Chlorinated Solvent Bioremediation: Fundamentals and Practical Application for Remedial Project Managers

Presented by:

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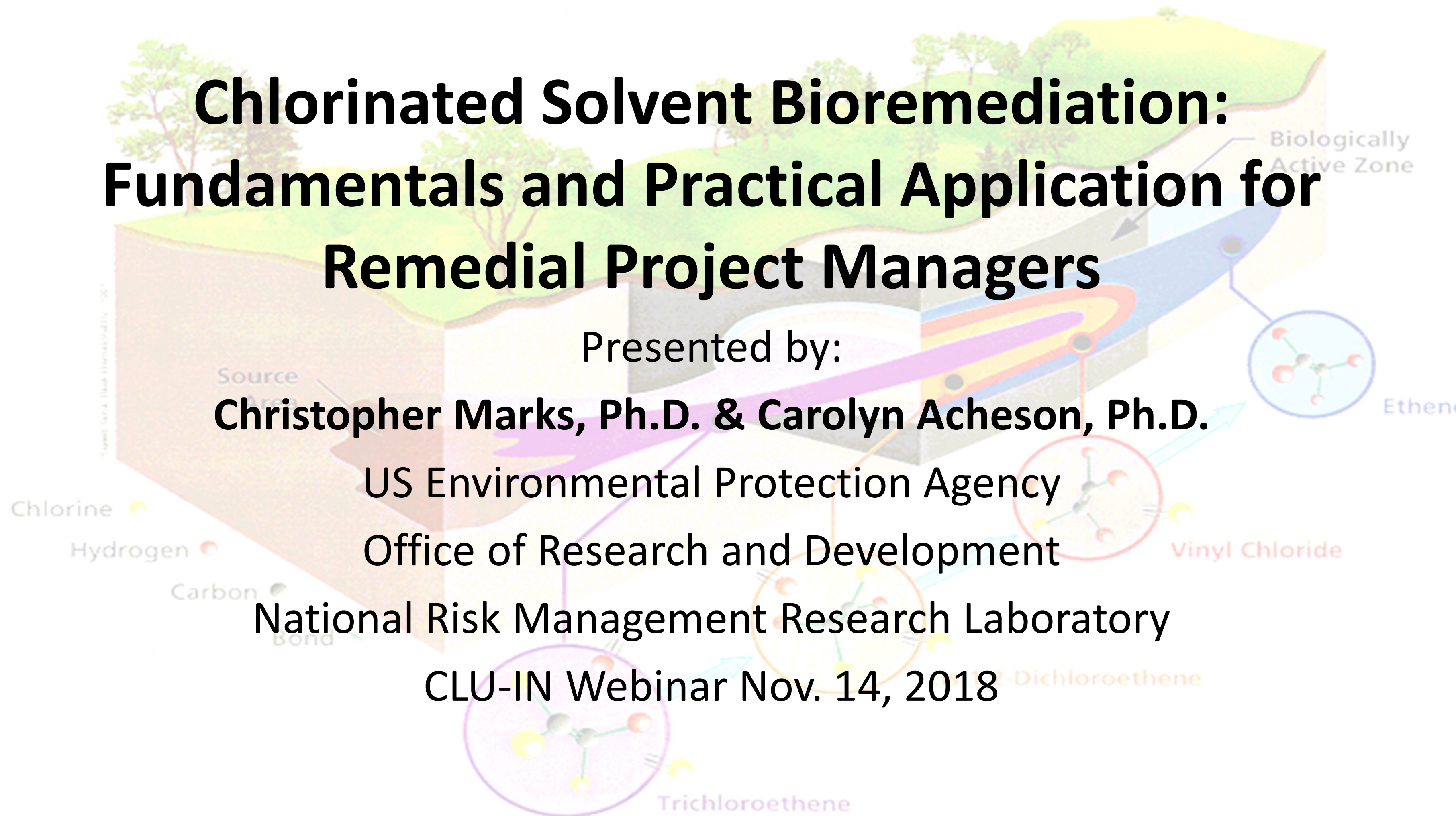
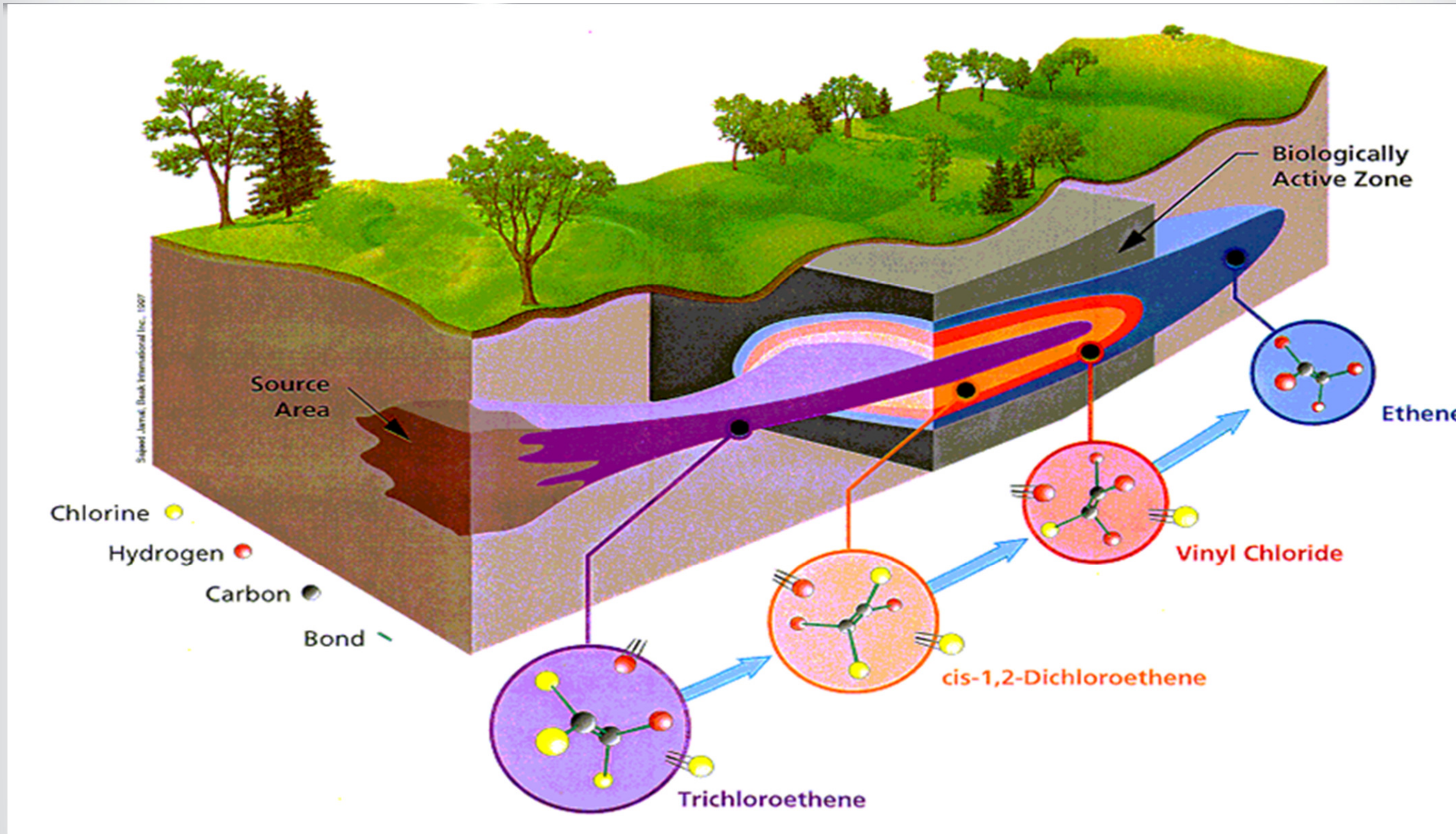


Source: Accelerated Bioremediation of Chlorinated Solvents, Interstate Technology and Regulatory Council and Remediation and Technology Development Forum, 2003

Bioremediation of Chlorinated Solvents



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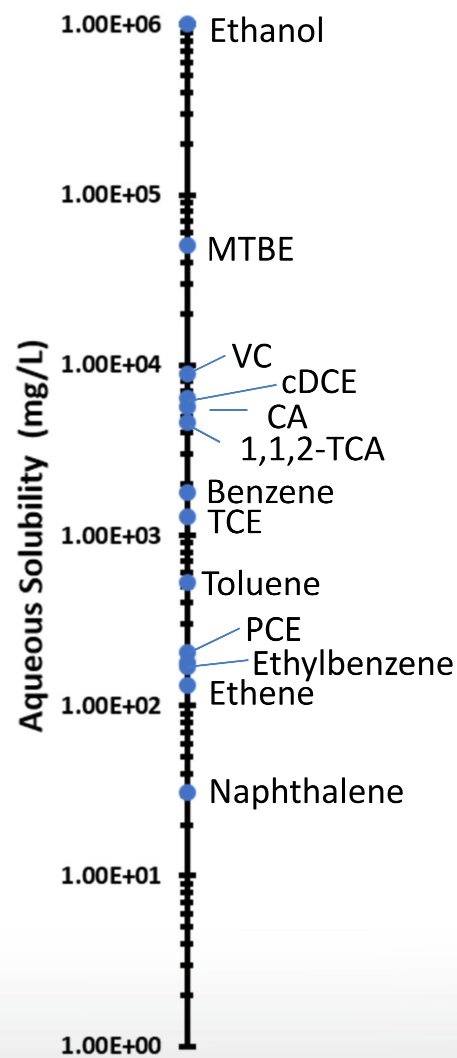
Part I: Introduction to Chlorinated Solvent Properties and Anaerobic Reductive Dechlorination

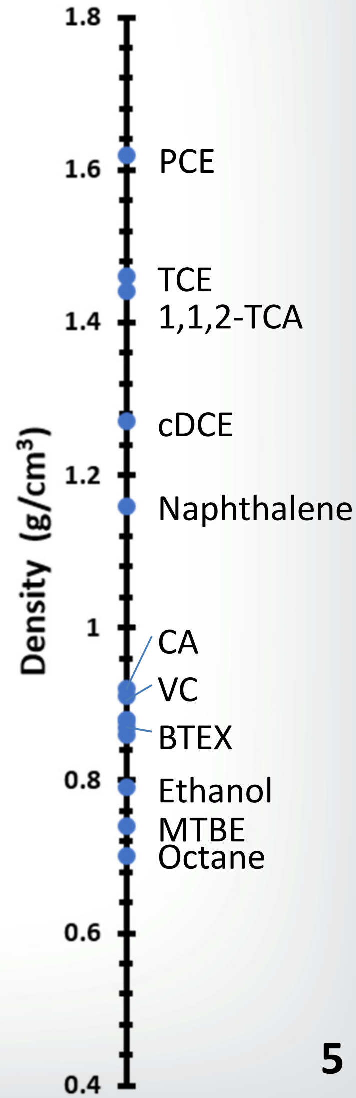
Terminology

- **Anaerobic:** Microbial metabolic processes occurring in the absence of oxygen.
- **Anaerobic Reductive Dechlorination:** The biological removal of a chlorine atom from an organic compound and replacement with a hydrogen atom in a reducing environment.
- **Biodegradation aka biotransformation:** Biologically mediated reactions which convert one chemical to another. For example, PCE is converted to TCE when anaerobic reductive reactions remove a chlorine molecule.
- **Bioremediation:** The engineered approaches using microorganisms to biodegrade contaminants.
- **Biostimulation:** The addition of organic electron donors and nutrients to enhance the rate of reductive dechlorination by the native microflora.
- **Bioaugmentation:** The addition of beneficial microorganisms to enhance the capacity for reductive dichlorination.
- **Dense nonaqueous-phase liquid (DNAPL):** An organic liquid that is more dense than water and is not miscible in water.
- **Monitored Natural Attenuation (MNA):** A remediation approach that involves routine contaminant monitoring and relies on the natural contaminant attenuation processes through physical, chemical, and biological mechanisms without intervention.

Key Properties of Chlorinated Solvents

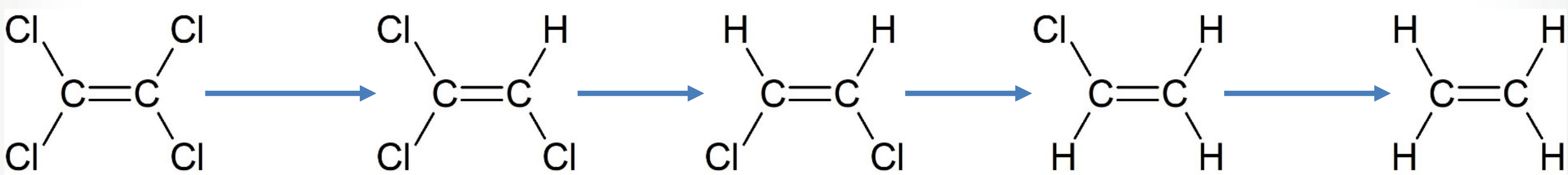
- **Aqueous Solubility:** Some chlorinated ethenes and ethanes have higher solubility in water as compared to other common NAPL groundwater contaminants such as BTEX hydrocarbons.
- **Density (or Specific Gravity):** Polychlorinated ethenes/ethanes are more dense than water, will sink within groundwater systems.
- **Miscibility:** Immiscible (do not mix) with water and form distinct liquid-liquid phases (NAPL).
- **Viscosity:** Low viscosity (readily flow), even lower than water. These compounds will rapidly infiltrate soil profiles.
- **Volatility:** Highly volatile compounds that will readily partition to the gas phase and form vapor plumes in the vadose zone.





Sequential Microbial Reductive Dechlorination Pathway

<u>Chloroethenes -</u> Alternative DCE isomers may be produced through abiotic reactions



PCE   TCE   1,2-*cis*DCE (cDCE)   Vinyl chloride (VC)   Ethene

<u>Chloroethanes</u>

1,1,1-TCA   1,1-DCA   Chloroethane (CA)   Ethane

Part II: Microbial Players and Processes Responsible for Anaerobic Reductive Dehalogenation

What are Microorganisms?

- Microbes are tiny (<0.2 – 750 μm) single-celled organisms that are ubiquitous in any and all habitats.
- Groundwater may typically contain 10^3 – 10^6 cells/mL.
- Obtain required sources of carbon, nitrogen, phosphorous, nutrients, etc. from their habitat.
- They make their energy through coupled oxidation-reduction reactions of both organic and inorganic compounds and drive the majority of planetary elemental cycles (e.g. C, N, P, S, etc.).
- Usually live in complex diverse communities.
- Have extremely diverse metabolic capacities with species acting as generalists (lots of potential substrates) and specialists (single or select few metabolic processes)
- Microbial communities are responsive to environmental changes such as contamination.

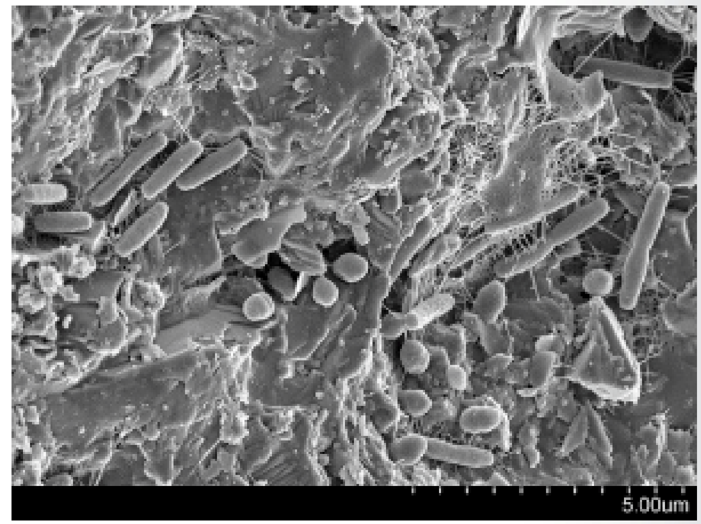
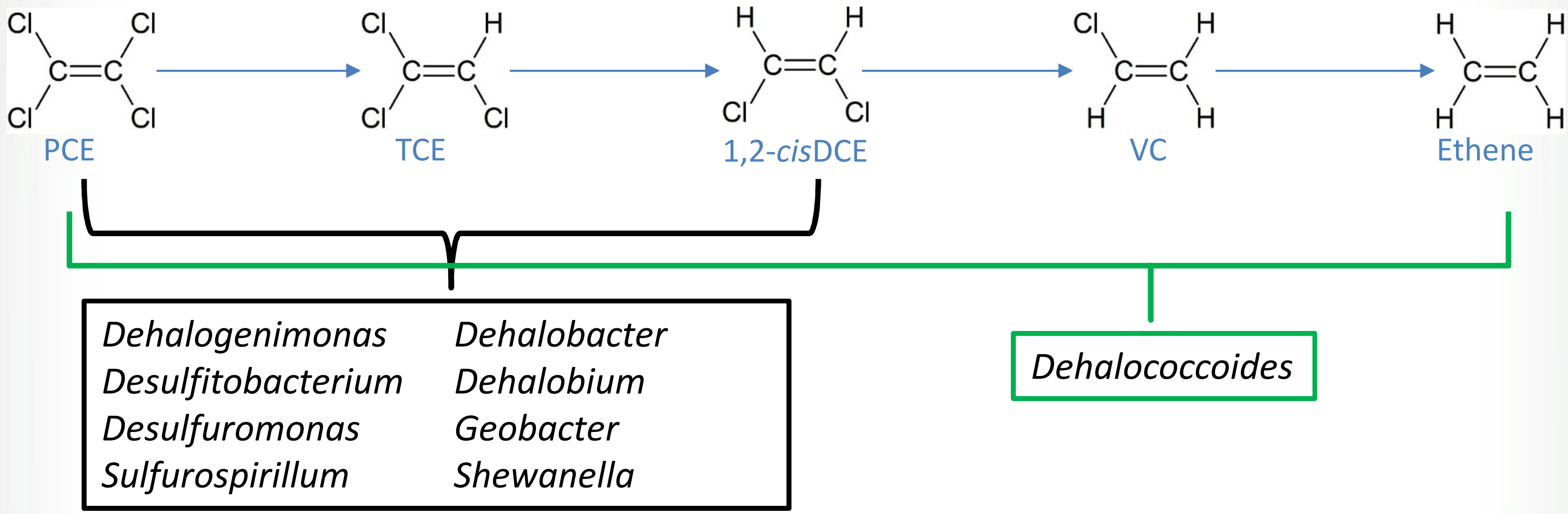


