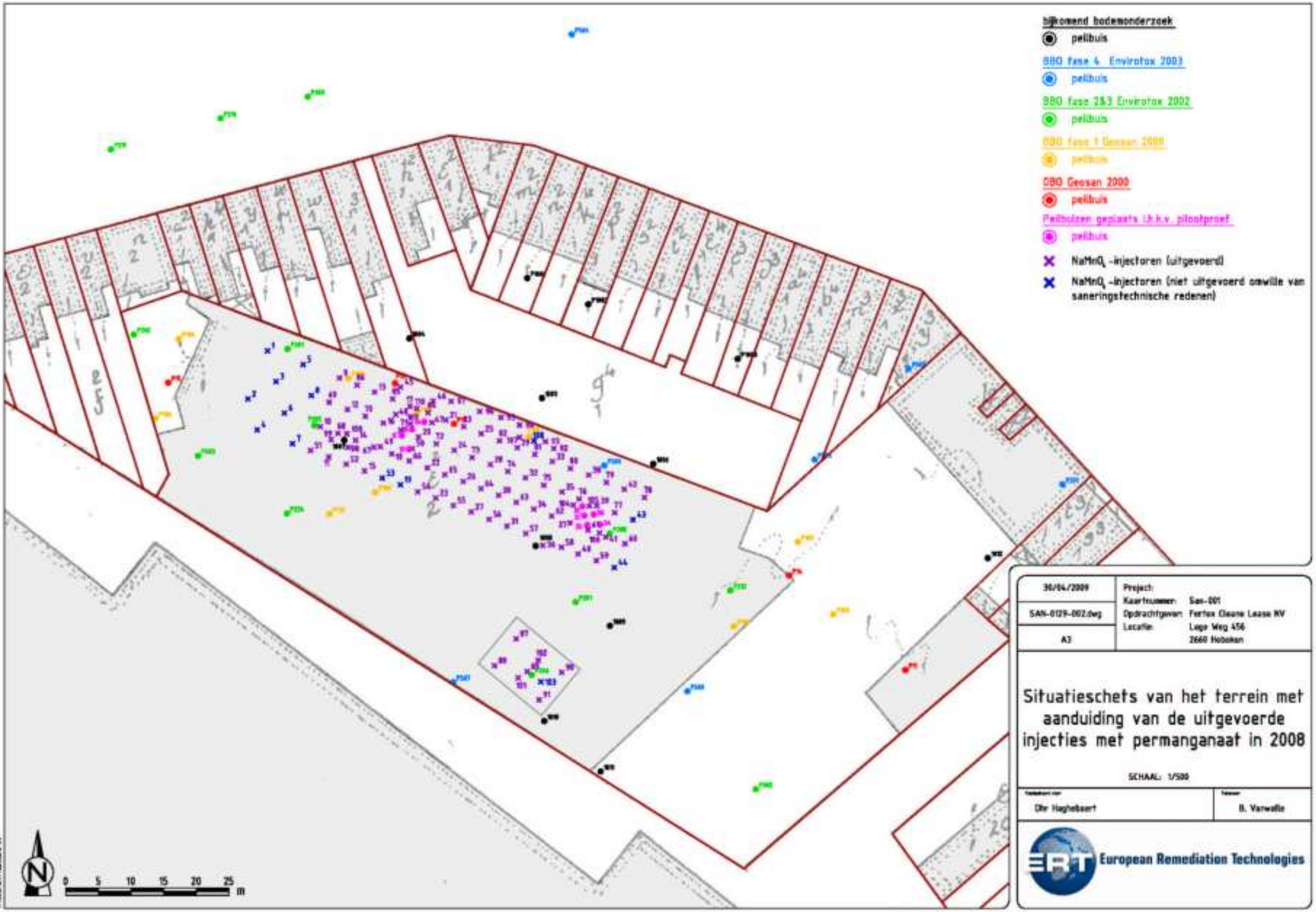
Food Grade refined and blended vegetal oils for reductive dehalogenation



CAP18™

RemOx L and CAP18-ME®-results (Zone 1)

