Headquarters U.S. Air Force

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Natural Attenuation as a Remediation Approach

U.S. AIR FORCE

Presented by

Todd Wiedemeier
Parsons Engineering Science, Inc.

todd.wiedemeier@parsons.com
(303) 831-8100

Overview

- In 1993 the US Air Force began an initiative to evaluate natural attenuation at numerous sites across the country
- The results of this effort changed the way natural attenuation was viewed as a remediation approach
- This workshop will focus on what we learned from the effort

Acknowledgements

- Numerous People were Involved in this Effort Including:
- U.S. Air Force
  - Col. Ross Miller, Jerry Hansen, Patrick Haas, and Jim Gonzales
- Parsons Engineering Science
  - Bruce Henry, John Hicks, Doug Downey, and many others

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Section 1
Overview of Natural Attenuation

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Presented by

Todd Wiedemeier
Parsons Engineering Science, Inc.

todd.wiedemeier@parsons.com
(303) 831-8100

Terminology

- Natural Attenuation
- Monitored Natural Attenuation
- Intrinsic Bioremediation
- Intrinsic Remediation
- Passive Bioremediation

Terminology - Con’t

- Natural Assimilation
- “Wink and Walk” Approach
- No Action Alternative
- Bioprocrastination

Definitions

- Natural Attenuation
  - Dispersion, Dilution, Sorption, Volatilization, Abiotic Degradation, and Biodegradation
- Intrinsic Bioremediation
  - Natural Biodegradation

Monitored Natural Attenuation

- **Innovative Remedial Approach**
- **Used to Remediate Organic Contaminants Dissolved in Groundwater**
- **In Some Cases can Also be Used for Inorganic Contaminants**
- **Relies on Natural Processes of Contaminant Attenuation**

EPA Definition - Monitored Natural Attenuation

The term Monitored Natural Attenuation Refers to the Reliance on Natural Attenuation Processes (Within the Context of a Carefully Controlled and Monitored Site Cleanup Approach) to Achieve Site-Specific Remedial Objectives Within a Time Frame that is Reasonable Compared to Other Methods

EPA Definition - Natural Attenuation Processes

A Variety of Physical, Chemical, or Biological Processes that, Under Favorable Conditions, act Without Human Intervention to Reduce the Mass, Toxicity, Mobility, Volume, or Concentration of Contaminants in Soil or Groundwater

EPA Definition - Natural Attenuation Processes

These In-Situ Processes Include Biodegradation, Dispersion, Dilution, Sorption, Volatilization, and Chemical or Biological Stabilization, Transformation, of Destruction of Contaminants

Benefits of Natural Attenuation

- Less Generation or Transfer of Wastes
- Less Intrusive as Fewer Surface Structures are Required
- May be Applied to all or Part of a Given Site, Depending on Site Conditions and Cleanup Objectives

Benefits Of Natural Attenuation

- **Natural Attenuation may be Used in Conjunction with, or as a Follow-Up to, Other (Active) Remedial Measures**

- **Overall Costs will Likely be Lower than with Active Remediation (With the Possible Exception of Small Fuel Spills)**

Potential Drawbacks of Natural Attenuation

- **Longer Time Frames may be Required to Achieve Remediation Objectives, Compared to Active Remediation**

- **Site Characterization may be More Complex and Costly**

- **Toxicity of Transformed Products may Exceed that of the Parent Compound**

Potential Drawbacks of Natural Attenuation

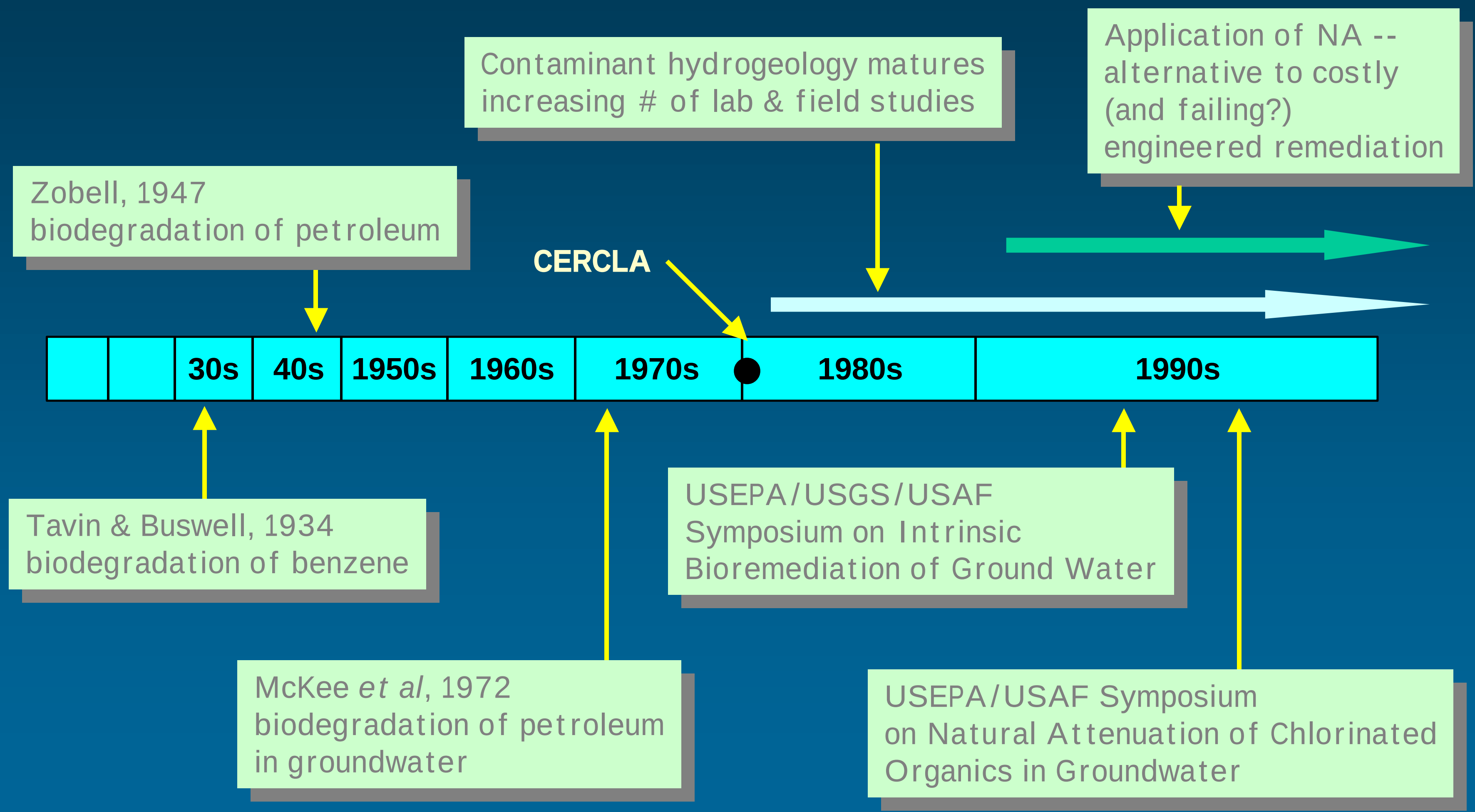
- Responsibility Must be Assumed for Long-Term Monitoring and its Associated Cost, and Implementation of Institutional Controls

- Potential Exists for Continued Migration

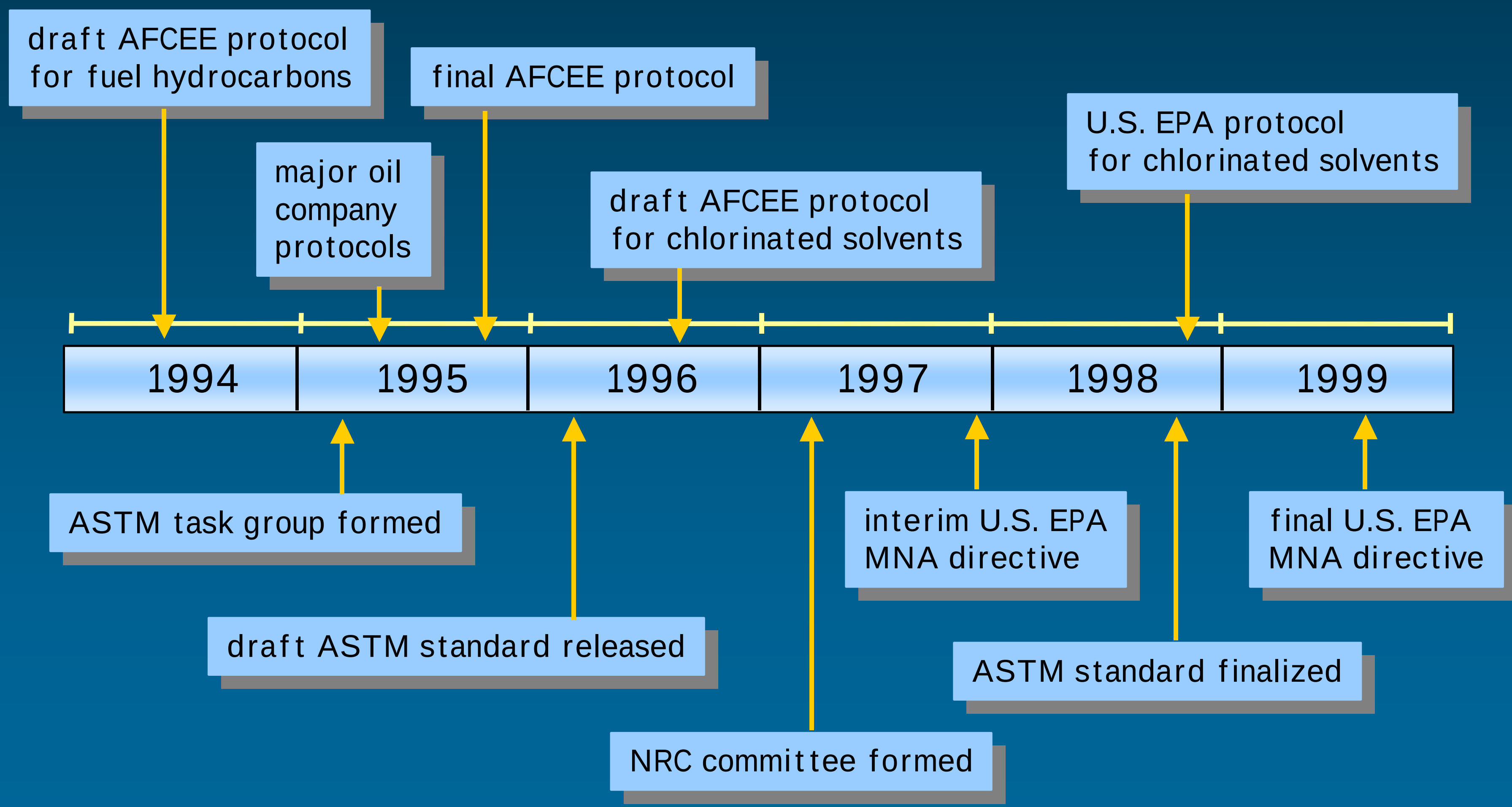
Potential Drawbacks of Natural Attenuation

- **The Hydrogeologic and Geochemical Conditions Amenable to Natural Attenuation are Likely to Change over Time and Could Result in Renewed Mobility of Previously Stabilized Contaminants and May Adversely Impact Remedial Effectiveness**
- **More Extensive Outreach Efforts may be Required in Order to Gain Public Acceptance of Natural Attenuation**

Monitored Natural Attenuation Timeline



Monitored Natural Attenuation Timeline



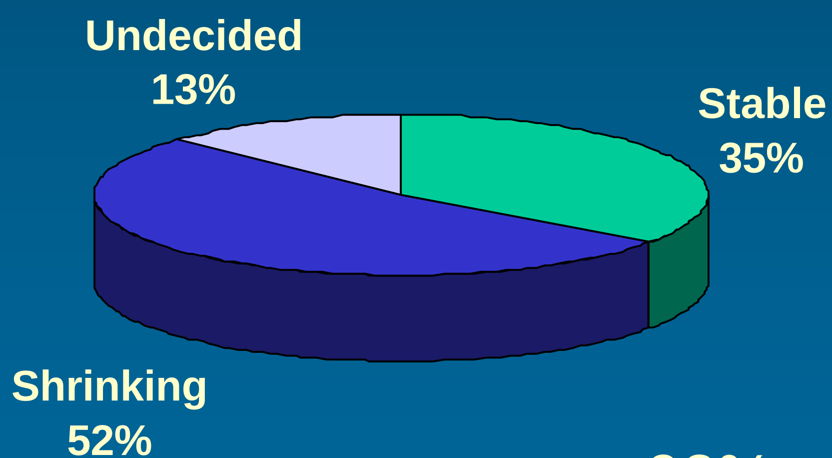
How Do Plumes Really Behave?

- **In the Mid 1990's Several Plume-a-Thons were Completed by:**
  - **Lawrence Livermore National Laboratory**
  - **Texas Bureau of Economic Geology**
  - **Chevron**

Groundwater Solute Plume Studies

1995 - Chevron Oil study

- Evaluation of 119 gasoline station hydrocarbon spills: unpublished data
- Evaluated historical data from 119 service stations

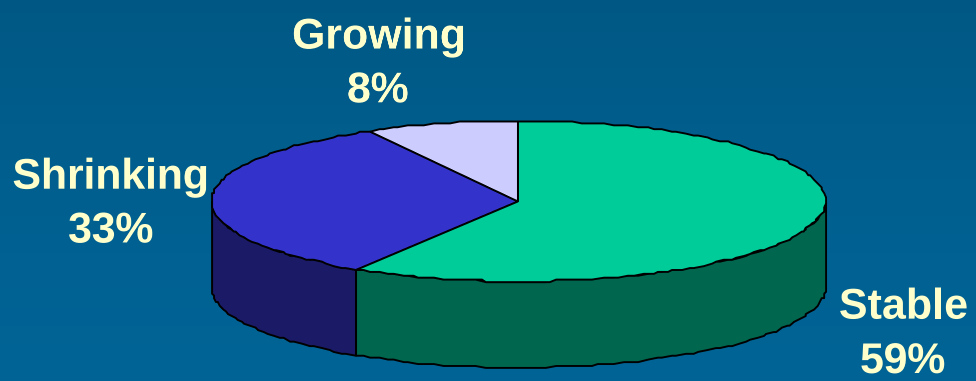


92% of plumes < 200 feet long

Groundwater Solute Plume Studies (cont'd)

1995 - Lawrence Livermore National Laboratory Report

- **Study for California State Water Resources Control Board ("Plume-a-thon")**
- **Evaluated historical data from over 1000 fuel spills**

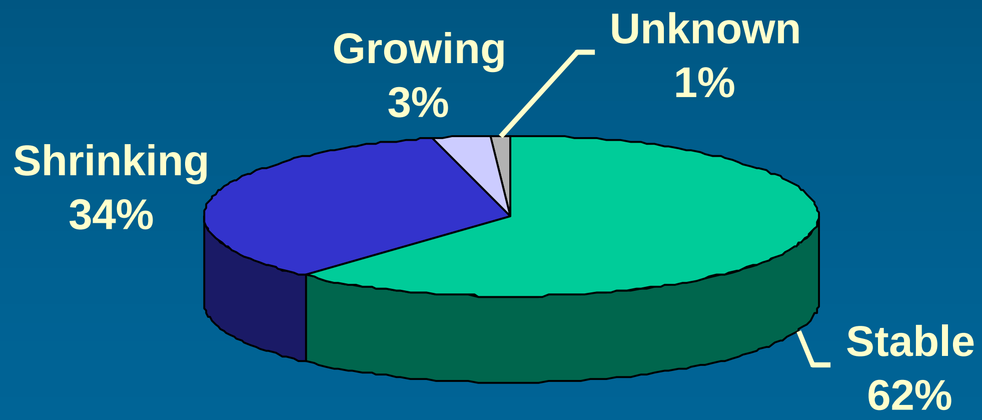


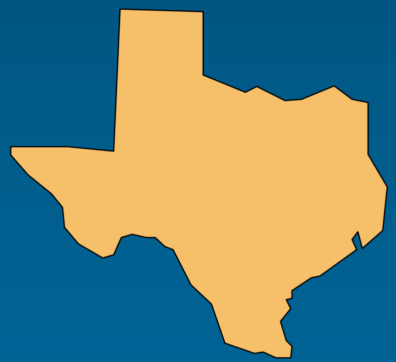
Most plumes < 250 feet long

Groundwater Solute Plume Studies (cont'd)

1997 - Texas fuel hydrocarbon plume study

- **Mace *et al* -- Texas Bureau of Economic Geology**
- **Evaluated historical data from 605 fuel sites**

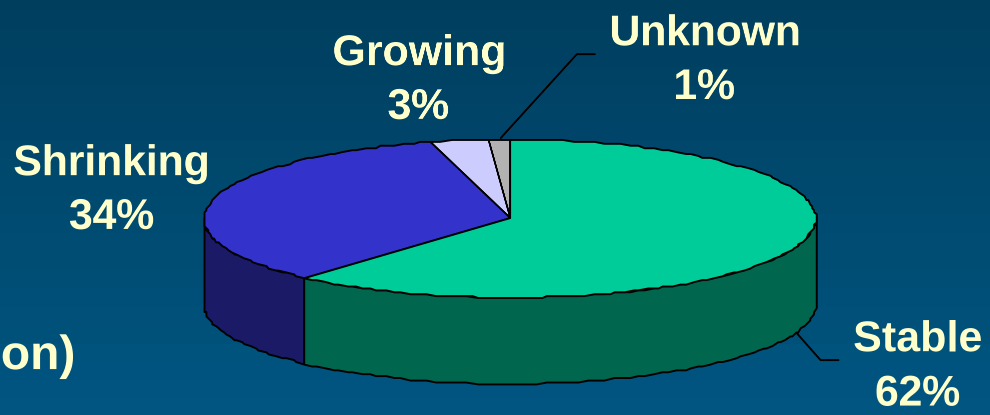




75% of plumes < 250 feet long

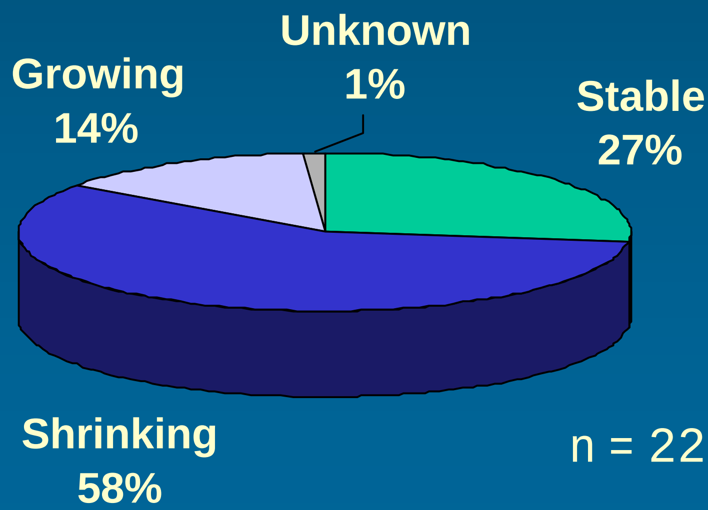
Texas Plume Study

Plume Length

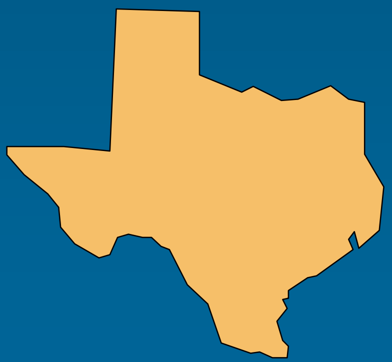


n = 219

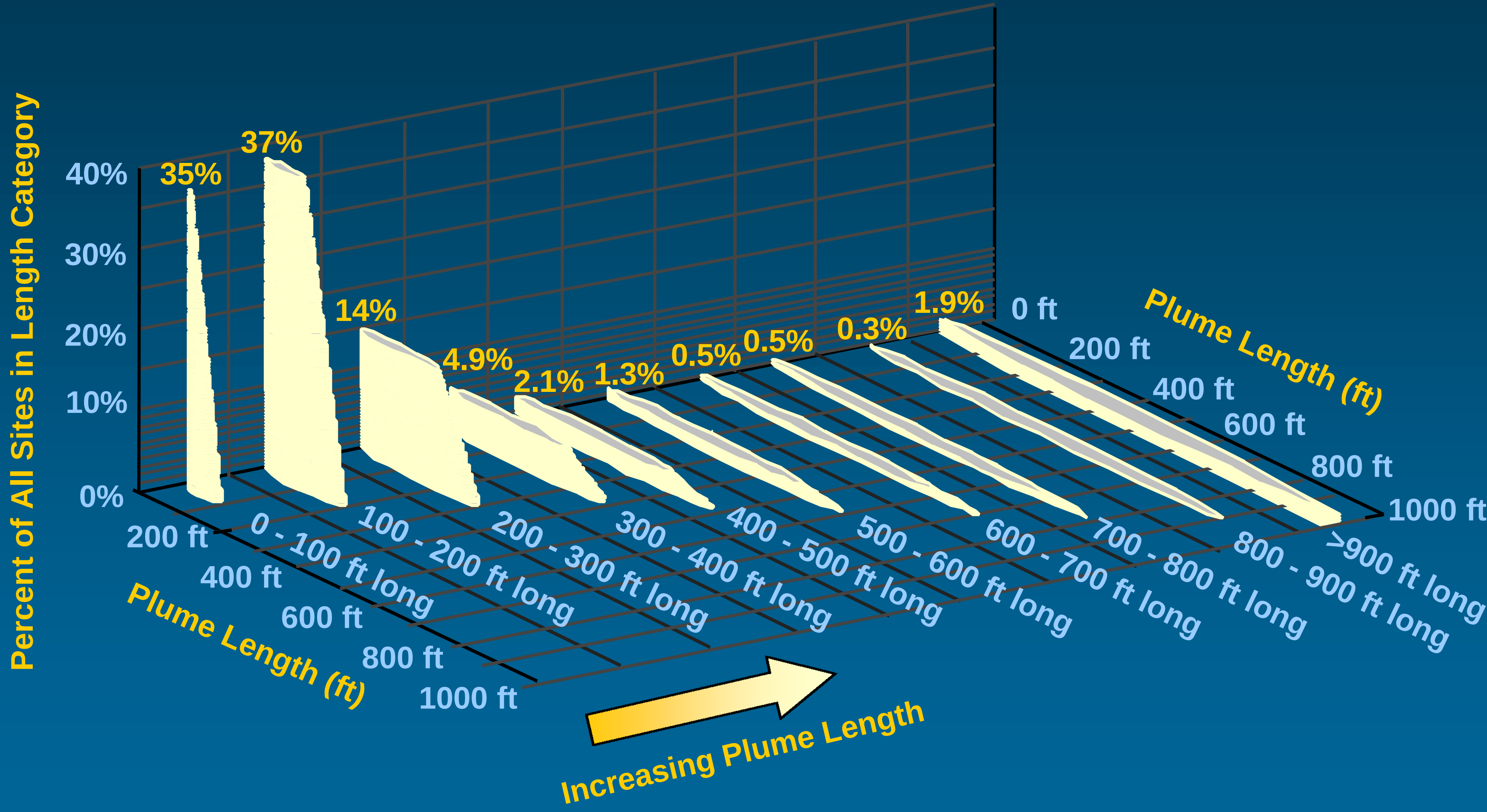
Plume Mass (ave. concentration)