Image by Lewis Lab (Northeastern University) from https://soilsmatter.wordpress.com/2014/09/02/the-living-soil/

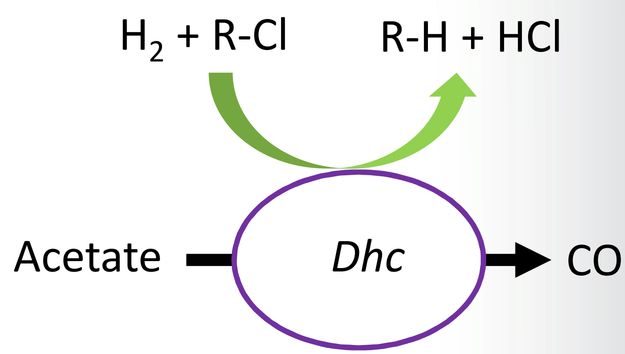
Diversity of Microorganisms Capable of Anaerobic Reductive Dechlorination of Chlorinated Alkanes & Alkenes

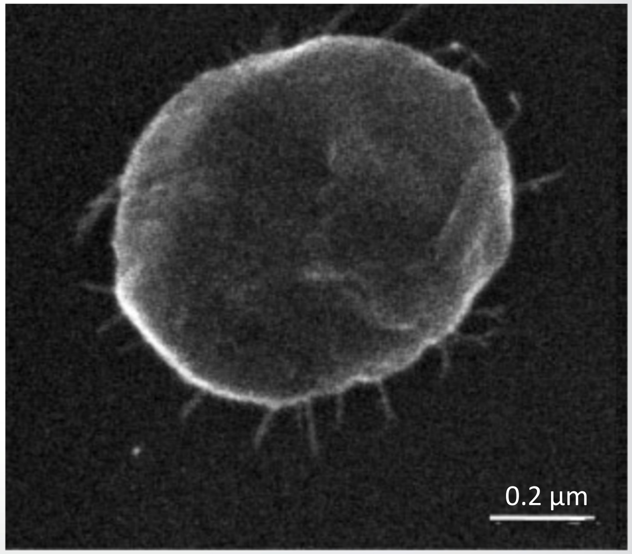


- Many different microbial species are capable of partial reductive dechlorination.
- Only species of *Dehalococcoides* have been shown to dechlorinate VC to ethene.
- Environmental investigations have revealed that complete reductive dechlorination of PCE and TCE is only observed in groundwaters with detectable *Dehalococcoides* populations

Dehalococcoides mccartyi (Dhc): the Model Dehalogenating Microorganism

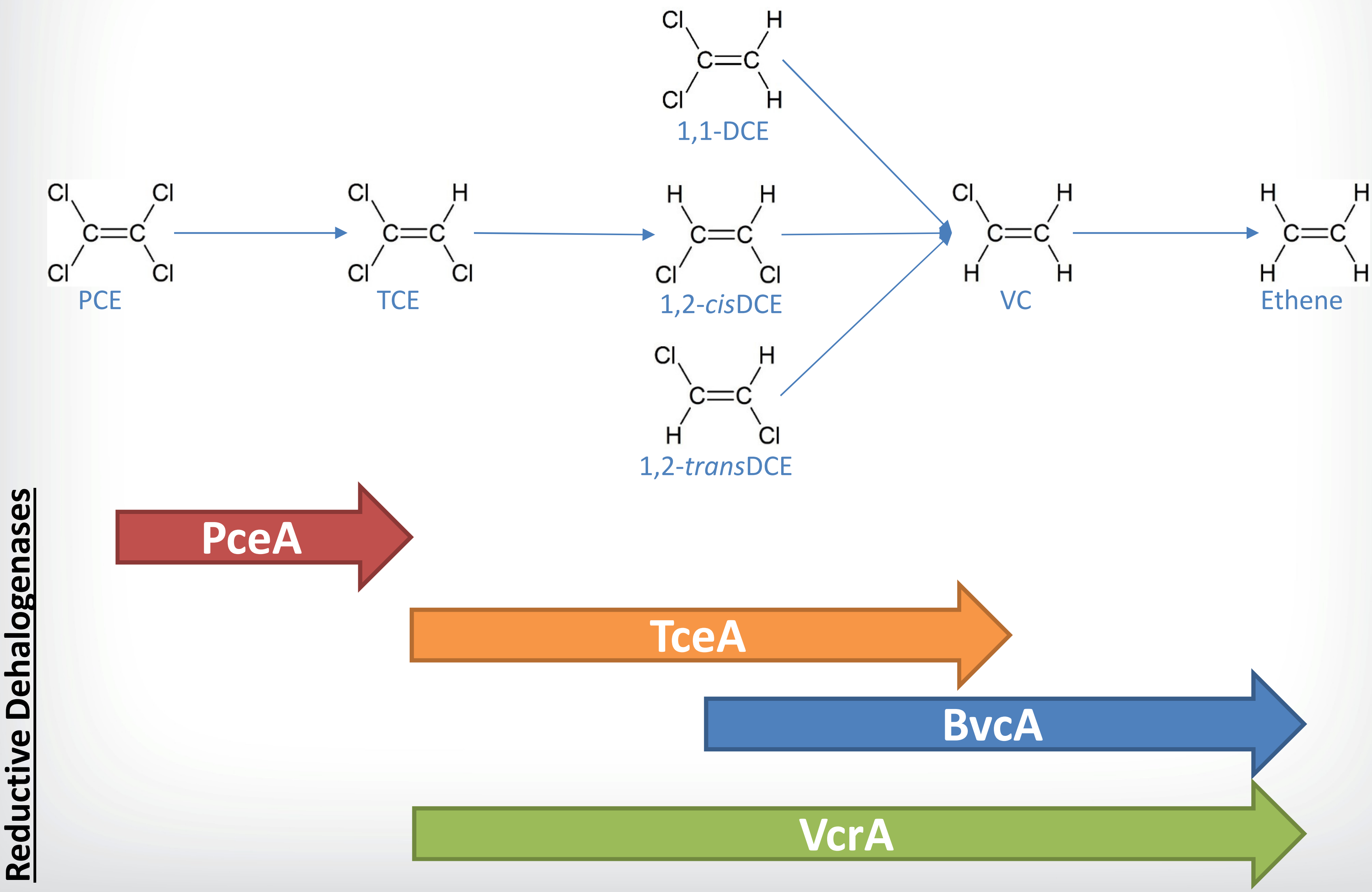
- Obligate organohalide-respiring organism. Makes all of it's energy from reductive dehalogenation.
- Requires strictly anoxic and reducing-conditions in the environment
- Dehalogenation activity at temperatures 15 - 30°C and pH 6.5 – 8.0.
- Requires acetate, hydrogen (electron donor), and vitamin B12 production from other microorganisms in the environment
- Capable of dehalogenating a wide range of chlorinated/brominated contaminants: alkanes, alkenes, and aromatic compounds.
- Different strains have different reductive dechlorination capacities:
  - Some strains can degrade VC to ethene, while others produce cDCE or VC as toxic end products
  - Differences are based upon the different reductive dehalogenase genes they possess.



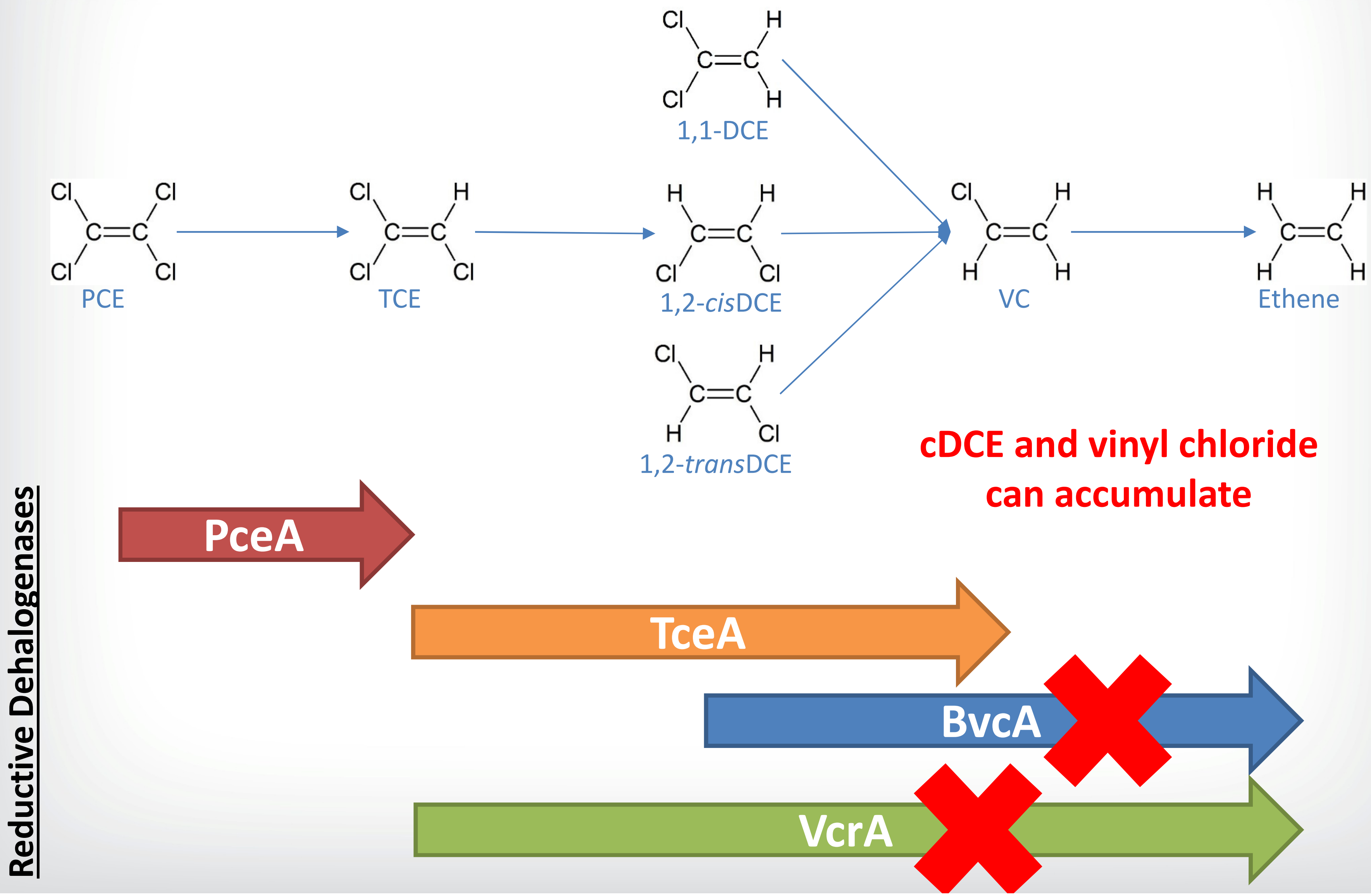


Source: Löffler et al. (2013) IJSEM 63, 625-635

The Various Reductive Dehalogenase Enzymes



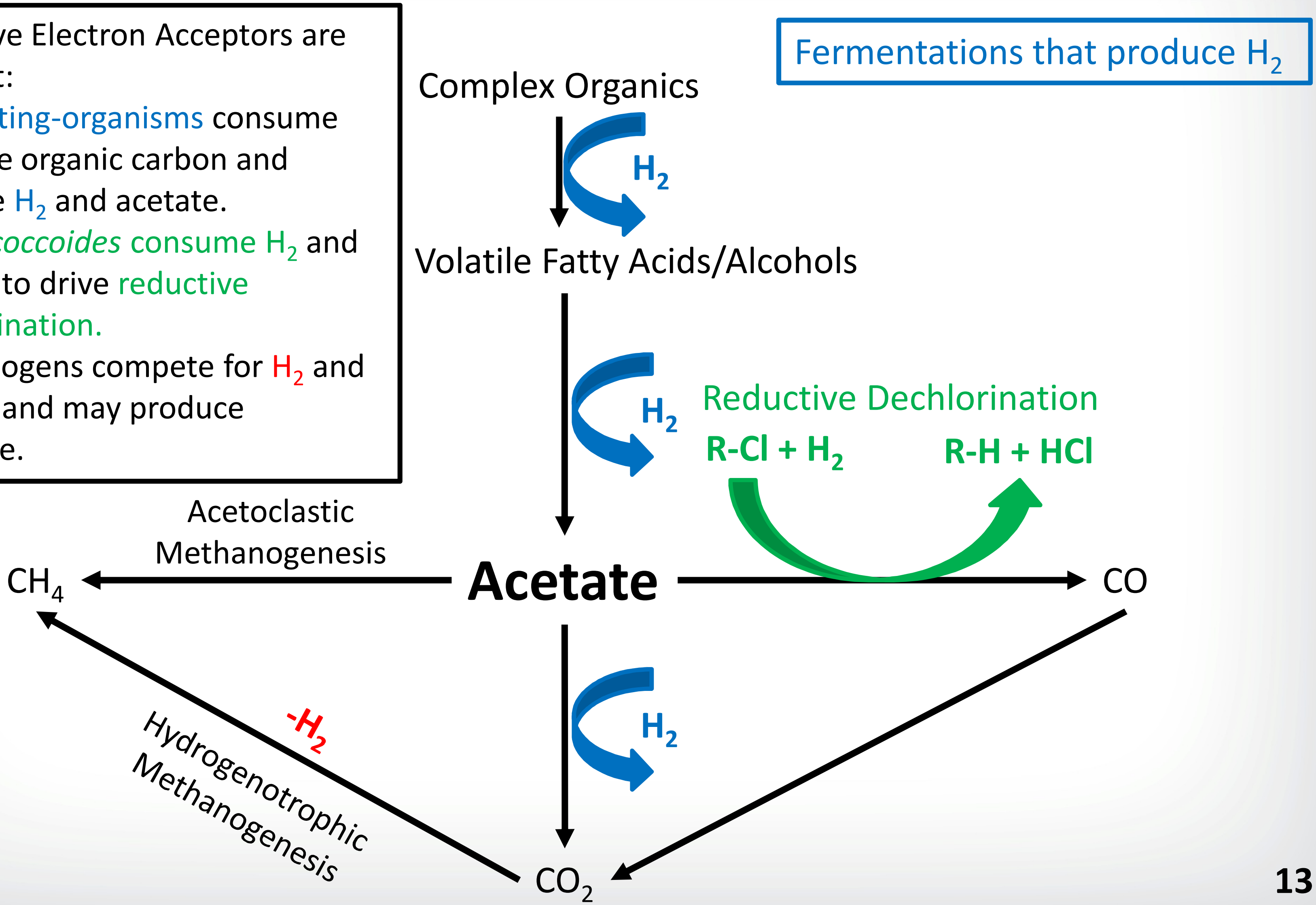
Reductive Dehalogenase Genes Effect Treatment



The Subsurface Anaerobic Food Web

If Alternative Electron Acceptors are **not** Present:

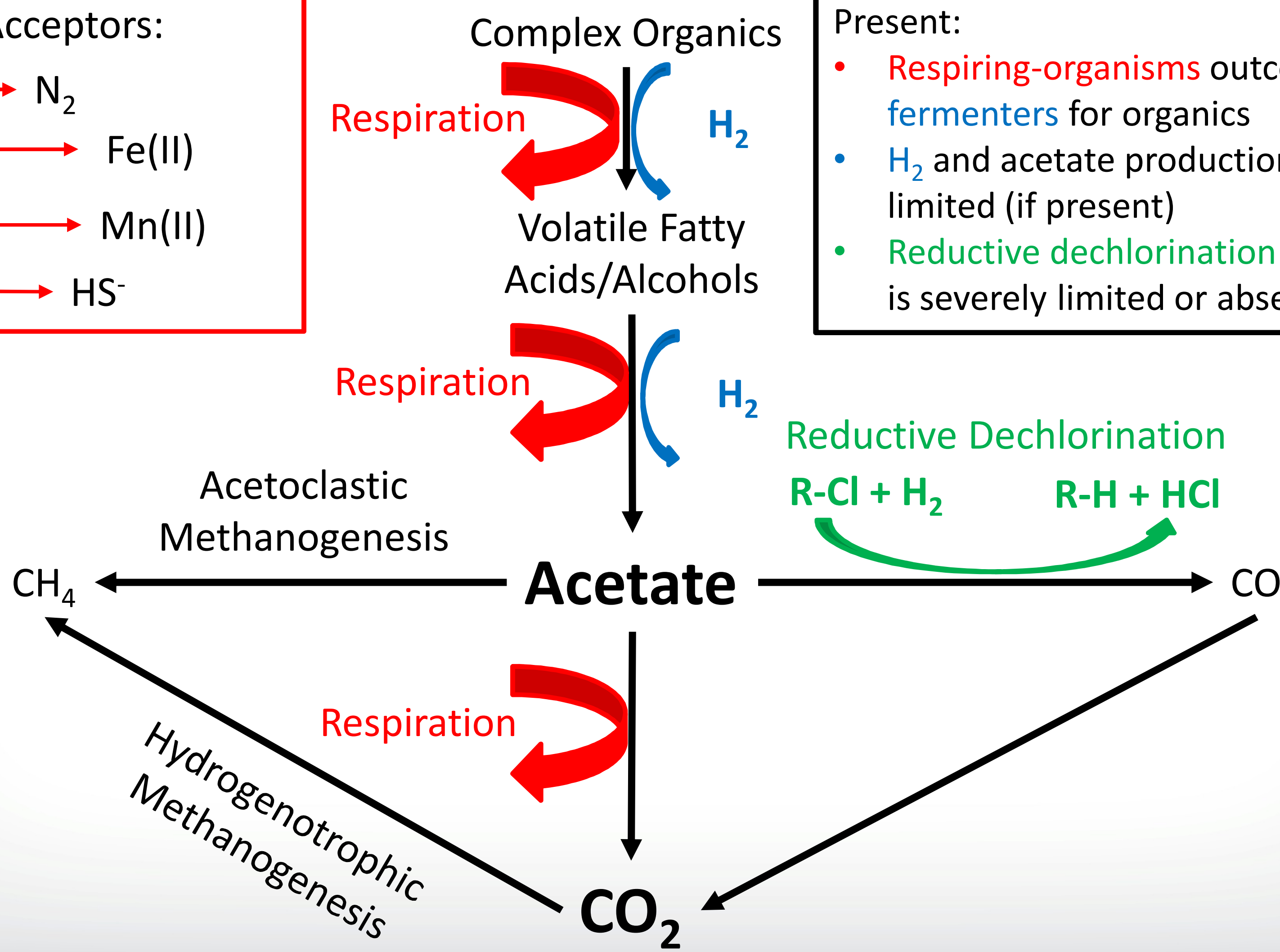
- Fermenting-organisms consume available organic carbon and produce H_2 and acetate.
- *Dehalococcoides* consume H_2 and acetate to drive reductive dechlorination.
- Methanogens compete for H_2 and acetate and may produce methane.



