Practical Considerations for Pilot Tests of Reductive Reagents

Evonik | Soil and Groundwater Remediation
March 1, 2023 | Daniel Leigh

Introduction

Why this presentation?

Our technical group regularly discuss projects we are involved with and have observed common practices that make projects successful and some that make projects less than successful. This presentation is intended to help the everyday practitioner understand the main aspects of making a pilot test successful based on our collective experience.

What this presentation is intended to:

Provide some ideas on the practical aspects of conducting pilot tests based on Evonik’s Team’s collective experience at hundreds of sites around the world with various reductive reagents

What this presentation is not intended to be:

A guidance document for conducting a pilot or full-scale application of reductive reagents at any specific site. We are glad to participate in your project and can provide input and review your results.

Presentation Outline:

Reductive Processes
Planning your Project
Applying your Reagents
Performance Monitoring
Data Evaluation

Why Not Just Conduct Laboratory Bench Tests?

Reductive technologies applied over 30 years and follow well-defined –understood patterns

Bench tests can be very useful and may be necessary for some situations

- Mixed or unusual contaminants
- Very high concentrations
- Extreme conditions (i.e., high salinity, very low, very high pH)

Evonik has a complete testing laboratory in Tonawanda, New York

Bench tests are usually conducted under ideal conditions, not site conditions

- Usually conducted at higher temperature (~20C/68F)
- Typically, major and minor nutrients are added to increase results
- Reagents and matrices are homogenized and mixed to increase contact time and reaction rates

Bench tests can take months to over a year to fully complete. This delays the remedial process.

Most representative data are generated during field pilot tests.

Reductive Processes

Biological, Abiotic and Biogeochemical Reduction

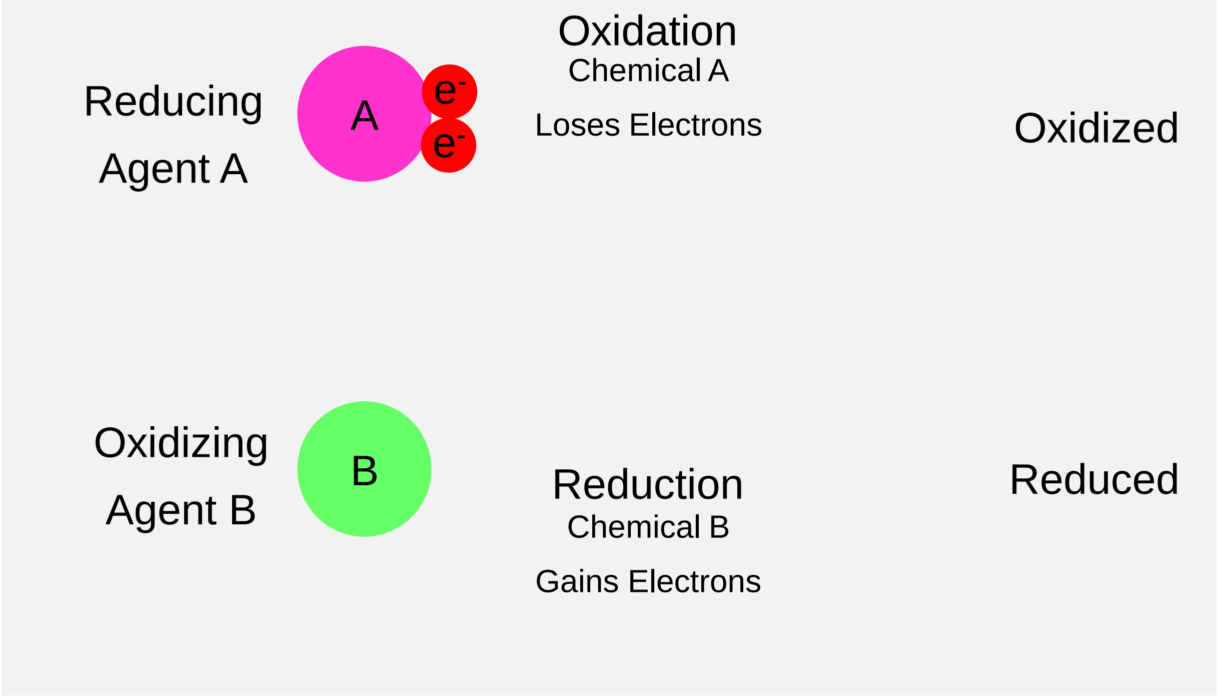
Biological, Abiotic and Biogeochemical Reductive Treatment Occurs by an Oxidation-Reduction (Redox) Reaction.

Oxidation – Reduction: Definition

“a type of chemical reaction in which the **oxidation states** of atoms are changed”

This occurs by transfer of electrons between chemical species

Oxidation of one chemical results in the reduction of another.
Reduction of one chemical results in the oxidation of another.



Reducing Agent A

Oxidation
Chemical A
Loses Electrons

Oxidized

Oxidizing Agent B

Reduction
Chemical B
Gains Electrons

Reduced

Oxidation is the ***loss*** of electrons or an *increase* in the oxidation state of an atom, an ion, or of certain atoms in a molecule.

Reduction is the ***gain*** of electrons or a ***decrease*** in the oxidation state of an atom, an ion, or of certain atoms in a molecule (a reduction in oxidation state).

Reductive Treatment is where the Relatively **Oxidized** contaminant becomes the **Reduced** chemical

Reductive Treatment of Chlorinated Organic Contaminants

CVOCs are “relatively oxidized” = electron acceptor
Treatment by adding a “relatively reduced” compound = electron donor

Biological treatment

- Apply organic substrate (electron donor; e.g., ELS)
- Bacteria transfer electrons from the donor to the acceptor to reduce the oxidized contaminants to non-toxic chemicals.
- Bacteria reduce the oxidized contaminants to less soluble reduced chemicals (e.g., Chromium [VI] to [III])

Abiotic treatment

- Apply an inorganic reduced chemical (e.g., ZVI,).
- Relatively oxidized contaminant is reduced to non-toxic end products by contact with reduced chemical (CVOCs).
- Relatively oxidized soluble contaminant is reduced to a less soluble form (e.g., Cr[VI] to Cr[III])

Biogeochemical treatment

- Apply organic substrate (e.g., ELS) and an inorganic electron acceptor (e.g., sulfate) (e.g., Geoform Reagents)
- Bacteria use organic substrate to reduce the sulfate creating a reactive reduced mineral (e.g., pyrite (FeS_2)
- Relatively oxidized contaminant is reduced to less toxic chemical by contact with reduced mineral.
- Relatively oxidized soluble contaminant is reduced to a less soluble chemical (e.g., Cr[VI] to Cr[III]) or by combining the metal with a reduced ion (e.g, arsenic/arsenopyrite).

Electron donors for H_2 production

Molasses

Starch

Cheese whey

Emulsified vegetable oil

Corn syrup

Lactose

Glucose

Ethanol

Methanol

Propanol

Lecithin

Glycerol, xylitol, sorbitol

Acetic acid and its salts

Lactic acid and its salts

Propionic acid and its salts

Citric acid and its salts

Various Bean Oils (soy, guar)

Benzoic acid and its salts

Oleic acid and its salts

Polylactate esters of fatty acids (e.g.., Glycerol tripolylactate)

Food process byproducts including milk whey or yeast extract

Complex organic material such as wood chips

Complex sugars

Molecular H_2

Only H_2 has been shown to be an electron donor for cis 1,2-DCE and vinyl chloride conversion to ethene

Draft General Waste Discharge Requirements for
In Situ Groundwater Remediation – Santa Ana Water Quality Control Board CA, 2013

Chemical Reducing / Reductive degradation

Ferrous Chloride

Ferrous Carbonate

Ferrous Gluconate

Sorbitol Cysteinate

Sodium Sulfide

Calcium Polysulfide

Sodium Dithionite

Zero Valent Metals

Zero Valent Zinc

Zero-Valent Iron

- Granular
- Emulsified
- Micro-scale
- Nano-scale
- Sulfidized

Draft General Waste Discharge Requirements for
In Situ Groundwater Remediation – Santa Ana Water Quality Control Board CA, 2013

Planning the Project

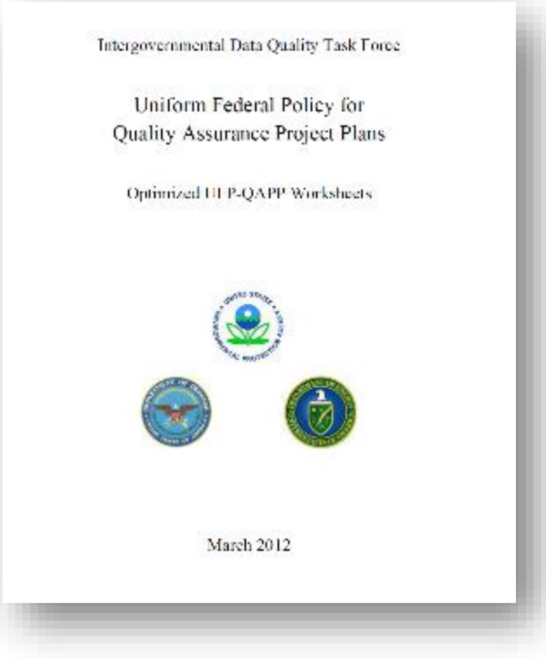
"… as we know, there are ***known knowns;*** *there are things we know we know. We also know there are* ***known unknowns;*** *that is to say we know there are some things we do not know. But there are also* ***unknown unknowns****- the ones we don't know we don't know."*

– Donald Rumsfeld

Knowing the Knowable Unknowns

Questions to ask and answer when planning a pilot test:

- What is the environmental question that is being answered?
- What will the data be used for?
- What types of data are needed (matrix, target analytes, analytical groups, field screening, onsite analytical or offsite laboratory techniques, sampling techniques)?
- Are there any special data quality needs, field or laboratory, in order to support environmental decisions?
- Where, when, and how should the data be collected/generated?