n = 227



Percentage of Plumes of Different Lengths (604) Sites



Natural Attenuation

- Determination is Site Specific
- Site Characterization Must be Geared Toward Supporting this Remedial Option
- Burden of Proof is on the Proponent, Not the Regulator
- Can be Scientifically Supported

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Section 1 – Con't
Physical, Chemical, and Biological Mechanisms of Natural Attenuation

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Presented by

Todd Wiedemeier
Parsons Engineering Science, Inc.

todd.wiedemeier@parsons.com
(303) 831-8100

Mechanisms of Natural Attenuation

- There are several physical, chemical, and/or biological mechanisms causing natural contaminant attenuation in the subsurface

- These mechanisms can be broken down into nondestructive and destructive attenuation mechanisms

Non-Destructive Attenuation Mechanisms

Results in Decreasing Contaminant Concentrations But Not Removal of Contaminant Mass

- **Sorption**
- **Dispersion**
- **Dilution from Recharge**
- **Volatilization**

Destructive Attenuation Mechanisms

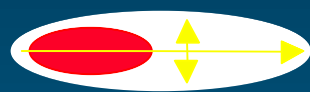
Results in Removal of Contaminant Mass

- **Biological**
  - **Primary Growth Substrate Utilization**
  - **Cometabolism**
- **Abiotic**
  - **Hydrolysis**
  - **Dehydrohalogenation**

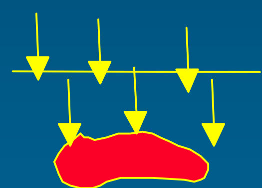
Major Natural Attenuation Mechanisms

Non-Destructive

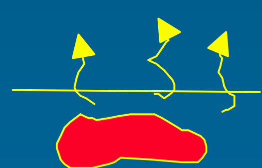
- Dispersion



- Sorption $K_d = (K_{oc})*(f_{oc})$
- Dilution

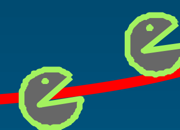


- Volatilization



Destructive

- Biodegradation



- Abiotic Reactions (hydrolysis)

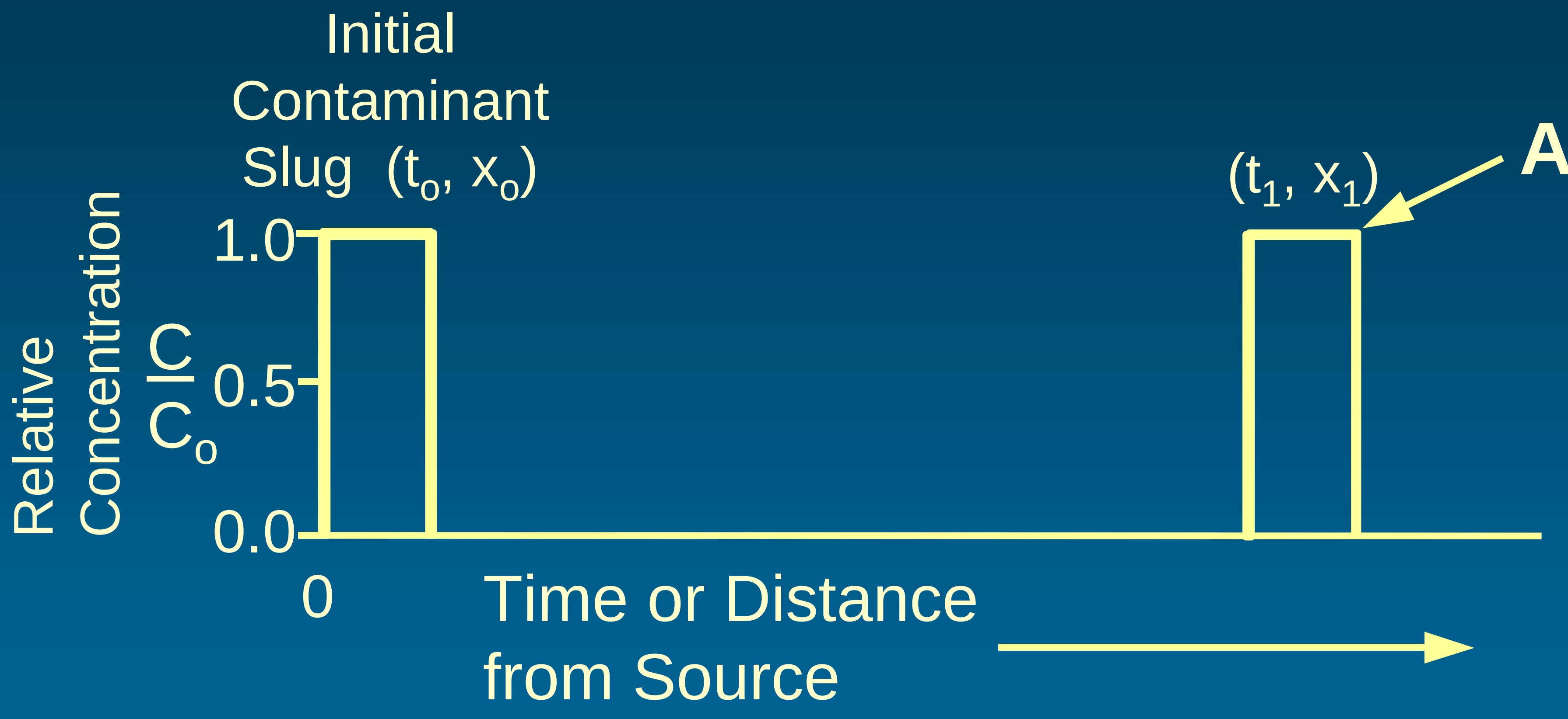
Advection

- Although Advection is Not a Natural Attenuation Process, It is the Major Mechanism Driving Contaminants Downgradient

Advection

- Transport of Solutes by the Bulk Movement of Groundwater
- Solute Behaves Like a Water Molecule
- Solute Moves at the Average Seepage Velocity of the Groundwater

Instantaneous Source - Advection Only



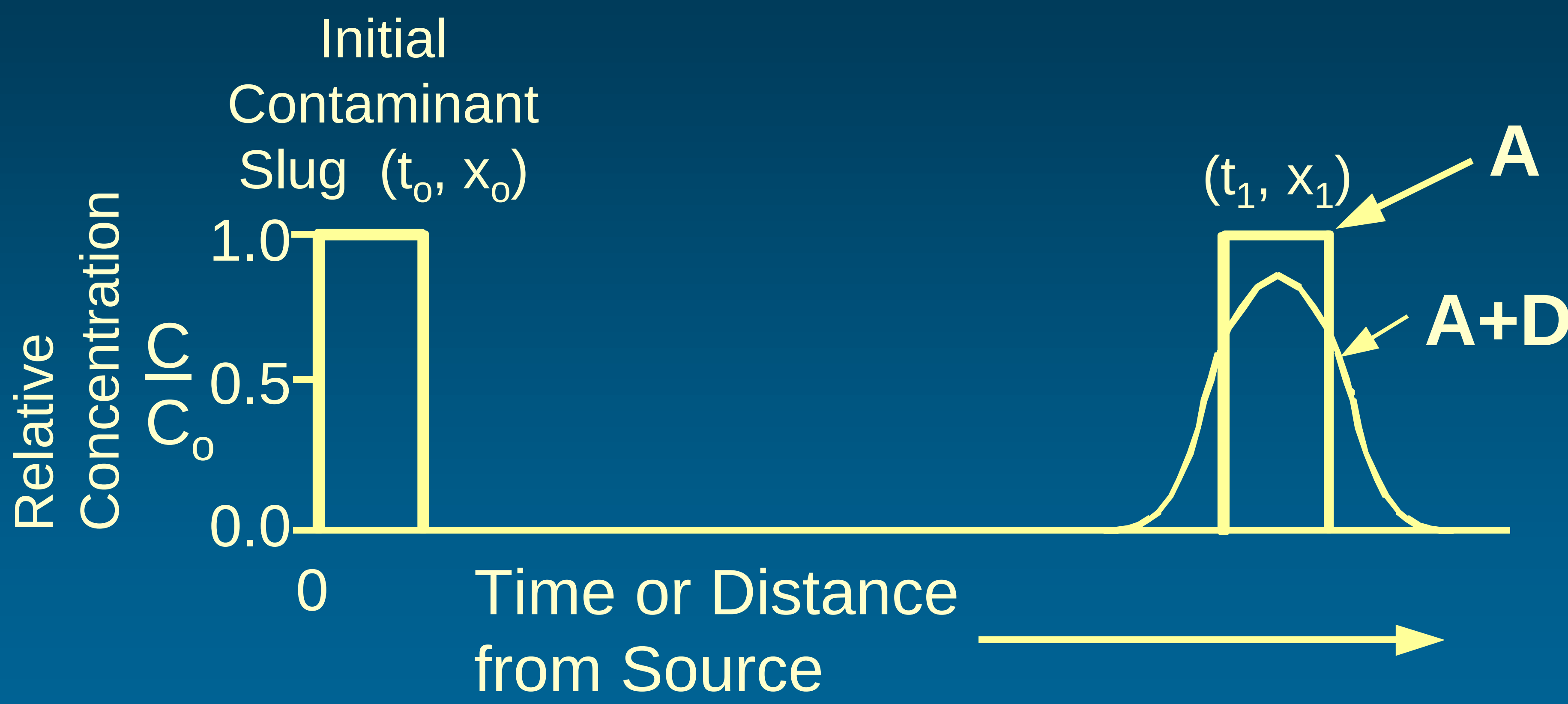
Hydrodynamic Dispersion

- Caused by Velocity Variations During Advective Transport
- Results in Longitudinal (x) and Transverse (y and z) Spreading of Solute Plume (3D phenomenon)
- Two Components

  1) Molecular Diffusion

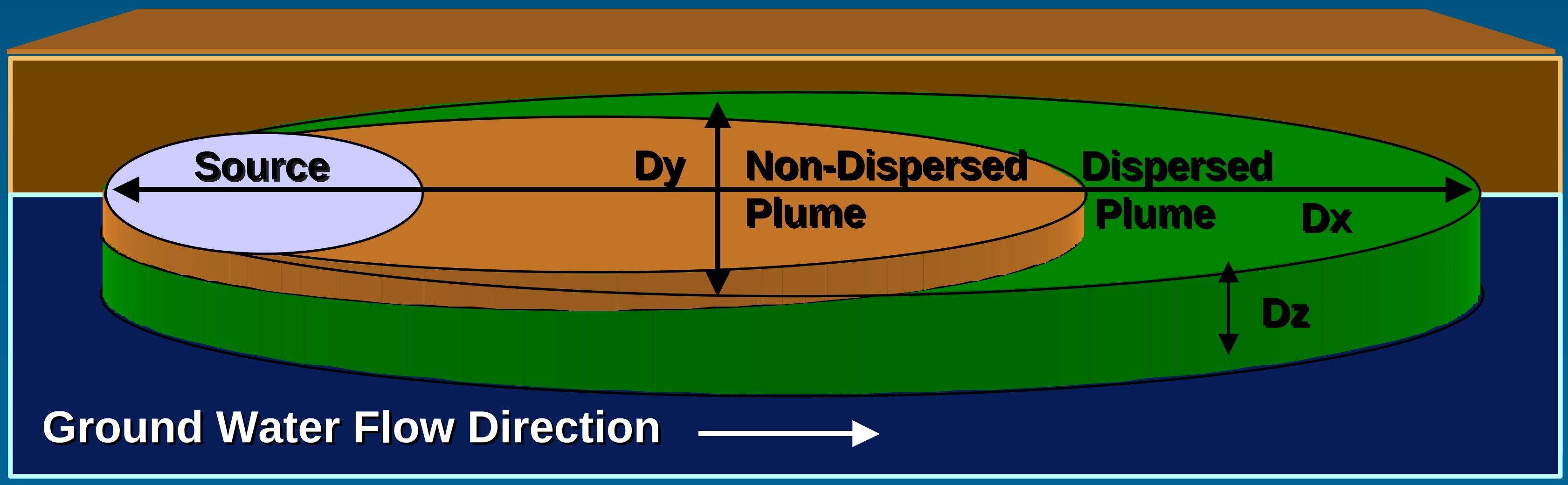
  2) Mechanical Dispersion

Instantaneous Source with Advection and Dispersion



Dispersion

- Dispersion results in the 3D mixing of the contaminants, but doesn't affect the total mass present.
- The extent of mixing caused by dispersion is characterized by a dispersion coefficient (Dx, Dy, Dz).
- Dispersion Coefficient = advection x dispersivity.

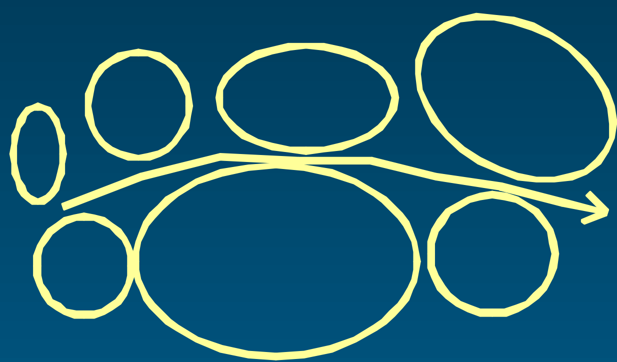


Mechanical Dispersion

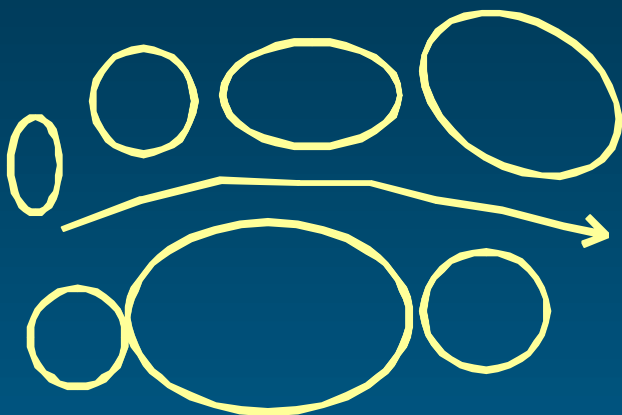
- **Mechanical Mixing**

- **Three Mechanisms**
  1) **Variable Pore Size**
  2) **Variable Flow Length (Tortuosity)**
  3) **Pore-Throat Friction**