The Subsurface Anaerobic Food Web

Respiration of Alternative Electron Acceptors:

- NO_3^- → N_2
- Fe(III) → Fe(II)
- Mn(IV) → Mn(II)
- SO_4^{2-} → HS^-



If Alternative Electron Acceptors are Present:

- Respiring-organisms outcompete fermenters for organics
- H_2 and acetate production are very limited (if present)
- Reductive dechlorination capacity is severely limited or absent

Part III: Chlorinated Solvent Behavior in the Terrestrial Subsurface

DNAPL Plume Life Cycle: Early Stage

- Initial migration is predominantly downward into the subsurface.
- Heterogeneity of the subsurface profile greatly influences distribution.
- Ganglia (DNAPL disconnected from the main body) may form in pore spaces and flow paths in both saturated and vadose zones.
- Pools of DNAPL may form on low-permeability zones if sufficient contaminant is present.

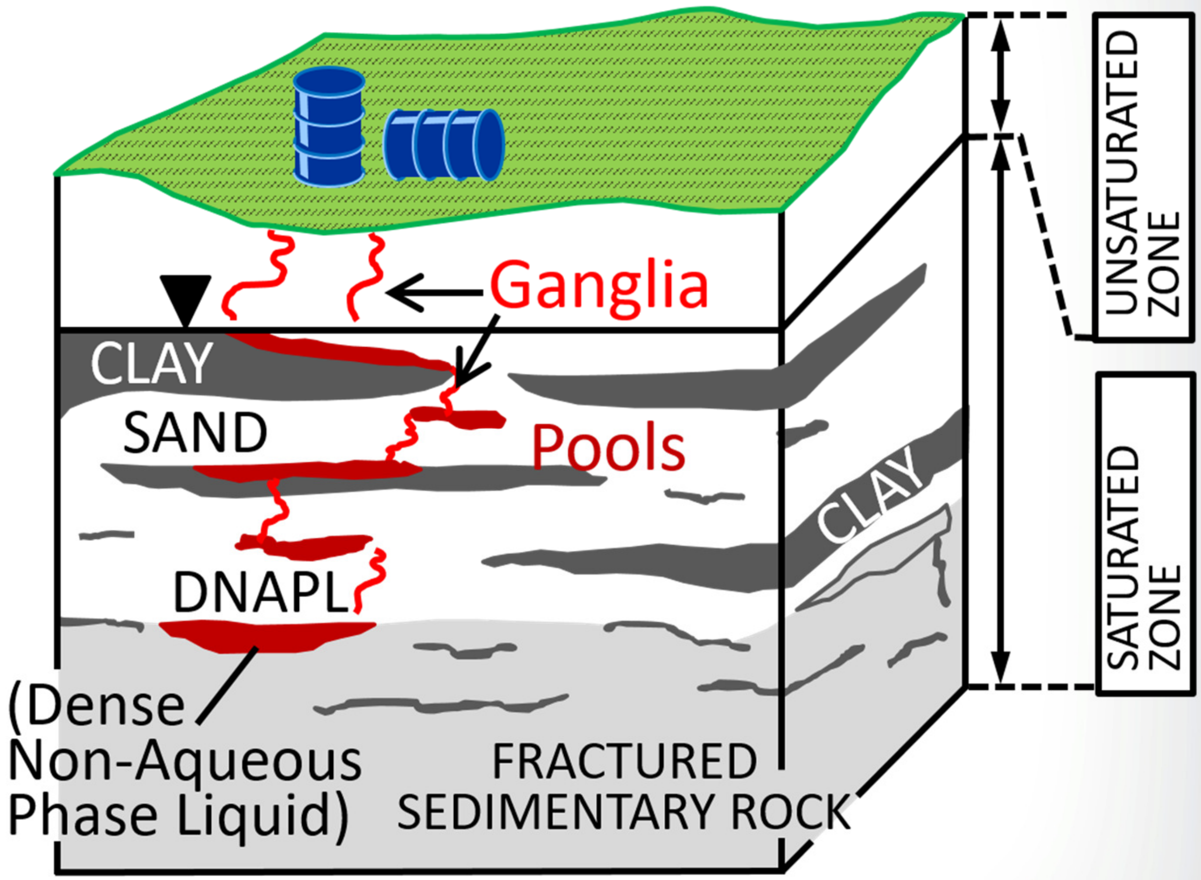


Image source: Stroo et al. (2012) ES&T 46 (12):6438-6447

DNAPL Plume Life Cycle: Mature Stage

- Horizontal plume development
  - Liquid (DNAPL) flow driven by gravity
  - Dissolved-phase driven by groundwater flow
  - Vapor plume develops in vadose zone from volatilization of DNAPL plume
- Sorption into low-permeability zones occurs

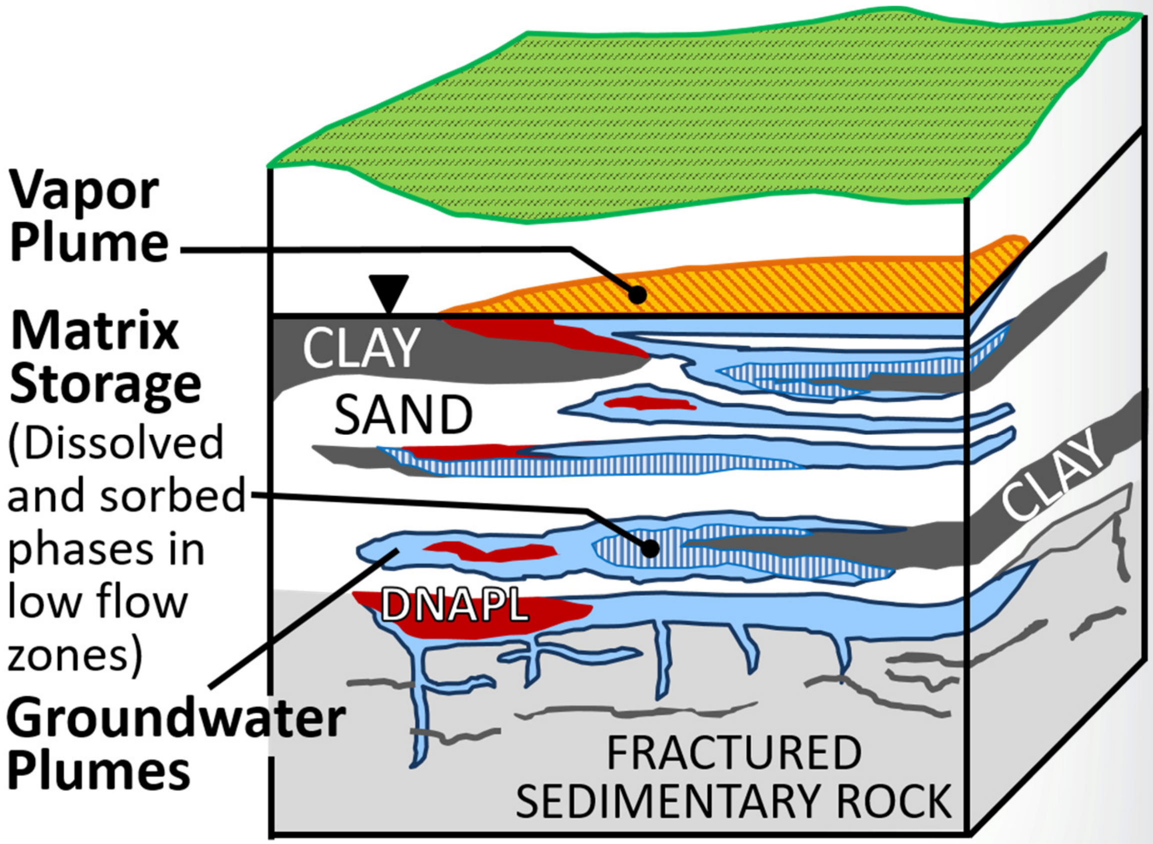
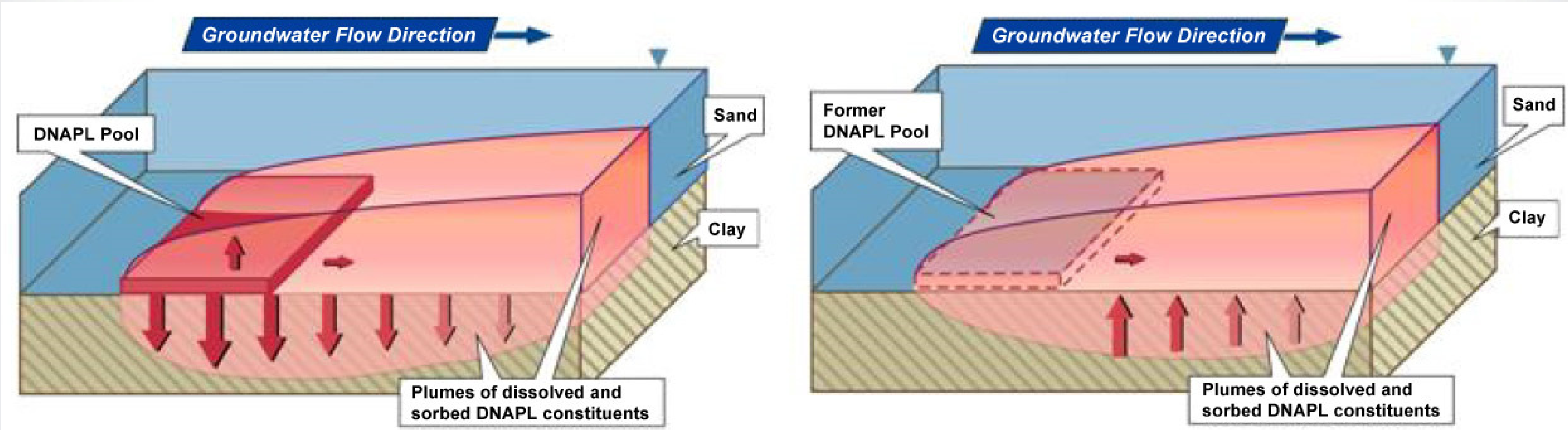


Image source: Stroo et al. (2012) ES&T 46 (12):6438-6447

Back Diffusion from Clay



- DNAPL pools are initially the predominant source of dissolved-phase contaminants
- Sorption into the underlying low-permeability clay layer occurs while the DNAPL pool is present.
- Once the DNAPL pool is gone (removal or dissolution), the chlorinated solvents stored within the low-permeability zone now diffuse back into the higher-permeability saturated zone.
- The clay layer now becomes a significant source of dissolved phase plume contaminants.

Image source: Sale, T.C. and C. Newell. (2011) ESTCP Project ER-05 30.

Consequences of Fractured Bedrock

- High density and low viscosity drive DNAPL downward within bedrock.
- Fractures act as preferential flow paths:
  - Early movement is mostly downward.
  - Groundwater flow drives dissolved-phase plume development along fractures with time
- Sorption into rock matrices occurs around fractures with time
- Fracture network complexity makes DNAPL location and quantification challenging

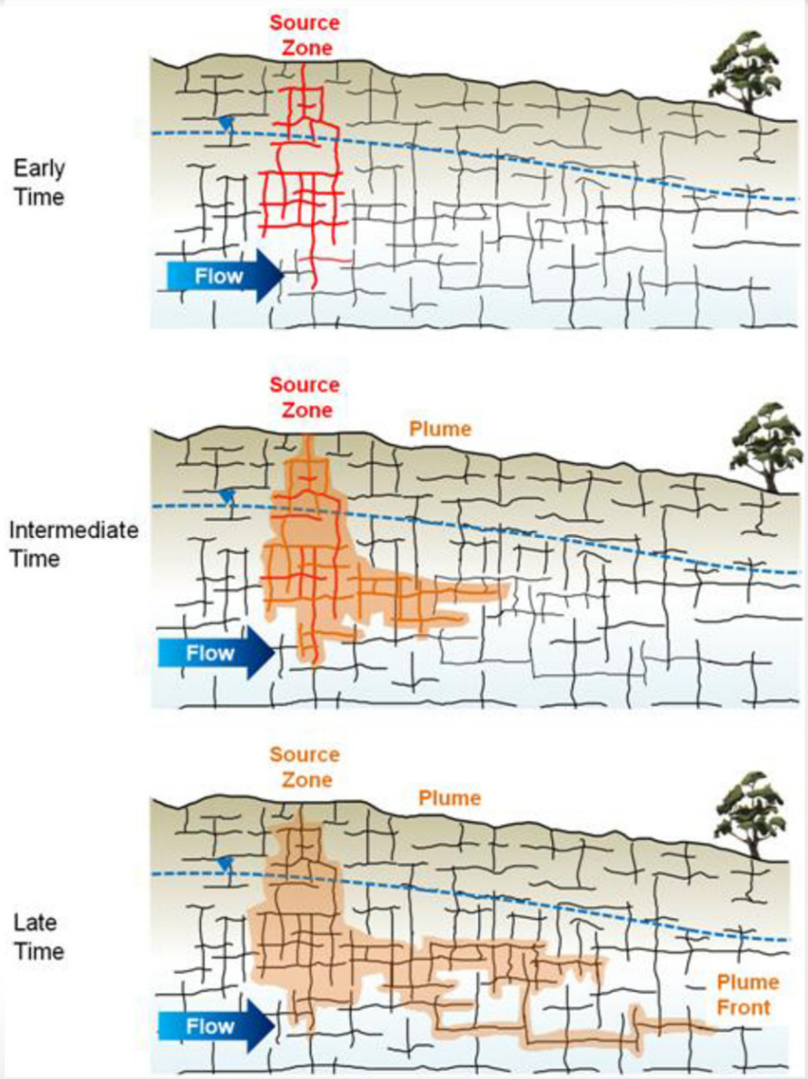


Image source: Parker et al. (2012) AQUA (Am06052):101-116

Part IV: Strategies for the Bioremediation of Chlorinated Solvents via Anaerobic Reductive Dechlorination

Passive Treatment: Monitored Natural Attenuation (MNA)

- Natural attenuation relies on physical, chemical, and biological contaminant reduction mechanisms (e.g. biodegradation, volatilization, dilution, etc.) native to the site.
- Continued thorough **monitoring** of contaminant and transformation product concentrations is essential throughout the remediation project.
- MNA may be used as the sole remediation strategy, but is commonly applied in conjunction with or following active treatment measures.
- Lines of evidence to support the use of MNA:
  - Presence of transformation and terminal end products (e.g. ethene without accumulation of VC)
  - Presence of the required microorganisms (*Dehalococcoides* with *bvcA* and/or *vcrA* genes)
  - Sufficient site characteristics to support the process (reducing conditions, anoxia, circumneutral pH, sufficient electron donor, etc.)
  - Degradation rates (bench or field studies) sufficient to achieve remediation objectives within reasonable timeframe and low exposure risk.

Active Treatment: Biostimulation

- **Biostimulation:** The addition of organic electron donors and nutrients to enhance the rate of reductive dichlorination by the native microflora.
- The essential stimulant for chlorinated solvents is readily fermentable organic materials to serve as electron donors.