Intergovernmental Data Quality Task Force

Uniform Federal Policy for
Quality Assurance Project Plans

Optimized UFP-QAPP Worksheets

March 2012

SAP Worksheet #11: Project Quality Objectives/Systematic Planning Process Statements
(UFP-QAPP Manual Section 2.6.1)

Reagent Selection for Soil & Groundwater Remediation

Planning the Project

Reagent by Treatment Process

Reductive Destruction

Biological
① ELS® Microemulsion
② ELS® Liquid Concentrate

Biological and Chemical
EHC ISCR Portfolio
③ EHC® Liquid
④ EHC® Reagent
⑤ EHC® Plus

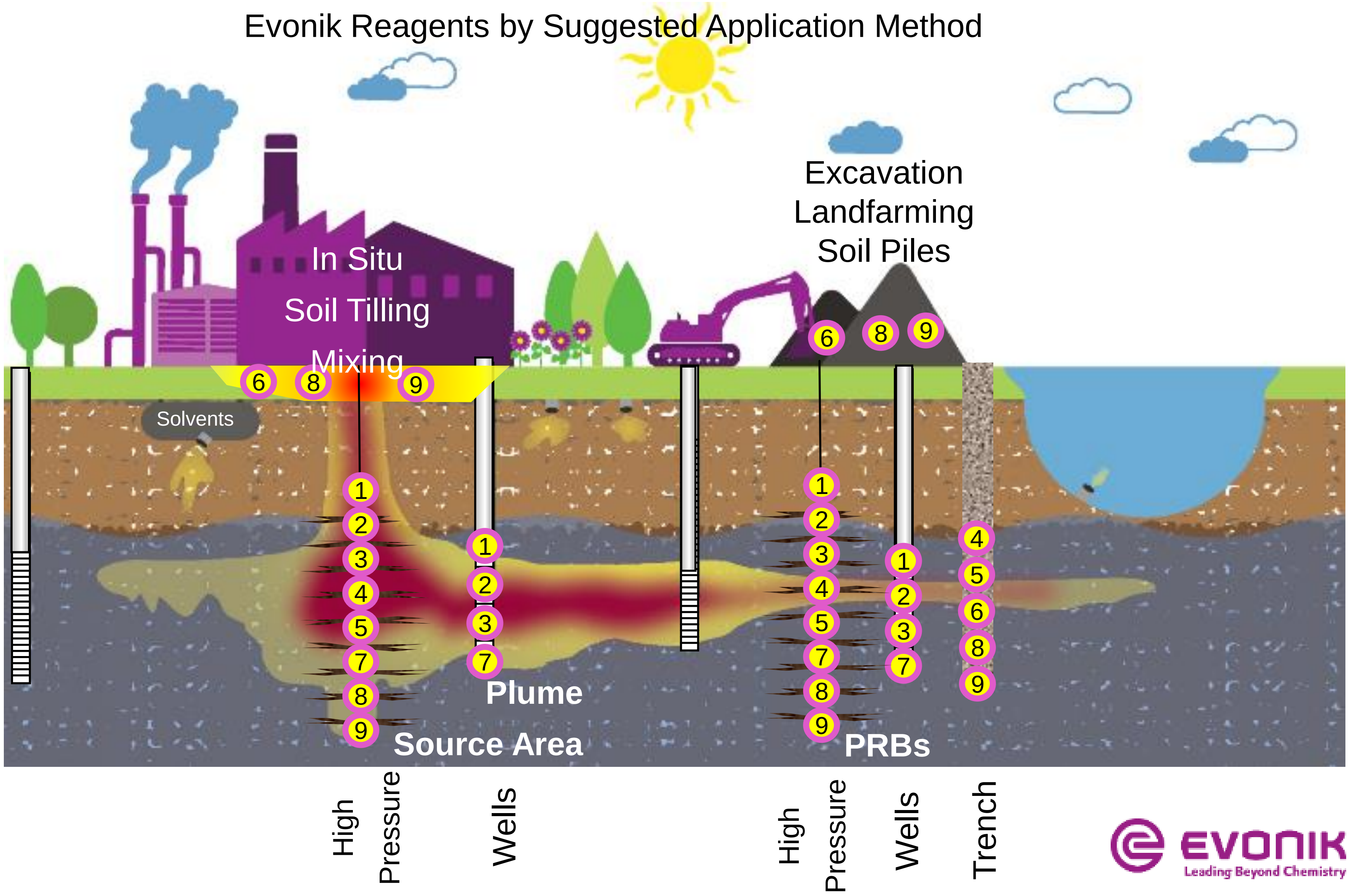
⑥ Daramend® Reagent

Biological, Chemical and Biogeochemical
GeoForm® Reagents
⑦ Geoform® Soluble
⑧ Geoform® Extended

Metals Treatment:

⑨ MetaFix® Reagents

Evonik Reagents by Suggested Application Method



Dosing: Part Science, Part Art, Part Other ???

Step 1. Determine Stoichiometric Requirement

Stoichiometry (counting electrons)

Electron donor must be ≥ Electron acceptors

Electron donor = reagent

Electron acceptor =

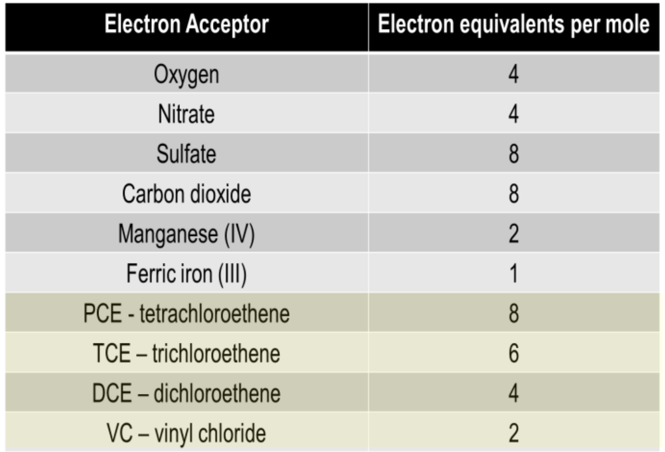
- Contaminant (CVOCs)
- Competing Electron acceptors:

  Oxygen, nitrate, manganese, arsenic, ferric iron, sulfate

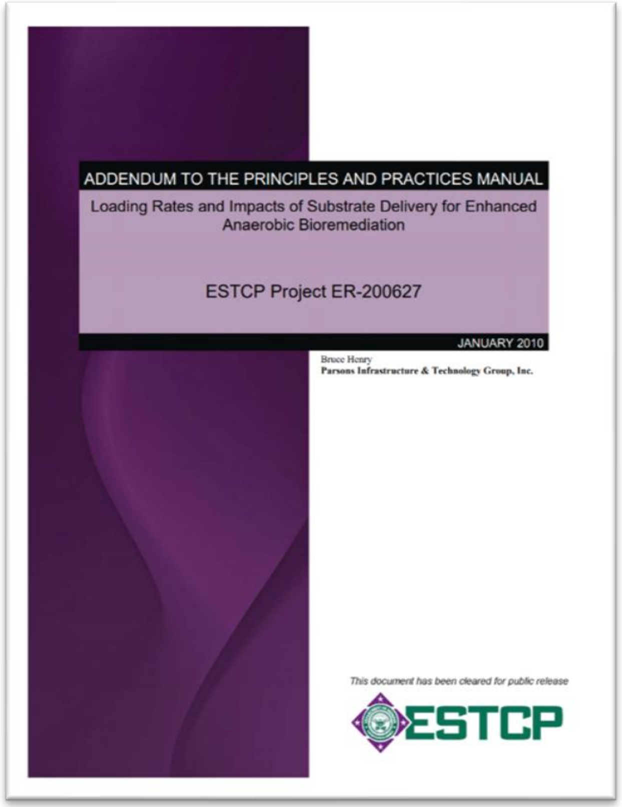
Dissolved, adsorbed or in solid form in treatment area and;

Dissolved flux

Electron Donor	Electron equivalent per mole
acetate	4
proprinoate	3
lactate	2
fructose/glucose	12
sucrose/lactose	24
linoleic acid	50
glycerol	7
lecithin	122



Electron Acceptor	Electron equivalents per mole
Oxygen	4
Nitrate	4
Sulfate	8
Carbon dioxide	8
Manganese (IV)	2
Ferric iron (III)	1
PCE - tetrachloroethene	8
TCE – trichloroethene	6
DCE – dichloroethene	4
VC – vinyl chloride	2



ADDENDUM TO THE PRINCIPLES AND PRACTICES MANUAL

Loading Rates and Impacts of Substrate Delivery for Enhanced Anaerobic Bioremediation

ESTCP Project ER-200627

JANUARY 2010

Bruce Henry
Parsons Infrastructure & Technology Group, Inc.