Mechanical Dispersion - Effect of Pore Size



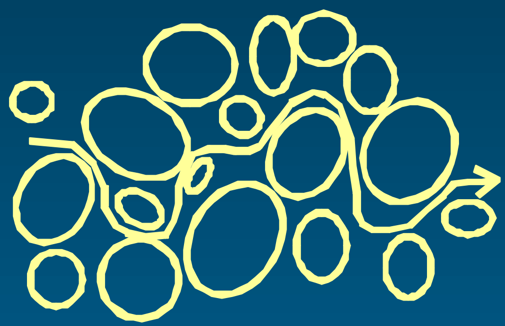
Small,
Fast



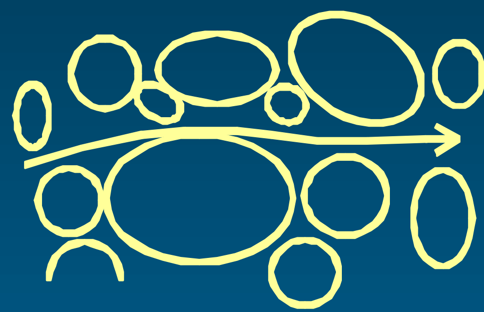
Large,
Slow

Q = vA = Constant

Mechanical Dispersion - Effect of Tortuosity

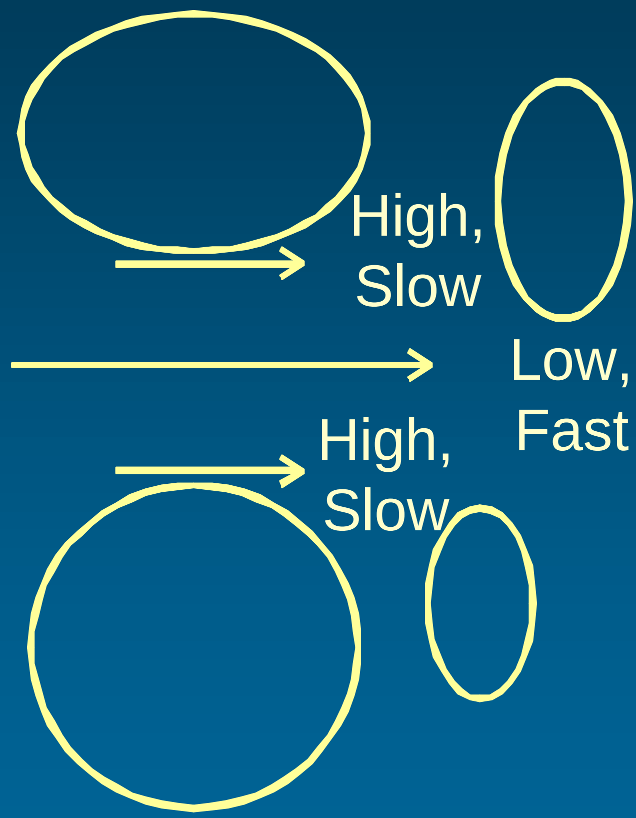


High
(Long Flow Path)
Slow



Low
(Short Flow Path)
Fast

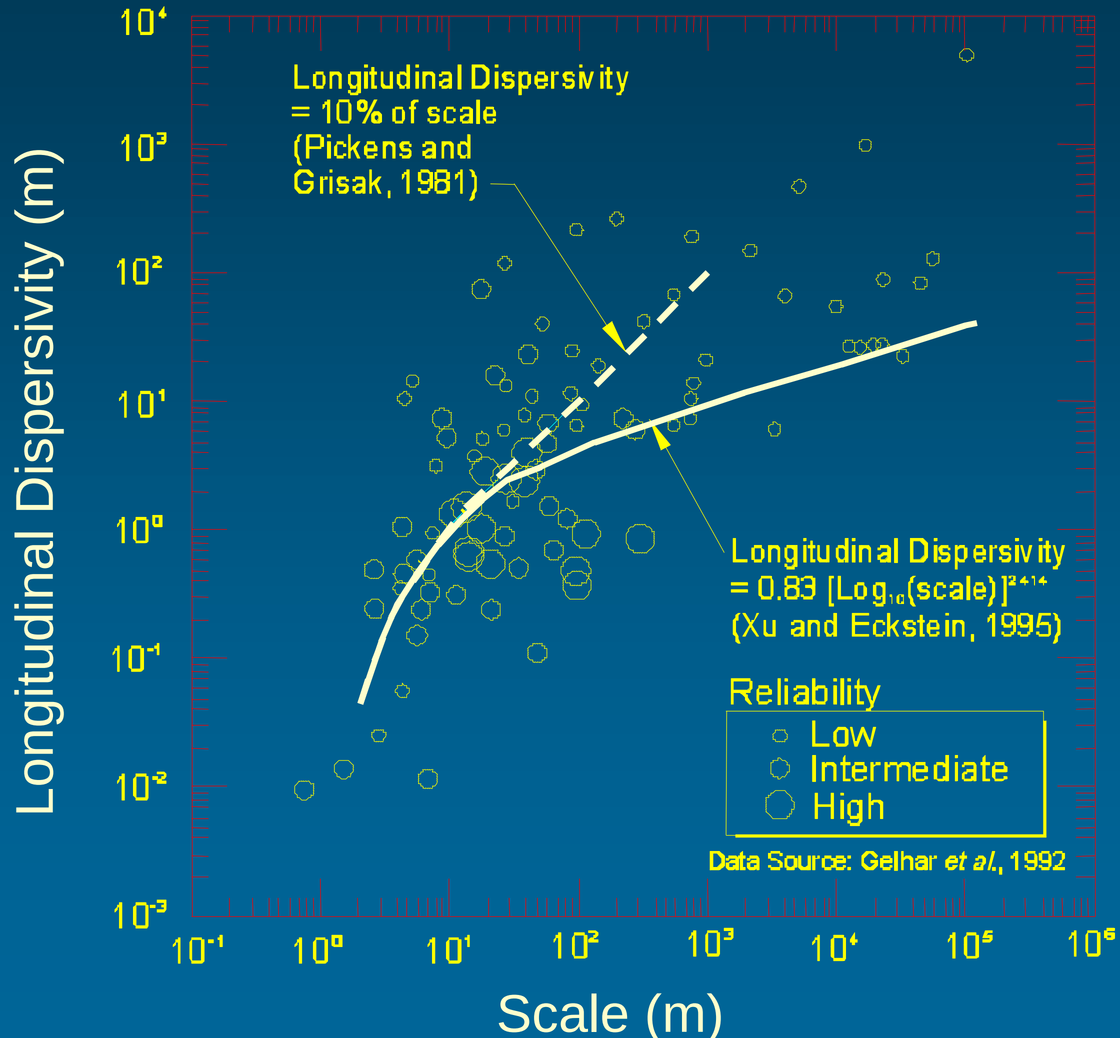
Mechanical Dispersion - Pore-Throat Friction



Estimating Dispersivity

- Assume 1/10th of Plume Length
- Method of Xu and Eckstein (1995)

Relationship Between Dispersivity and Scale



*Dispersivity Estimate**

$$\alpha_x = 0.83(\mathrm{Log}L_p)^{2.414}$$

α_x = longitudinal dispersivity

L_p = plume length

* From Xu and Eckstein (1995)

Overview of Sorption

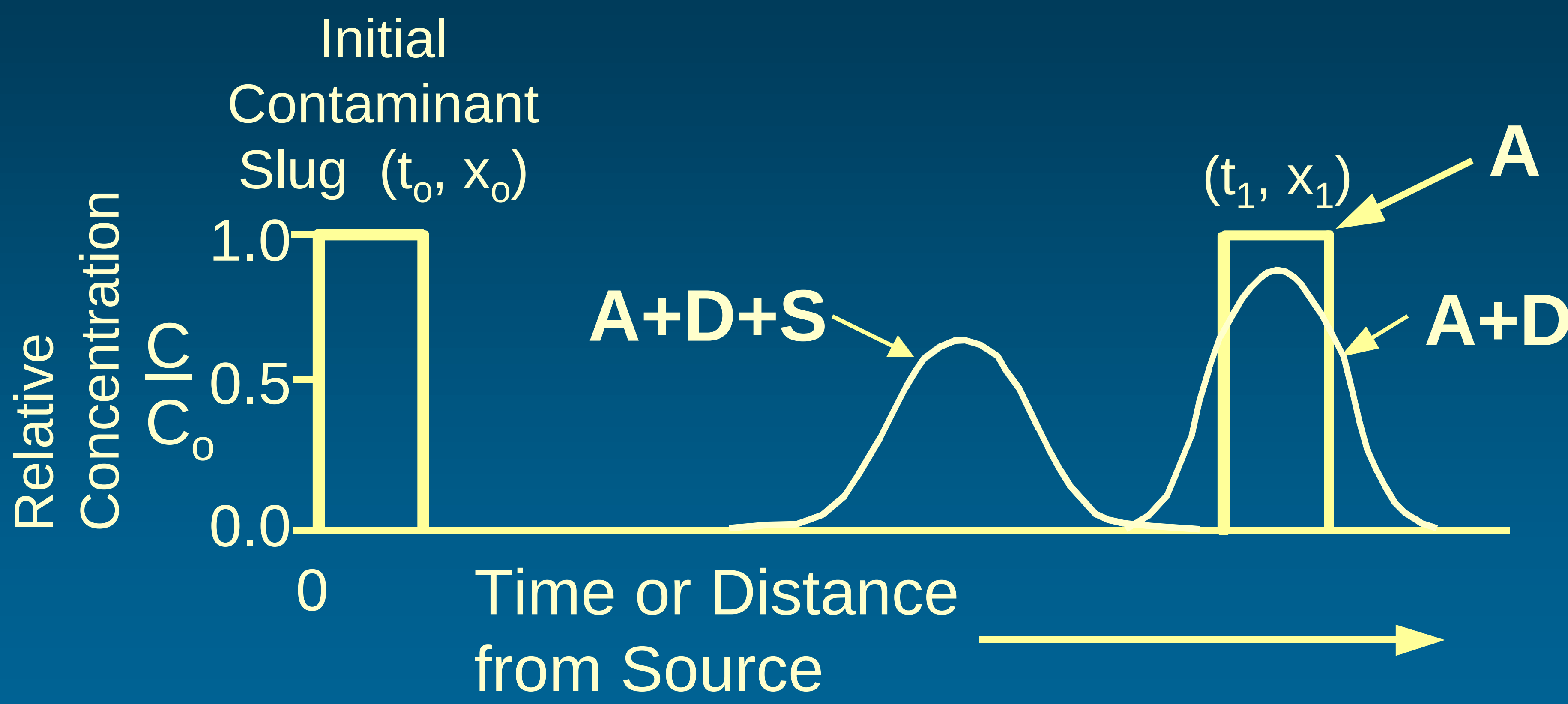
- **Organic Carbon and Clay Mineral Fractions Generally Act as Sorption Sites (Large SA to V Ratio and Surface Properties)**

- **Organic Carbon Fraction Most Important if > 0.1% of the Aquifer Matrix by Weight**

Overview of Sorption

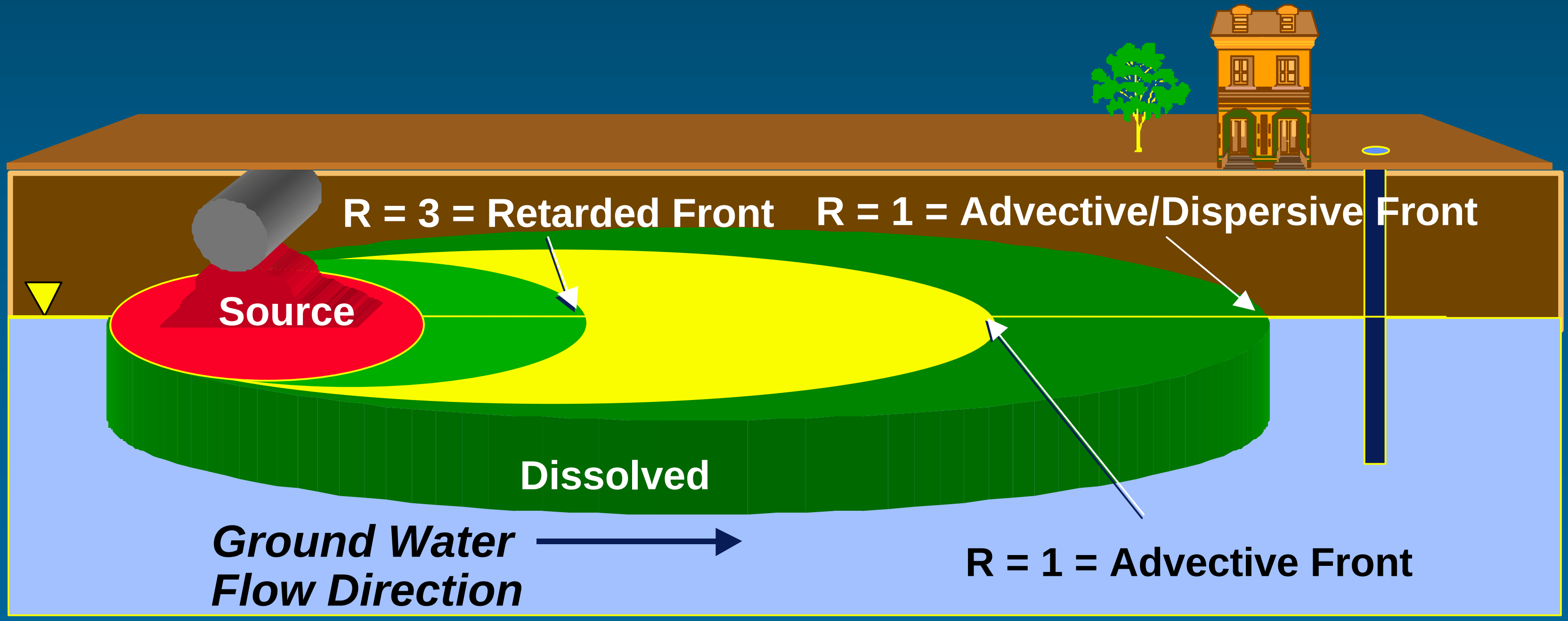
- Important Process
- Causes Slowing (Retardation) of Plume Relative to Groundwater
- Quantified (Estimated) Using Coefficient of Retardation (R)

Instantaneous Source: Advection, Dispersion, and Sorption



Sorption

- Retardation causes dissolved compounds to migrate slower than the ground water.
- The figure below compares advective plume. migration due to the flow of ground water (R = 1) versus the retarded plume migration (R = 3).



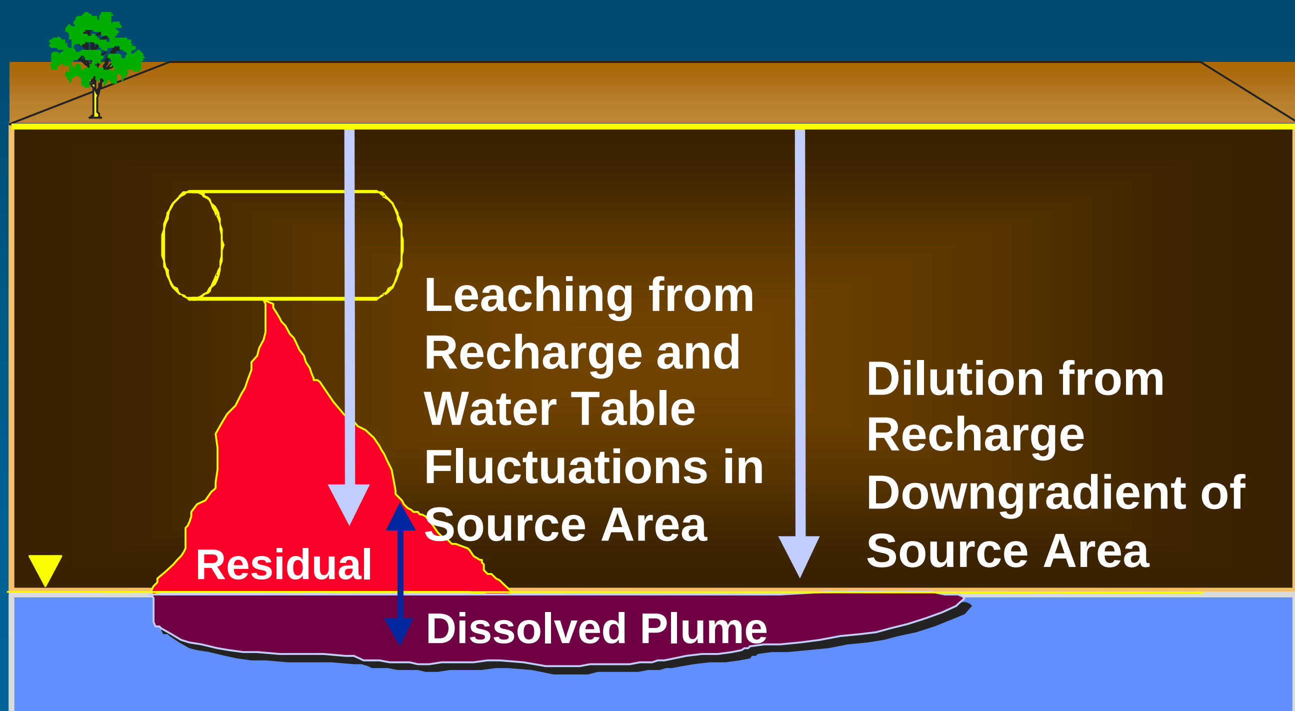
Dilution By Recharge

- Recharge Events and Water Table Fluctuations Leach Contaminants From Soil Into Groundwater in the Source Area.

- Recharge Events Dilute Dissolved Plumes Downgradient From the Source Area

Dilution By Recharge

Comparison of Soil Leaching (Source Area) vs. Dilution by Recharge (Downgradient)



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Section 1 – Con't
General Microbiology

Presented by

Todd Wiedemeier
Parsons Engineering Science, Inc.

todd.wiedemeier@parsons.com
(303) 831-8100

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Characteristics of Microbes

- The Mass of Microbes on/in the Earth is Greater than the Sum of the Mass for all Other Living Things on this Planet!
- There are more Microbial cells in and on the Human Body than Human Cells – by an Order of Magnitude!
- Rapid Growth and Metabolism and Genetic Plasticity they can Rapidly Adjust to a Variety of Environments

Primary Factors Affecting Population Size

1) Type and Amount of Organic Material Present

2) Type and Amount of Electron Acceptors Present

3) Water Content

Primary Factors Affecting Population Size

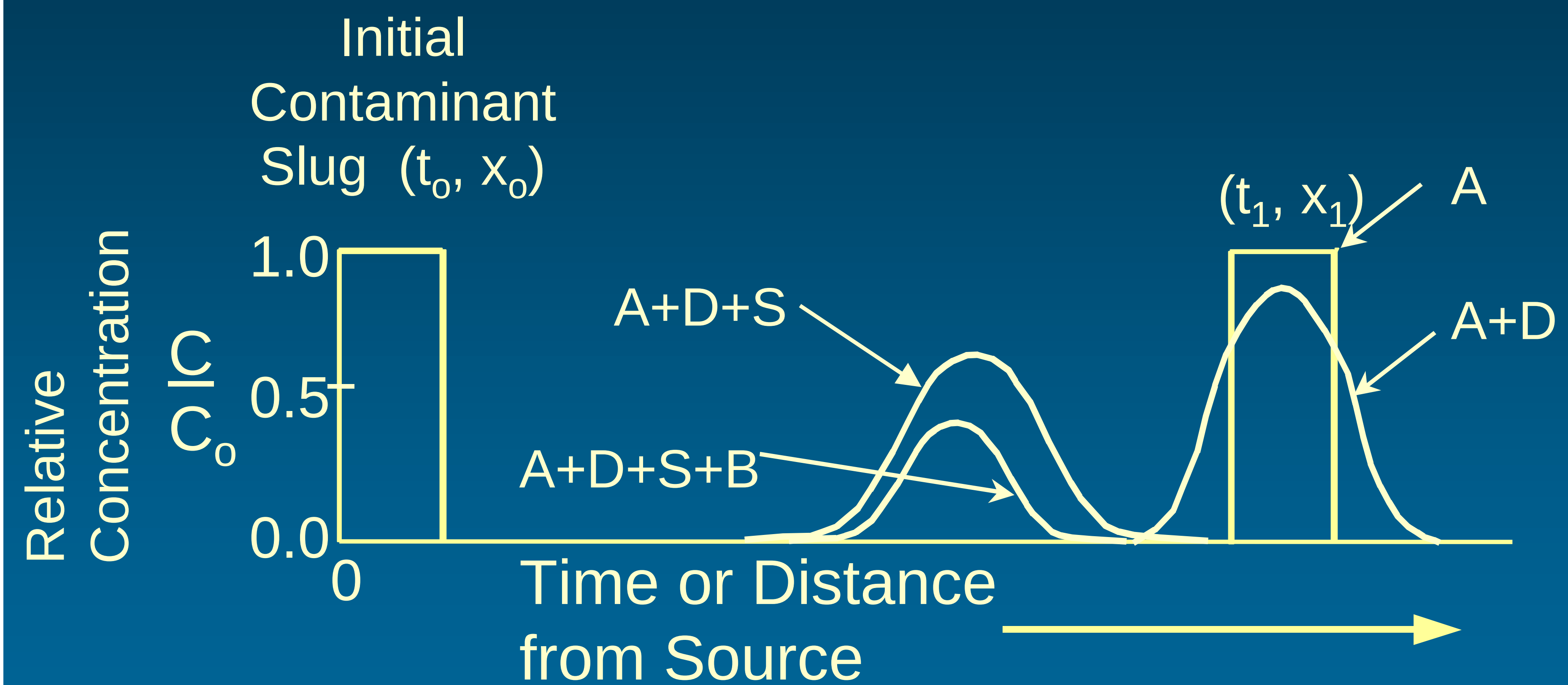
4) Temperature

5) pH (6 - 8 Optimal)

6) Presence of Toxic Materials

7) Concentration of Inorganic Nutrients (Nitrogen, Phosphorous)