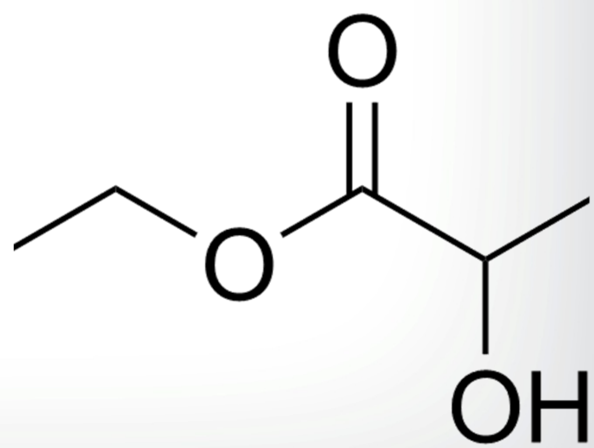
Soluble Substrates (e.g. lactate or molasses):

  - Rapidly consumed by subsurface microorganisms
  - Can be applied as a water solution
  - Injected continuously or with high frequency

Slow-release Substrates (e.g. ethyl lactate or vegetable oils):

  - Consumed over prolonged times by subsurface microbial communities
  - Applied as water emulsions (more uniform distribution) or as straight oils (less uniform distribution)
  - Injected only once or possibly every few years

- Growth-supporting nutrients (nitrogen, phosphorus, etc.) may also be added to further support microbial activities.
- Can also be used to drive groundwater to anoxic reducing-conditions.



Active Treatment: Bioaugmentation

- **Bioaugmentation:** The addition of beneficial organisms to promote contaminant biodegradation.
- Bioaugmentation cultures for ARD are mixed communities containing:
  - *Dehalococcoides* with genes for complete dehalogenation
  - Microbes capable of fermenting complex and simple organics to supply acetate, hydrogen, vitamin B12.
- Cultures must be handled and applied in the field to maintain cell viability (i.e. reducing-conditions).
- Bioaugmentation can only be effective if the groundwater chemistry is conducive to the growth/activity of the supplied organisms. Biostimulation is used to ensure the groundwater conditions are appropriate and then bioaugmentation is applied.
- Bioaugmentation is an effective strategy to deal with accumulated cDCE or VC within chlorinated solvent plumes. It may also be used to increase the rate of anaerobic reductive dechlorination.

https://toxics.usgs.gov/highlights/bioaugmentation.html

Biologically-based Permeable Reactive Barriers (PRBs)

- Engineered porous subsurface structures composed of reactive substrates to treat groundwater contaminants as they flow through the unit.
- They rely on passive hydraulic processes to route the contaminant plume through the wall for remediation.
- PRB solid substrates can be mulch, compost, chitin, etc.
- PRBs are installed by trenching/excavation and are generally only used at sites with shallow contamination.
- Can be applied in different ways:
  - Source zone-treatment by placing perpendicular to groundwater flow-path to intercept contaminant plume.
  - Upstream of contaminant plume to remove alternative electron acceptors to promote better source zone treatment conditions.
- Key considerations are placement location, substrate material reaction rates, and retention times to ensure adequate contaminant biodegradation within the PRB.

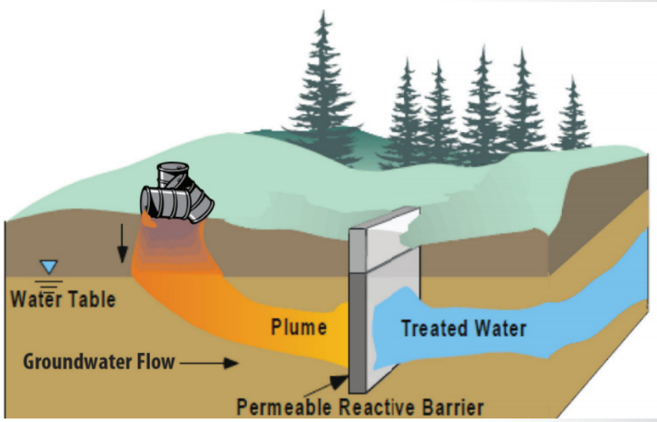


Image source: US EPA from http://hazmatmag.com/2017/10/in-situ-remediation-of-tetrachloroethylene-and-its-intermediates-in-groundwater

Image source: https://archive.epa.gov/ada/web/html/prb.html

Conceptual Site Models are Essential

- **Conceptual Site Models (CSMs)** show the potential source area and current plume characteristics (e.g. size & concentrations)
- CSMs provide essential information for treatment strategy decision making, so developing a high quality CSM must be the first step in building a remedial action plan at every site.
- CSMs reflect the content they are based upon:
  - More high quality data = better CSM
  - Low quality and/or low data coverage = poor CSM
  - "Garbage In means Garbage Out"
- CSMs should be "living documents" that are updated as new site data becomes available.

- Key elements of a high-quality CSM:
  - Geology and hydrogeology
  - Contaminant types, distribution, fate, and transport
  - Proposed release zone and mechanism
  - Potential exposure mechanisms
  - Groundwater physicochemical conditions

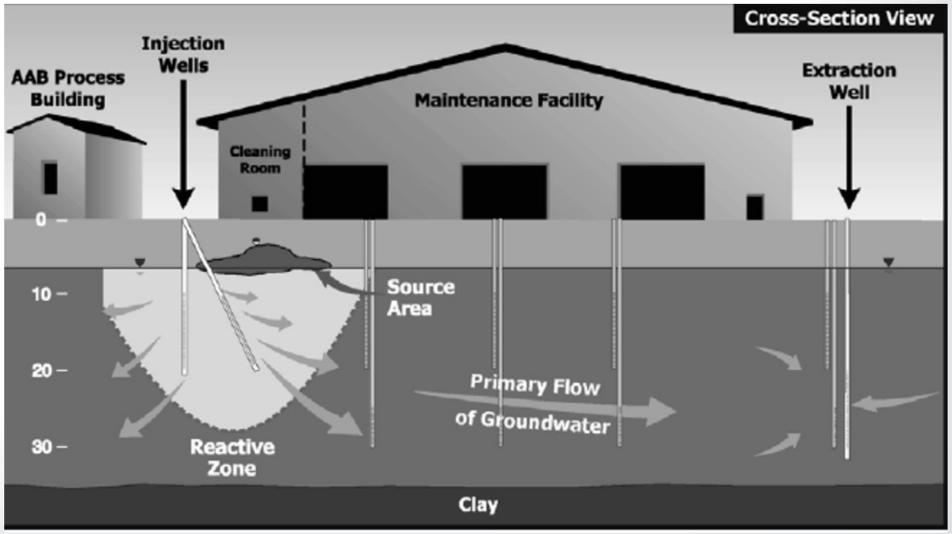


Image source: https://www.esaa.org/wp-content/uploads/2015/06/05-Paper09.pdf

Recommended Monitoring

Baseline and Each Groundwater Sampling:

- Chlorinated solvents and transformation products (PCE, TCE, DCE, VC)
- Dissolved gases
  - methane, ethane, and ethene
  - Oxygen (DO)
- Organic carbon: usually as total (TOC) and/or dissolved organic carbon (DOC)
- Alternative electron acceptors: nitrate, iron, manganese, sulfate
- Groundwater physicochemistry:
  - Oxidation-reduction potential (ORP),
  - pH, temperature, conductivity
  - Alkalinity and chloride

Molecular Monitoring (qPCR):

- *Dehalococcoides* 16S rRNA gene (*Dhc*)
- Reductive dehalogenase genes: *tceA, bvcA, vcrA*
- Baseline to determine if augmentation is needed
- Routinely to monitor introduced organisms if bioaugmentation used.

Others that may be helpful:

- Major cations: baseline recommended and as needed
- Sulfide: routinely if high sulfate concentrations (>20 mg/L) are present

Data from: https://clu-in.org/techfocus/default.focus/sec/Bioremediation/cat/Anaerobic_Bioremediation_(Direct)

Part V: Evaluating Treatment Performance

Evaluating if anaerobic reductive dechlorination is working at a site

Multiple lines of evidence :

- Is there a reducing environment?
  - Geochemical data
  - Groundwater VOC data
- Is reductive dechlorination occurring?
  - Groundwater VOC data – **moles rather than mass**
  - Evaluate dilution vs treatment
    - Mole fractions
    - Tracers
- Is there evidence of complete mineralization?
  - Groundwater VOC data
  - Bench or pilot scale data
  - Microbiological data

All data is not required but may be helpful

In general, more data = stronger conceptual site model

Practical Considerations

Is the data reliable?

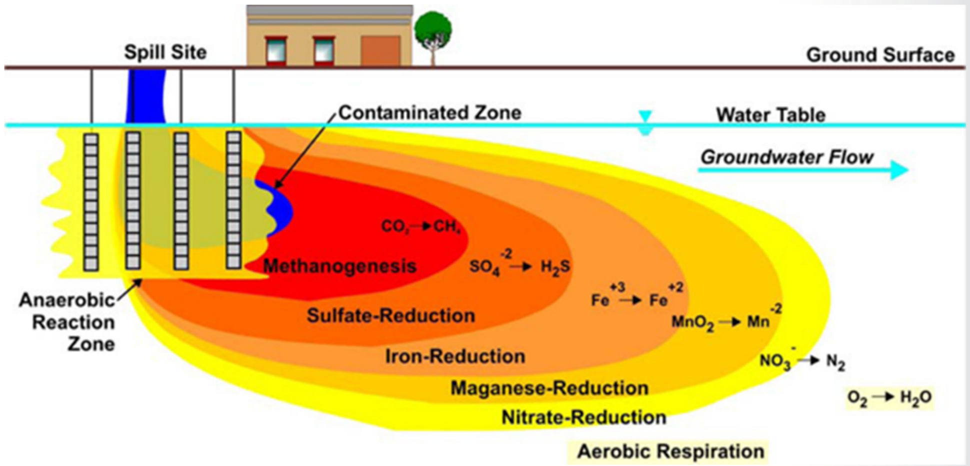
- Were appropriate sampling methods used?
- Were appropriate measurement methods used?
- What are the calibration ranges for probes?
- When were probes calibrated or checked?

Reducing Environment Needed

Conditions must be and stay anaerobic

Examine the groundwater data

- Depletion of electron acceptors (NO_3^-, SO_4^{-2})
- No dissolved oxygen < 1mg/L[1]
- Field ORP < -100 mV [1]
- Depletion of electron donors (ED) – often reported as TOC
- Observation of anaerobic products such as methane or ethane



Anaerobic microbes use electron acceptors in preferential order: nitrate, manganese, ferric iron, sulfate, and carbon dioxide (Source: Parsons 2004).

Other measurements must be supportive of ARD such as 5 < pH < 9 [1]

[1] U.S. EPA. Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water. EPA/600/R-98/128.

Reducing Environment ? Example Data I

elapsed time (days)	TOC (mg/L)	Sulfate as Sulfur (mg/L)	Methane (µg/L)	Ethene (µg/L)	Ethane (µg/L)	pH	DO (mg/L)	ORP (mV)
0	328	100	7270	1050	42.5	7.08	0.07	-172
25	254	--	--	--	--	6.31	3.19	-221
31	236	400	7730	935	36.6	6.6	0.77	-116
63	324	200	9120	2210	69.8	6.96	0.27	-174
95	293	200	10400	1720	60.4	7.35	0.2	-174
129	144	100	9910	1110	36.9	7.21	2.75	-139

Electron donor added throughout pilot

- ORP < - 100 mV
- DO mostly < 1 mg/L
- pH neutral
- TOC and sulfate decreasing
- Methane, ethene, and ethane increasing

Conclusion

- **Evidence of reducing environment suitable for ARD based on ORP, pH, methane, and most sulfate data**
- **DO probe may not be reliable**

Reducing Environment ? Example Data 2

elapsed time	TOC	Sulfate as Sulfur	Methane	Ethene	Ethane	pH	DO	ORP
(days)	(mg/L)	(mg/L)	(µg/L)	(µg/L)	(µg/L)		(mg/L)	(mV)
-490	22	--	3880	27.1	2	6.32	0.17	-190.2
-397	--	--	--	--	--	6.37	0.96	-41.9
-315	23.6	1000	5350	954	76.7	6.14	0.73	-137
-49	28.1	--	3110	56.6	6.8	6.57	0.06	-87.1
-14	19.5	1560	4850	143	13.7	6.68	1.31	-139.7
28	10.5	1960	3000	113	4.8	6.15	5.09	-129
57	11.9	1900	2600	282	7.3	6.48	1.75	-326.9
83	11.7	1810	2770	45	2.5	7.13	0.32	-146.2
111	10.9	1840	3890	57.7	5.8	6.24	0.1	-226.6

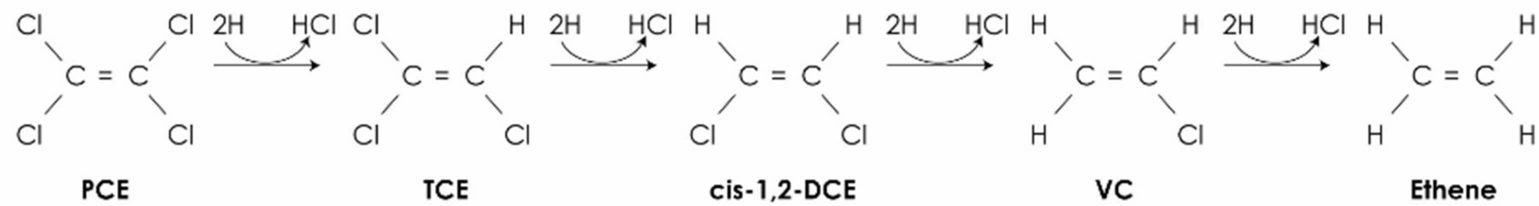
After day 0 (shaded), electron donor added continuously and ground water recirculation system started – data as reported

- ORP < -100 mV
- DO increase, not correlated to ORP
- pH neutral
- TOC low and sulfate increasing
- Methane, ethene, and ethane decreasing

Conclusion

- **Conditions marginal for ARD**
- **GW recirculation may be changing concentrations**
- **DO probe may not be reliable**
- **More ED may be needed**

Is Reductive Dechlorination Occurring?



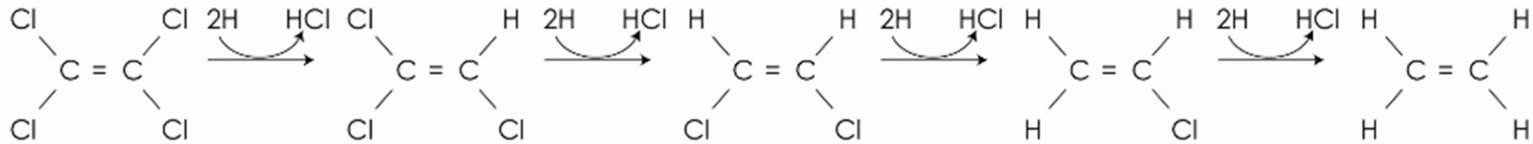
Lines of Evidence

- Mass Balance based on chemical data
  - Sequential conversion of solvents to ethene or ethane
  - Generation of chloride
    - Not useful for marine influenced sites
    - > 2x background [1]
- Dilution vs Treatment
  - Use tracers
  - Proportions of solvents changing with time

Use a molar basis

[1] U.S. EPA. Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water. EPA/600/R-98/128.

Molar Basis



	PCE	TCE	cis-1,2-DCE	VC	Ethene
Molecular Weight (g/mole)	165.8	131.4	96.95	62.50	28.05
Mass basis (mg/L)	165.8	131.4	96.95	62.50	28.05
Mole Basis (mmole/L)	1	1	1	1	1

Data Interpretation Tools I

Chemical	Mass Conc (mg/L)	Molecular Weight (g/mole)	Mole Conc (mmoles/L or mM)
PCE	0	165.8	0
TCE	40	131.4	**0.3**
cDCE	0.54	96.95	0.005
VC	0	62.50	0
Ethene	0	28.05	0
Total			**0.305**

Mole based data – Concentration expressed in moles/L

Molar Conc TCE = Mass Conc of TCE/ molecular weight of TCE

Molar sum of chlorinated solvents - Units moles/L

- Sum of all molar concentrations in the degradation pathway

Total Conc = Mol Conc$_{PCE}$ + Mol Conc$_{TCE}$ + Mol Conc$_{cDCE}$ + Mol Conc$_{VC}$ + Mol Conc$_{Ethene}$

Data Interpretation Tools 2

Chemical	Mass Conc (mg/L)	MW (g/mole)	Mole Conc (mM)	Mole Fraction
PCE	0	165.8	0	0
TCE	40	131.4	0.3	0.98
cDCE	0.54	96.95	0.005	0.02
VC	0	62.50	0	0
Ethene	0	28.05	0	0
Total			0.305	

Mole fractions – No units

- Ratio of molar concentration of a solvent to total conc
- Useful in evaluating dilution vs treatment

$$\text{MF TCE} = \frac{\text{Mol Conc}_{\text{TCE}}}{\text{Total Conc}}$$

Data Interpretation Tools 3

Chemical	Mass Conc (mg/L)	MW (g/mole)	Mole Conc (mM)	Mole Fraction	Chlorines/ molecule	Calc Cl number
PCE	0	165.8	0	0	4	**4*0**
TCE	40	131.4	0.3	0.98	3	**3*0.3**
cDCE	0.54	96.95	0.005	0.02	2	**2*0.005**
VC	0	62.50	0	0	1	**1*0**
Ethene	0	28.05	0	0	0	
Total			**0.305**			**2.98**

Chlorine number – no units

$$\text{Cl Number} = \frac{(4 * \text{Mol Conc}_{PCE} + 3 * \text{Mol Conc}_{TCE} + 2 * \text{Mol Conc}_{DCE} + 1 * \text{Mol Conc}_{VC})}{\text{total conc}}$$