This document has been cleared for public release

ESTCP

Quantifying the organic contaminants

Organic compounds are adsorbed (partition) onto carbon

In saturated zone contaminants are in water and on aquifer matrix

Kd = Koc x foc

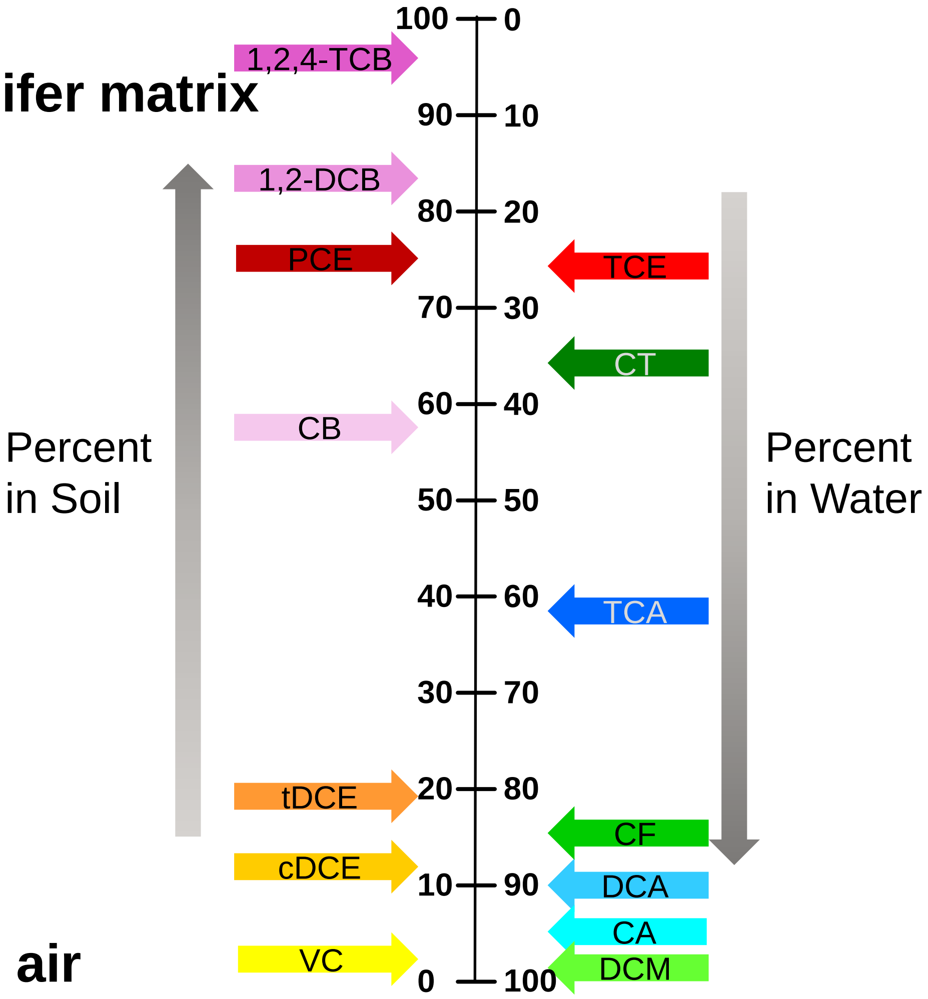
Kd = Soil partitioning coefficient
Koc = Organic carbon partitioning coefficient
foc = fraction of organic carbon in aquifer matrix

Each chemical has a specific water:soil (OC) ratio

Chlorinated Ethenes
Chlorinated Ethanes
Chlorinated Benzenes
Chlorinated Methanes

More reduced compounds more soluble/mobile

In unsaturated zone contaminants are in soil, water and air



From Installation Restoration Program Toxicology Guide 1989

Dosing: Part Science, Part Art, Part Other ???

Step 1 (continued). Determine Stoichiometry

Quantifying ambient sulfate concentration may be the most important factor for the dosing estimate.

Each mole of sulfate requires 9 H^+ equivalents to reduce to sulfide – More than PCE

Sulfate Reduction $SO_4^{2-} + 9H^+ + 8e^- \longrightarrow HS^- + 4H_2O \quad (Eh^0 = {}^-220)$

Sulfate concentration often/usually several orders of magnitude higher than CVOC concentration

Often 99% of reagent is applied for sulfate reduction

Step 2. Safety Factor: Typically 3X to 10X. You should evaluate this too.

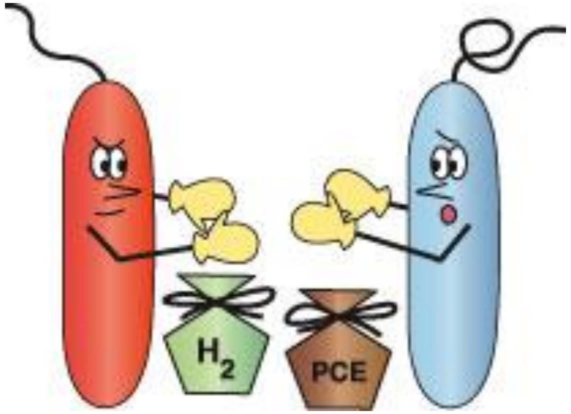
Step 3. Minimum and maximum recommended amount per application method determined

Step 4a. Soluble Reagents. Reasonable? Confirm concentrations are not at toxic levels (i.e., lactate and EVO inhibitory at ~ 50 g/L, ELS > 100 g/L. (Typically Target 1 to 5 g/L)

Step 4b. Solid Reagents. Reasonable? Confirm dosing within practical range for application method (Typically Target 0.1 to 0.5 wt % for injection, up to 5 % for soil mixing.

Is Bioaugmentation Necessary/Beneficial?

- Only one organism (Dehalococcoides *sp*) (Dhc) demonstrated to completely degrade PCE and TCE to ethene
- Dechlorinating organisms may not be present at sufficient concentrations at many sites.
  > $1x10^7$ Dhc cells/L considered necessary for remediation
- Cultures enriched for treatment of various contaminants are available (e.g., chloromethanes, chloroethanes)
- The indigenous organism may not be efficient at dechlorination.
- Indigenous organisms (e.g. methanogenic bacteria) may outcompete dechlorinators such as *Dhc* for H_2.
- Final step may be co-metabolic, which is slow



www.mdsg.umd.edu/CQ/v05n1/main/

Application

Injecting liquid reagents through wells

Conceptually must fill up pore space (likely less than total but more than effective porosity)

At low pressure (flow rates), liquids move as an expanding cylinder around well.

The distance distributed (during injection) is determined by the volume injected.

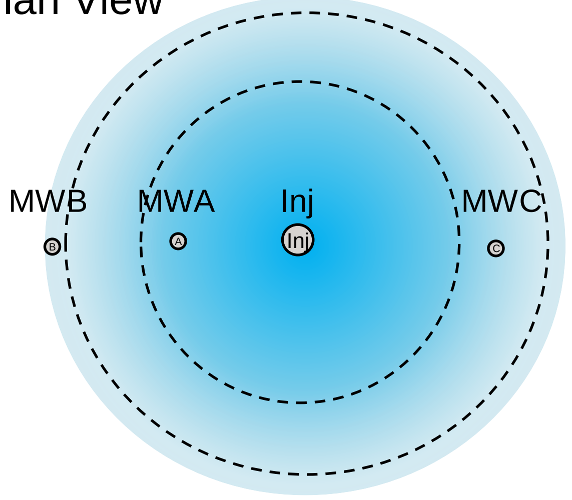
Injection concentration reduced by dilution and vertical and longitudinal dispersion

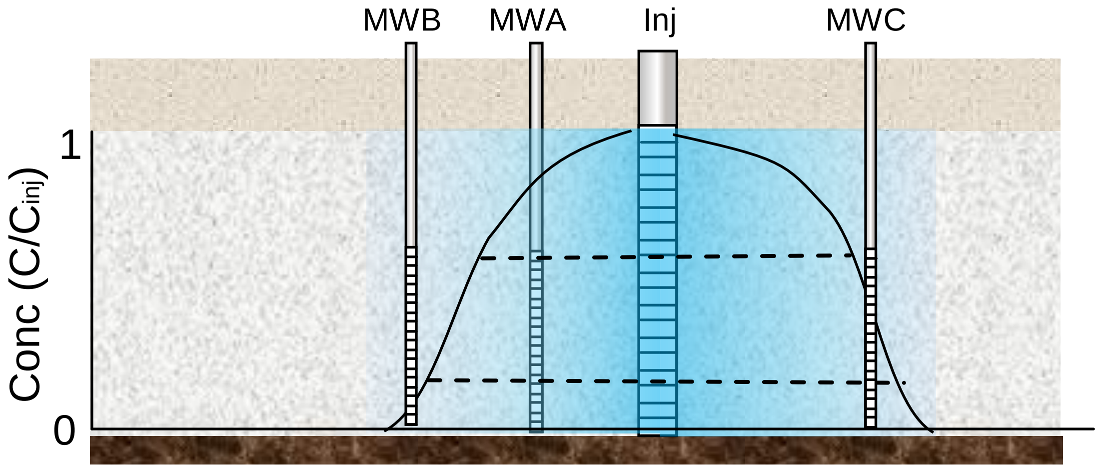
Within some distance you have sufficient or excess reagent for complete dechlorination (Inj & MWA) (Target Conc)

At some distance you do not have sufficient reagents for any dechlorination (MWB)

In between reagents only sufficient for incomplete/partial dechlorination (MWC)

Plan View





Cross Section View

Injection Rate - Faster is Better

Higher pressure = faster flow rates = better distribution

Darcy's Law

$$Q = -KA\frac{dh}{dl}$$

Flow rate is controlled by pressure (dh/dl)

Liquid reagents (emulsions, solutions) can be injected by low and high pressure systems

Benefit: Higher pressures = faster flow rates = reduced injection time = cost savings.

Benefit: Higher pressures increase flow into lower permeability zones = more effective treatment.

Concern: High pressure can result in surfacing of the reagent or distribution into undesired location (e.g., ground surface, utilities, basements, etc).

Concern: Some agencies limit injection pressures.

Goal: Optimize injection strategy to enhance treatment and reduce field time, while not creating adverse conditions.