Instantaneous Source: Advection, Dispersion, Sorption, Biodegradation

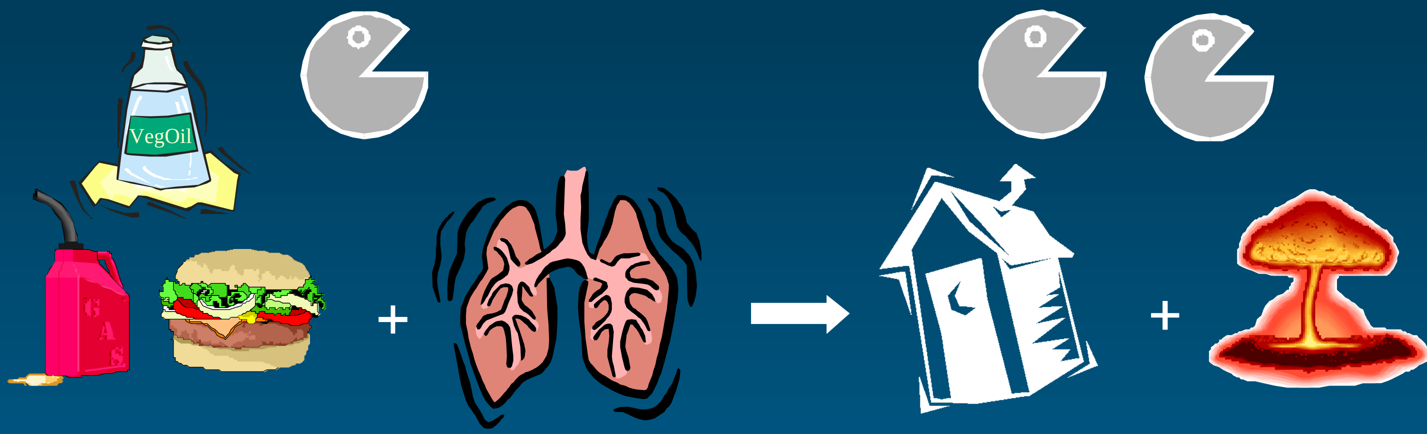


Biological Fate of Organic Contaminants

Two Broad Mechanisms

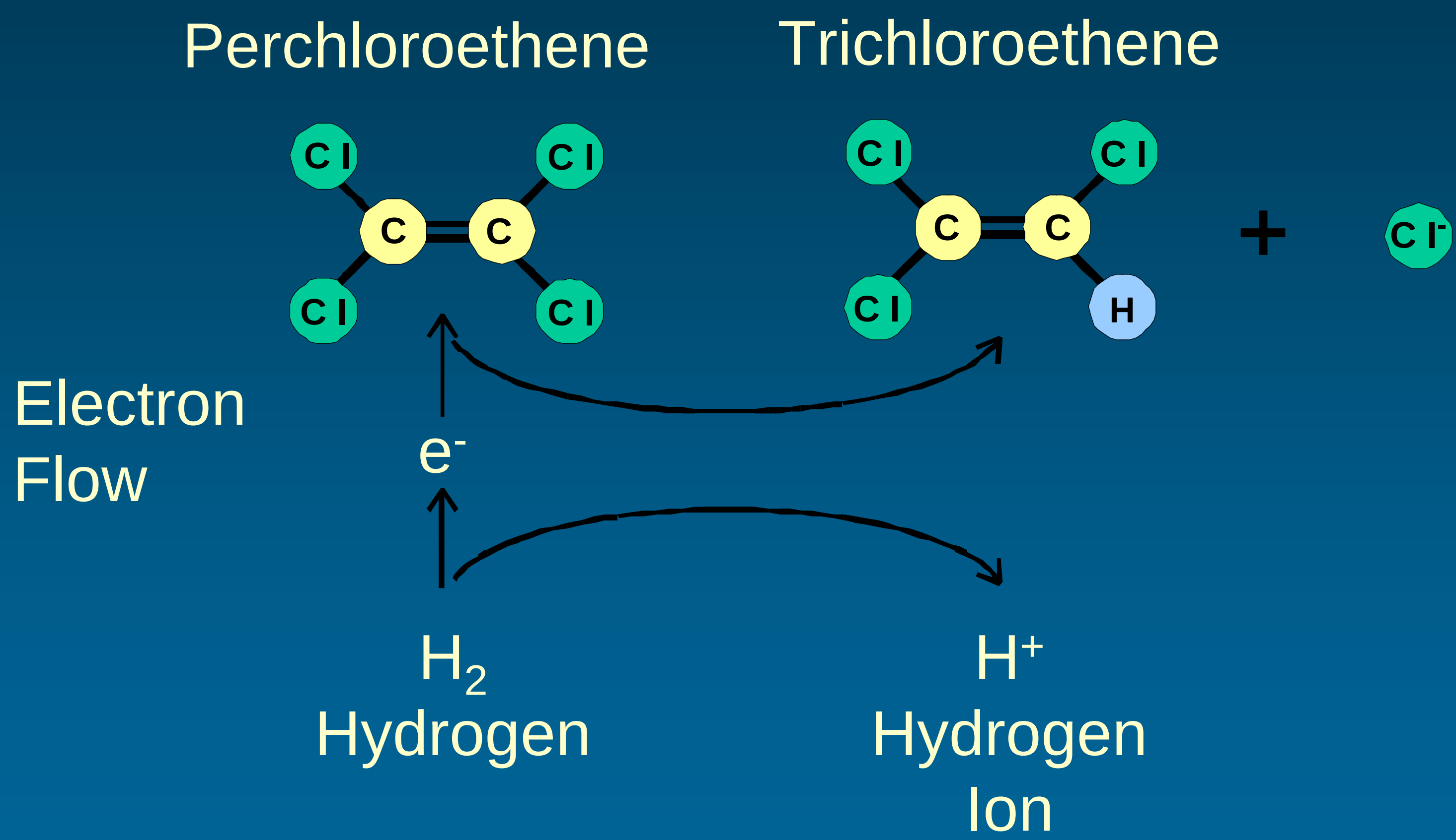
- **Use as a Primary Growth Substrate**
  - **Growth-Promoting Biological Oxidation (Electron Donor)**
  - **Growth-Promoting Biological Reduction - Halorespiration (Electron Acceptor)**
  - **Fermentation**
- **Cometabolism**

Use as Primary Growth Substrate



Electron Donor (food) + Electron Acceptor (something to breath) [O_2, NO_3^-, SO_4^{2-}, Fe(III), CO_2, Solvents] → Metabolic Byproducts [Fe(II), CH_4, CO_2, Alkalinity, Cl^-] + Energy

Reductive Dechlorination



Microbially-Mediated Processes of Contaminant Degradation

- **Aerobic Processes**
  - **Aerobic Respiration**
  - **Cometabolism (Co-Oxidation)**

Microbially-Mediated Processes of Contaminant Degradation

- **Anaerobic Processes**
  - **Denitrification, Mn (IV) Reduction, Fe(III) Reduction, Sulfate Reduction, Methanogenesis**
  - **Halorespiration (Reductive Dechlorination)**
  - **Cometabolism (Co-Reduction/Reductive Dechlorination)**

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Section 1 – Con't
Biodegradation of Petroleum Hydrocarbons

U.S. AIR FORCE

Presented by

Todd Wiedemeier
Parsons Engineering Science, Inc.

todd.wiedemeier@parsons.com
(303) 831-8100

BTEX Biodegradation

- Numerous Researchers Have Shown that BTEX Biodegrades via:
  - Aerobic Respiration
  - Denitrification
  - Mn(IV) Reduction
  - Fe(III) Reduction
  - Sulfate Reduction
  - Methanogenesis

BTEX Biodegradation via Aerobic Respiration

- **Barker, et al., 1987, Natural attenuation of aromatic hydrocarbons in a shallow sand aquifer: GWMR, Winter 1987: 64-71. (B,T,X)**
- **Thomas, et al., 1990, Biodegradation of BTEX in subsurface materials contaminated with gasoline: Water Science Technology 22:53-62 (B,T,E,X)**

Benzene Oxidation/Aerobic Respiration

$$7.5\ O_2 + C_6H_6 \longrightarrow 6\ CO_2 + 3H_2O$$

$$\Delta G^o_r = -3566 \text{ kJ/mole Benzene}$$

Mass Ratio of O_2 to C_6H_6 = 3.1:1

0.32 mg C_6H_6 Degraded per mg O_2 Consumed

Average BTEX Utilization Factor (O_2) = 3.14

(Average Mass Ratio of O_2 to BTEX)

BTEX Biodegradation/Denitrification

- **Evans, et al., 1991, Degradation of toluene and m-xylene and transformation of o-xylene by denitrifying enrichment cultures: Appl. Environ. Microbiol., 57:450-454 (T,X)**
- **Major et al., 1988, Biotransformation of benzene by denitrification in aquifer sand: Ground Water, 26:8-14 (B)**

BTEX Biodegradation/Denitrification

- **Hutchins, et al., 1991, Biodegradation of aromatic hydrocarbons by aquifer microorganisms under denitrifying conditions: Environ. Sci. Technol., 25:68-76 (B,T,E,X)**

Benzene Oxidation/Denitrification

$$6NO_3^- + 6H^+ + C_6H_6 \longrightarrow 6\,CO_2 + 6H_2O + 3N_{2(g)}$$

ΔG^o_r = -3245 kJ/mole Benzene

Mass Ratio of NO_3^- to C_6H_6 = 4.8:1

0.2 mg C_6H_6 Degraded per mg NO_3^- Consumed

Average BTEX Utilization Factor (NO_3^-) = 4.9
(Average Mass Ratio of NO_3^- to BTEX)

BTEX Biodegradation via Fe(III) Reduction

- **Lovley, D.R., et al., 1989, Oxidation of aromatic contaminants coupled to microbial iron reduction: Nature, 339:297-300 (T)**
- **Lovley, D.R., et al., 1994, Stimulated anoxic biodegradation of aromatic hydrocarbons using Fe(III) ligands: Nature 370:128-131 (B)**

Benzene Oxidation/Fe(III) Reduction

$$60H^{+} + 30Fe(OH)_3 + C_6H_6 \longrightarrow 6\ CO_2 + 30Fe^{2+} + 78H_2O$$

ΔG^o_r = -2343 kJ/mole Benzene

Mass Ratio of $Fe(OH)_3$ to C_6H_6 = 41:1

Mass Ratio of Fe^{2+}Produced to to C_6H_6 Degraded = 16:1

0.06 mg C_6H_6 Degraded per mg Fe^{2+} Produced

Average BTEX Utilization Factor (Fe) = 21.8

(Average Mass Ratio of Fe^{2+} Produced to BTEX Degraded)

BTEX Biodegradation via Sulfate Reduction

- **Lovley, et al., 1995, Benzene oxidation coupled to sulfate reduction: Appl. & Env. Micro., v. 61, no. 3, p. 953-958 (B)**
- **Thierrin, et al., 1995, A ground-water tracer test with deuterated compounds for monitoring in situ biodegradation and retardation of aromatic hydrocarbons: Ground Water 33:3, p. 469-475 (T,X, Napthalene)**

Benzene Oxidation/Sulfate Reduction

$$3.75SO_4^{-2} + 7.5H^+ + C_6H_6 \longrightarrow 6CO_2 + 3H_2O + 3.75H_2S$$

ΔG^o_r = -340 kJ/mole Benzene

Mass Ratio of SO_4^{-2} to C_6H_6 = 4.6:1

0.22 mg C_6H_6 Degraded per mg SO_4^{-2} Consumed

Average BTEX Utilization Factor (SO_4^{-2}) = 4.7

(Average Mass Ratio of SO_4^{-2} to BTEX)

BTEX Biodegradation via Methanogenesis

- **Grbic-Galic and Vogel, 1987, Transformation of Toluene and Benzene by mixed methanogenic cultures: Appl. Environ. Microbiol., 53:554-260 (B,T)**
- **Thierrin, et al., 1995, A ground-water tracer test with deuterated compounds for monitoring in situ biodegradation and retardation of aromatic hydrocarbons: Ground Water 33:3, p. 469-475 (T,X, Napthalene)**

BTEX Biodegradation via Methanogenesis

- **Wilson, et al., 1986, Biotransformations of selected alkylbenzenes and halogenated aliphatic hydrocarbons in methanogenic aquifer material: A microcosm study: Environ. Sci. Technol., 20:997-1002. (B,T,E,X)**

Methanogenesis

According to Chapelle (1993)

- *Methanogenic respiration ……. is one of the most important respirative pathways found in anaerobic subsurface environments*

Benzene Oxidation/ Methanogenesis

$$4H_2O + C_6H_6 \longrightarrow 2.25CO_2 + 3.75CH_4$$

$$\Delta G^o_r = -135 \text{ kJ/mole Benzene}$$

Mass Ratio of CH_4 Produced to C_6H_6 Degraded = 0.8:1

1.25 mg C_6H_6 Degraded per mg CH_4 Produced

Average BTEX Utilization Factor (CH_4) = 0.78
(Average Mass Ratio of CH_4 Produced
to BTEX Degraded)

Benzene Oxidation/ Methanogenesis

Methanogenesis is a Two-Step Process that Involves Fermentation and Respiration

Step 1 Produces Acetate and Hydrogen via Fermentation

$$C_6H_6 + 6\ H_2O \longrightarrow 3CH_3COOH + 3H_2$$

Benzene Oxidation/ Methanogenesis

Step 2 Produces Methane, Water, and Carbon Dioxide
via Fermentation and Respiration

$$3CH_3COOH \longrightarrow 3CH_4 + 3CO_2$$

$$3H_2 + 0.75CO_2 \longrightarrow 0.75CH_4 + 1.5H_2O$$

Relative Importance of Terminal Electron Acceptor Processes

	Wurtsmith AFB, MI	Travis AFB, CA	Pope AFB,NC	Seymor Johnson AFB, NC	
aerobic respiration	2720	1216	2400	5820	mg/L
denitrification	5174	3234	1408	880	mg/L
iron reduction	913	743	2580	1450	mg/L
sulfate reduction	2312	23,730	2100	8400	mg/L
methanogenesis	1776	6950	62,000	3460	mg/L
EAC	12,895	35,873	70,488	20,010	mg/L
Total BTEX	3126	67,000	8180	13,800	mg/L

Relative Importance of Terminal Electron Acceptor Processes

	Westover AFRES, MA FT-03	Westover AFRES, MA FT-08	Griffis AFB, NY	Rickenbac-ker ANGB, OH	
aerobic respiration	3200	3140	1396	480	μg/L
denitrification	1760	3520	10,714	7330	μg/L
iron reduction	27,500	12,800	1134	823	μg/L
sulfate reduction	7290	2550	17,860	20,250	μg/L
methanogenesis	230	5500	9070	9841	μg/L
EAC	39,980	27,510	40,174	38,724	μg/L
Total BTEX	1657	32,557	12,840	963	μg/L

Relative Importance of Terminal Electron Acceptor Processes

	MacDill AFB, FL ST-56	MacDill AFB, FL ST-57	MacDill AFB, FL OT-24	Langley AFB, VA	
aerobic respiration	770	666	411	2029	mg/L
denitrification	1144	92	--	4805	mg/L
iron reduction	230	960	600	500	mg/L
sulfate reduction	22,000	13,560	796	17,682	mg/L
methanogenesis	17,400	19,710	12,620	10,240	mg/L
EAC	41,544	34,988	14,427	35,256	mg/L
Total BTEX	29,636	680	2840	68	mg/L

Relative Importance of Terminal Electron Acceptor Processes

	Elmendorf AFB, AK Hanger 10	Elmendorf AFB, AK ST-41	King Salmon, AFB, AK FT-101	King Salmon, AFB, AK Naknek	
aerobic respiration	260	4030	2870	3730	mg/L
denitrification	13,200	12,300	2552	--	mg/L
iron reduction	410	1860	115	2020	mg/L
sulfate reduction	5460	12,400	1470	--	mg/L
methanogenesis	11,600	1900	238	7190	mg/L
EAC	30,930	32,490	7245	12,940	mg/L
Total BTEX	22,200	30,600	10,100	5260	mg/L

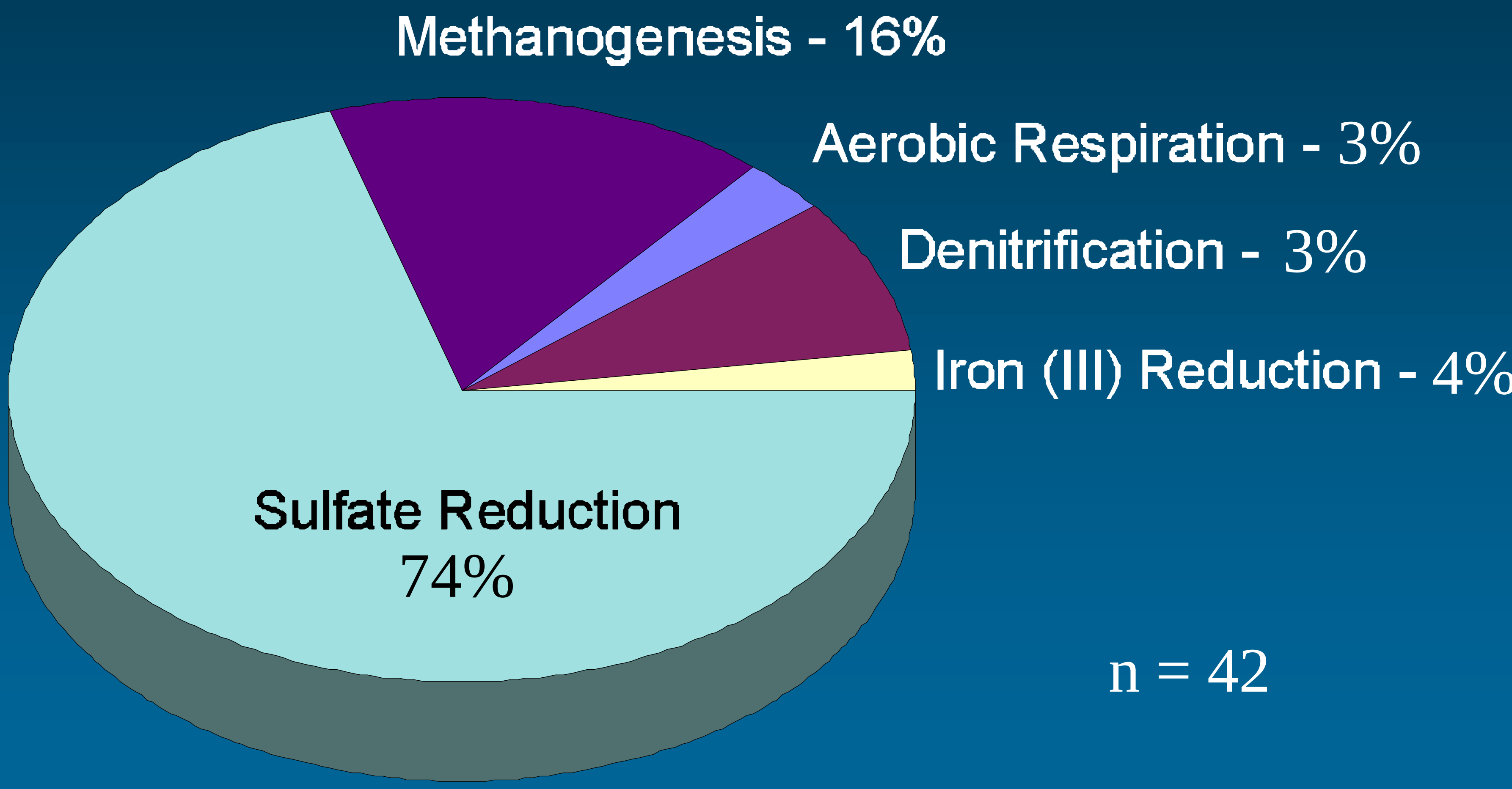
Relative Importance of Terminal Electron Acceptor Processes

	Hill AFB, UT	Patrick AFB, FL	Battle Creek ANGB, MI	Madison ANGB, WI	
aerobic respiration	1920	1200	1800	2300	μg/L
denitrification	7392	--	1144	9240	μg/L
iron reduction	2550	90	550	700	μg/L
sulfate reduction	21,000	--	2800	5250	μg/L
methanogenesis	2560	17,400	10,800	15,000	μg/L
EAC	35,422	18,690	17,094	32,490	μg/L
Total BTEX	21,475	7304	3552	28,000	μg/L

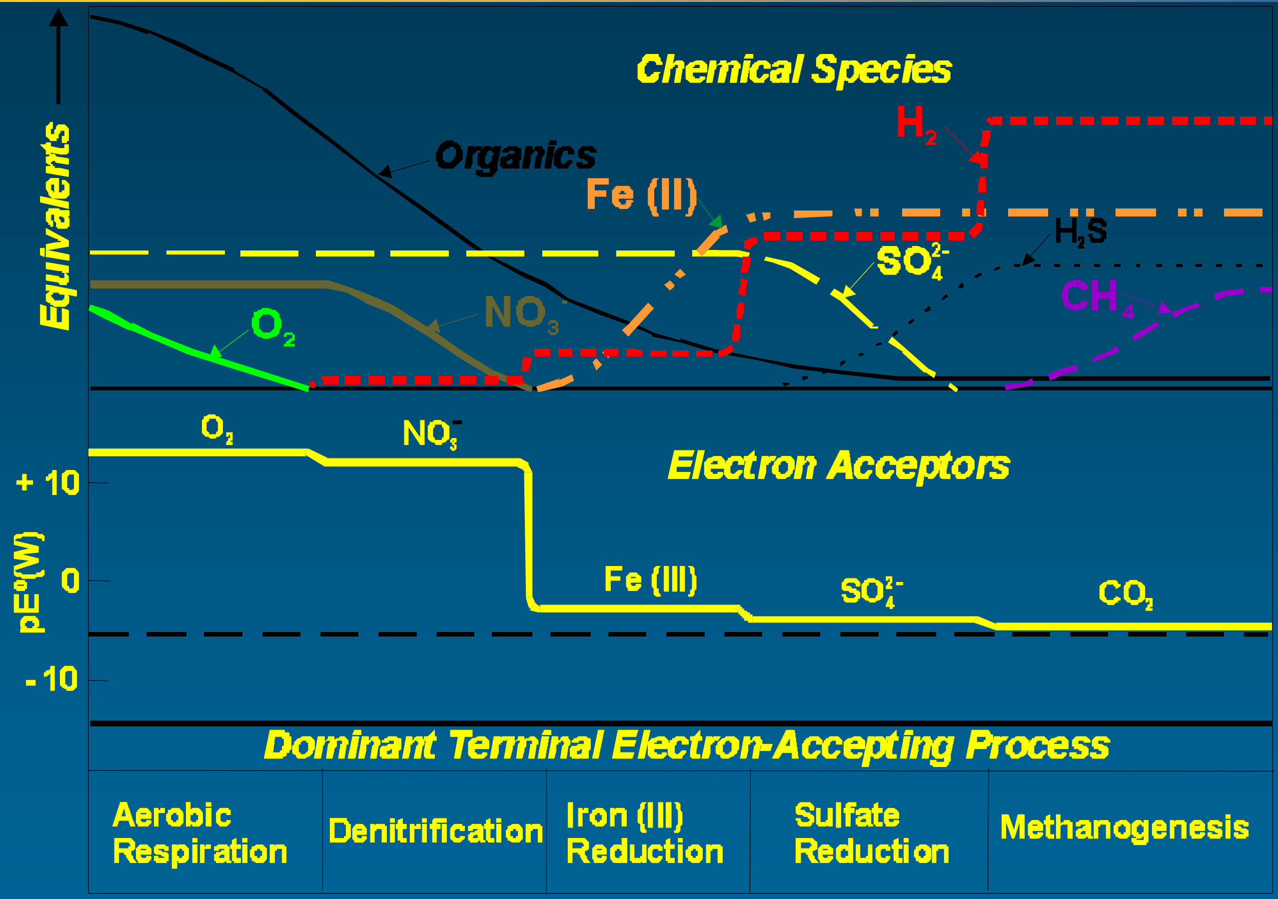
Relative Importance of Terminal Electron Acceptor Processes