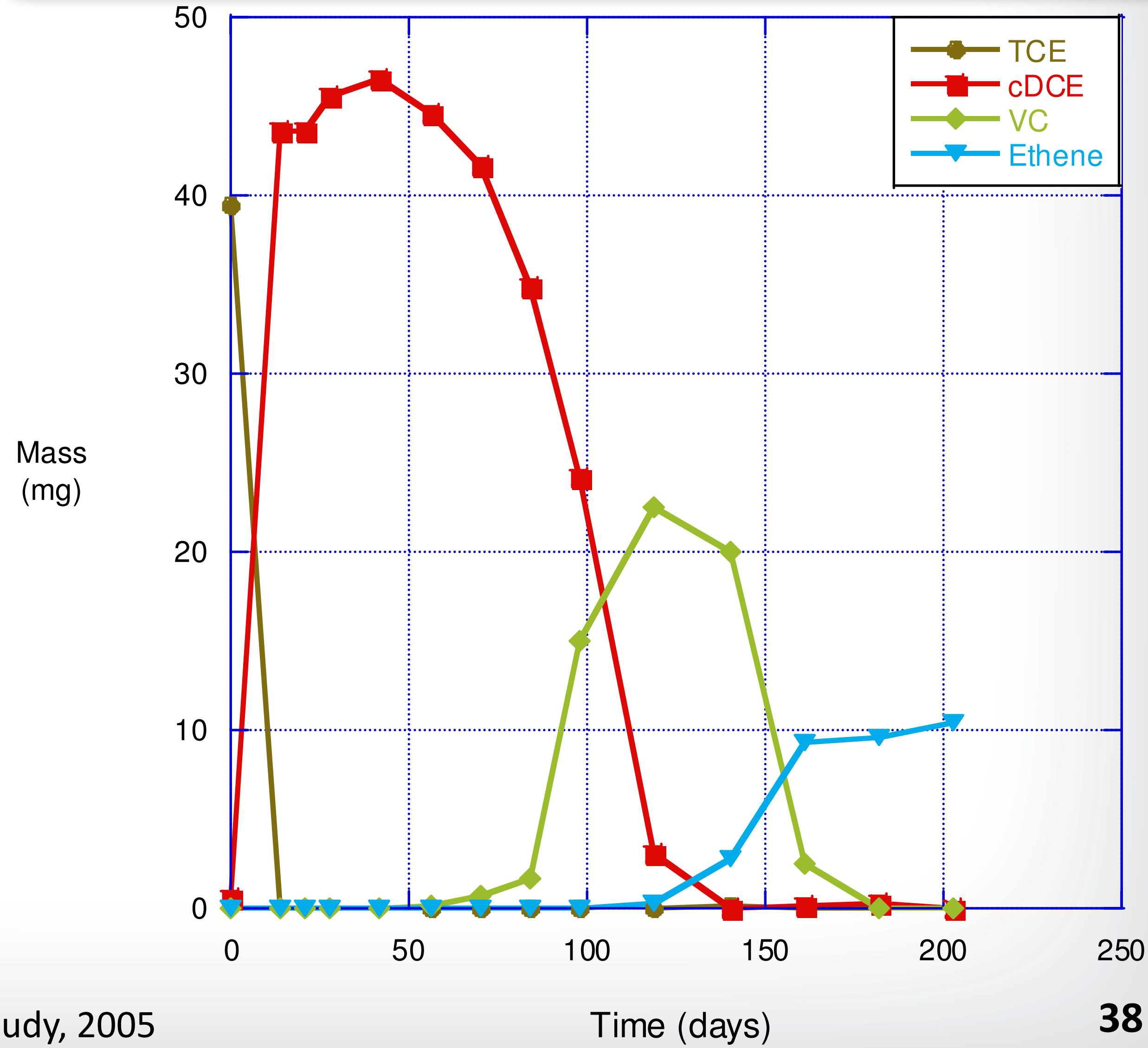
- Useful in evaluating the extent of dechlorination
- Average number of chlorine per solvent molecule

- PCE dominated system, Cl num. = 4
- DCE dominated system, Cl num. = 2
- Complete dechlorination, Cl num. = 0

Example – Mass Basis

Example Data

- Shows sequential conversion of solvents
- Difficult to determine if molar conversion is occurring
- Next slide – same data on molar basis

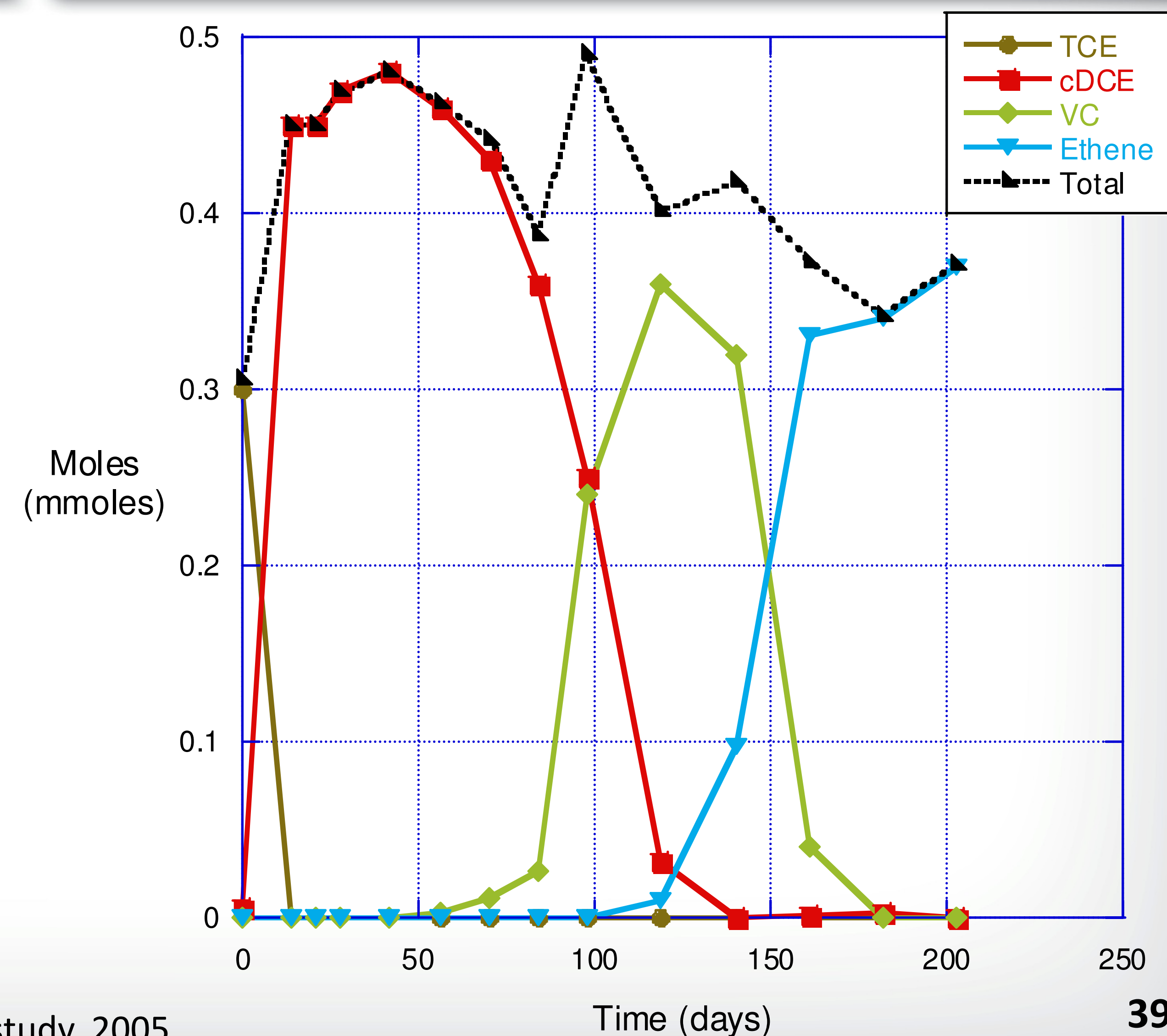


Data from SiREM, RTDF/SABRE study, 2005

Example – Mole Basis

Example Data

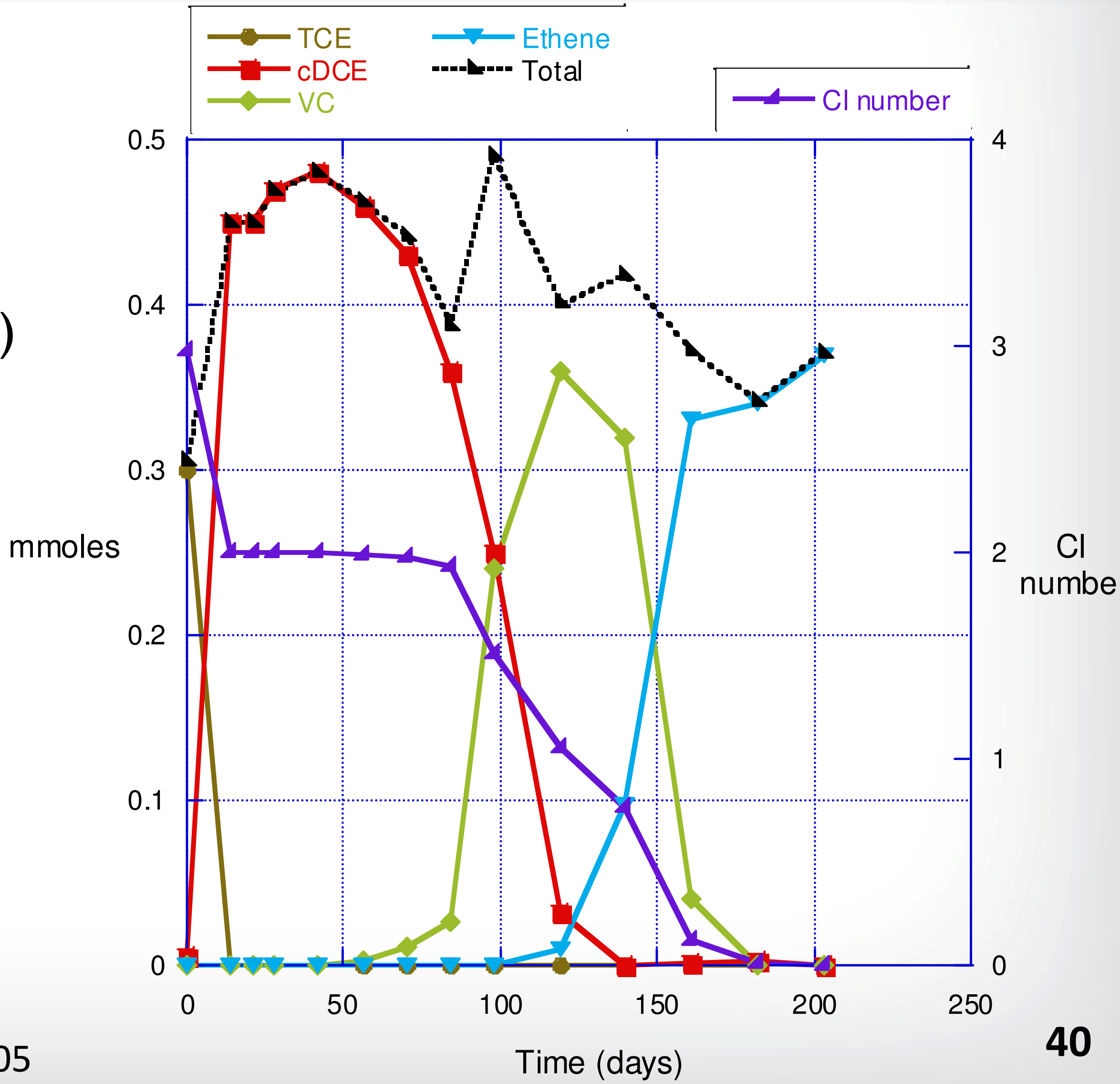
- Shows sequential conversion of solvents
- Approximately equimolar amounts of solvents
- By 200 days, only ethene – complete conversion
- Easier to see trends



Data from SiREM, RTDF/SABRE study, 2005

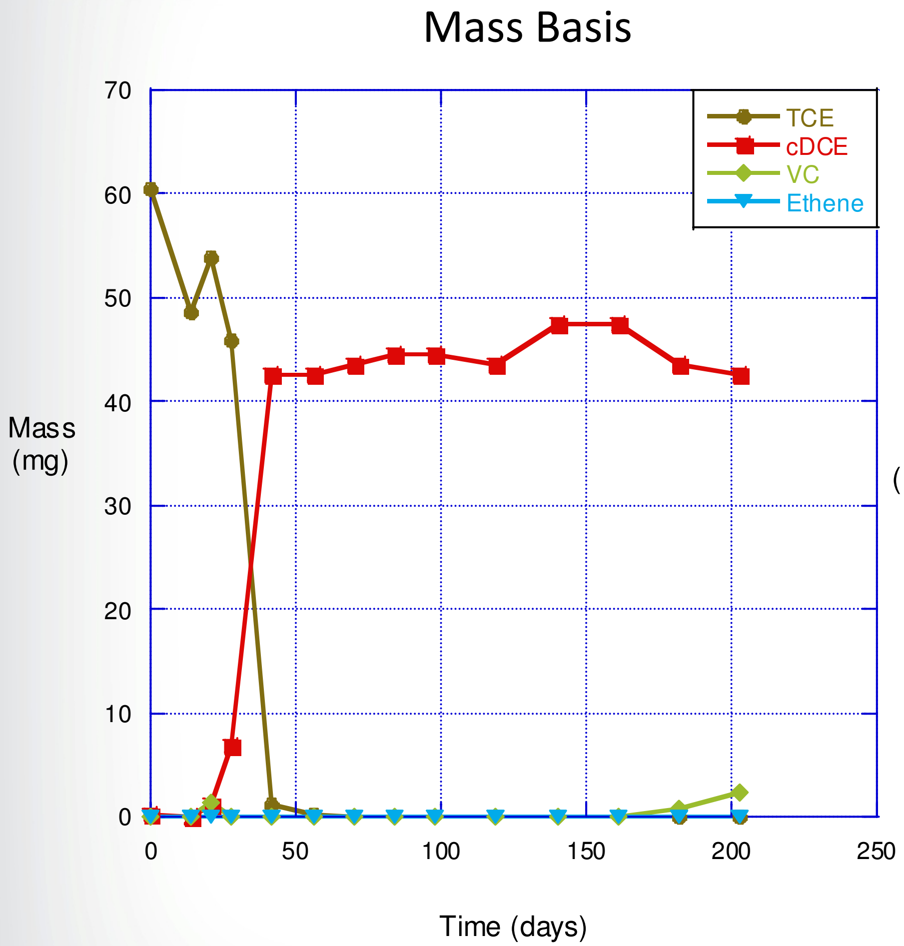
Mole Basis with Chlorine Number

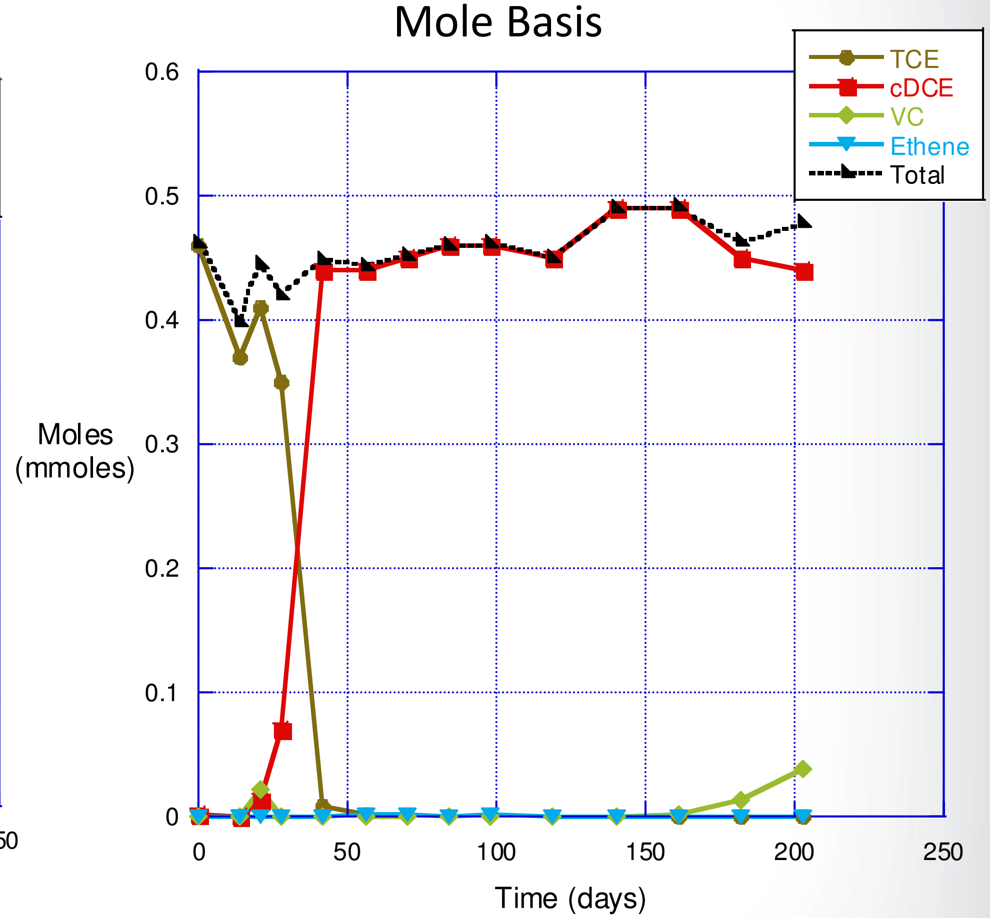
- Cl number shows dechlorination progress
  - starting around 3 (TCE)
  - moving through 2 (cDCE)
  - ending up at 0 (Ethene)
- This ED type and amount was sufficient for full dechlorination
- This microbial community is capable of full dechlorination