Injecting Solids/Slurries (EHC®, GEOFORM® ER, Microscale ZVI

Require high pressure to inject

Tend to fracture the aquifer rather than fill pore space

Not as mobile as emulsified or soluble reagents

Last substantially longer

Injecting solids (Fine ZVI) through wells

Higher flow pressure = higher flow rates = farther distribution

ZVI Very dense and tends to fall out of suspension at rate dependent on size/particle density

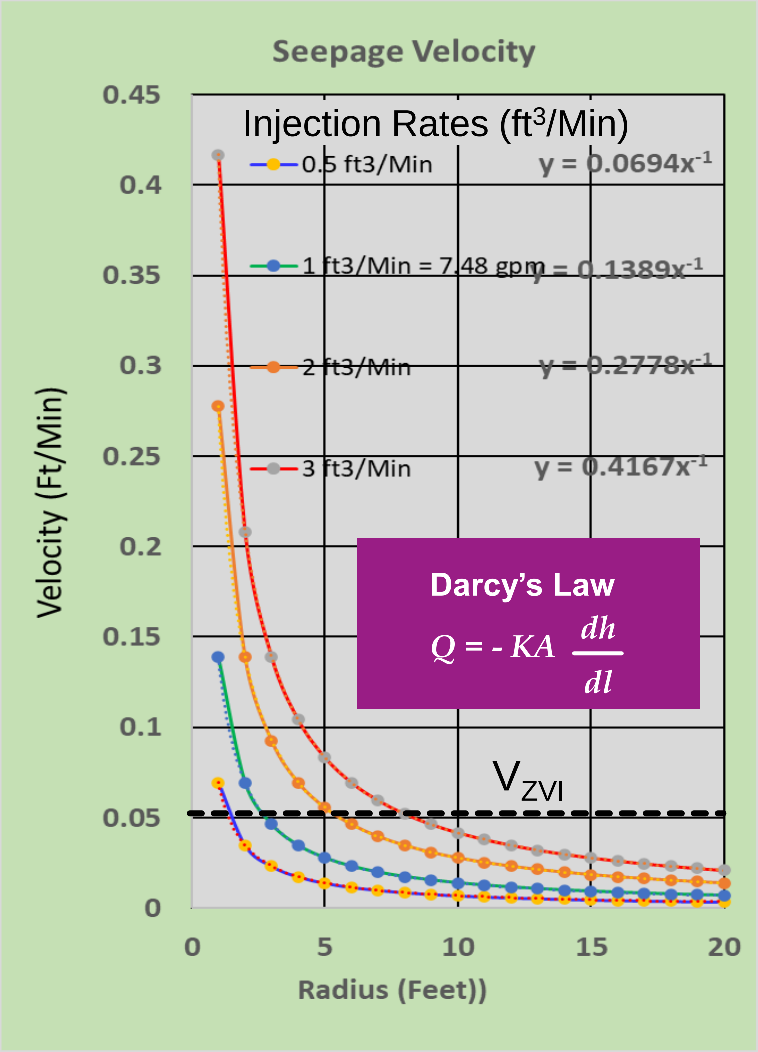
Very fine ZVI Can be suspended in flowing water

ZVI suspension depends on flow rate (velocity) of water

Water velocity decreases as it flows away from injection well

Want iron to be distributed efficiently but not to flow out of your treatment area by advective transport

Velocity can be reduced by increasing viscosity (add guar)



Performance Monitoring

Solid Reagent Distribution

You can use a typical monitoring wells system to determine reagent distribution

Microscale iron can pass through an 0.01 inch slotted screen
  0.01 inch = 254 microns, 0.02 inch = 508 microns.

Most ZVI for remediation in range of 1 to 300 microns.

Use a suspended magnet during injection to confirm distribution of the iron

Can use wells to monitor for iron and organic distribution
- Usual ways involve post injection soil boring and looking for the reagent
  - i.e., visual observation, laboratory analysis, magnetic susceptibility

Look for change in color to identify organic component

Analyze for TOC to compare concentration in well to injected concentration to estimate effectiveness of distribution.

Microscale ZVI on magnet collected from monitor well

Use surrogates to quantify reagent distribution

Determine the effectiveness of your distribution to evaluate effectiveness of reagents and to determine appropriate design of the full-scale distribution system.

Unless you are injecting a single type of reagent (e.g., lactate), you need to analyze for a surrogate to determine reagent distribution

Typical surrogates include:

- TOC Total Organic Carbon
  - DOC Dissolved Organic Carbon
- Alkalinity
  - Acetate, Propionate
- Iron
  - Ferrous
  - ZVI
- Sulfate

Why analyze for TOC?

The total organic carbon (TOC) is a measure for the content of carbon dissolved and undissolved organic substances in water.

EPA suggests TOC greater than 20 mg/L is favorable for anaerobic dechlorination of CAHs

Organic carbon does not directly contribute to dechlorination, only the H_2

However, TOC <u>approximately</u> correlates to the amount amount of molecular hydrogen (H_2) available [compound specific]

TOC is an easy and cost effective measure of organic substrate and potential H_2 in water.

TOC used as a surrogate for determining organic substrate distribution and availability

Organic Substrates Estimation – Total Organic Carbon (TOC)

TOC fractions calculated for various organic substrates:

Sodium Lactate ($C_3H_5NaO_3$) - Organic carbon fraction (C) = 0.32

Lactic Acid($C_3H_6O_3$) - Organic carbon fraction (C) = 0.40

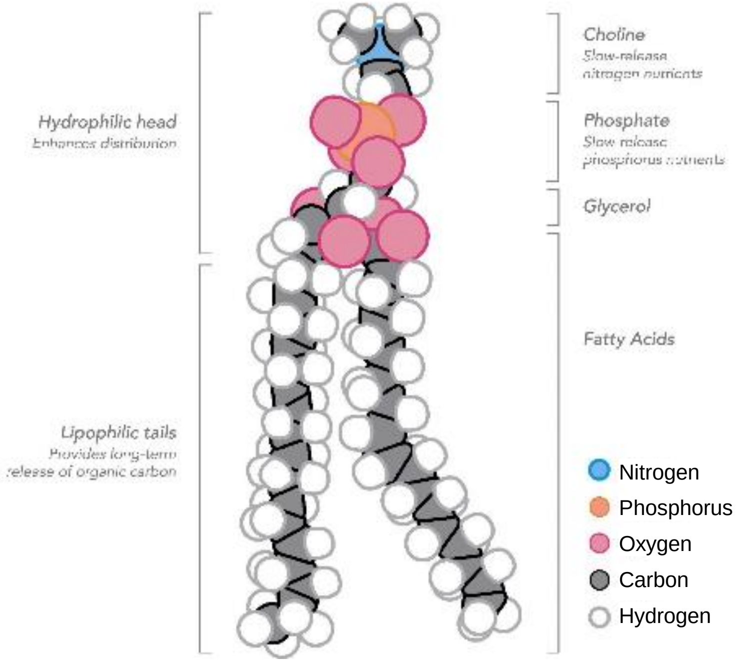
Glycerol ($C_3H_8O_3$) - Organic carbon fraction (C) = 0.39

Lineolic Acid (Soy Oil) ($C_{18}H_{32}O_2$) - Organic carbon fraction (C) = 0.77

ELS concentrate is composed of lecithin

Lecithin - $C_{42}H_{82}NO_8P$ – Organic carbon fraction (C) = 0.66

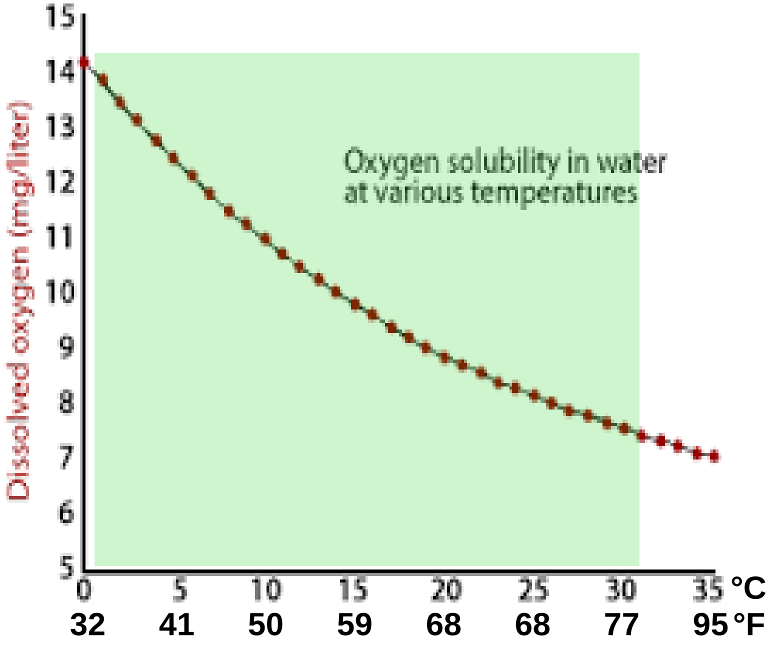
Lecithin minus nitrate & phosphate ($C_{42}H_{82}O_1$) - Organic carbon fraction (C) = 0.84



Lecithin Molecule

Most organic substrates are blends of various organic compounds and usually have preservatives and/or surfactants at various ratios and water that alter the pure TOC fraction

Dissolved oxygen (DO) and other field measured parameters



The Dissolved Oxygen (DO) Problem

Often DO concentrations are higher than the solubility of oxygen in water.

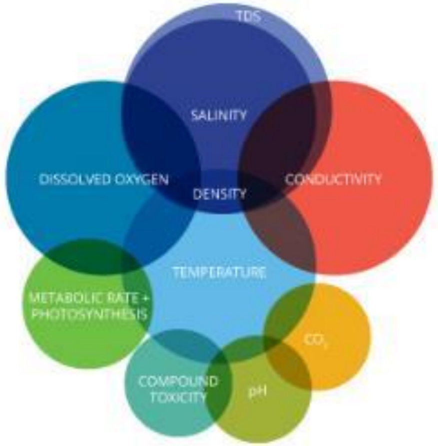
High DO concentrations should be a red flag for field personnel.