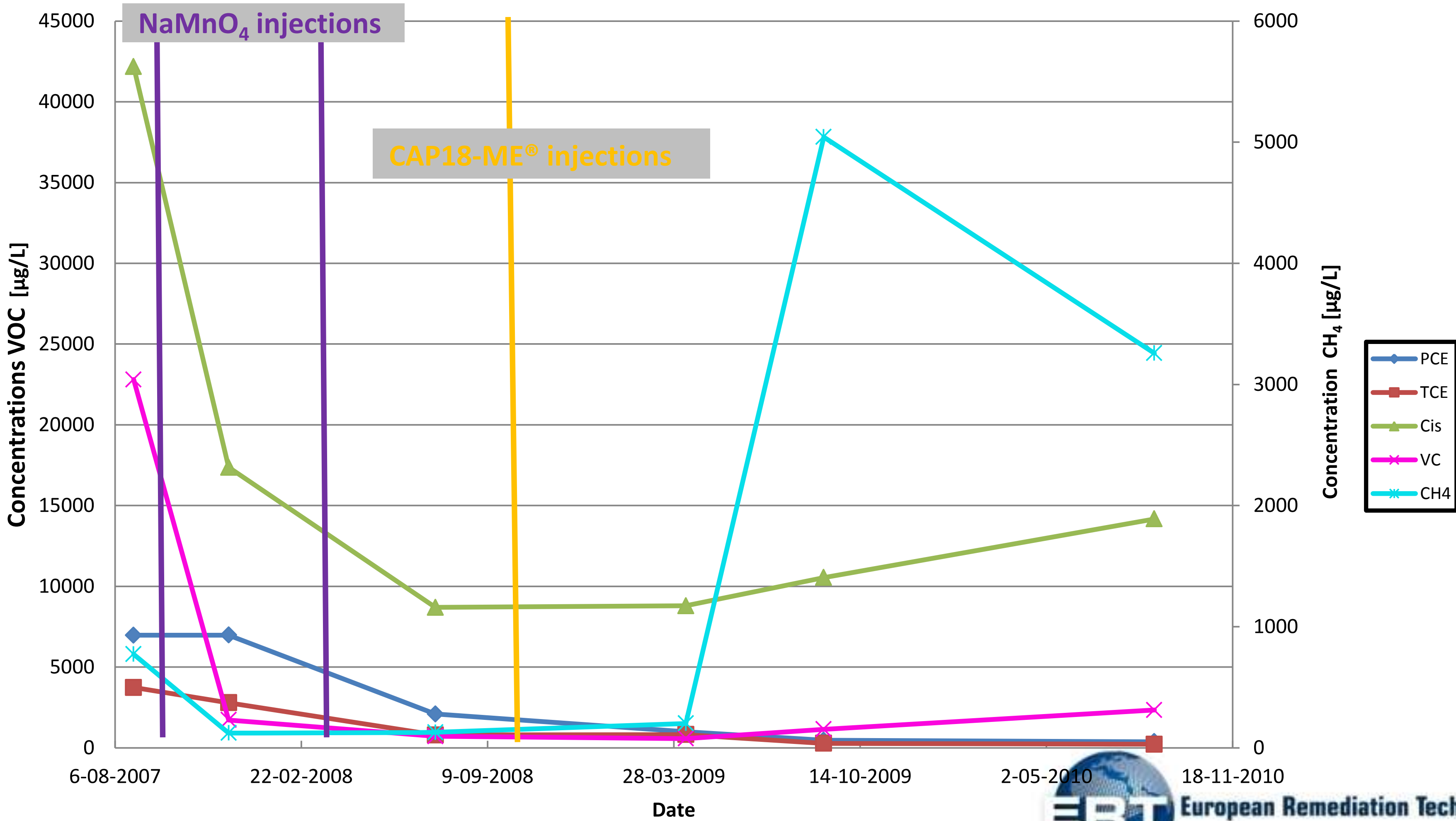
CAPISCO™-project region Antwerp


bijkomend bodemonderzoek
pelibuis
BBO fase 4 Envirotox 2003
pelibuis
BBO fase 2&3 Envirotox 2002
pelibuis
pelibuis
OBO Geosan 2000
pelibuis
Peilbuizen geplaatst i.h.k.v. pilootproef
pelibuis
NaMnO4 -injectoren (uitgevoerd)
NaMnO4 -injectoren (niet uitgevoerd omwille van saneringstechnische redenen)
30/04/2009
SAN-0129-002.dwg
A3
Project:
Kaartnummer: San-001
Opdrachtgever: Fortex Cleane Lease NV
Locatie: Lage Weg 456
2660 Hoboken
Situatieschets van het terrein met aanduiding van de uitgevoerde injecties met permanganaat in 2008
SCHAAL: 1/500
Dhr Haghebaert
B. Vanwalle
European Remediation Technologies
0 5 10 15 20 25 m
N

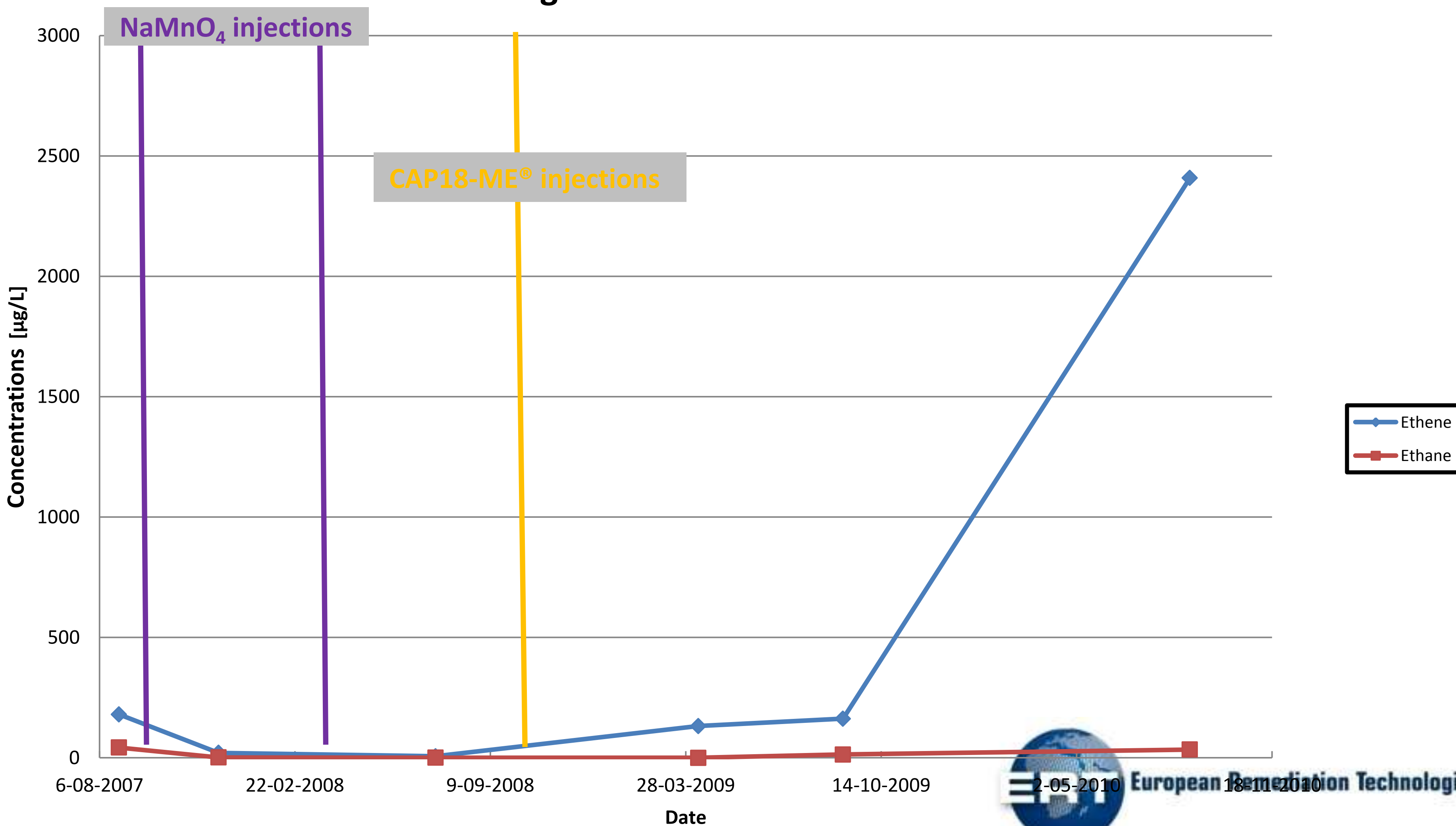
Full scale design :