Data from SiREM, RTDF/SABRE study, 2005

Example Incomplete Treatment



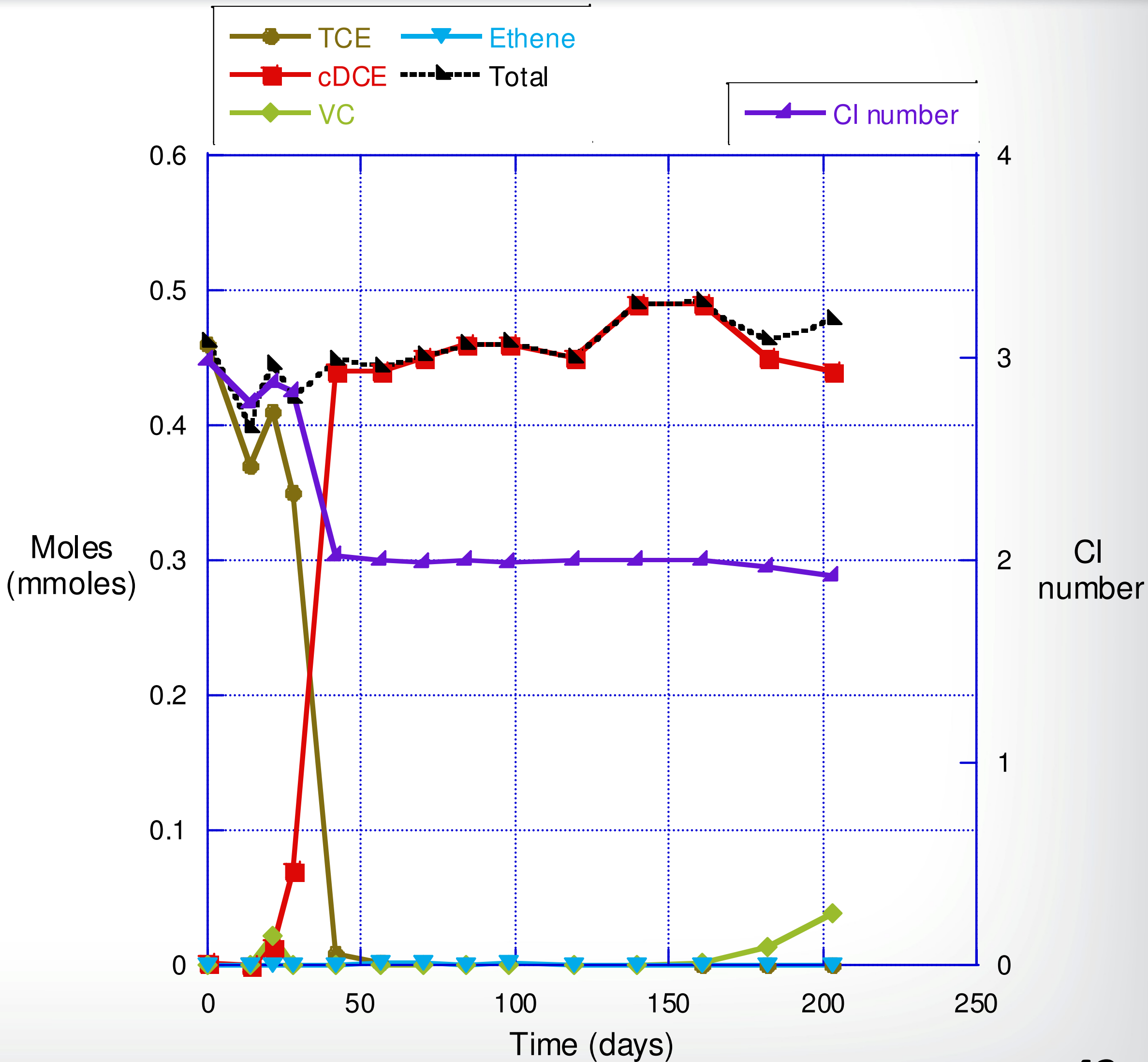


- Both show decrease in TCE and increase in cDCE
- Mole Basis shows one to one conversion

Data from SiREM, RTDF/SABRE study, 2005

Incomplete Treatment with Chlorine Number

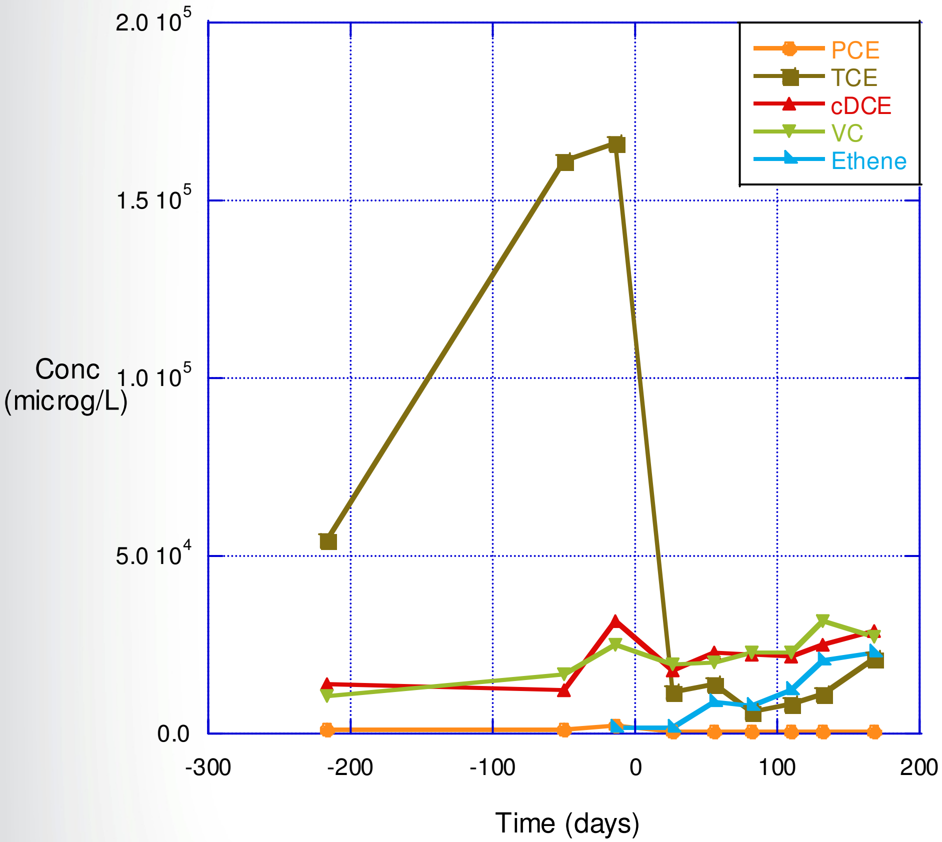
- Cl number shows the limited process of dechlorination
  - starting around 3 (TCE)
  - staying at 2 (cDCE)
- Progress may be limited by
  - type of ED
  - quantity of ED
  - microbial community
- Because the 1st microcosm showed complete dechlorination, problem
  - is probably the type or amount of ED
  - but different ED can cultivate a different microbial community



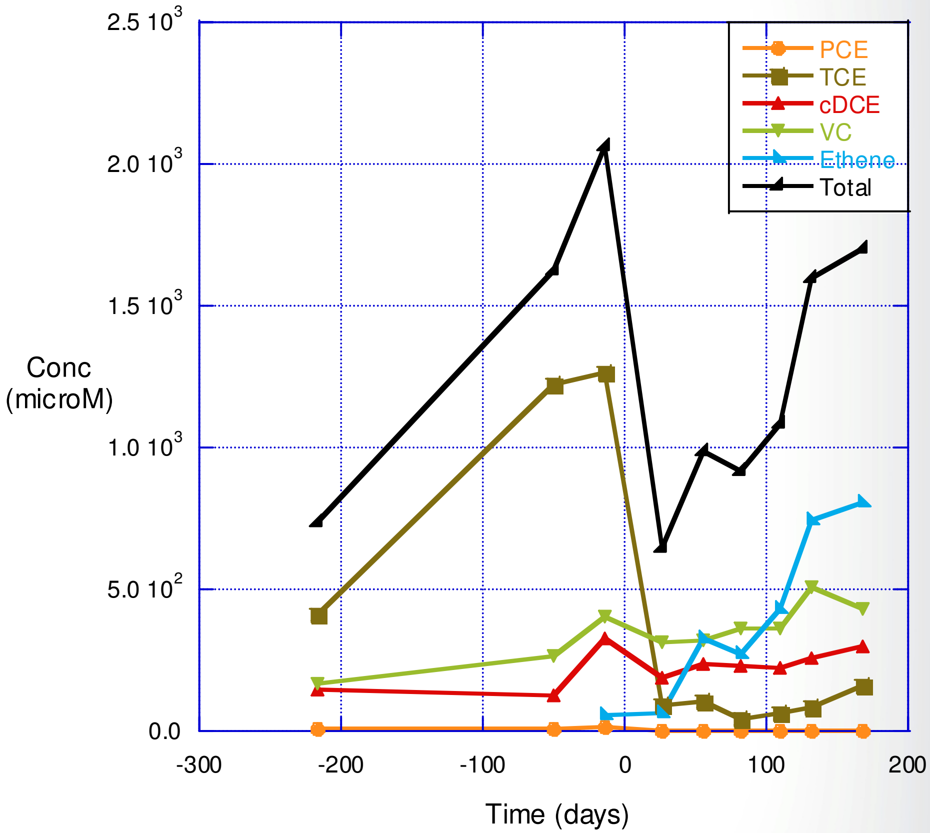
Data from SiREM, RTDF/SABRE study, 2005

Example from Groundwater Well – Mass and Mole bases

Mass Basis



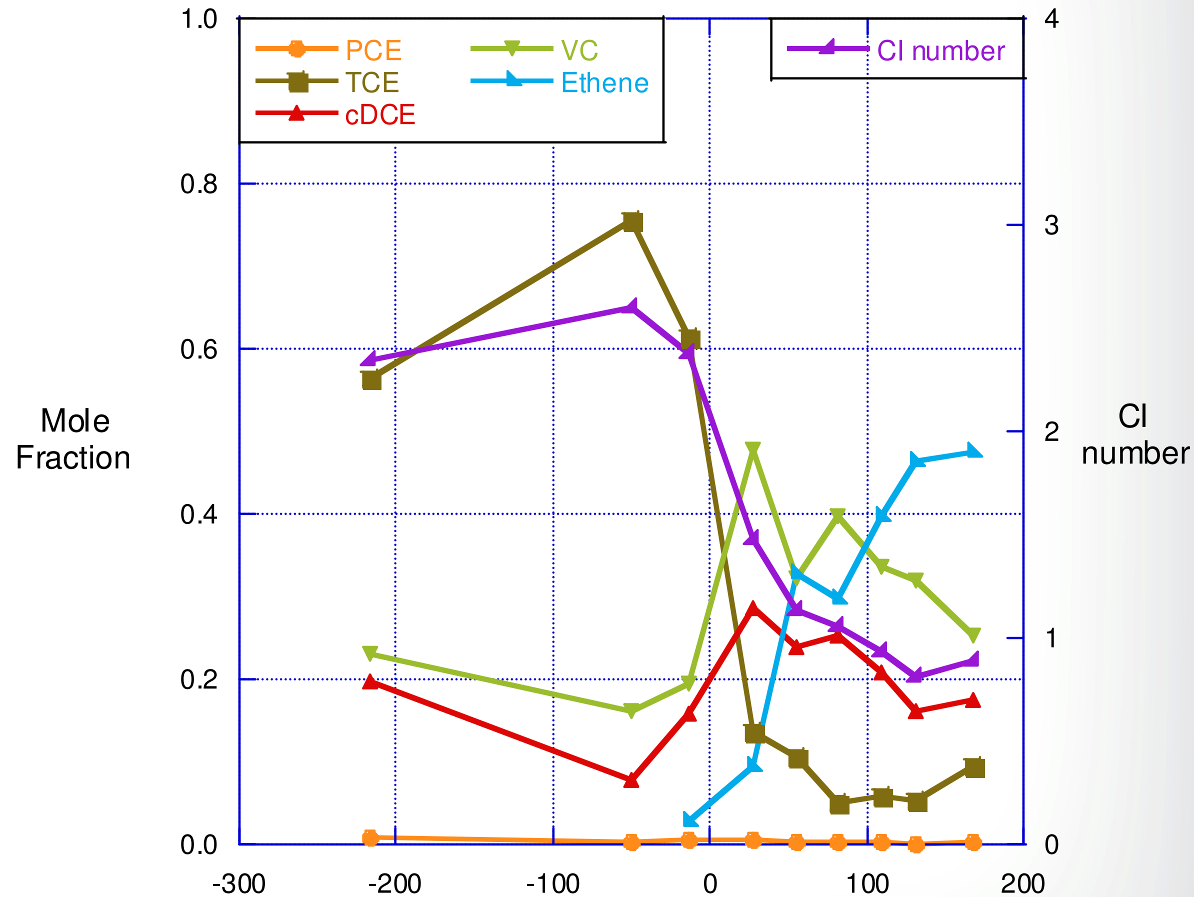
Mole Basis



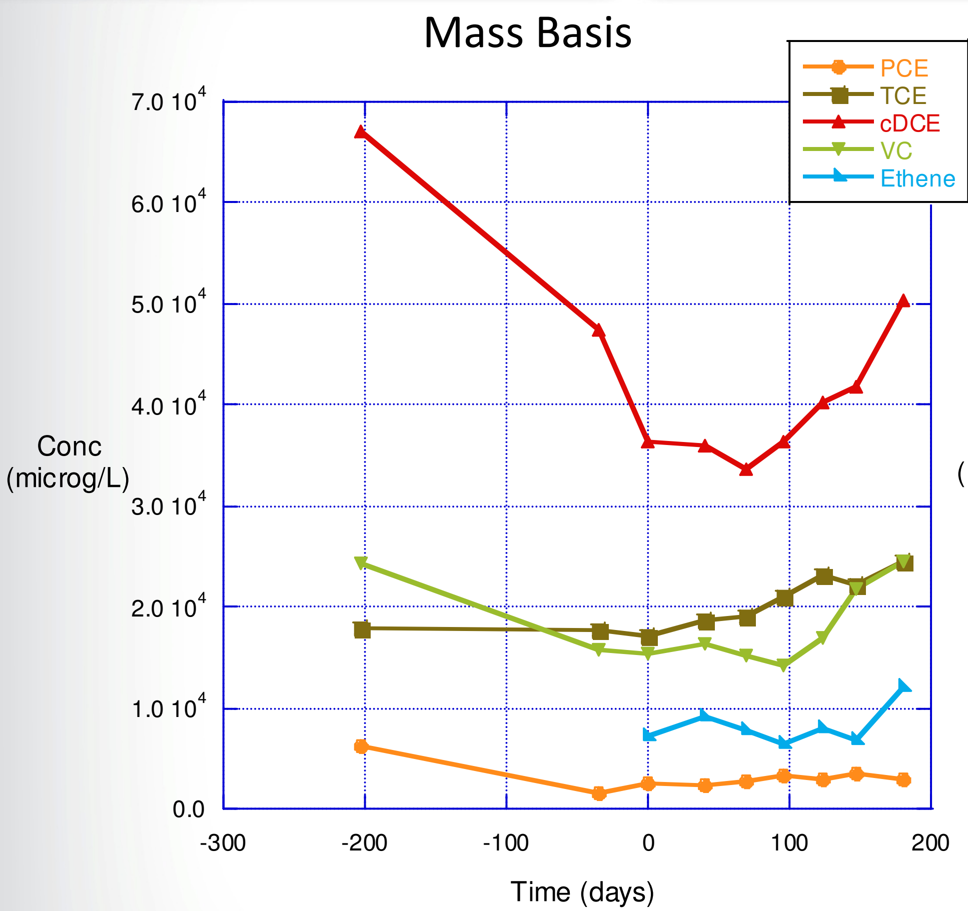
- At day 0, added ED and changed the GW flow pattern – potential for treatment and dilution
- Both graphs show decrease in TCE and changes in other species – **hard to distinguish treatment from dilution**

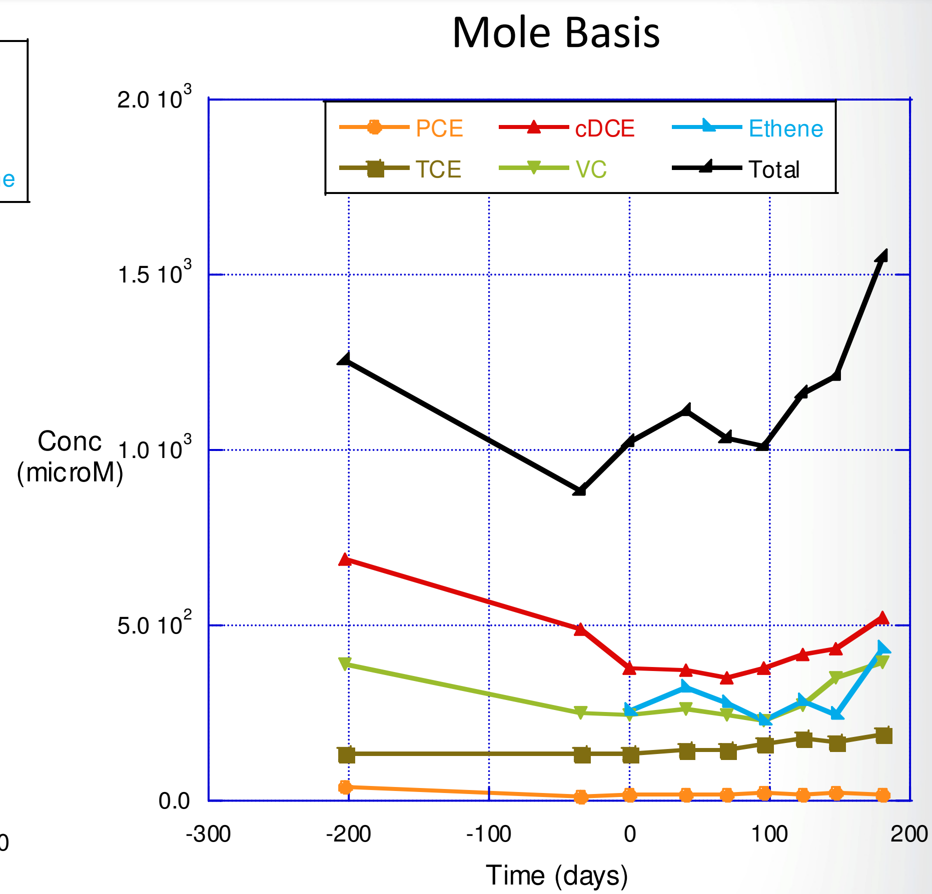
Example from Groundwater Well – Mole Fractions and Chlorine Number