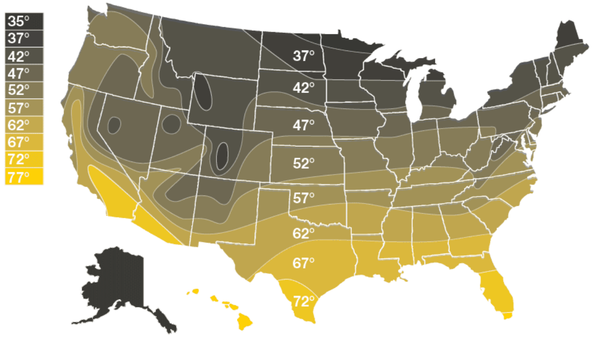
Check equipment or acknowledge outside the assumed range.

Some DO meters report % saturation as well as mg/L.

Temperature affects other water quality parameter.

- Metabolic rates and photosynthesis production
- Compound toxicity
- Dissolved oxygen and other dissolved gas concentrations
- Conductivity and salinity
- Oxidation reduction potential (ORP)
- pH
- Water Density





https://www.fondriest.com/environmental-measurements/parameters/water-quality/water-temperature/

Data Evaluation

Convert CVOC lab data to molar concentrations

Regulatory standards are based on the mass concentration of a contaminant (e.g., µg/L, mg/L)

Reductive process change the mass of a molecule (contaminant), not the number molecules

(i.e., 1 mole of PCE → 1 mole of TCE → 1 mole of DCE → 1 mole VC)

To evaluate the degradation process we want to count the molecules

To convert data to molar concentrations

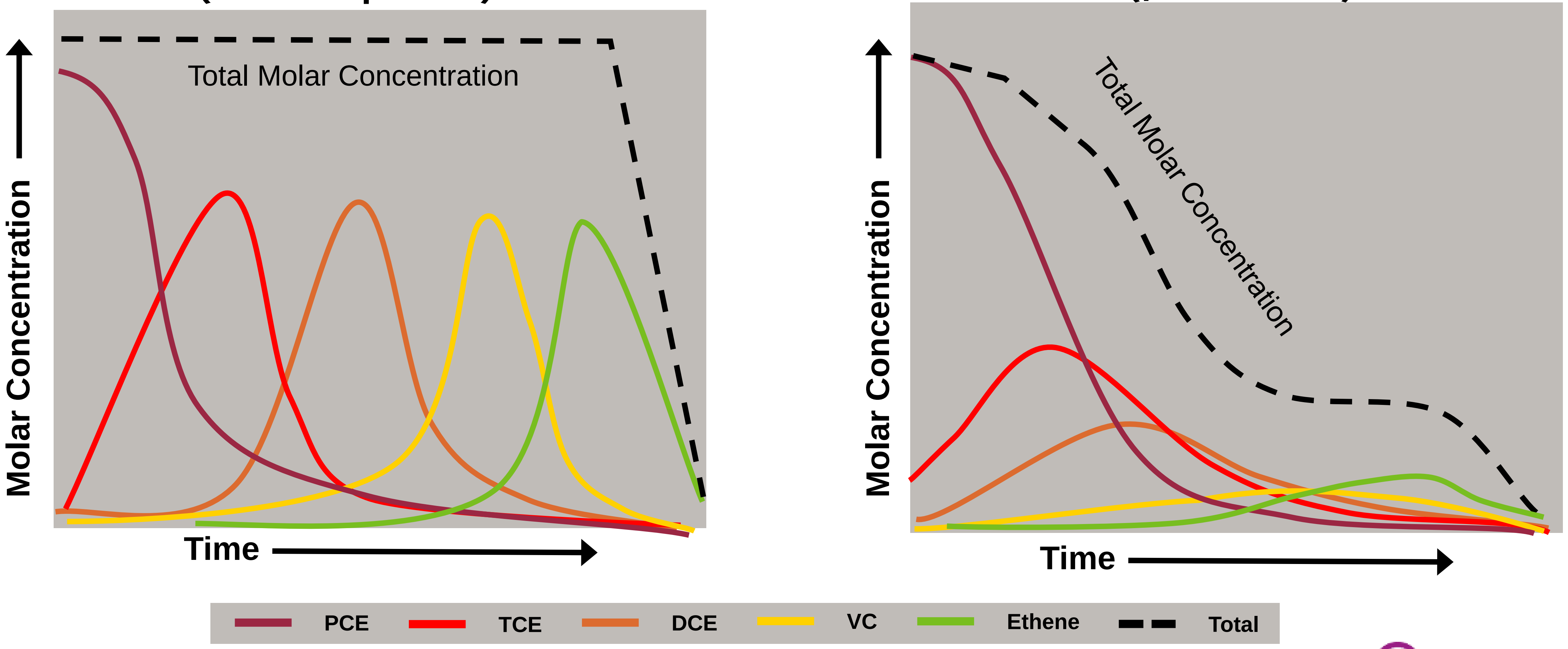
Divide concentration by formula weight

µg/L/FW = µmol/L, mg/L/FW = mmol/L

Sum total molar concentrations

Compound	Formula	Formula Weight	Total Reduction in Weight (%)
Tetrachlorothene	C_2Cl_4	165.8	0%
Trichloroethene	C_2Cl_3H	131.8	21%
Dichloroethene	$C_2Cl_2H_2$	96.9	42%
Vinyl Chloride	C_2ClH_3	62.5	62%
Ethene	C_2H_4	28.0	83%
Ethane	C_2H_6	30.1	82%
Trichloroethane	$C_2Cl_3H_3$	133.4	0%
Dichloroethane	$C_2Cl_2H_4$	98.9	26%
Chloroethane	C_2ClH_5	64.5	52%
Ethane	C_2H_6	30.1	77%

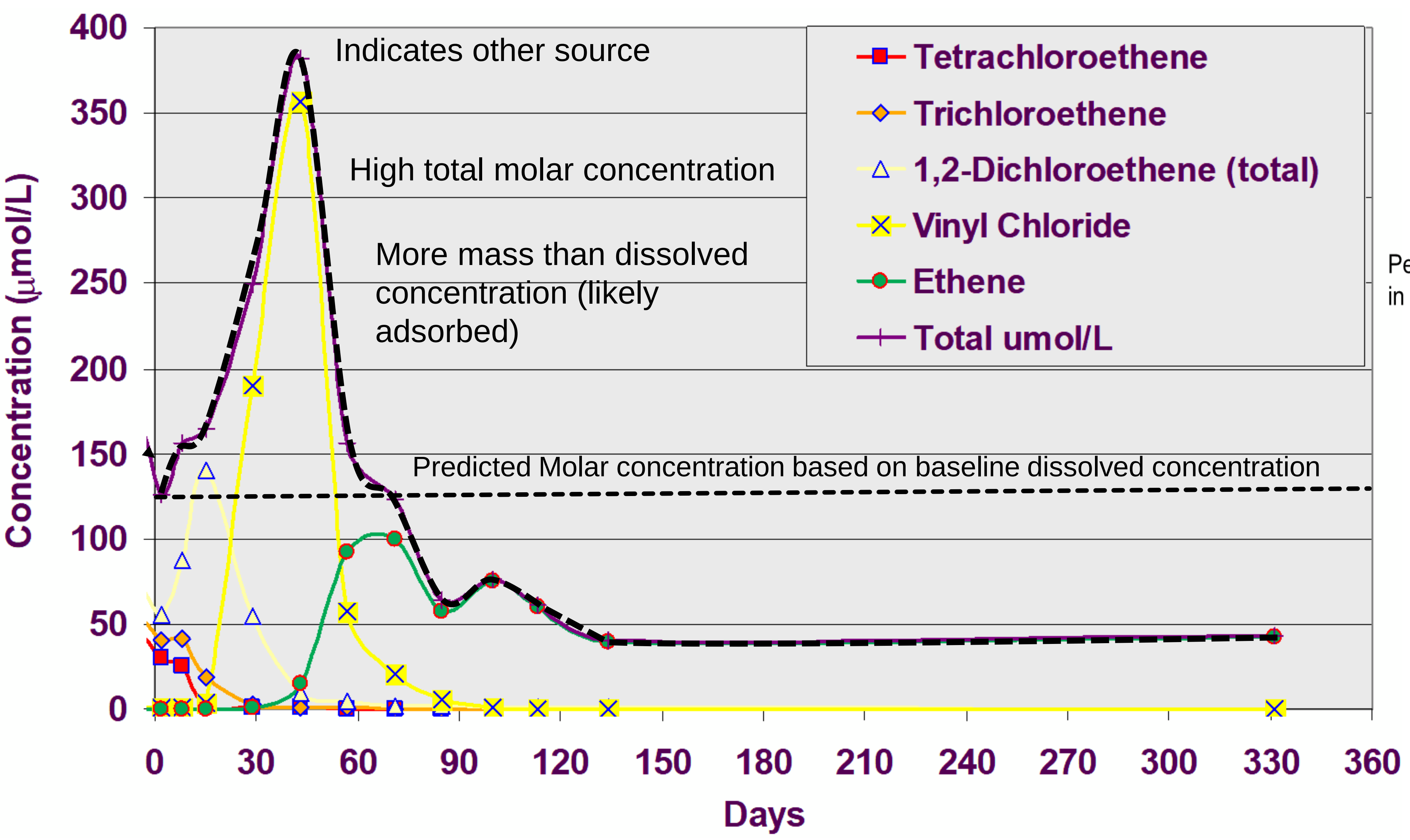
Expected Degradation Trends



Biological Degradation (Chlororespiration)