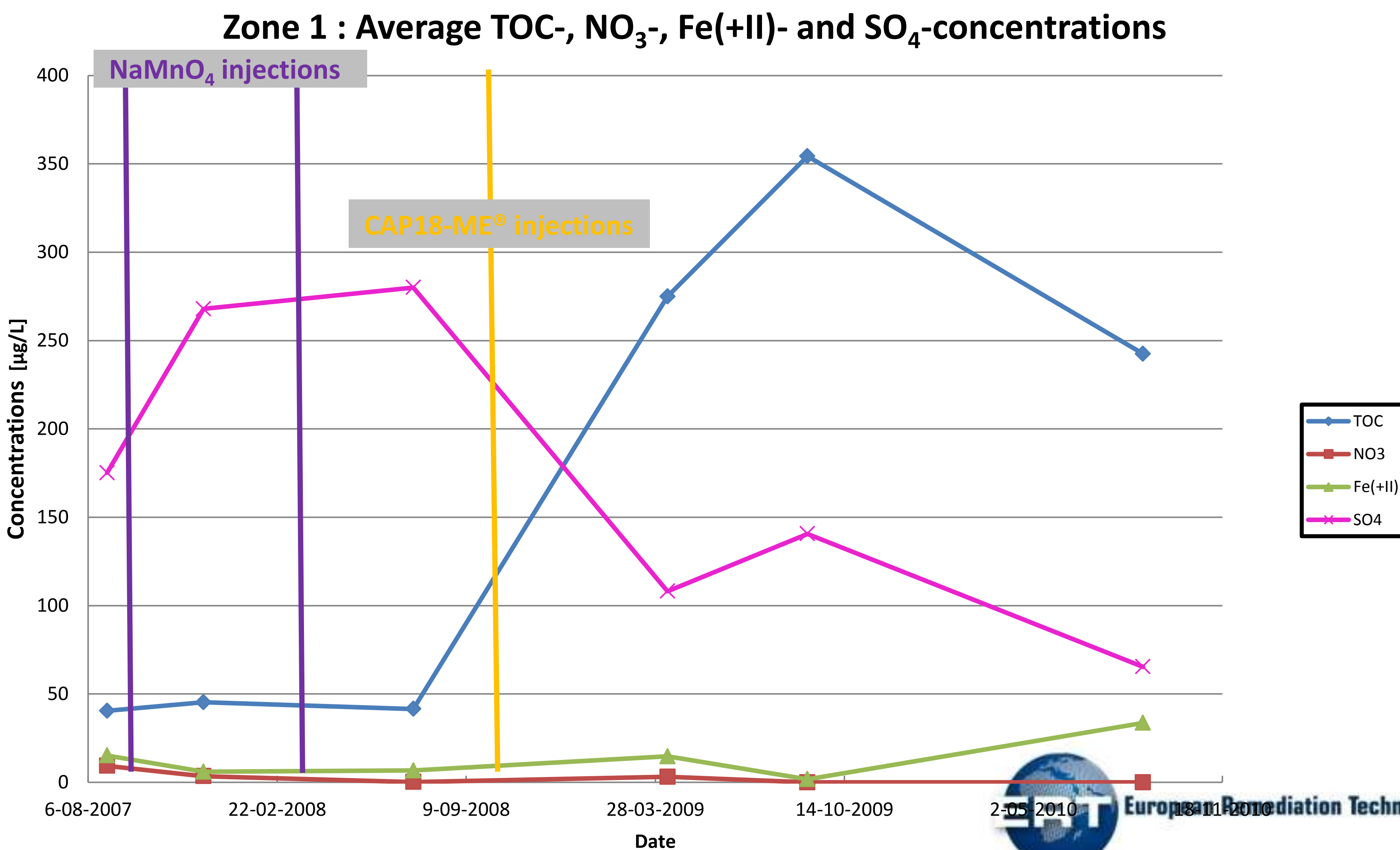
- ***Injections via 'direct push' :***
  - ✓ *August 2007 :* 6.720 kg $NaMnO_4$ 40 % diluted till 8% divided into circa 45 injectors.
  - ✓ *March 2008 :* 5.440 kg $NaMnO_4$ 40 % diluted till 4% injected via circa 100 injectors.
  - ✓ *October 2008 :* 2.950 kg CAP18-ME® injected into 82 injectors(source).
- ***Conclusion :*** decrease of VOCs is sufficient to justify the after-treatment with CAP18-ME® (October 2008).

Zone 1 : Average VOC- and CH_4-concentrations



Zone 1 : Average ethene and ethane concentrations





European Remediation Technologies

REDUCTION of the pollutants :

Pollution	After $NaMnO_4$	After CAP18-ME®
PCE	70%	95%
TCE	79%	94%
Cis	79%	66%
VC	97%	90%

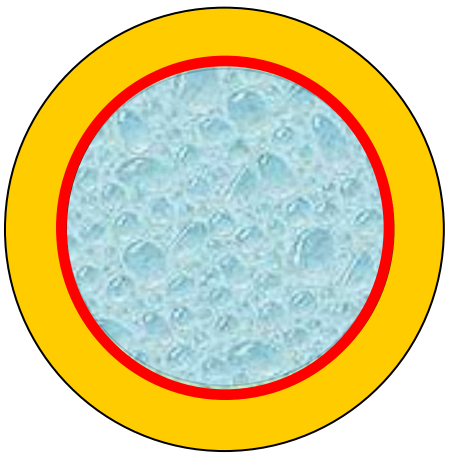


CARUS REMEDIATION TECHNOLOGIES

Zero Valent Iron (ISCR) and Reductive Dechlorination (BIO)