	Plattsburg AFB, NY	Elgin AFB, FL	Offutt AFB, NE FPT-A3	Myrtis Beach, SC	
aerobic respiration	3200	380	200	120	mg/L
denitrification	748	--	--	--	mg/L
iron reduction	490	410	870	1600	mg/L
sulfate reduction	4100	1060	6950	4500	mg/L
methanogenesis	400	15,150	28,780	22,000	mg/L
EAC	8938	17,000	36,800	28,200	mg/L
Total BTEX	6010	3682	3230	18,270	mg/L

Relative Importance of Biodegradation Mechanisms



Geochemical Evolution of Groundwater



After: Bouwer and McCarty, 1984

Time →

← Distance From Source

Findings of Intrinsic Bioremediation Evaluations - Fuel Hydrocarbons

- **Intrinsic Bioremediation is Occurring at 100% of Sites Studied**
- **Typically Sulfate Reducing or Methanogenic**
- **Most Plumes Not Migrating**
- **NAPL Source Reduction = Key**
- **Natural Attenuation Protective at > 80% of Sites**

Conclusions

- Anaerobic Processes More Important than Once Thought
- In General, Greater than 90% of BTEX Mass is Destroyed by Anaerobic Processes

Headquarters U.S. Air Force

I n t e g r i t y - S e r v i c e - E x c e l l e n c e

Section 1 – Con't
Biodegradation of Chlorinated Solvents

U.S. AIR FORCE

Presented by

Todd Wiedemeier
Parsons Engineering Science, Inc.

todd.wiedemeier@parsons.com
(303) 831-8100

Chlorinated Solvent Biodegradation

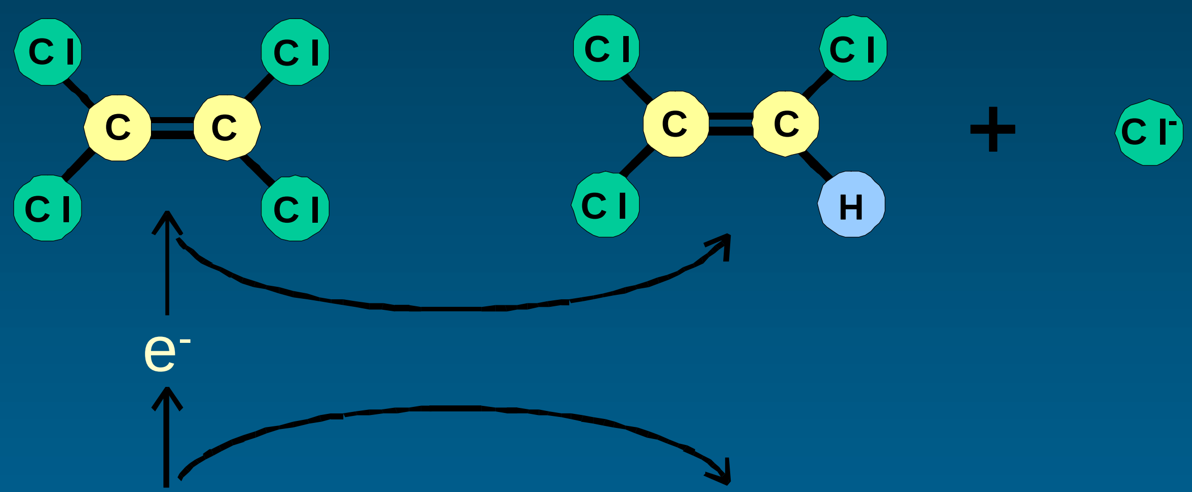
- Numerous Researchers Have Shown that Chlorinated Solvents Biodegrade via:
  - Aerobic Respiration (DCE, VC, Chlorobenzenes)
  - Fe(III) Reduction (DCE, VC)
  - Halorespiration (Most Solvents)
  - Cometabolism (TCE)

Reductive Dechlorination - Halorespiration

- **Reductive Dechlorination is the Only Biological Mechanism Known to Degrade the Common Chlorinated Solvents (PCE, TCE, TCA, and CT) in Most Groundwater Systems**

Reductive Dechlorination

Perchloroethene Trichloroethene



Electron Flow

e^-

H_2
Hydrogen

H^+
Hydrogen Ion

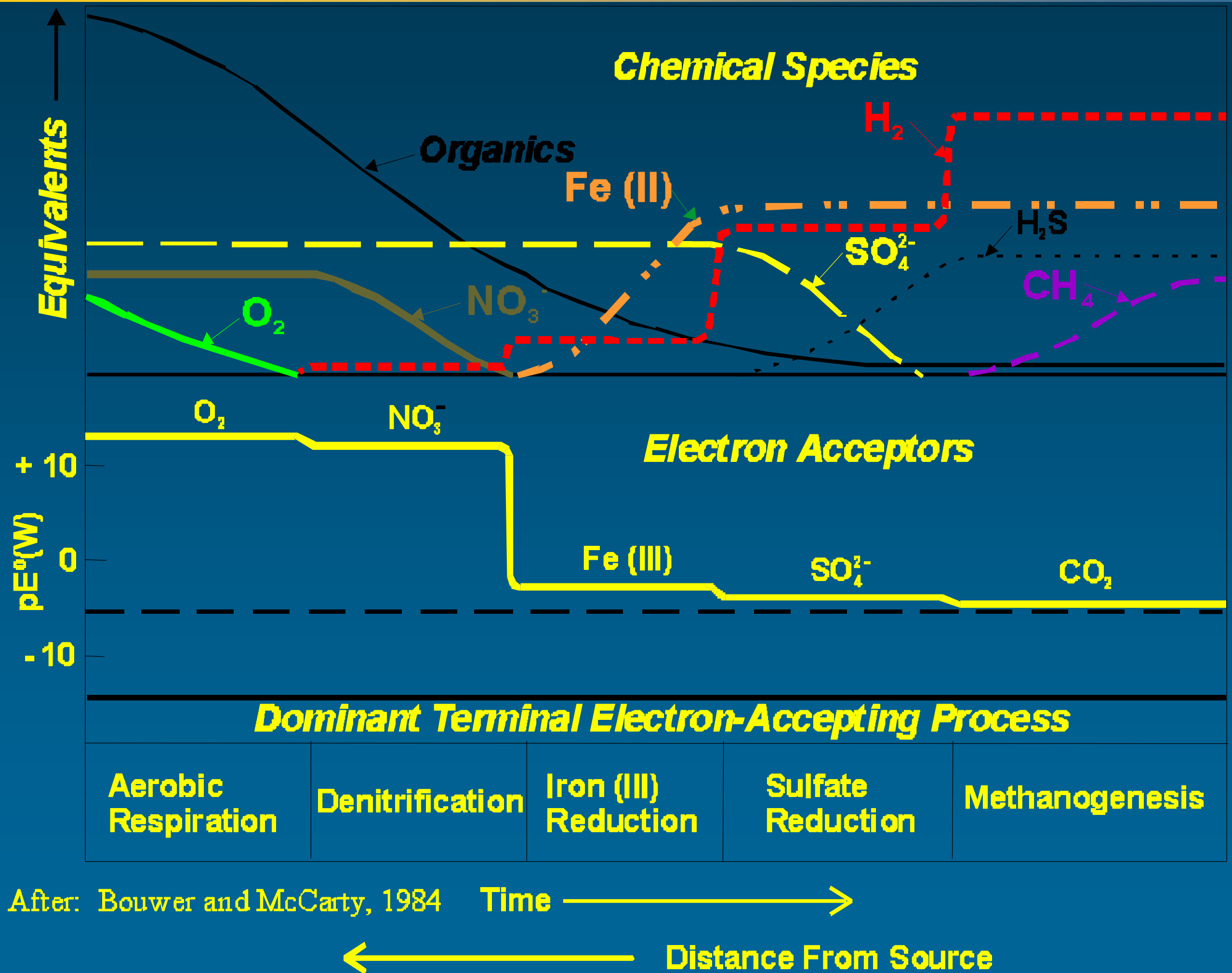
Requirements for Halorespiration

- **Halorespiring Bacteria**
- **Electron Donor (for Carbon and Hydrogen)**
- **Strongly Reducing Conditions (Sulfate Reducing or Methanogenic)**
- **Hydrogen Concentrations > 1 nM**

"Foot Race for Hydrogen"

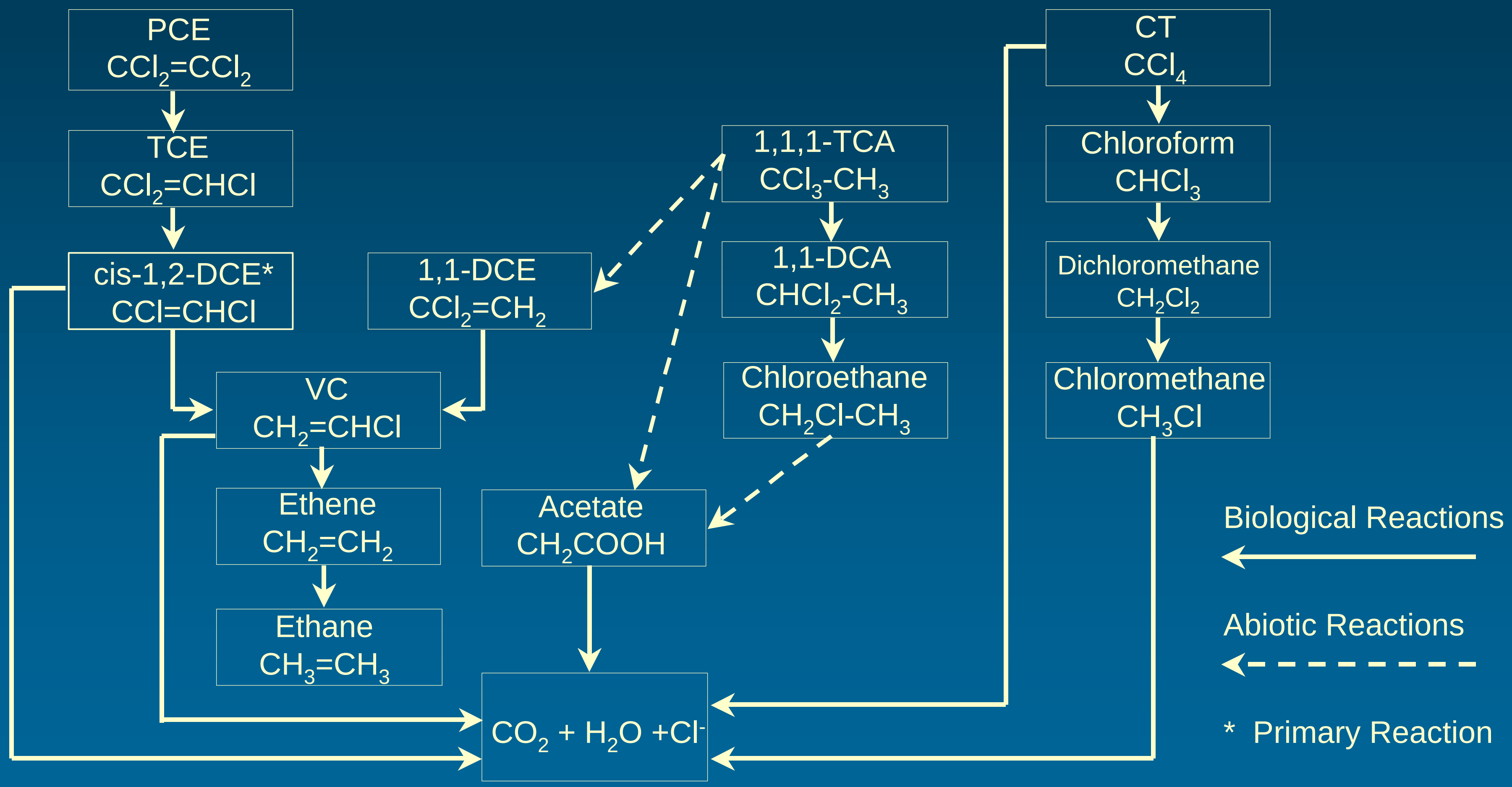
- **Reductive Dechlorination is in a "Foot Race" with Competing Donor Uses**
  - » Gossett and Zinder, 1996, EPA/540/R-96/509
  - **If Too Little Electron Donor is Present then not Enough H_2 is Produced to Sustain Reductive Dechlorination**

Geochemical Evolution of Groundwater

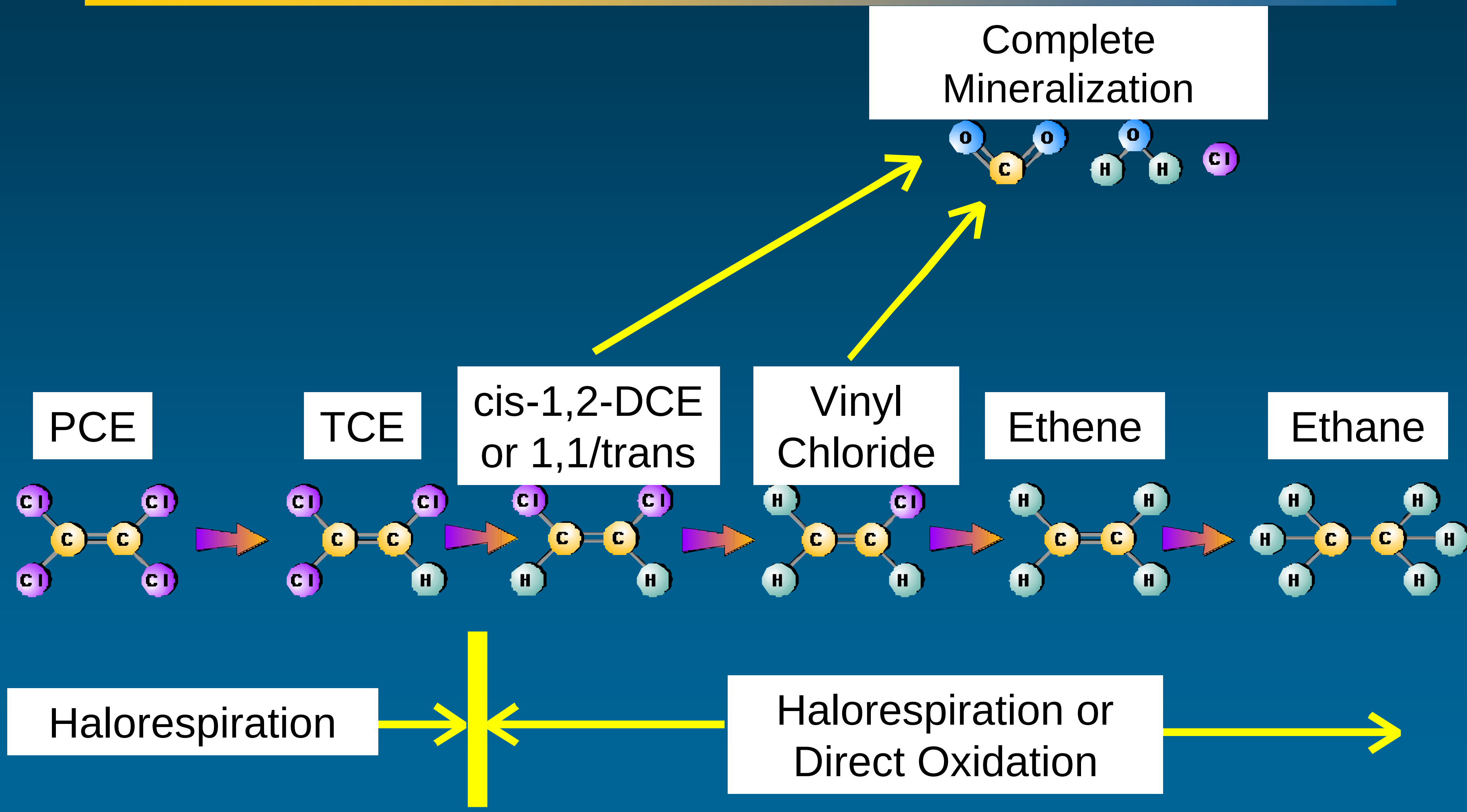


After: Bouwer and McCarty, 1984

Abiotic and Biological Transformation Pathways

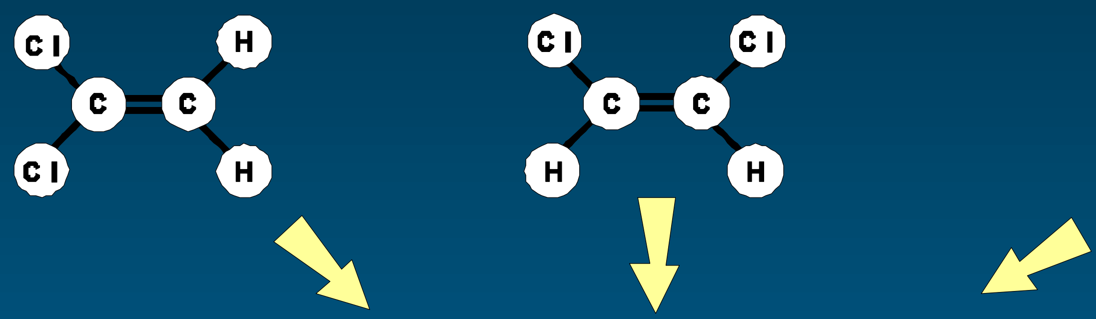


Chlorinated Ethene Degradation

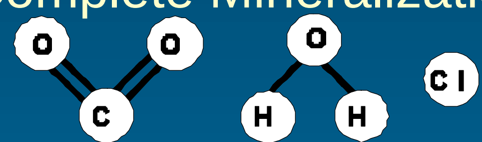


Growth-Promoting Biological Oxidation Pathways for Ethenes

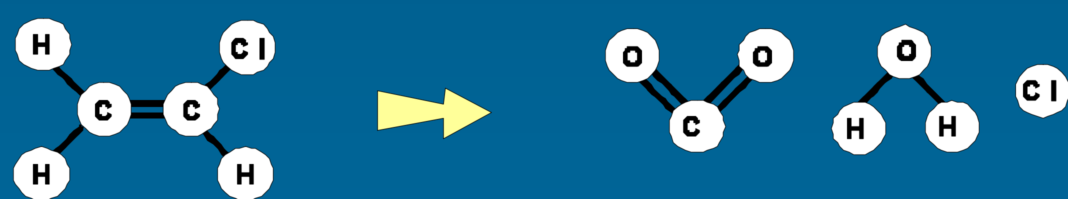
1,1-Dichloroethene   cis-1,2-Dichloroethene   trans-1,2-Dichloroethene