- After 0, decrease in TCE relative to other species – probably not just dilution
- More gradual decrease in cDCE and VC with increase in ethene – indicating treatment occurring
- **Cl number draws all the data together** – some conversion but add'l treatment needed



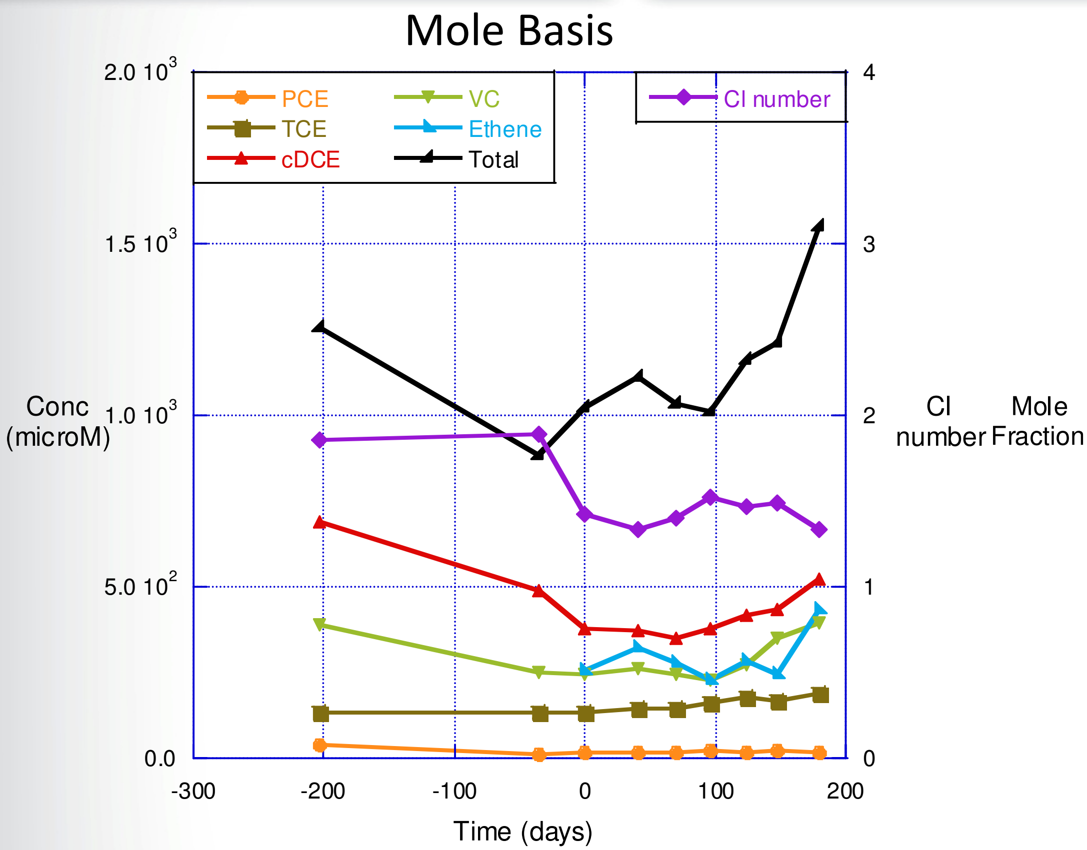
Another Groundwater Well Example

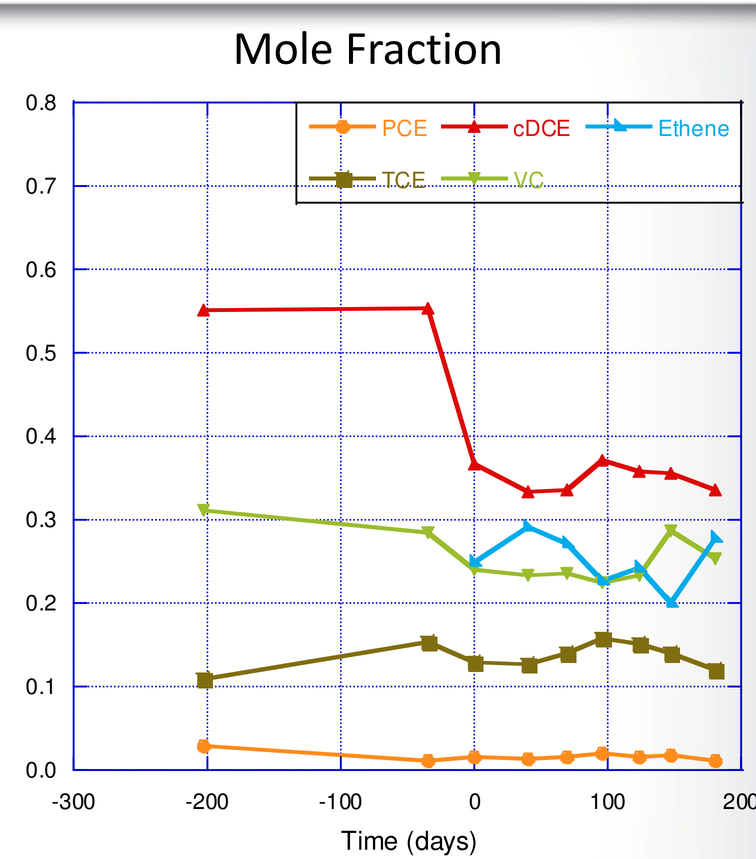




- After day 0, ED donor added continuously and GW flow pattern changed
- Mass based graph similar upward trend after day 0 for many species
- Mole based graph also show increasing amounts of solvents

Concentration and Mole Fraction





- Mole Basis shows Cl number – step change = not enough treatment/dilution
- Mole fraction
  - different shaped curves for cDCE, VC, and Ethene
  - High variability – need more data

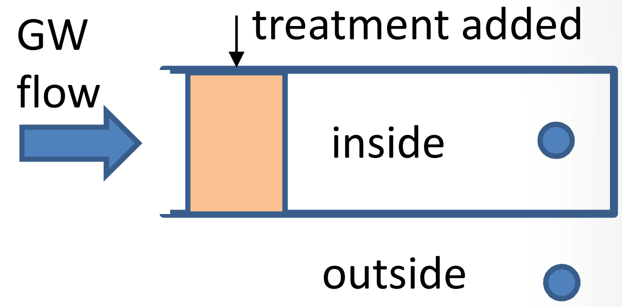
Good Data or Bad data?

- Will show data tables or graphs
- Via chat – suggest interpretation

Reducing conditions?

Table shows data from inside (shaded) and outside a test cell

- ORP
- DO
- Sulfate/Sulfide
- Anaerobic gases



Date	well location	sulfate mg/L	sulfide mg/L	methane mg/L	ethene mg/L	pH	DO mg/L	ORP mV
Jun-95	inside	-	-	-	-	6.56	1.7	292
May-96		-	-	-	-	6.75	3.4	319
Jun-97		170	< 1	0.69	-	6.46	0.45	85
Mar-98		146	< 1	2.8	-	6.38	0.65	-61
Dec-98		42	< 1	3.6	0.09	6.85	1.1	-116
Jun-95	outside	-	-	-	-	6.75	3.4	319
May-96		-	-	-	-	6.84	2.4	126
Jun-97		28	< 1	0.007	-	6.83	1.6	178
Mar-98		24	< 1	0.009	-	6.74	1.6	332
Dec-98		38	< 1	0.85	0.02	7.23	2.3	245

From ITRC Bioremediation of Chlorinated Solvents, 2005

Reducing conditions?

Table shows data from inside (shaded) and outside a test cell

- ORP – one value < -100 mV inside cell
- DO - most > 1 mg/L
- Sulfate/Sulfide – sulfate higher in treatment cell
- Anaerobic gases – higher in treatment cell

- **Unlikely to be reducing conditions**
- **Maybe more data**
- **Check sample and analytical methods**

Date	well location	sulfate mg/L	sulfide mg/L	methane mg/L	ethene mg/L	pH	DO mg/L	ORP mV
Jun-95	inside	-	-	-	-	6.56	1.7	292
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From ITRC Bioremediation of Chlorinated Solvents, 2005

Reducing Environment?

- Day 0, ED added and GW flow pattern changed –
  therefore possible treatment and concentration changes
- Data as reported

	Analytical Results						Field Measurements			
Elapsed time (days)	TOC	Sulfate as Sulfur	Nitrogen, Ammonia	Methane	Ethene	Ethane	pH	EC	DO	ORP
	(mg/L)	(µg/L)						(µS/cm)	(mg/L)	(mV)
0	LNAPL Present; Well Not Sampled									
16	LNAPL Present; Well Not Sampled									
25	5,650	--	--	--	--	--	6.79	497	4.66	-129.9
31	3,880	425	--	3,640	8,300	129	5.75	17,284	0.89	-39
63	3,600	1,000	7.0	5,030	12,600	171	6.28	24,251	1.83	-46.9
95	3,610	433	5.2	5,520	15,900	182	6.55	37,650	0.44	-45.9
130	1,820	1,000	4.3	4,510	14,300	129	6.54	28,445	0.46	-25.2
172	3,880	620	5.8	3,320	10,800	161	5.61	61,408	3.01	-324
198	1,730	404	3.4	4,850	20,400	1.0	6.51	32,102	1.22	-91.9

Reducing Environment?

Elapsed time (days)	TOC	Sulfate as Sulfur	Nitrogen, Ammonia	Methane	Ethene	Ethane	pH	EC	DO	ORP
	Analytical Results						Field Measurements			
	(mg/L)	(µg/L)						(µS/cm)	(mg/L)	(mV)
0	LNAPL Present; Well Not Sampled									
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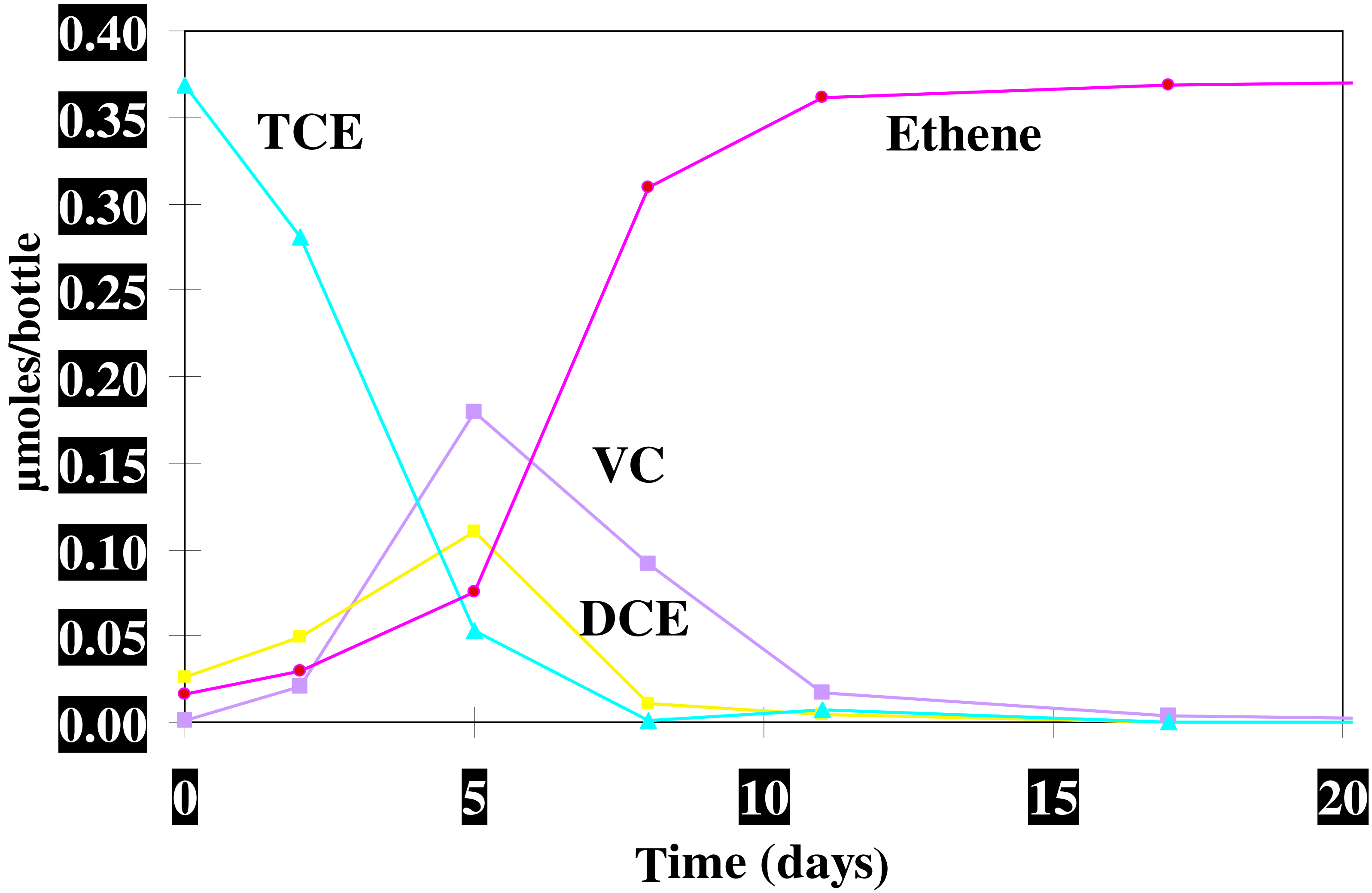
198	1,730	404	3.4	4,850	20,400	1.0	6.51	32,102	1.22	-91.9

- **Reducing environment - Questionable and high variability**
- **DO > 1 mg/L and ORP rarely < -100 mV**
- **Possibly reducing due to:**
  - **presence of methane, ethane and ethene**
  - **decreasing concentration of sulfate**

- **LNAPL**
- **Check sample and analytical methods**

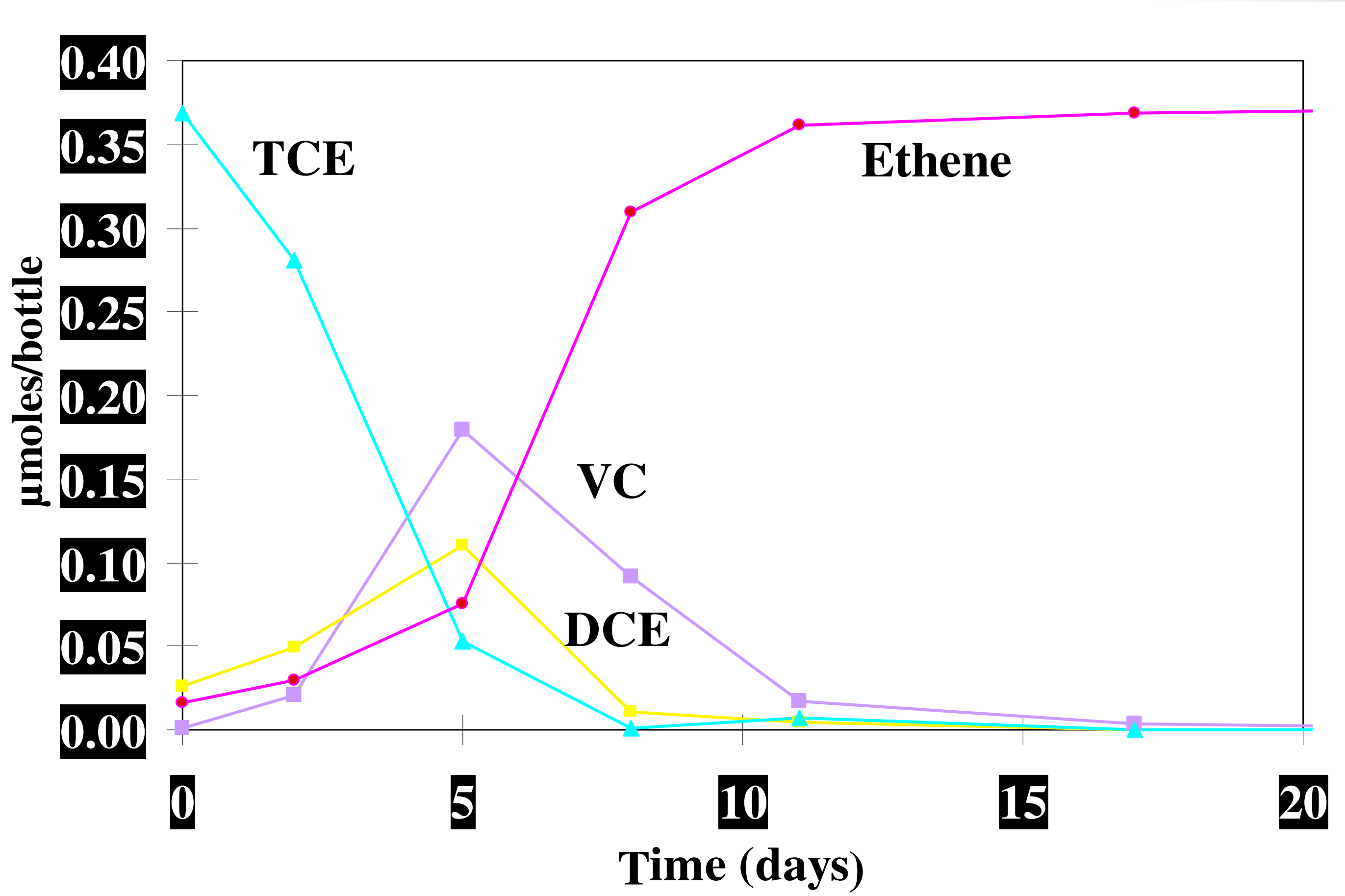
Microcosm Data – treatment or not?