CARUS®

EZVI with CAP 18

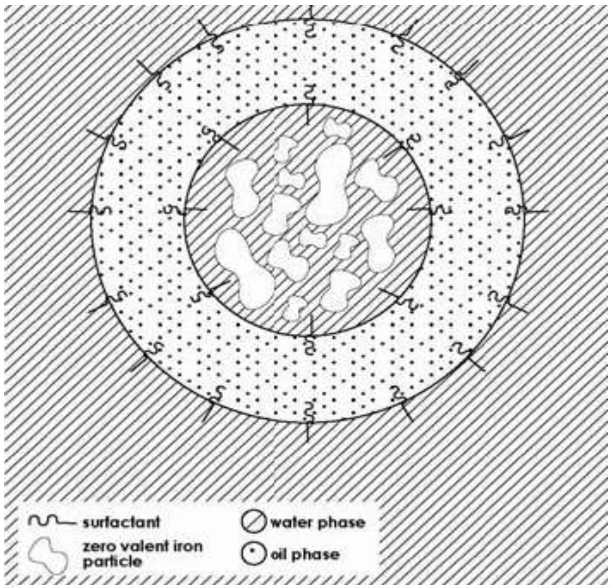


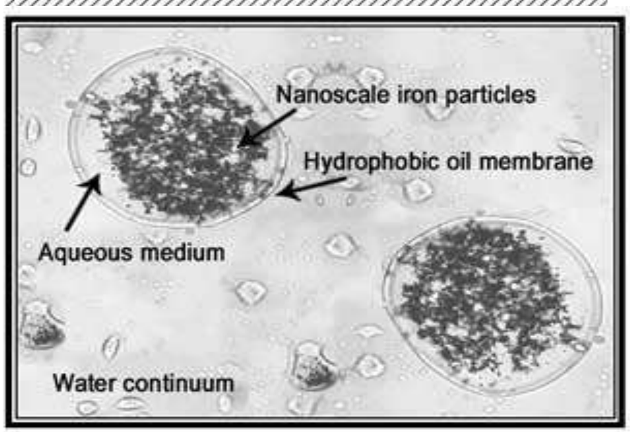
1) Micro Scale ZVI
2) Suspended in Water
3) Bound by a Polar Surfactant
4) Encased in CAP18

- This is referred to as a micelle
- The micelle is a few to 20 microns in size

CARUS®

EZVI



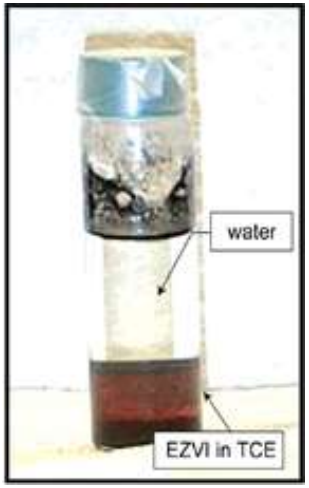


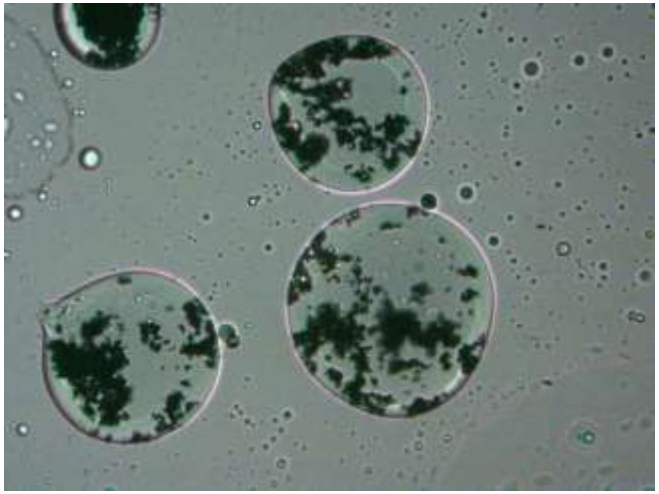
Quinn et. al., 2005

EZVI involves placing micro-scale zero-valent iron particles into a surfactant-stabilized, biodegradable water-in-oil emulsion. This emulsion is injected into DNAPL-contaminated zones of the subsurface. The DNAPL then phase partitions into the outer hydrophobic membrane of the emulsion and moves into the aqueous interior of the emulsion where the contaminant reacts with the zero-valent iron. Through a process known as reductive dehalogenation, the DNAPL and its daughter products are degraded into ethene and other benign end products. These by-products are further degraded through biological activity in the subsurface.