Abiotic / Biogeochemical Degradation (β elimination)

Increased concentration following treatment

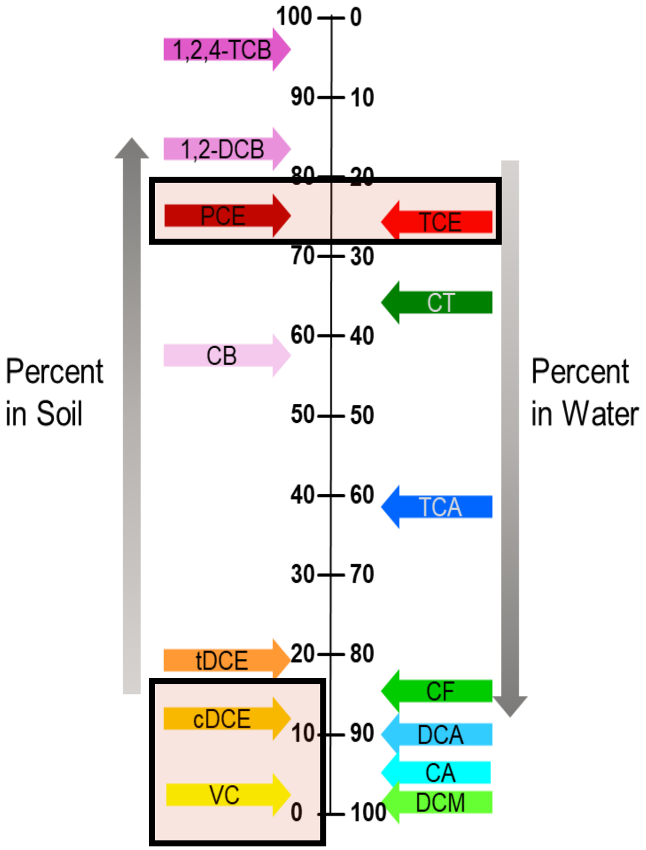


Indicates other source

High total molar concentration

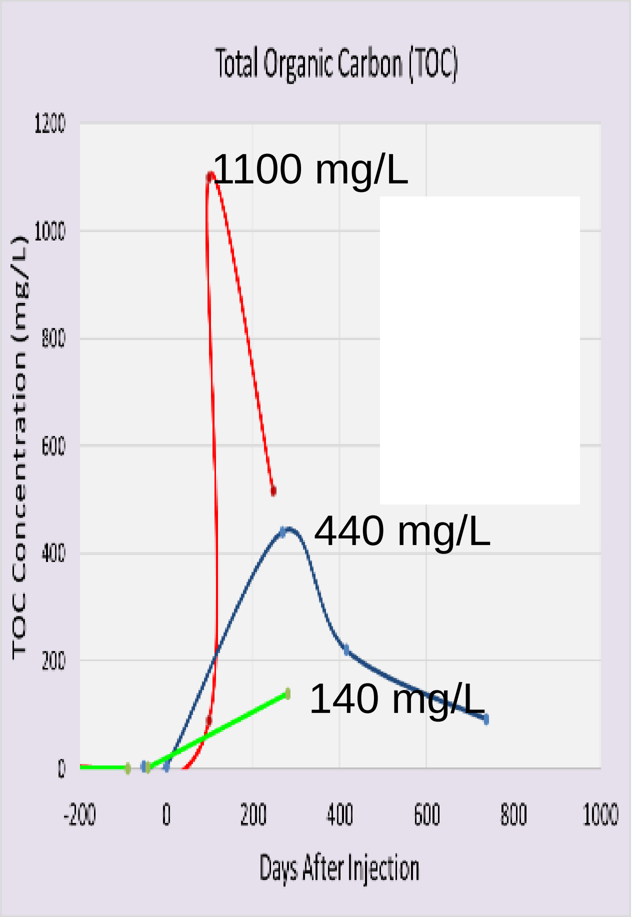
More mass than dissolved concentration (likely adsorbed)

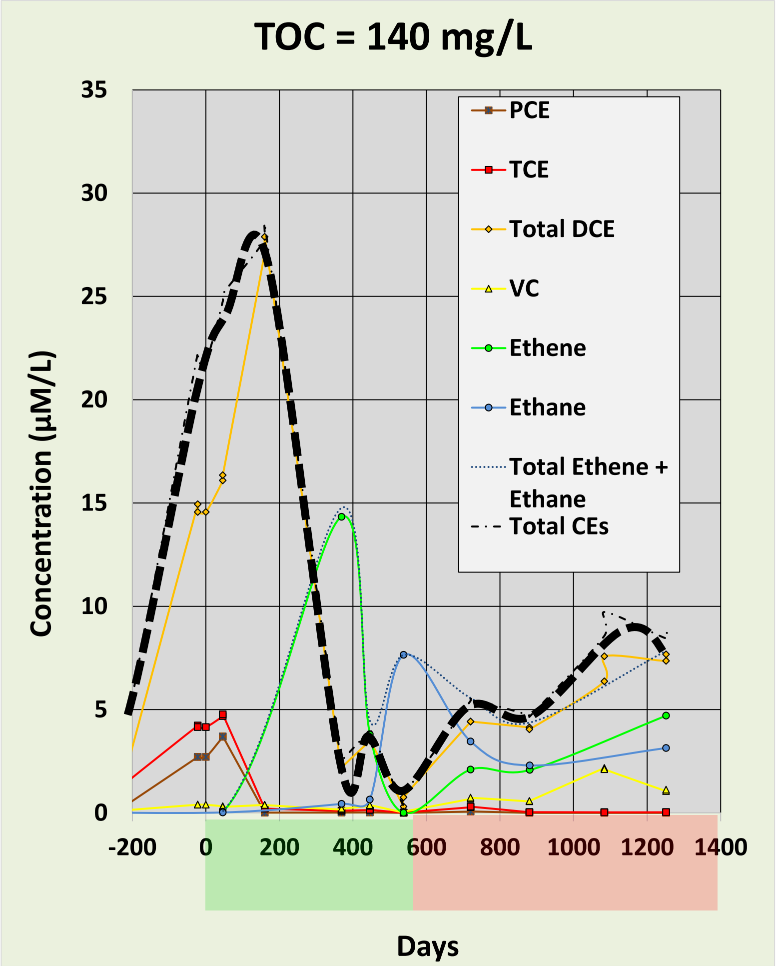
Predicted Molar concentration based on baseline dissolved concentration

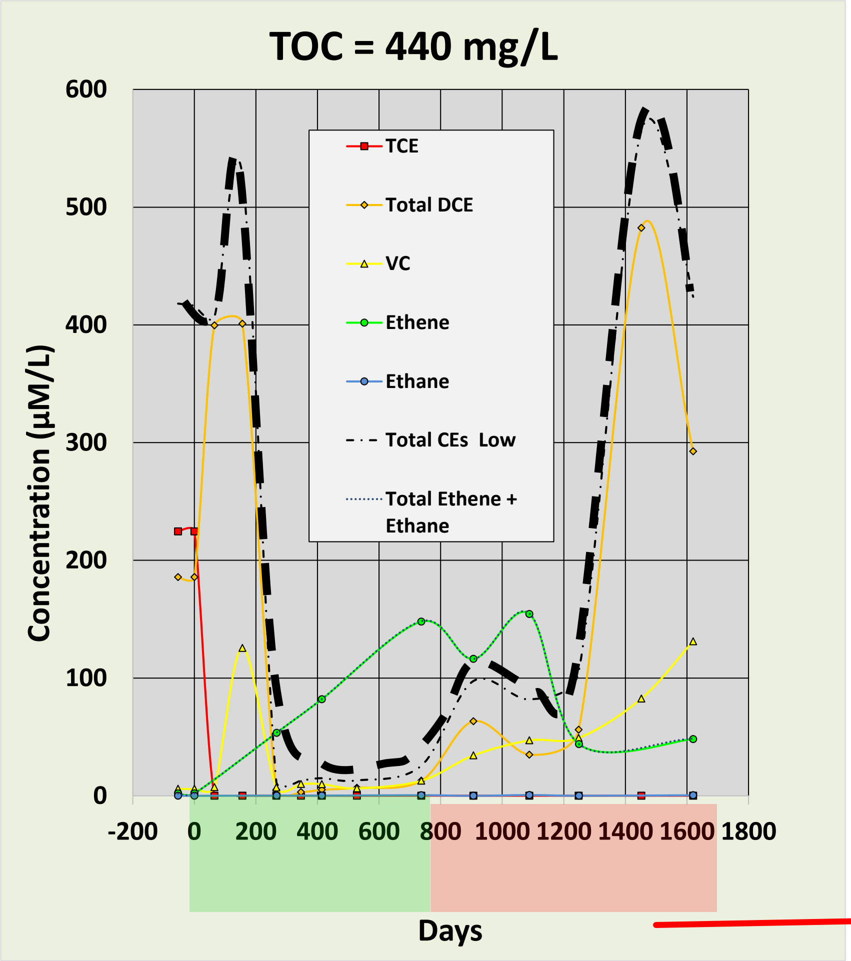


Degradation Extent & Longevity Correlates with TOC Concentration

GEOFORM® Soluble Application







Degradation

Rebound

~550 days for complete dechlorination

~Rebound begins ~ shortly thereafter

~290 days for complete dechlorination

Dechlorination maintained for ~ 750 days

Rebound Day ~750

Degradation Extent & Longevity Correlates with TOC Concentration

GEOFORM® Soluble Application

TOC changes over time due to:

Migration, biologic consumption,
Dilution, dispersion, adsorbtion

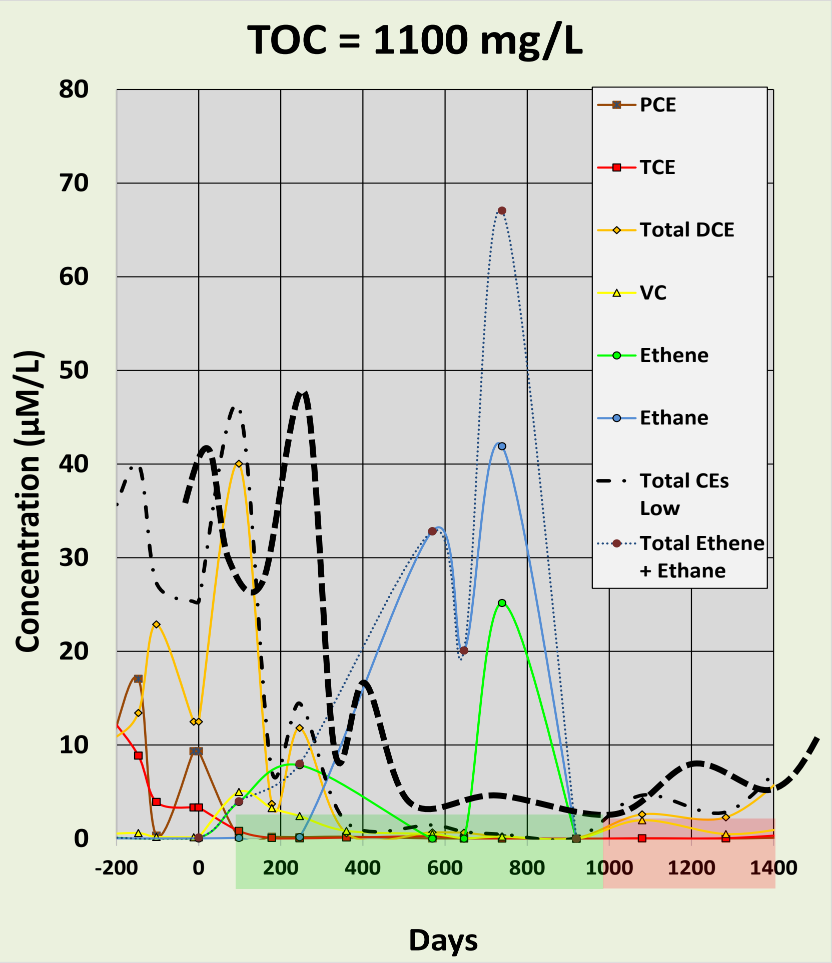
CEs inhibit CA reduction?

High TOC/reagent concentrations:

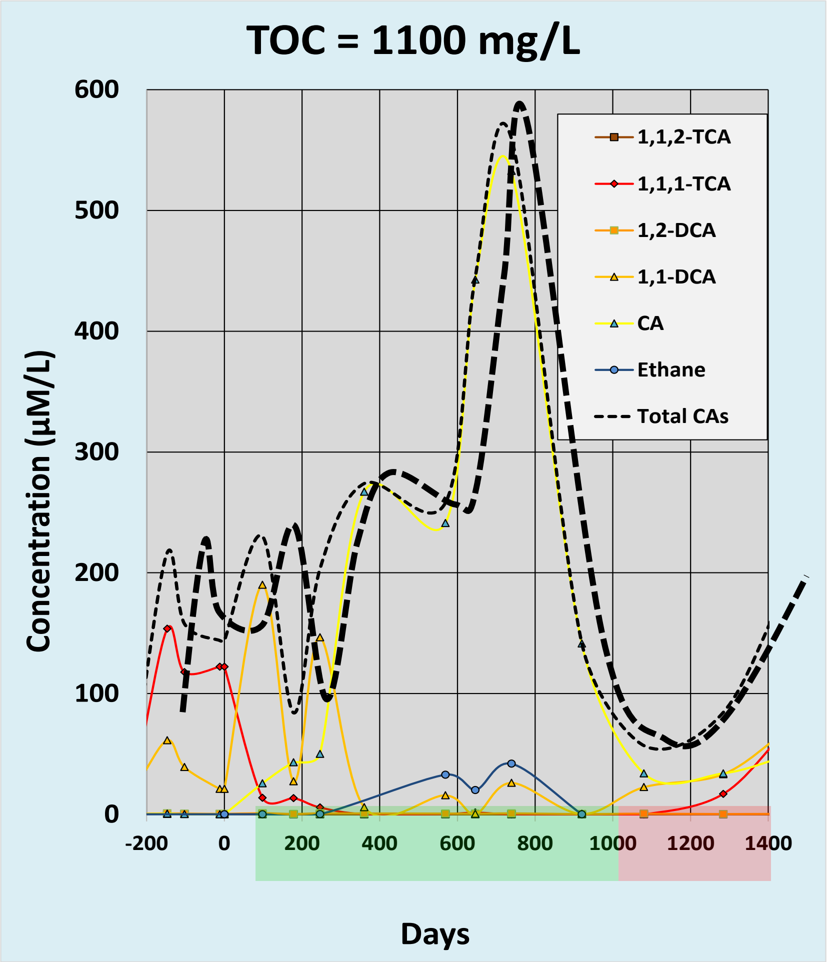
- Increase degradation rates
- Increase degradation time

Degradation

Rebound


TOC = 1100 mg/L

Dechlorination of CEs ~ Day 350
Rebound ~ Day 1000


TOC = 1100 mg/L

CA reduction occurs after CE
CA reduction nearly complete ~ day 1100

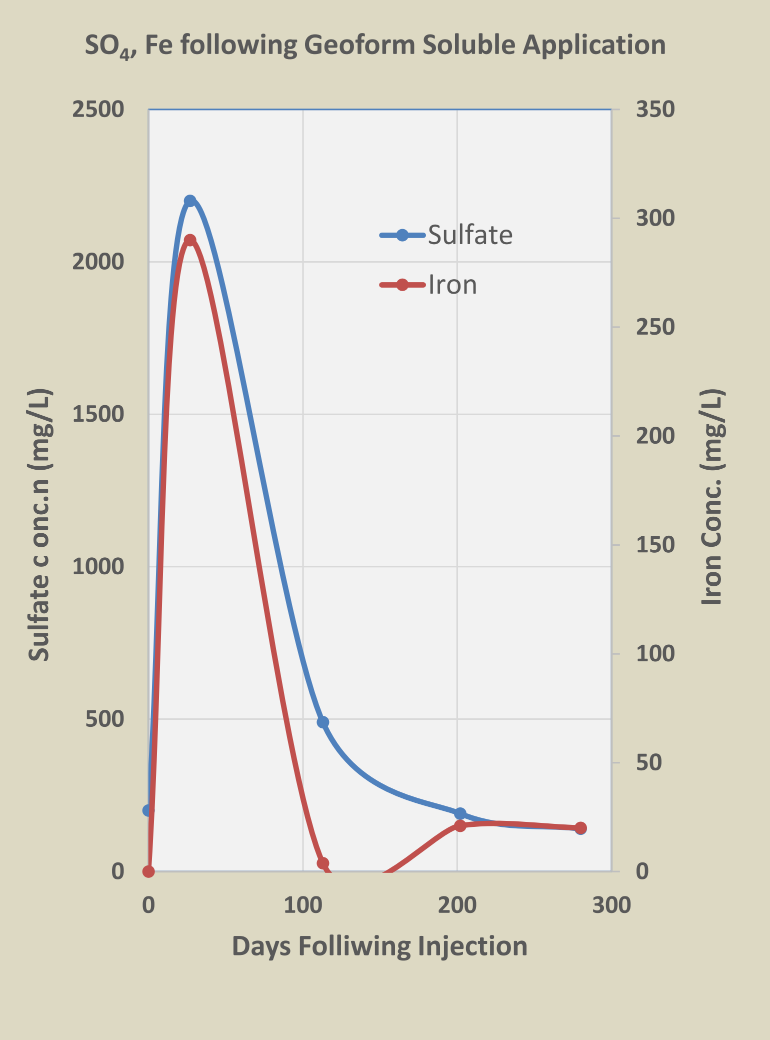
Confirming Reagent Distribution (no TOC Data)