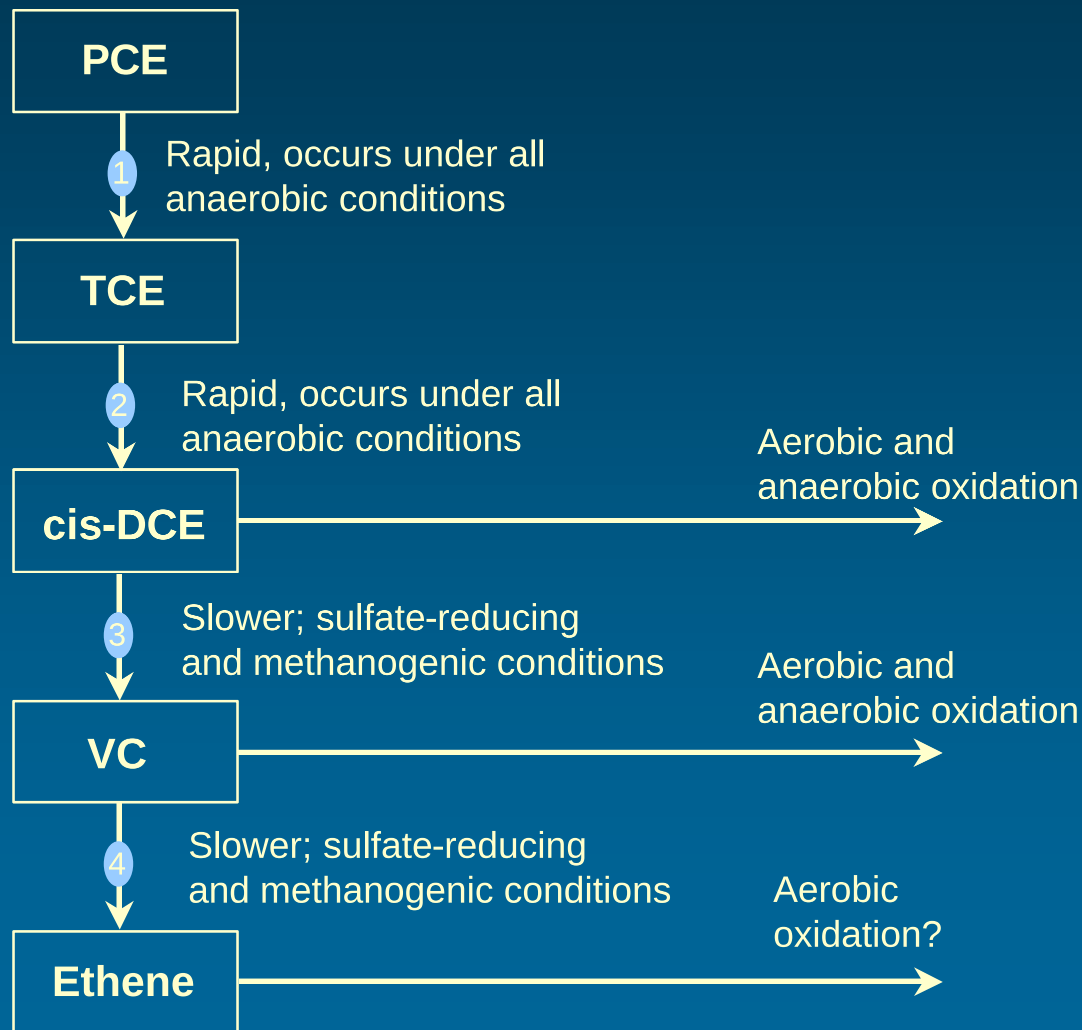
Complete Mineralization



Vinyl Chloride   Complete Mineralization

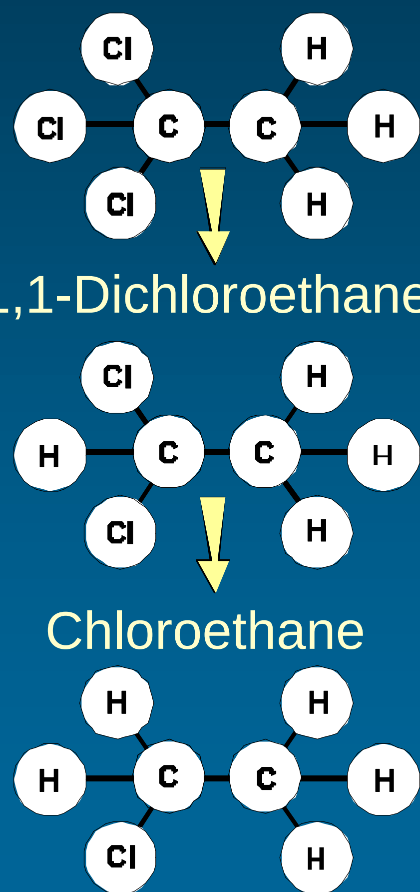


Chlorinated Ethene Degradation

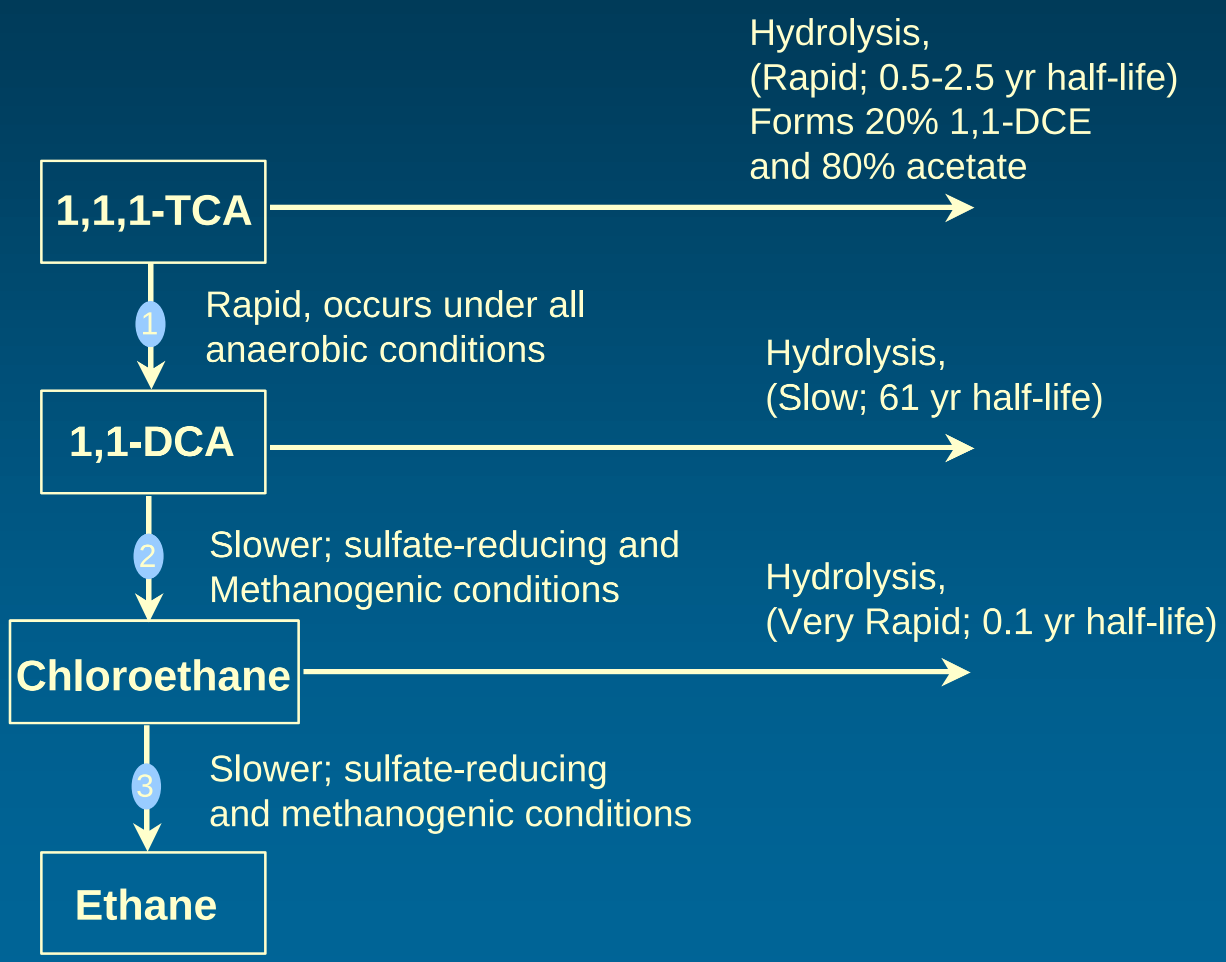


Reductive Dechlorination - Chlorinated Ethanes

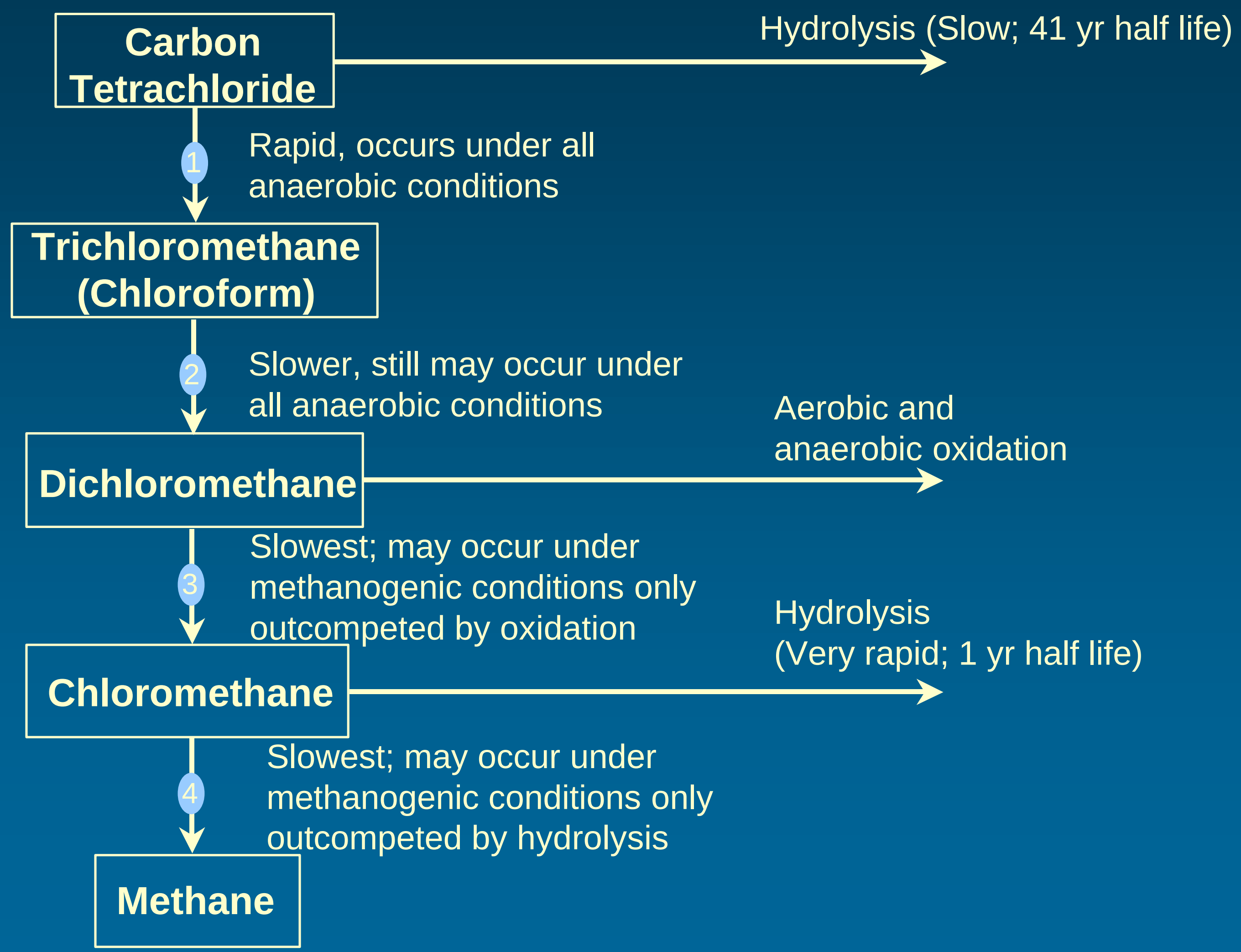
1,1,1-Trichloroethane



Chlorinated Ethane Degradation



Degradation Mechanisms - Chlorinated Methanes



Behavior of Chlorinated Solvent Plumes

- **Type 1 Behavior (Environment)**
  - **Primary Substrate Anthropogenic Carbon**
  - **Solvent Plume Dechlorinates**
- **Type 2 Behavior (Environment)**
  - **Primary Substrate Natural Carbon**
  - **Solvent Plume Dechlorinates**
- **Type 3 Behavior (Environment)**
  - **No Primary Substrate Low Organic Carbon**
  - **PCE, TCE, TCA, and CT Do Not Undergo Biological Reductive Dechlorination**

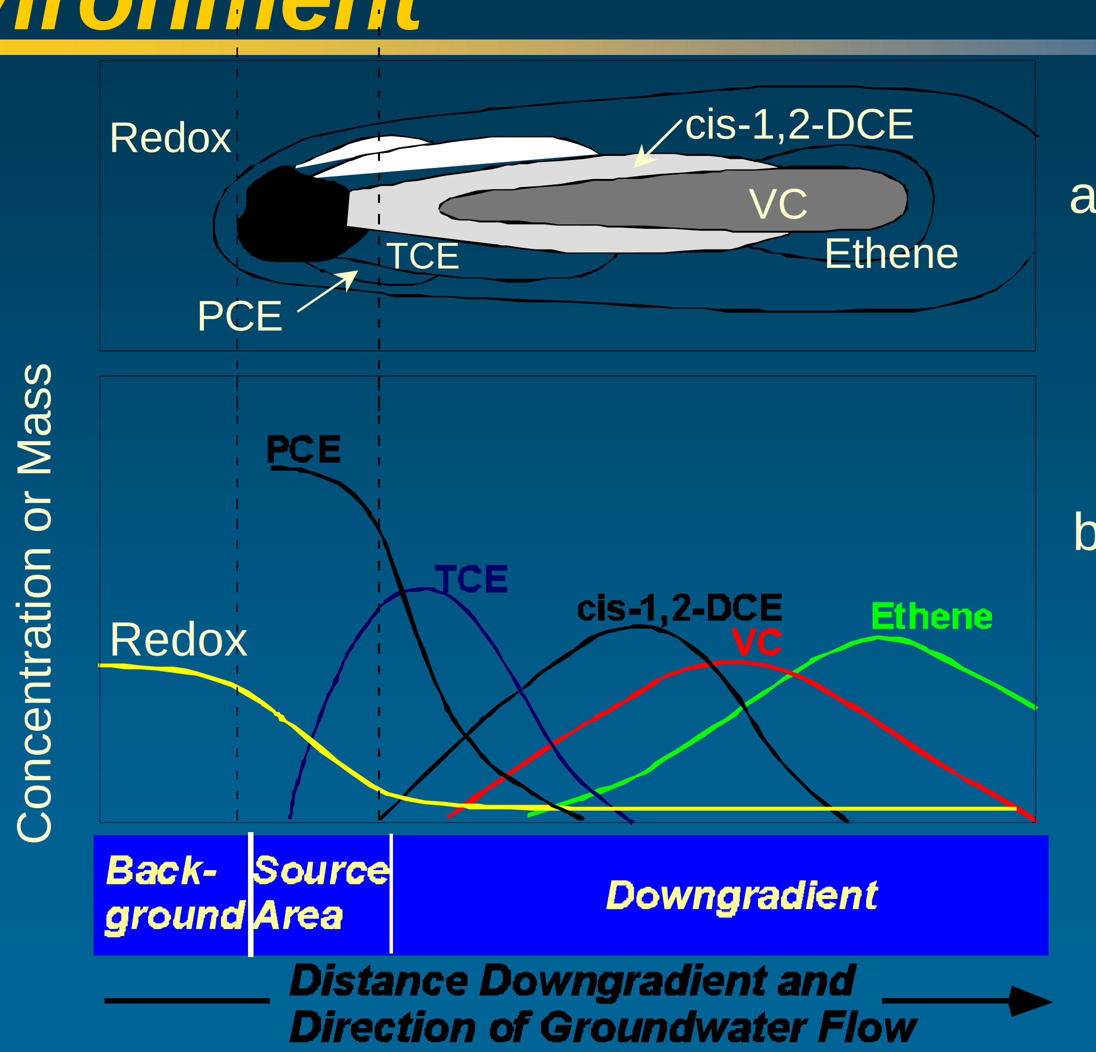
Type 1 Environment

- Primary Substrate is Anthropogenic Carbon
   - BTEX, Landfill Leacheate, etc.
- Anthropogenic Carbon Drives Dechlorination
- Several Questions Must be Answered

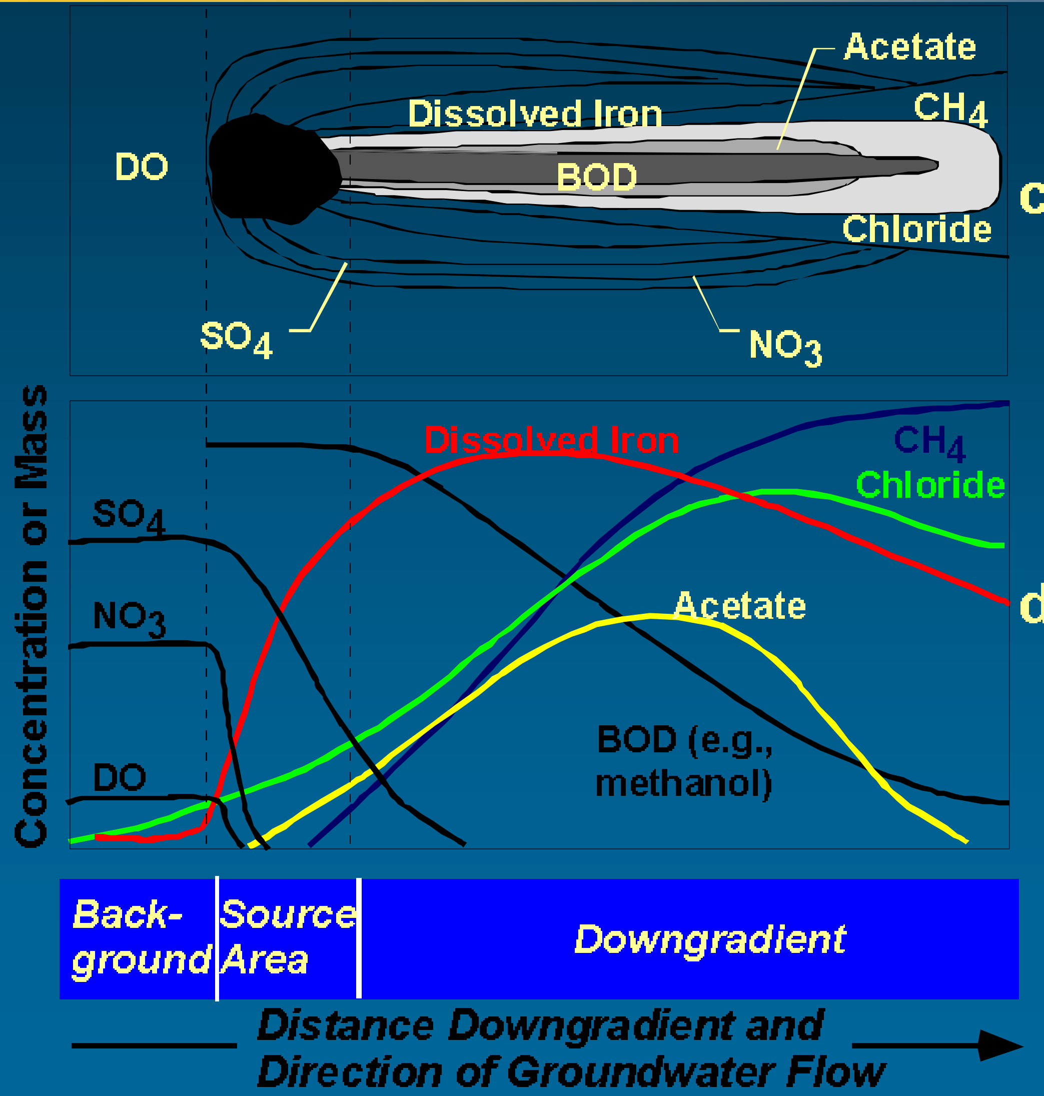
Type 1 Environment - Questions

- Does Electron Donor Supply Exceed Demand? (i.e., Is the Supply of Electron Donors Adequate)
- Will the Plume Strangle Before it Starves or Starve Before it Strangles?
- What is the Role of Competing Electron Acceptors
- Is Reductive Dechlorination Occurring
- Is Biodegradation Rate Adequate?