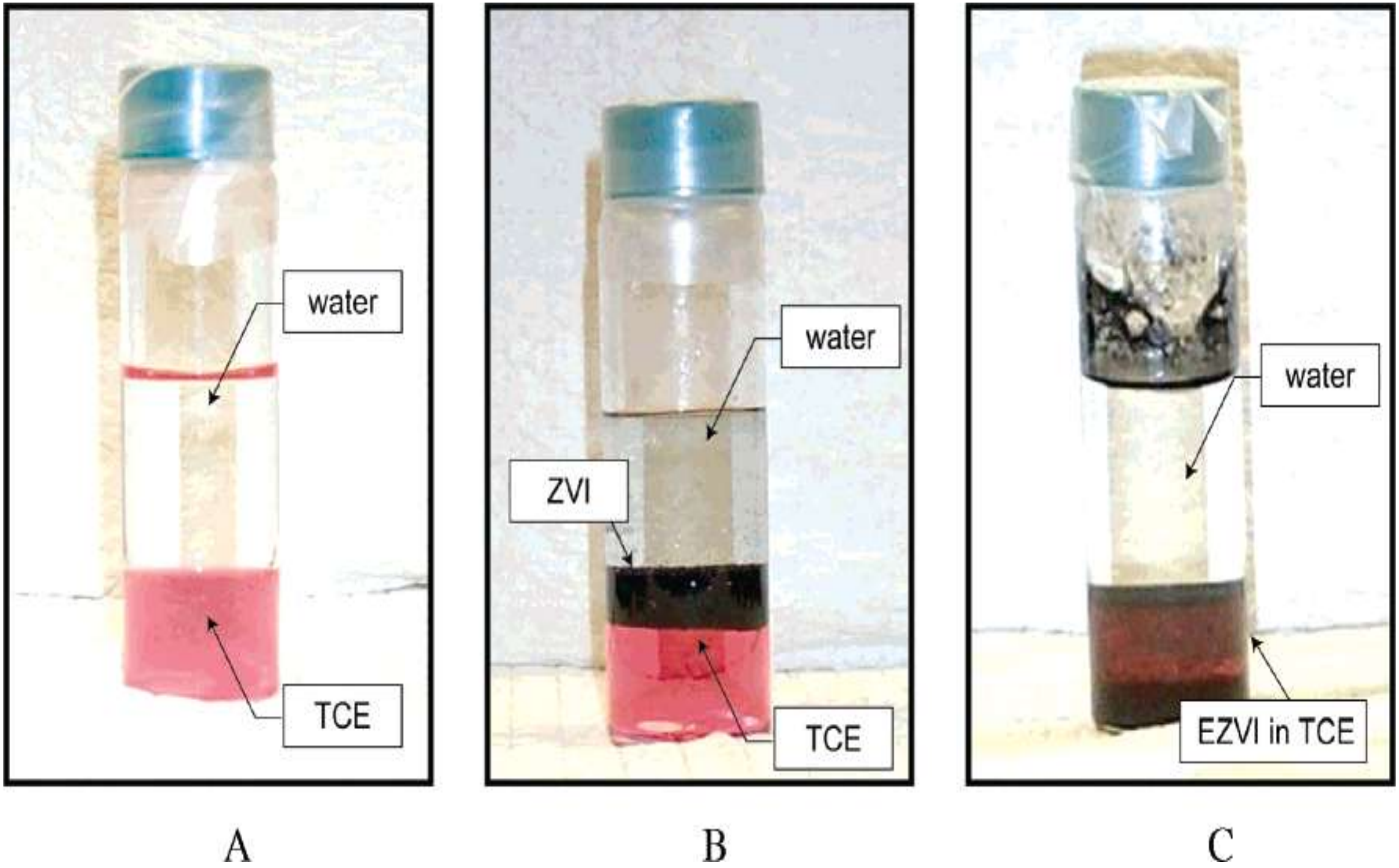
EZVI Characteristics

- EZVI acts as a DNAPL
- Hydrophobic exterior membrane mimics DNAPL characteristics
- EZVI is miscible with DNAPL globules, stringers, pools
- Dissolved phase VOC will preferentially partition into emulsion

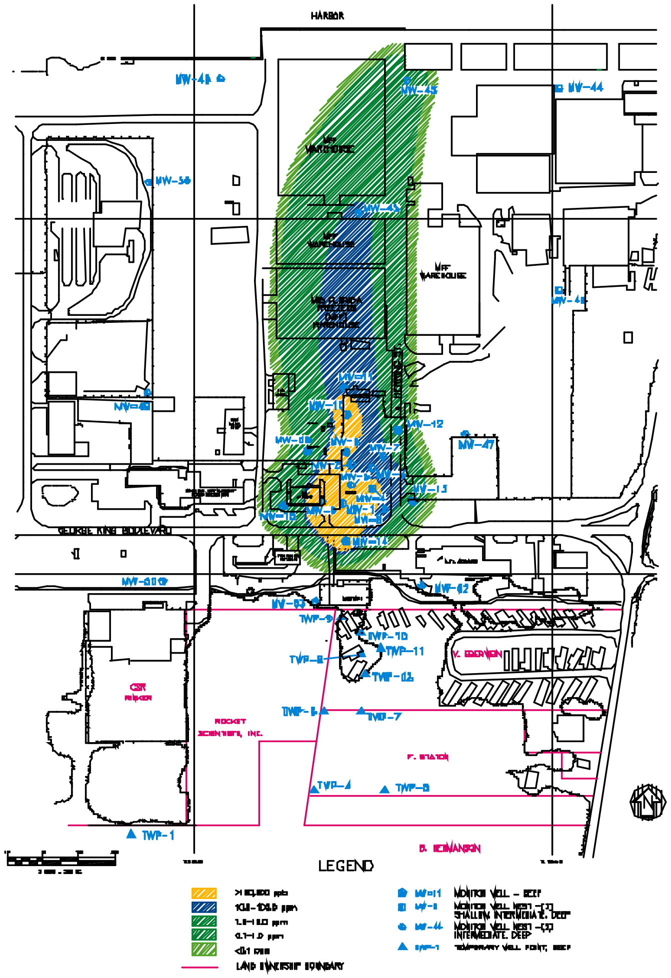




EZVI Characteristics



EZVI

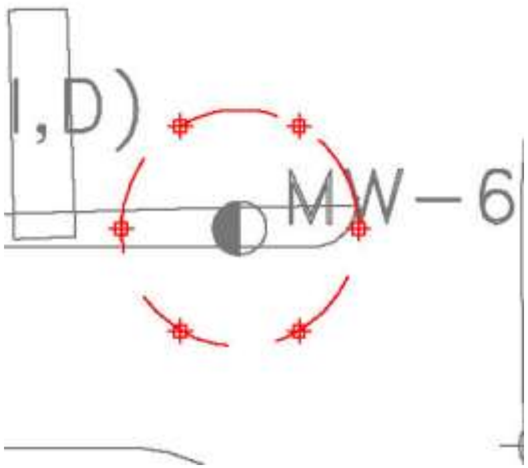


Private Client – Central Florida

TCE source area with dissolved plume

EZVI

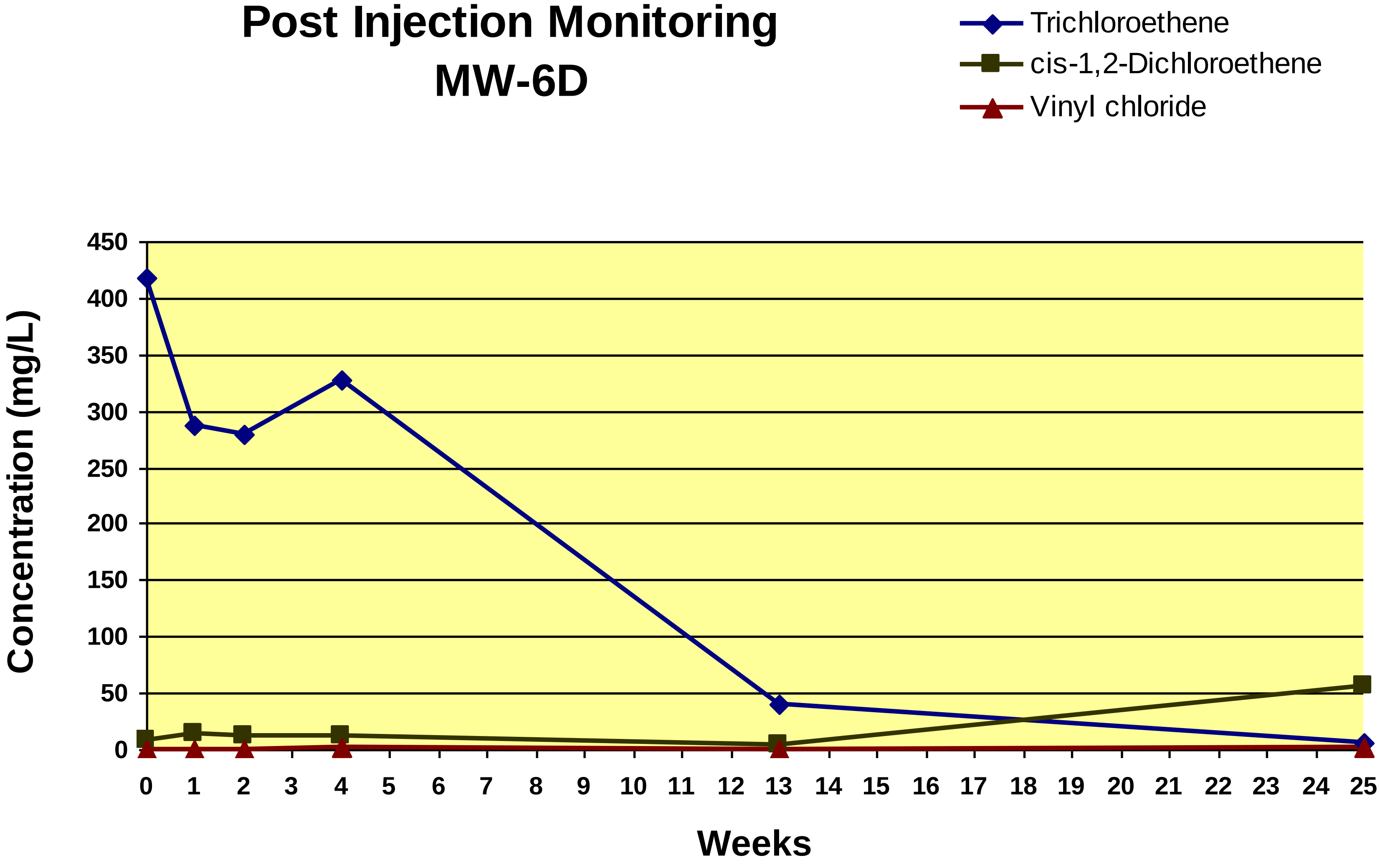
- Approach for Pilot Study was to focus EZVI injections on location of former UST and sump area that comprised the "bulls eye" for the source area.