From ITRC Bioremediation of Chlorinated Solvents, 2005

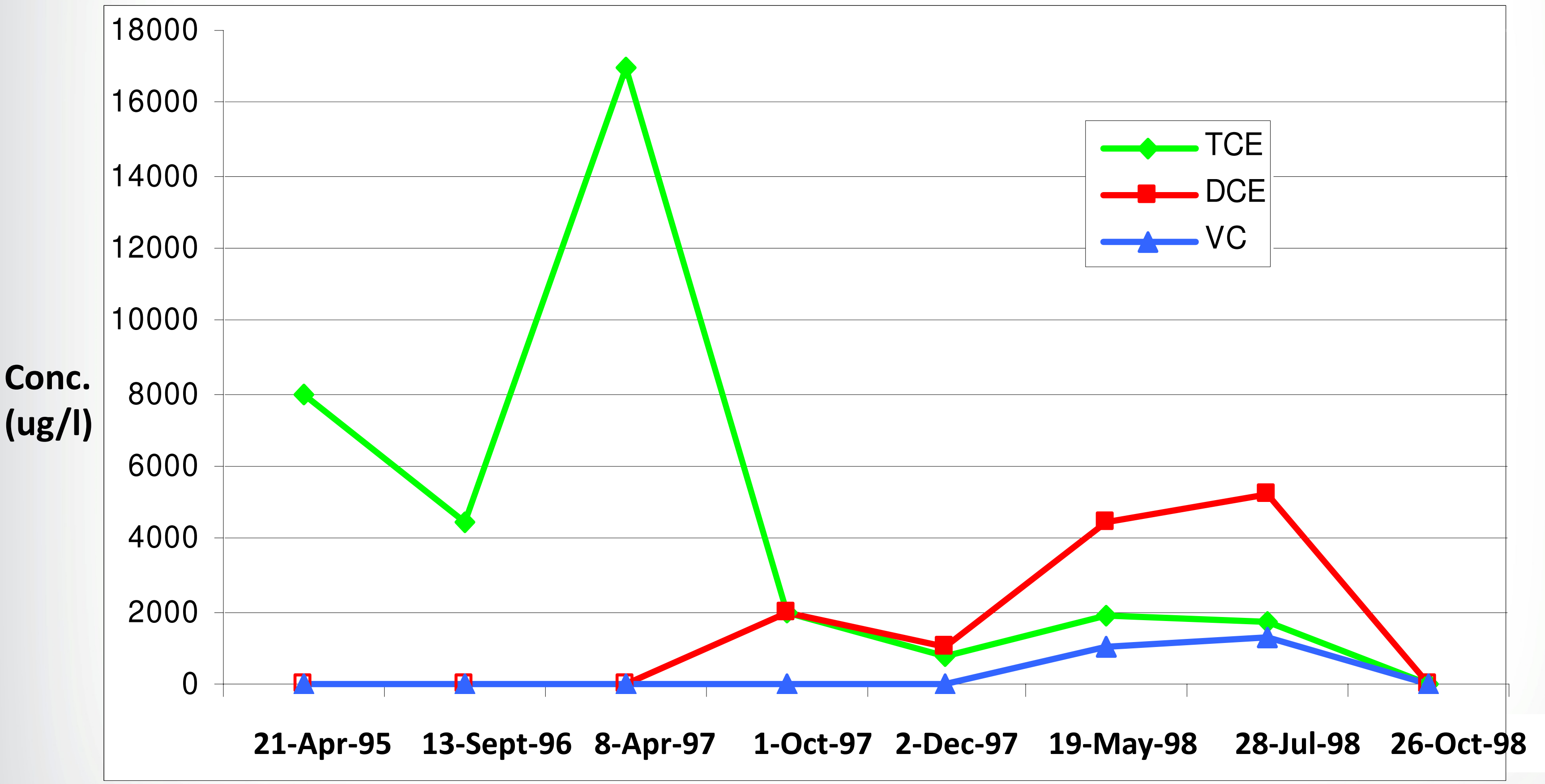
Treatment

- Molar basis
- X-axis is uniform
- Sequential conversion through pathway
- TCE = ethene
- Multiple non-detects for solvents



From ITRC Bioremediation of Chlorinated Solvents, 2005

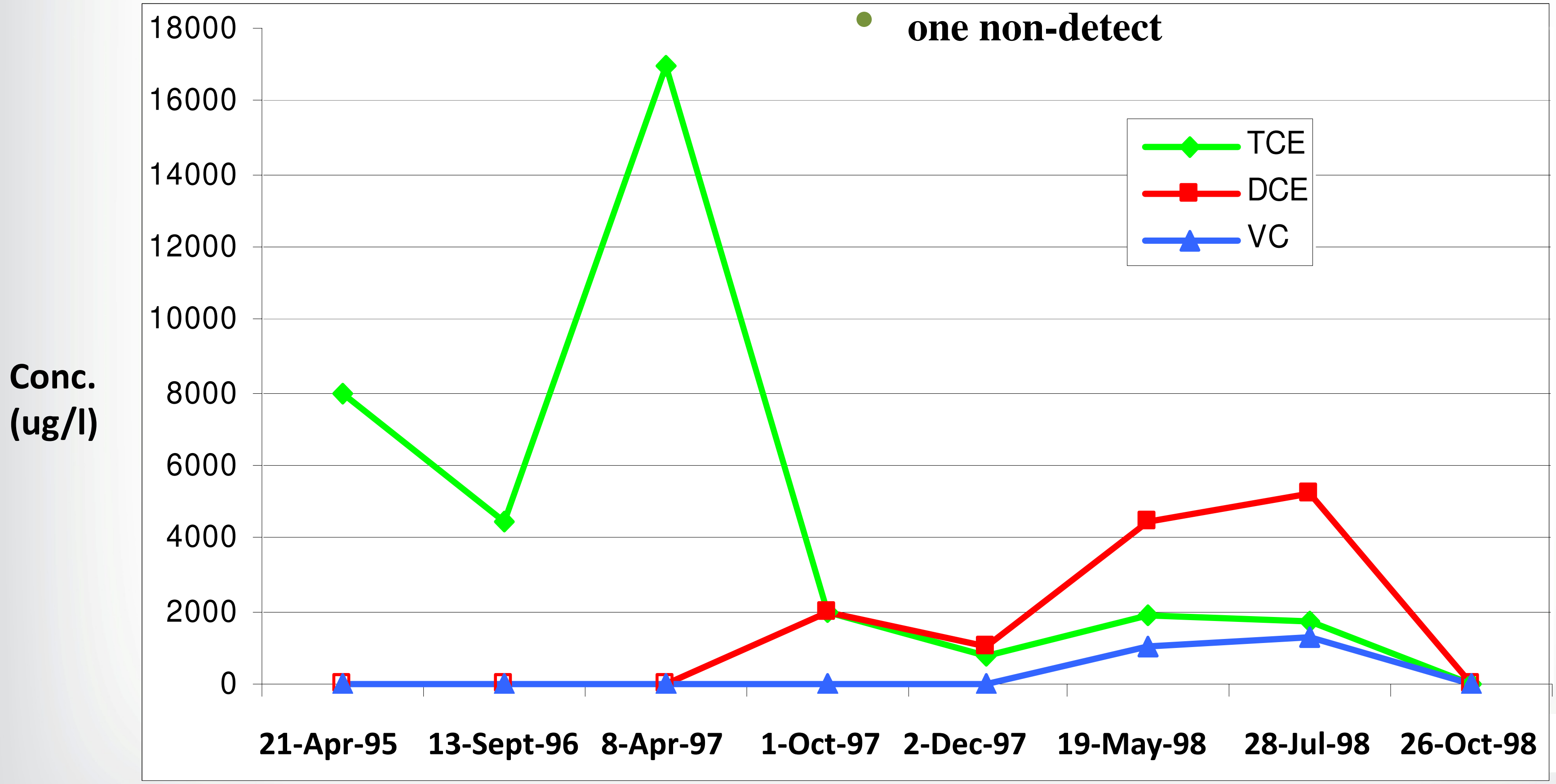
Groundwater data – treatment?



From ITRC Bioremediation of Chlorinated Solvents, 2005

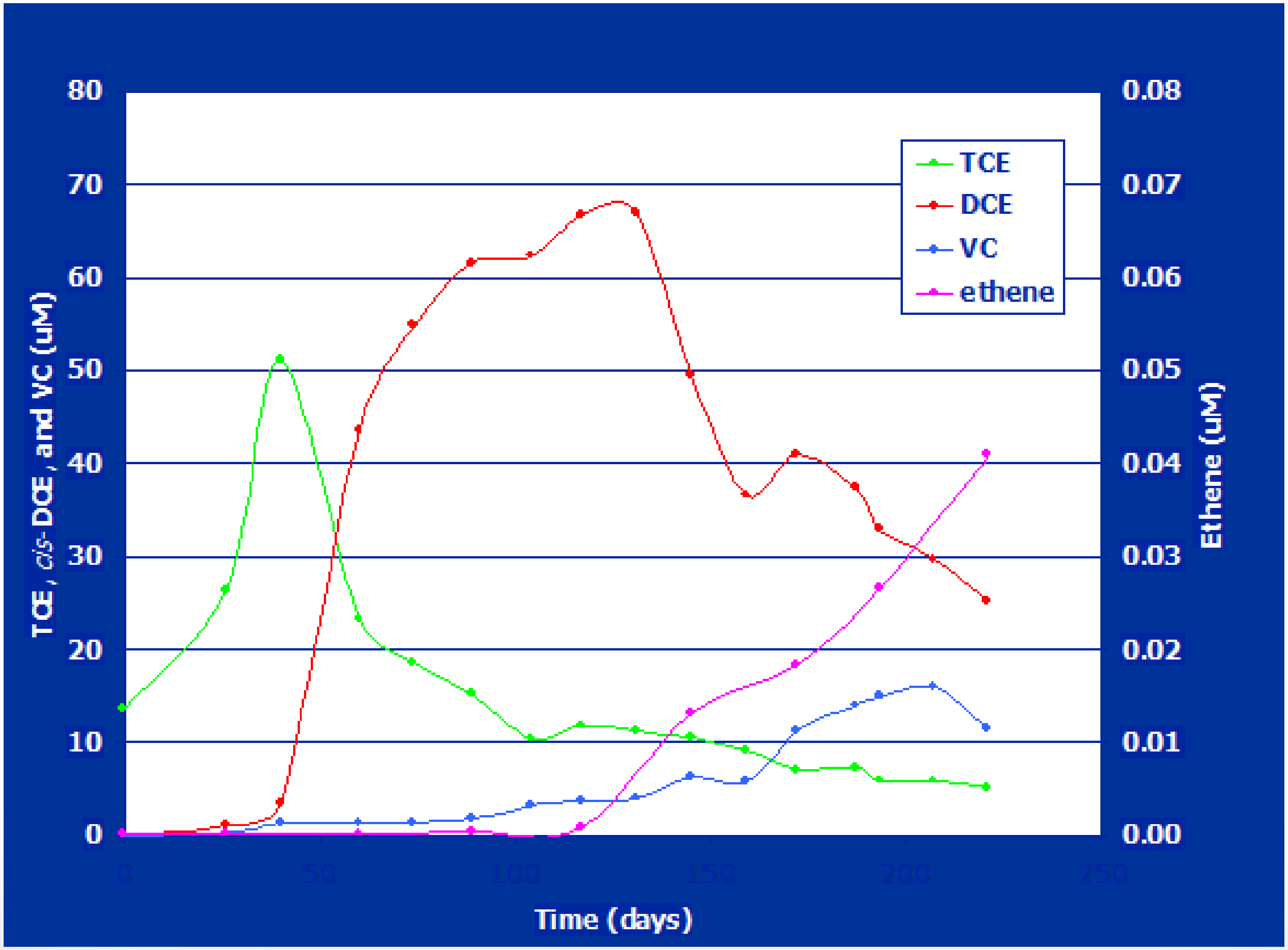
Bad data that looks good

- mass basis
- x-axis not consistent intervals
- no ethene or chloride data
- TCE decrease ≠ DCE increase
- one non-detect



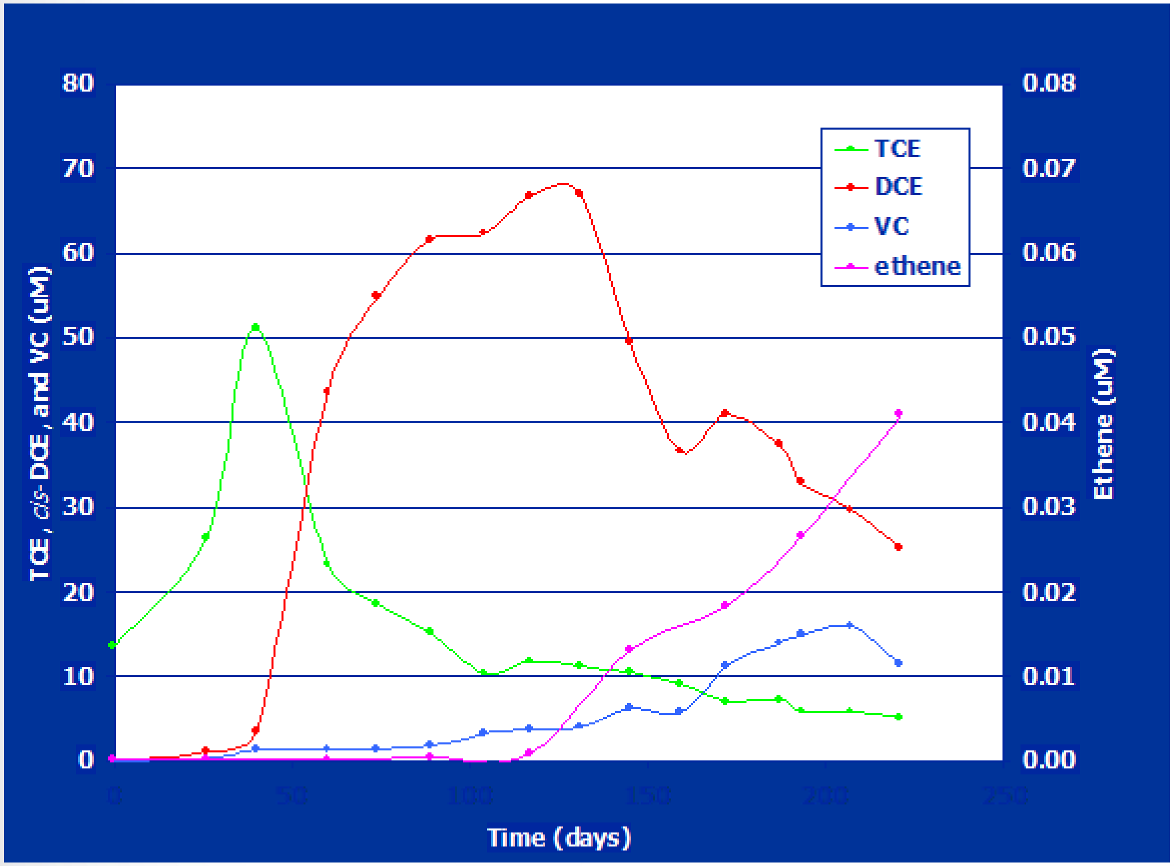
From ITRC Bioremediation of Chlorinated Solvents, 2005

Molar conversion?



From ITRC Bioremediation of Chlorinated Solvents, 2005

Molar conversion – not Ethene



- Mole basis
- Sequential conversion of TCE to DCE
- VC increases as DCE decreases but not proportional
- Includes ethene data
- But scale for ethene distorts amount relative to other solvents
- Possible that more ED needed or bioaugmentation

From ITRC Bioremediation of Chlorinated Solvents, 2005

More information

Technical Support Centers

- **Engineering Technical Support Center**
  - **https://www.epa.gov/land-research/engineering-technical-support-center-etsc**
  - **Ed Barth, Acting Director – Barth.Edwin@epa.gov**
  - **John McKernan, Director – McKernan.John@epa.gov**
- **Ground Water Technical Support Center**
  - **https://www.epa.gov/water-research/ground-water-technical-support-center-gwtsc**
  - **Dave Burden, Director – Burden.David@epa.gov**

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- **ITRC RTDF Bioremediation Consortium: Evan Cox, Dave Ellis, Paul Hadley, Ed Lutz, Dave Major, and Greg Sayles**
- **RPMs: Ron Leach, Mark Duffy**
- **SiREM: Sandra Dwortazek, Jeff Roberts**
  Harkness et al. J Contam Hydrol 2012 (131):100-18.