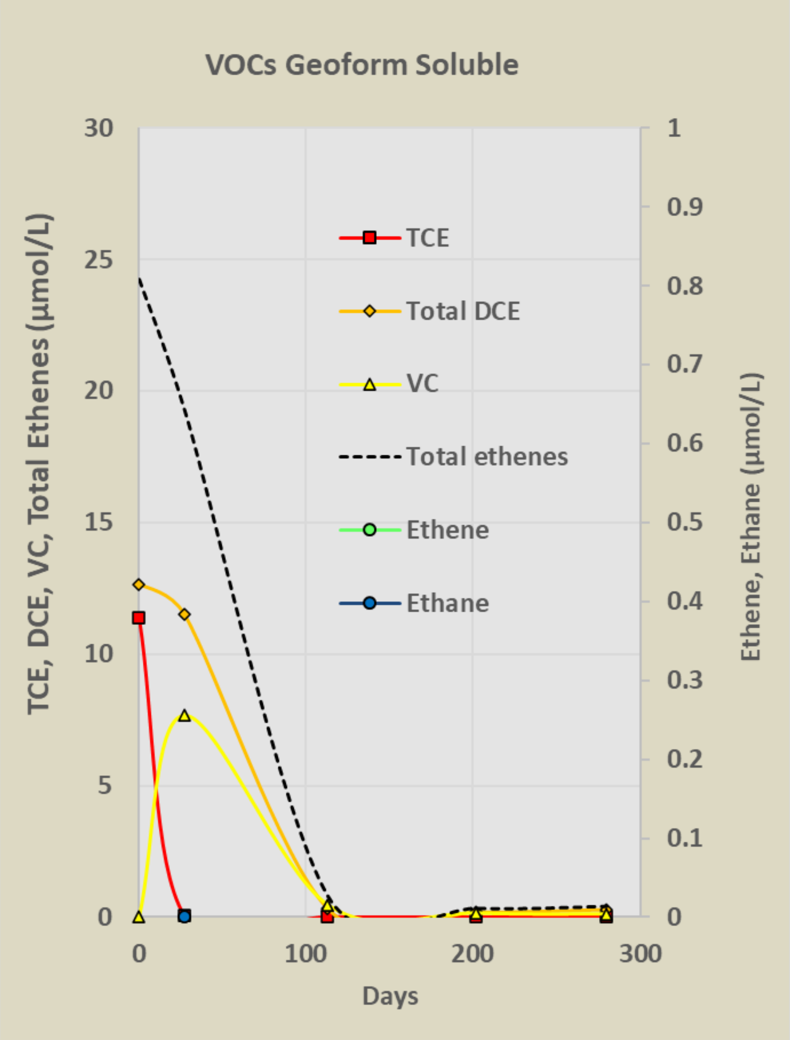
GEOFORM® Soluble Applied

TOC not collected

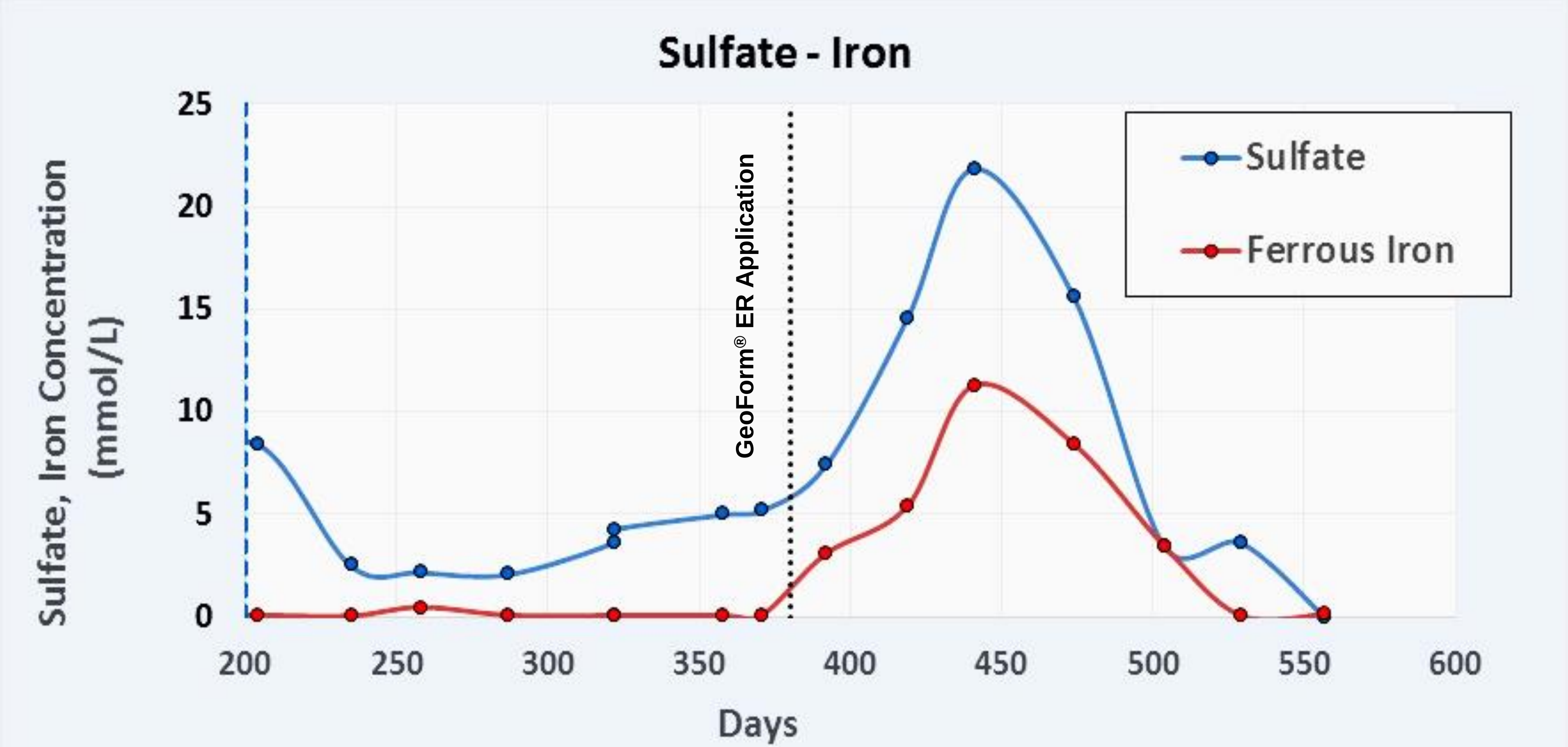
Fe and SO_4 used as surrogate to confirm reagent distribution

Data indicate both biological and abiotic (biogeochemical degradation)


SO_4, Fe following Geoform Soluble Application


VOCs Geoform Soluble

Confirming Reagent Distribution GEOFORM® ER

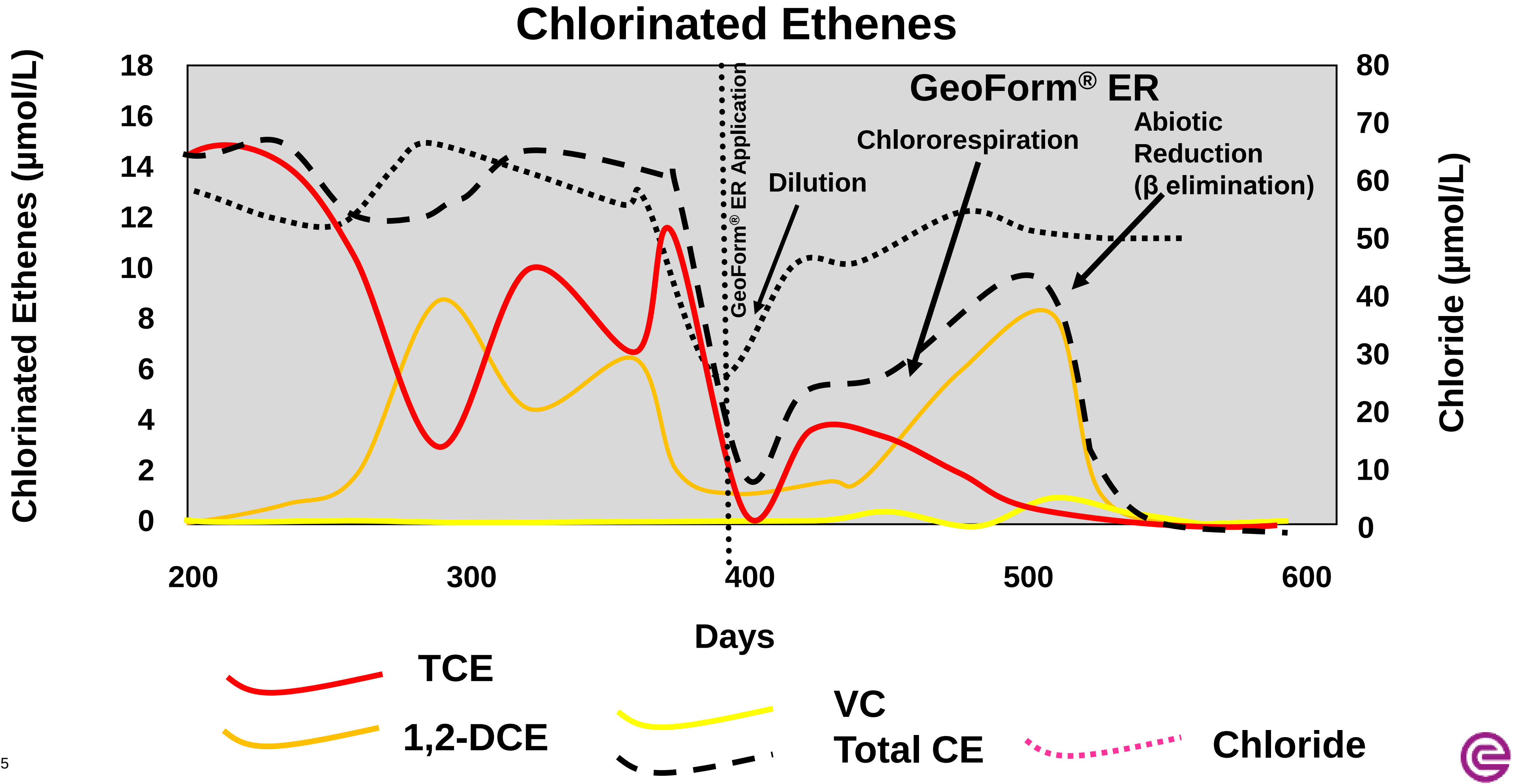


Sulfate FW = 96 Iron FW = 55

Sulfate and Iron Confirm Reagent distribution

GEOFORM® Extended Release

Not All Contaminant Reduction is Degradation



Summary

- Reductive remediation is not in the research stage anymore
- Field test are more informative and representative than bench tests
- Planning project is key to a successful and efficient pilot test
- Make sure you have more than enough reagent necessary to degrade all contaminants
- Need to have monitoring location in at least the area of highest reagent concentration.
- Expect some rebound during pilot tests
- TOC good surrogate for organic reagents (ELS, Geoform Soluble, EHC-L)
- Fe, SO_4, good surrogates for biogeochemical reagents (e.g., Geoform® ER & Geoform ® Soluble)

Questions?

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