- The injections were delivered to a deep zone (13 m) and an intermediate zone (10 m) that were separated by a low permeability layer.

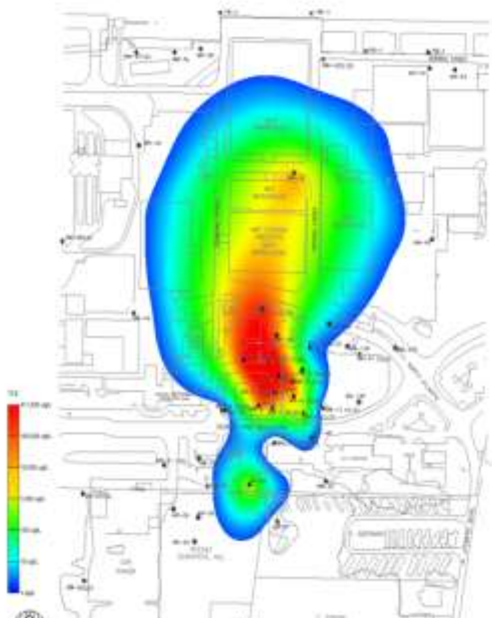
EZVI

Post Injection Monitoring
MW-6D

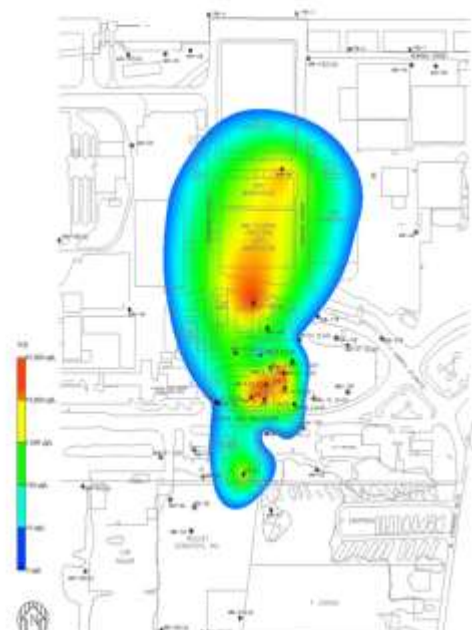


CARUS®

EZVI



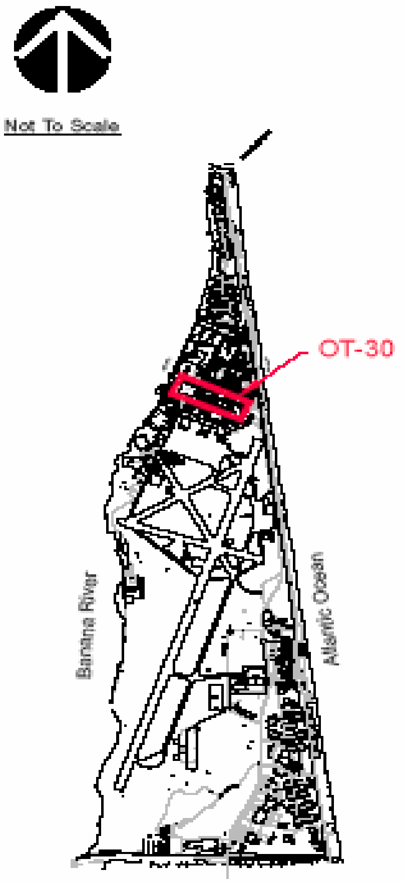
2008 TCE Plume
before EZVI

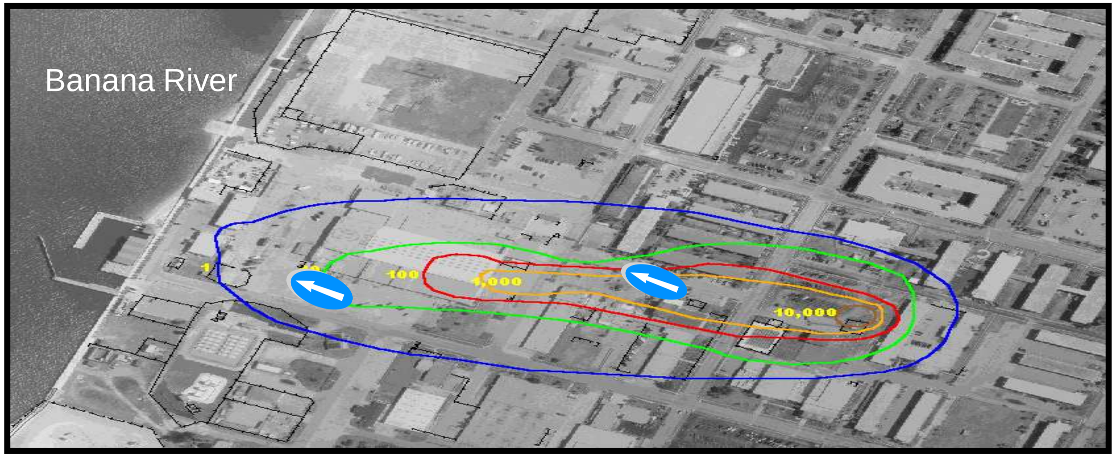


2009 TCE Plume
after EZVI

- 98% concentration reduction of TCE within 6 months
- 85% reduction of total organo-chlorine mass (i.e. TCE, DCE, VC)