Conceptual Model - Type 1 Environment



Conceptual Model - Type 1 Environment



Chemical Characteristics - Type 1 Environment

	Dissolved Oxygen		Nitrate (as N)		Sulfate		ORP	
Site	Plume (mg/L)	Back-ground (mg/L)	Plume (mg/L)	Back-ground (mg/L)	Plume (mg/L)	Back-ground (mg/L)	Plume (mV)	Back-ground (mV)
Site 1	0	9	< 0.05	1.2	< 0.1	20.4	-201	319
Site 2	0.1	9.9	< 0.05	6.02	3.02	13.6	-73	146
Site 3	0.02	1.54	1.09(D)	2.46 (D)	1.04	77	-238.3	-18.7
Site 4	0.1	3.3	< 0.05	1.52	< 0.5	391	-170	90
Site 5	0.46	7.95	< 0.05	2.4	< 0.05	13.1	-127	200
Site 6	0	13.4	< 0.05	9.1	6.57	938	-136	212
Site 7	0.15	8.93	< 0.05	5.57	< 0.5	76.7	-125	280
Site 8	0.21	10.75	< 0.05	9.5	1.3	36.8	-207	313

Chemical Characteristics - Type 1 Environment

	Iron (II)		Methane		Hydrogen		Chloride	
Site	Plume (mg/L)	Back-ground (mg/L)	Plume (mg/L)	Back-ground (mg/L)	Plume (nM)	Back-ground (nM)	Plume (mg/L)	Back-ground (mg/L)
Site 1	8.2	< 0.05	6.952	< 0.001	19.02	0.1	177	2.3
Site 2	15	< 0.1	3.55	< 0.001	< 0.1	< 0.1	25.3	1.05
Site 3	3.48	0.2	9.89	0.008	NA	NA	115	6.51
Site 4	26.3	< 0.05	22.45	< 0.01	NA	NA	213	3.6
Site 5	22.3	< 0.1	19.06	< 0.001	NA	NA	94	1.4
Site 6	16.5	< 0.05	19.2	< 0.01	0.648	0.001	53.3	1.5
Site 7	45.3	< 0.05	14.63	< 0.001	NA	NA	131	< 0.5
Site 8	288	< 0.01	2.2	< 0.001	NA	NA	57.6	0.9

Type 2 Environment

- **Primary Substrate is Natural Organic Carbon**
  - **Swamp Deposits, Wetlands, Peat, etc.**
- **Natural Organic Carbon Drives Reductive Dechlorination**
- **Several Questions Must be Answered**

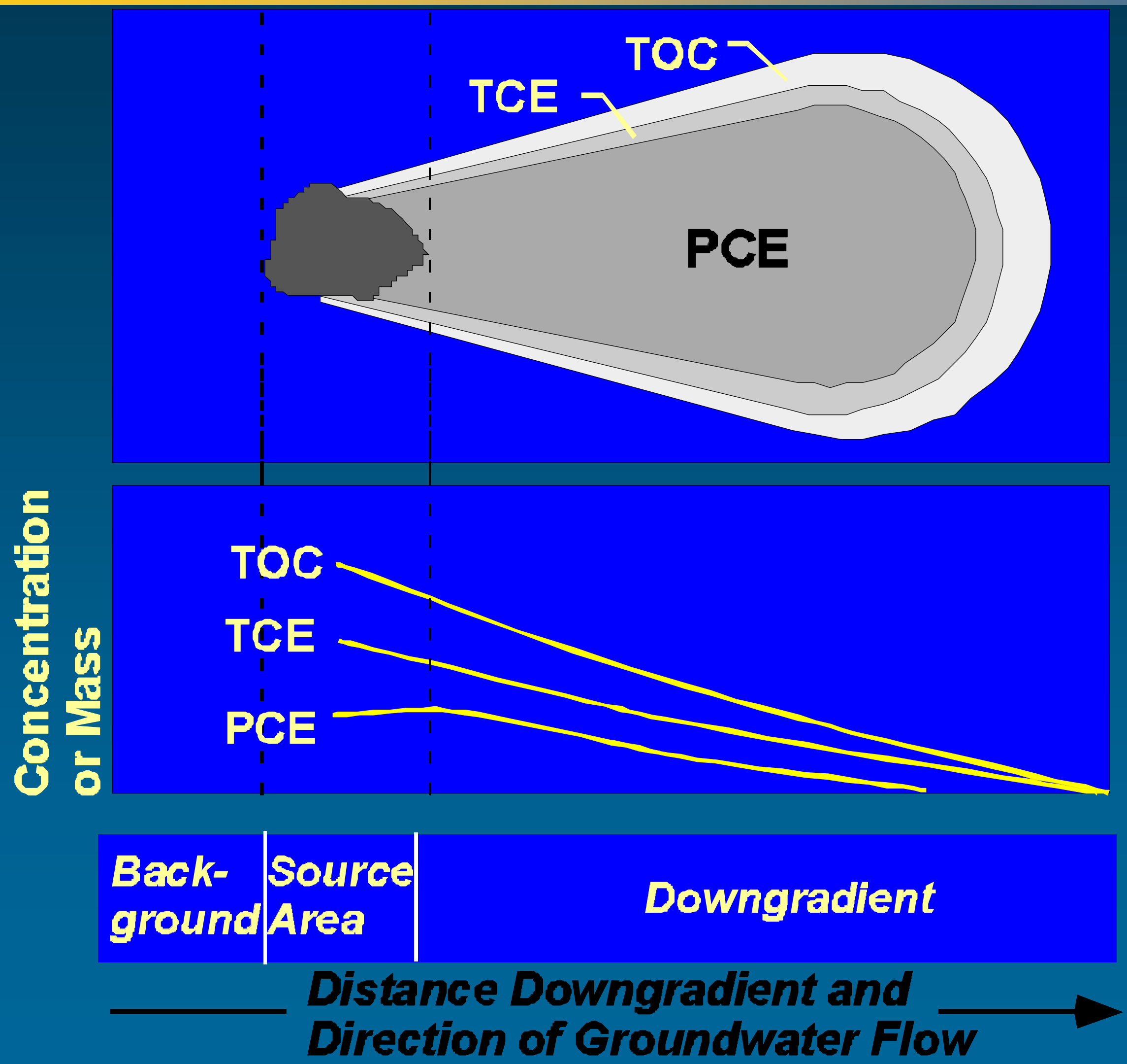
Type 2 Environment - Questions

- Does Electron Donor Supply Exceed Demand? (i.e., Is the Supply of Electron Donors Adequate)
- Will the Plume Strangle Before it Starves or Starve Before it Strangles?
- What is the Role of Competing Electron Acceptors
- Is Reductive Dechlorination Occurring
- Is Biodegradation Rate Adequate?

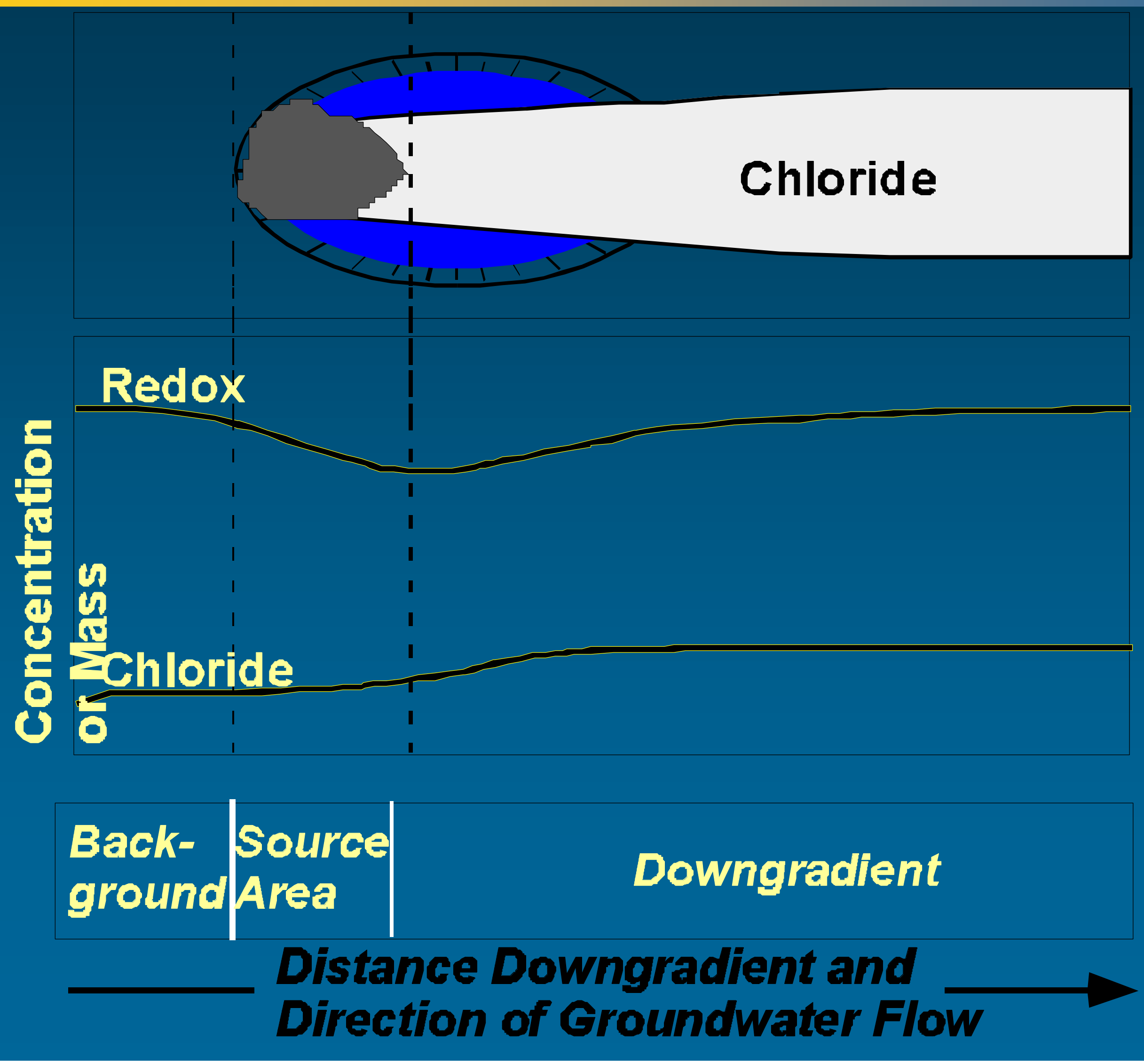
Type 3 Environment

- Low Natural Organic and Anthropogenic Carbon Concentrations
- Dissolved Oxygen (and Nitrate) Concentration(s) Greater than 1 mg/L
- Reductive Dechlorination Will Not Occur
  - Highly Halogenated Compounds Such as PCE, TCE, TCA, and CT will Not Degrade
- Oxidation of DCE, VC, etc. Can Occur