EZVI Full Scale DOD Facility





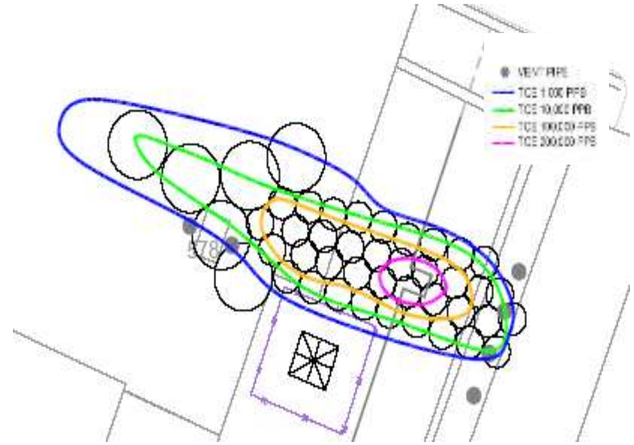
EZVI

Approach was to:

- Inject EZVI into source area where TCE concentrations exceeded 100 ppm; and

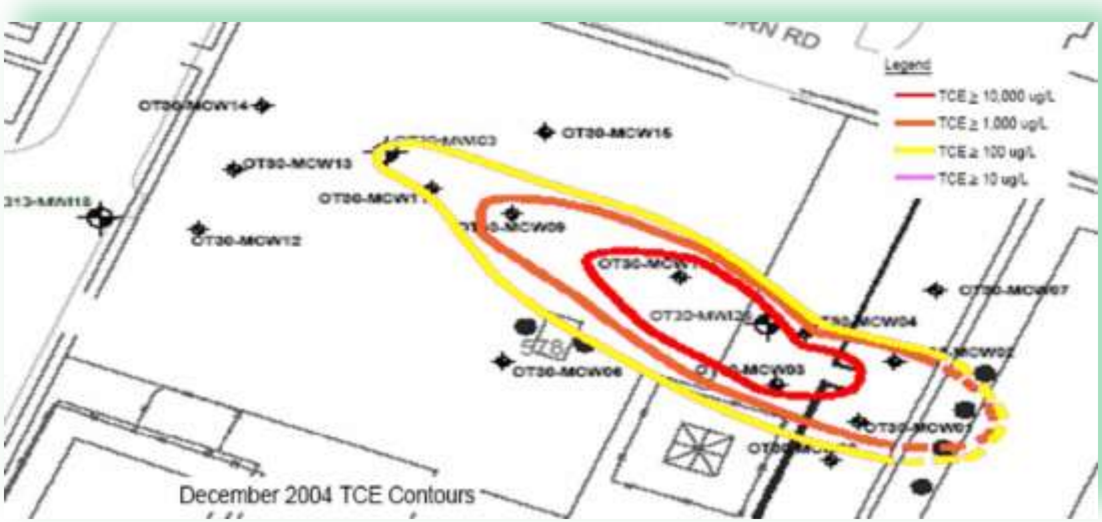
- Inject CAP18 down gradient of source area where TCE concentrations were between 10 – 100 ppm.

Injections were conducted so that source material was surrounded by EZVI and CAP18 with the highest concentration area being injected last.



CARUS®

EZVI



TCE
Before
and After
Treatment

CARUS®

EZVI

Benefits

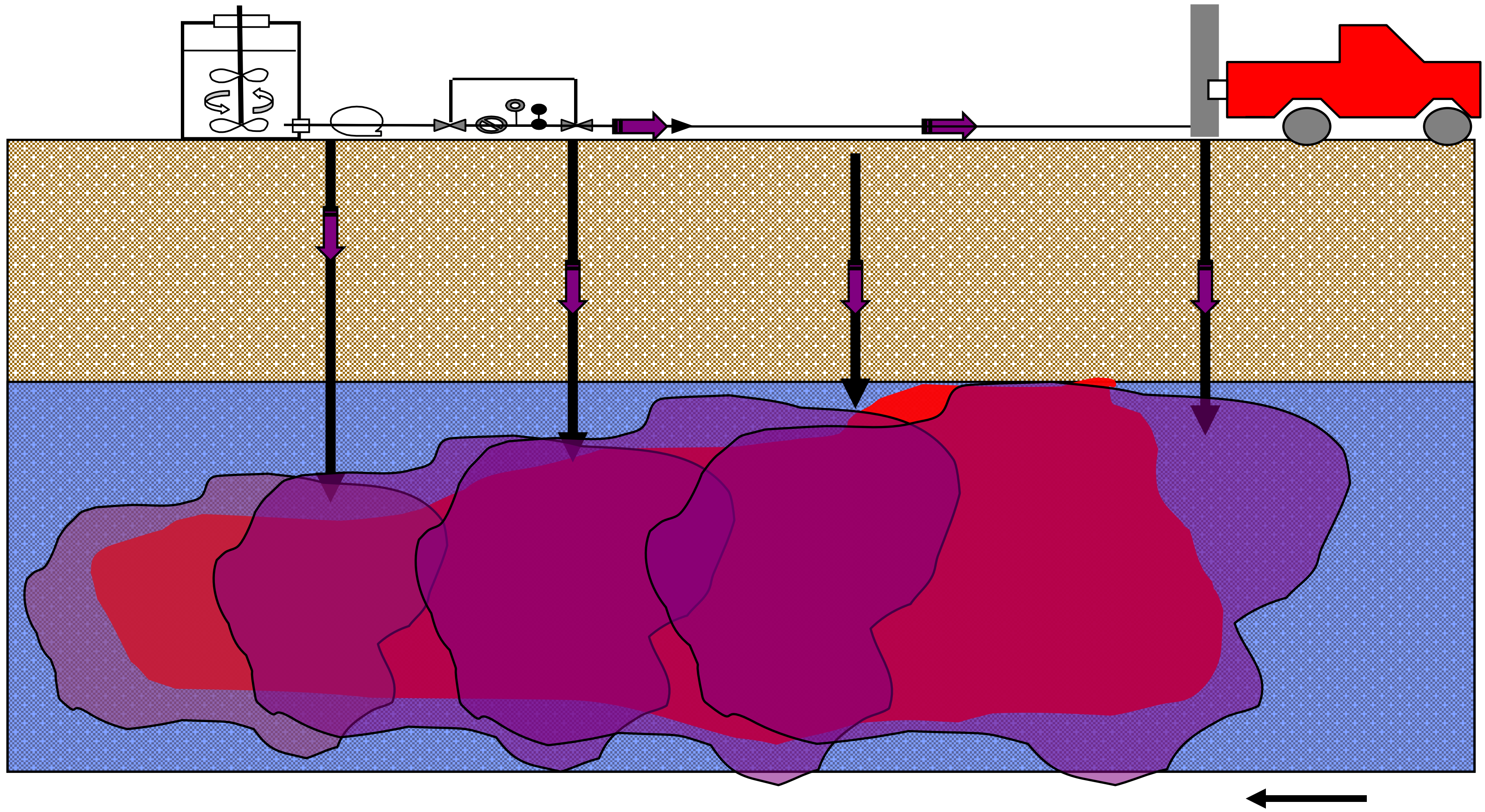
- Directly treats contaminant source
- Does not mobilize contaminant
- Requires less treatment time
- Cost competitive
- Generates less toxic & more easily degraded by-products
- Is environmentally friendly “GREEN”
- Is effective in oxidative or saline environments

Success Highlights

- Field-tested by the U.S. EPA under the SITE Program
- Used at commercial and government sites to treat both TCE and PCE
- Applied in multiple states, including; FL, AR, NC, TN, IL, OH, TX, LA, WV, MA
- 2005 Award for Excellence in Technology Transfer by the Federal Laboratory Consortium
- 2005 NASA Government Invention of the Year
- 2006 NASA Commercialization Invention of the Year
- 2007 NASA “ Technology Hall of Fame” Inductee

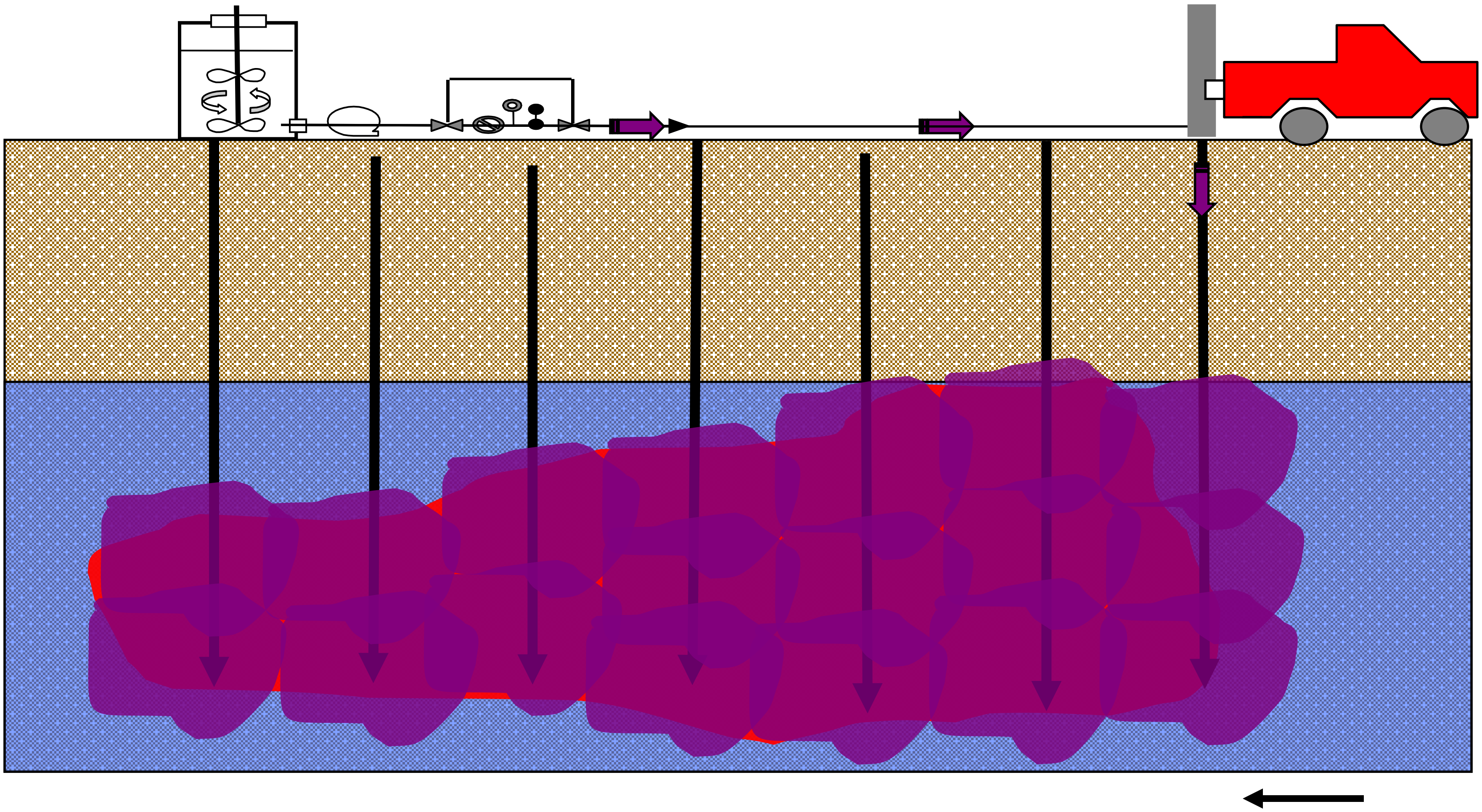
CARUS®

Simplified Injection



CARUS®

Simplified Direct Push Injection



CARUS®

Permanganate Injection Equipment

CARUS®

Permanganate Injection Equipment

Permanganate Injection Equipment

Permanganate Injection Equipment

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