Conceptual Model - Type 3 Environment – Dilution



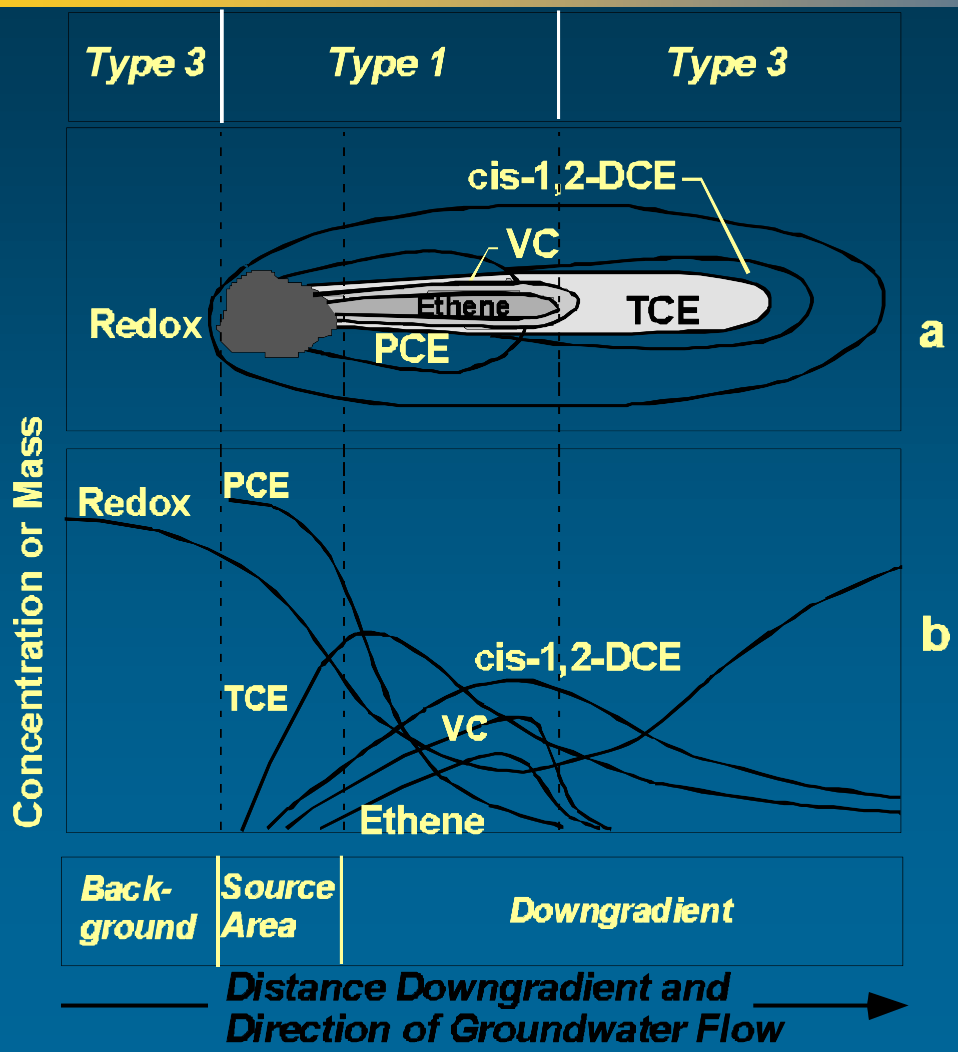
Conceptual Model - Type 3 Environment



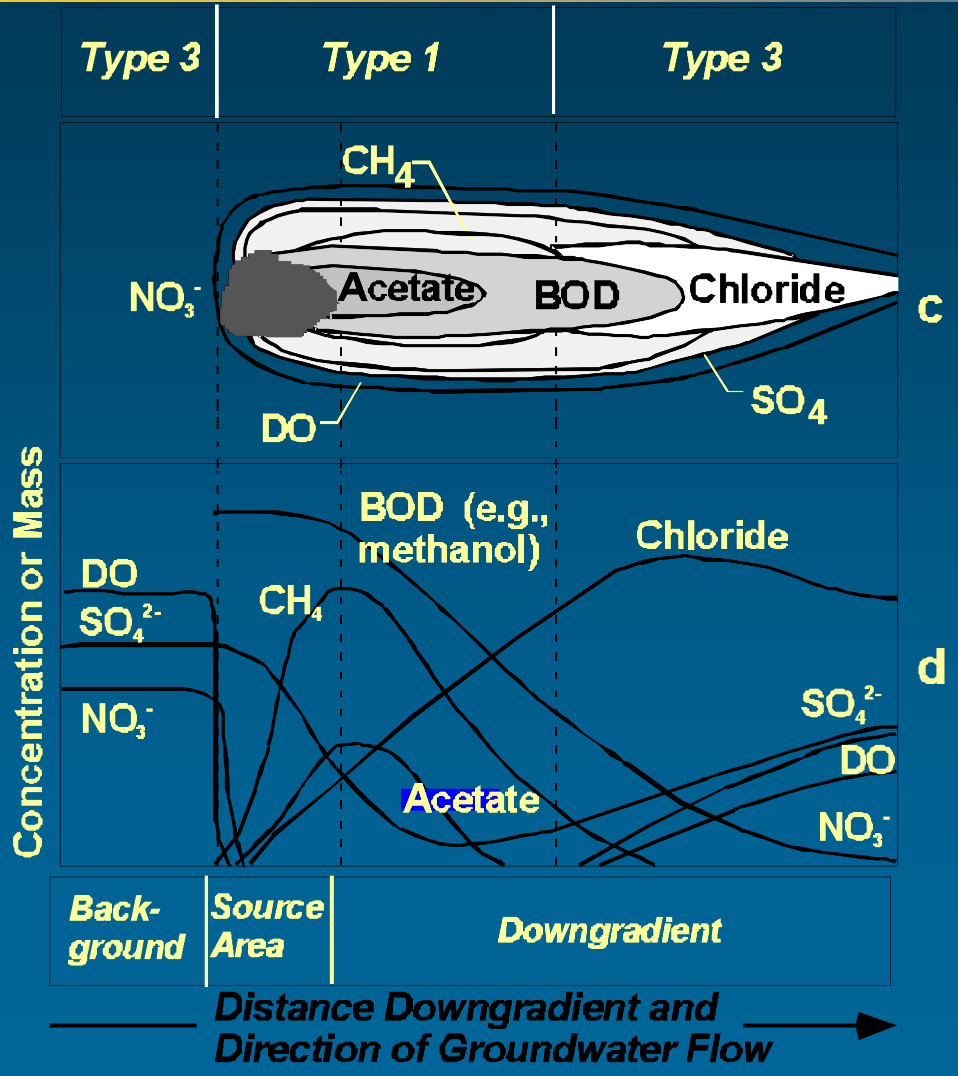
Mixed Environments

- Many Chlorinated Solvent Plumes Exhibit Mixed Behavior

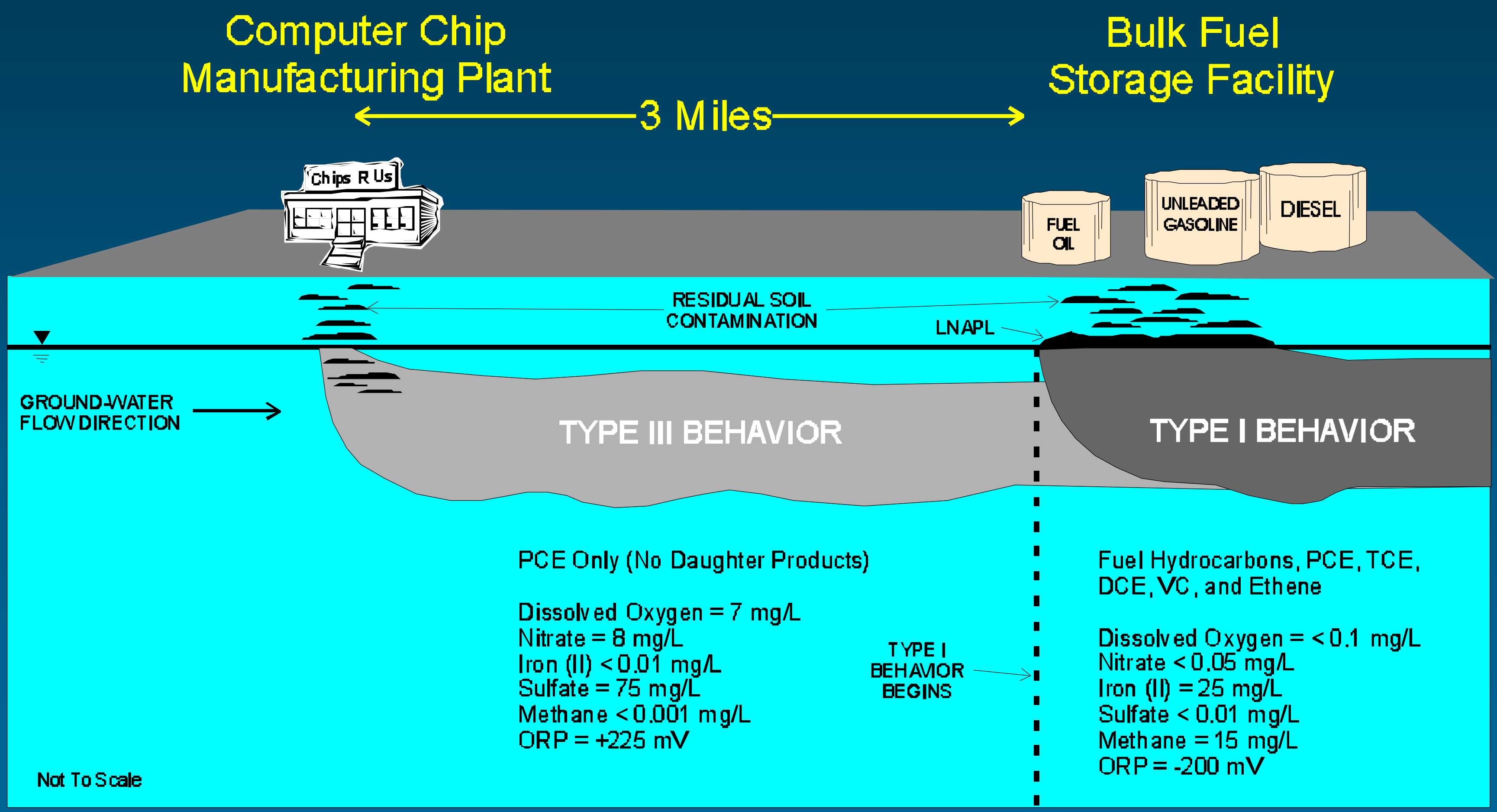
Conceptual Model - Mixed Environments



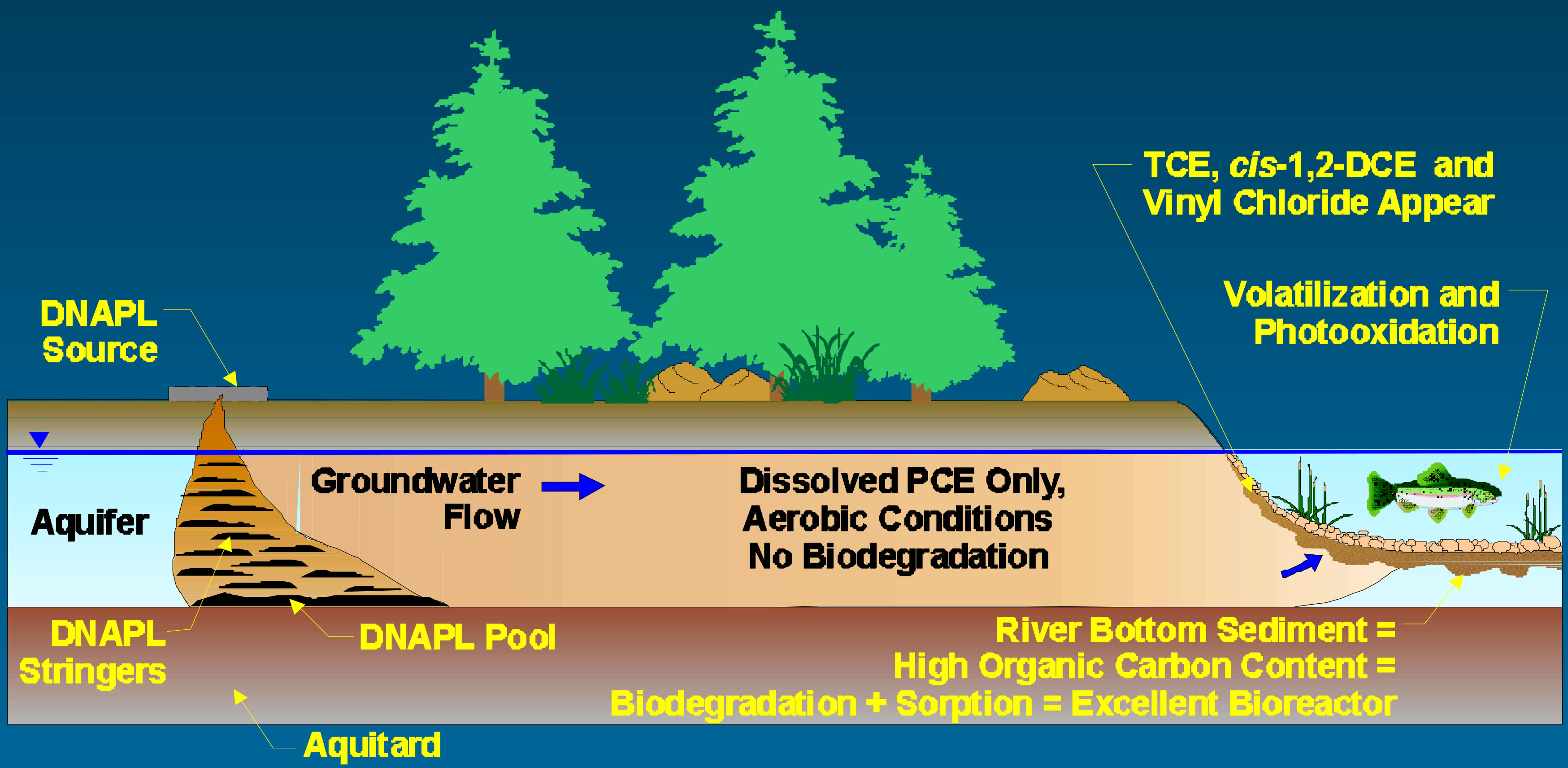
Conceptual Model - Mixed Environments



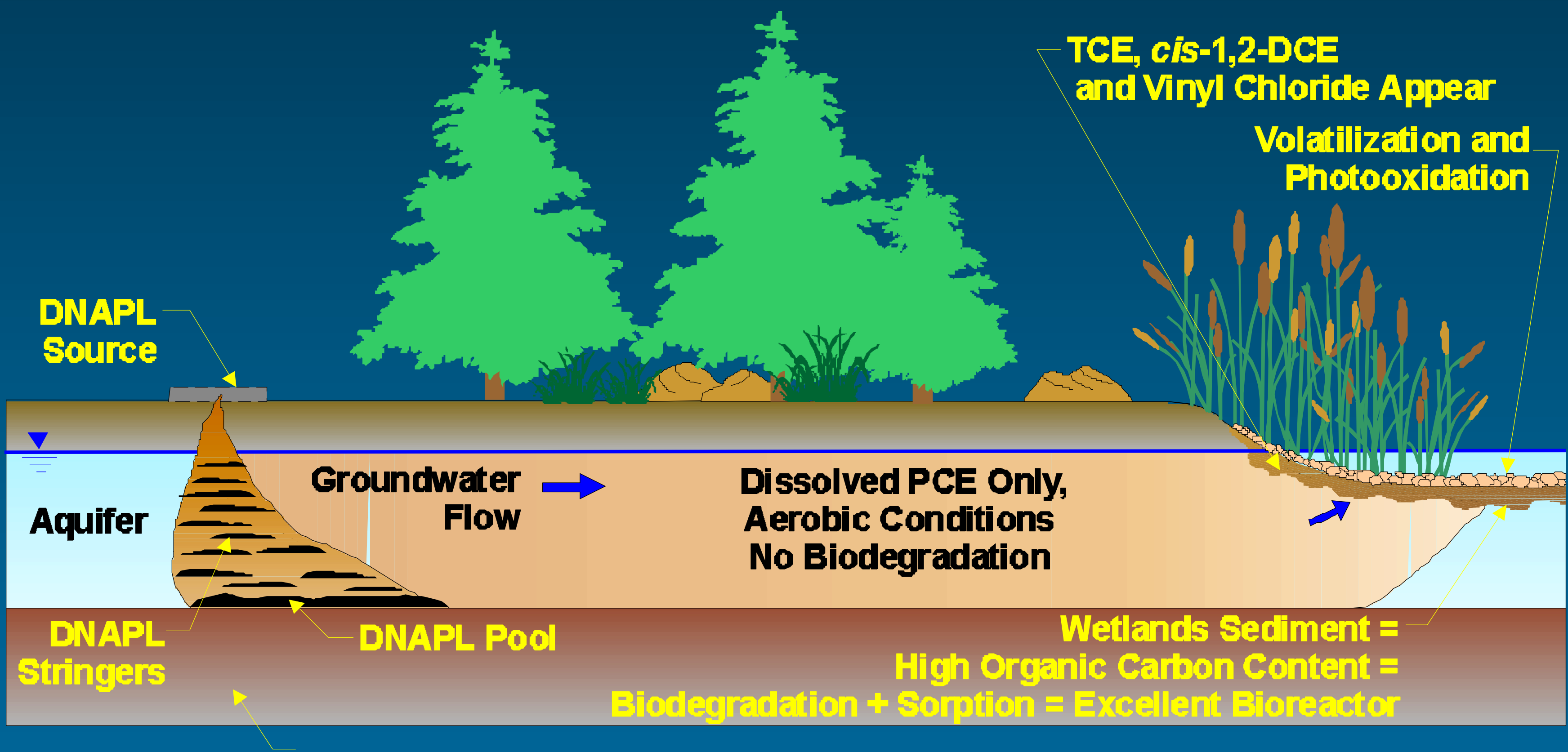
Mixed Environments



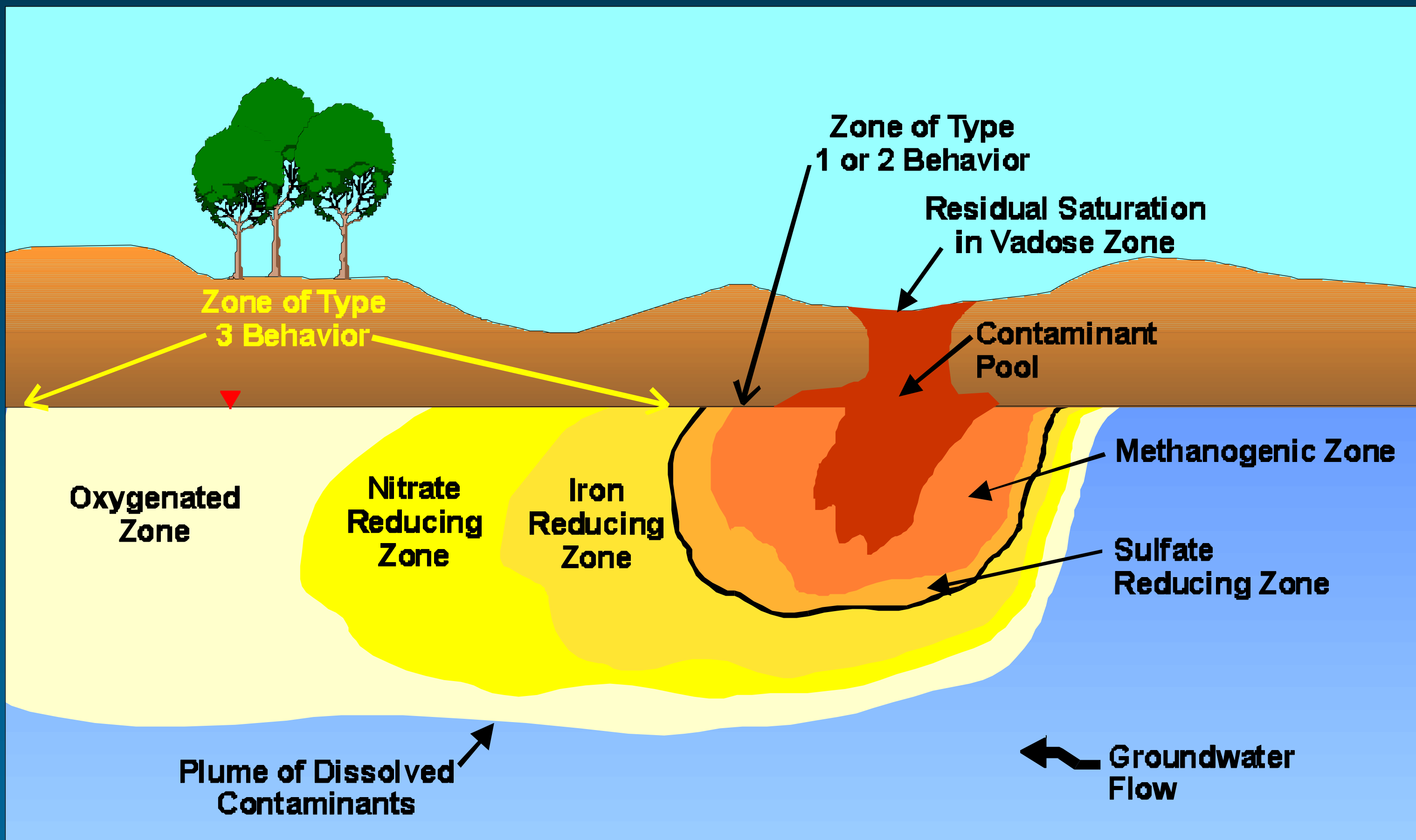
Mixed Environments



Mixed Environments



Conceptualization of Electron Acceptor Zones in the Subsurface



AFCEE Natural Attenuation Initiative – Chlorinated Solvents

- Began in 1995
- Total of 13 Sites were Evaluated Across the Country
- Additional Sites were Evaluated under the Risk-Based Corrective Action Program (Travis AFB) and Other Programs (Williams AFB and MMR)

Air Force Natural Attenuation Initiative for Chlorinated Solvents

Project Elements

- Site Visit/Kickoff Meeting
- Site-Specific Work Plan
- Field Site Characterization (Geoprobe® or CPT rig)
- Data Interpretation
- Contaminant Fate and Transport Modeling
- Treatability Study Report
- Final Regulatory Meeting

Groundwater Analytical Protocol Developed by AFCEE

- Contaminants/ Daughter Products
- Dissolved Oxygen
- Nitrate/Nitrite
- Fe(II)
- Sulfate/Sulfide
- Methane
- Oxidation/Reduction Potential (ORP)
- Carbon Dioxide
- Alkalinity
- pH
- Temperature
- Total Organic Carbon[a/]
- Ethene/Ethane[a/]
- Chloride[a/]
- Hydrogen[a/]

a/ Chlorinated Solvents Only

Wide Range of Site Characteristics

- Depths to groundwater ranging from 0 to 60 feet bgs
- Plume areas ranging from 1.6 to 210 acres
- Average groundwater temperatures ranging from 9.1 to 25.6 ºC
- Aquifer matrices ranging from clay to coarse sand and gravel
- TCE most pervasive, followed by cis-1,2-DCE

What Did We Learn from all This Variability?

- Solvent Plumes are Like Children, Each one is Different
- Plume Behavior (i.e., stable, shrinking, growing) Depends on Prevailing Groundwater Geochemistry
- Why?

Because …….

- The Common Chlorinated Solvents, PCE, TCE, Carbon Tetrachloride, and 1,1,1-TCA Predominantly Biodegrade in the Natural Environment via a process Called Reductive Dechlorination

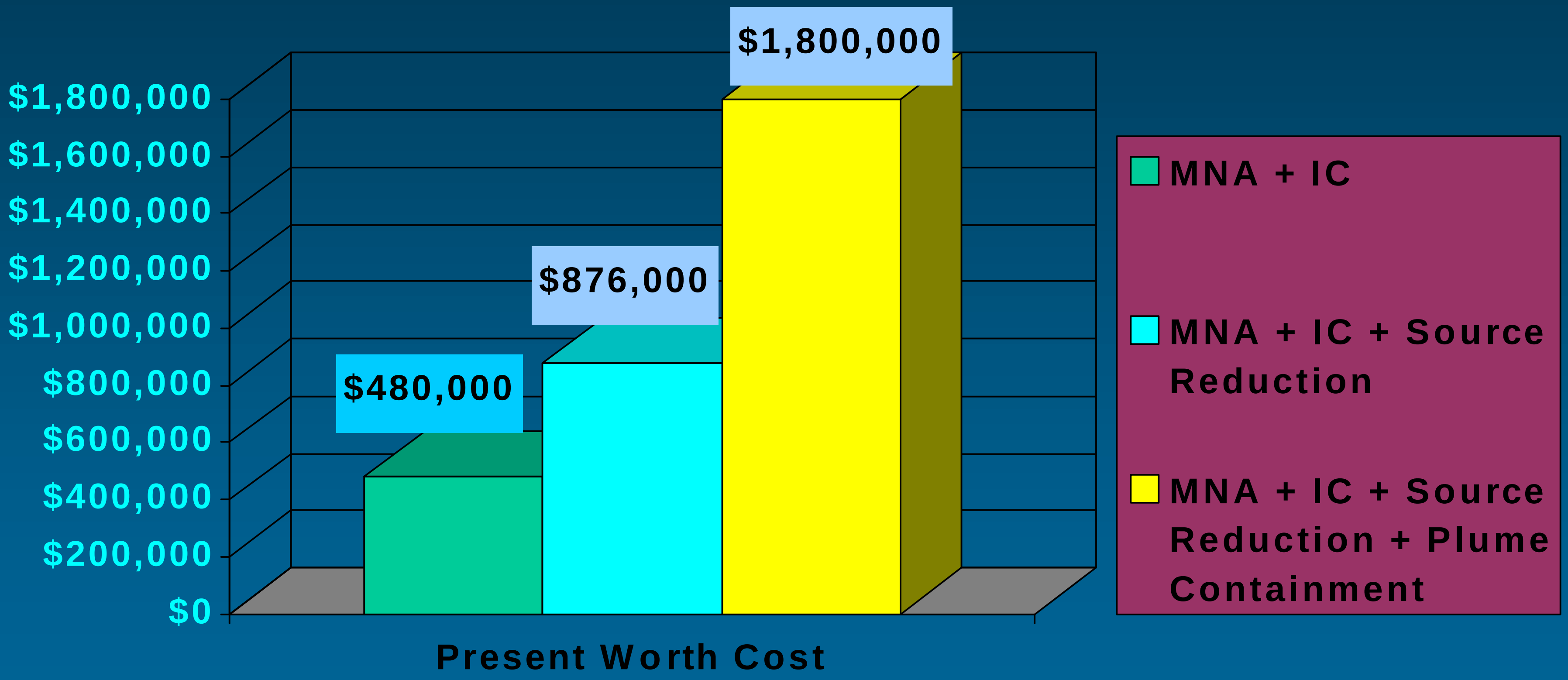
Solute Fate and Transport Modeling

- Out of 13 Plumes Models Predicted:
  - 2 Plumes at Steady-State
  - 1 Plume Expanding Along Sewer Line Corridors
  - 4 Plumes Discharging to a Surface Water Body
  - 6 Plumes Expanding (250 to 9,500 ft)

Proposed Remedial Alternatives

- MNA +IC: 2 sites (out of 14)
- MNA, IC, + engineered source reduction and/or hotspot pumping: 7 sites
- MNA, IC, + downgradient plume cutoff: 4 sites
- Insufficient data for recommendation: 1 site

Remedial Alternative Cost Comparisons



Findings of Natural Attenuation Evaluations - Solvents

- **Intrinsic Bioremediation Occurring at Approximately 88% of the Sites Studied (Biased, Probably 40%)**
- **Reductive Dechlorination Occurring at 100% of Sites Impacted with Fuels**
- **Surface Water Impacted at Many Sites**
- **6 of 13 Plumes Expected to Grow**

What Does all of This Mean?

- Some Form of Engineered Remediation may be Required at Many Sites
- Is Pump and Treat the Answer?
- ABSOLUTELY NOT!!!
- Why?

Engineered Bioremediation of Chlorinated Solvents

- **Because Pump and Treat is Expensive and Doesn’t Work**
- **The Limiting Factor at Many Sites Contaminated with Chlorinated Solvents is the Lack of Suitable Oxidizable Organic Carbon**

Engineered Bioremediation of Chlorinated Solvents

- **Many Types of Organic Substrate Have Been Added to Groundwater to Stimulate Biodegradation of Solvents Including:**
  - **Propionate**
  - **Lactate**
  - **Butyrate**
  - **Molasses**
  - **Hydrogen Releasing Compound®**
  - **Hydrogen (“Hindenberg Experiment”)**

Engineered Bioremediation of Chlorinated Solvents

- **All of These Materials are Added to Stimulate the Production of Hydrogen for Reductive Dechlorination**
- **All are Soluble to Some Extent in Water and Many are Miscible**
- **This Means Continuous Injection or at a Minimum, Multiple Injections (With the Exception of HRC®)**

VegOil for Engineered Bioremediation of Chlorinated Solvents

- **Injection of Food-Grade Vegetable Oil as a Carbon Substrate Looks Promising**
- **VegOil is a Non Aqueous Phase Which Means one Time Injection and Slow Dissolution**

Conclusions and Recommendations

- **Pounds of Contaminants Removed via Natural Attenuation Alone Should be Compared Against other Remedial Alternatives – People Will be Amazed**
- **If Engineered Remediation is Required the Focus Should be on In Situ Source Reduction Techniques**

Conclusions

- **Anaerobic Processes Paramount to Chlorinated Solvent Biodegradation**
- **The Common Solvents (PCE, TCE, TCA, and CT) Will Not Biodegrade Unless Strongly Anaerobic Conditions Predominate**

Differences - Fuel Hydrocarbon and Chlorinated Solvent Plumes

- **Fuel Hydrocarbon Biodegradation Will Always Proceed to Completion**
- **Chlorinated Solvent Biodegradation Dependent Upon Many Factors**
- **Chlorinated Solvent Plume Could Run Out of Primary Substrate Before Reductive Dechlorination is Complete**

Conclusions

- It Is Clear That We are Going to Have to Engineer Remediation at Many Sites Contaminated With Chlorinated Solvents
  - Carbon Addition may be the Key
  - The Problem is the Delivery Mechanism