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

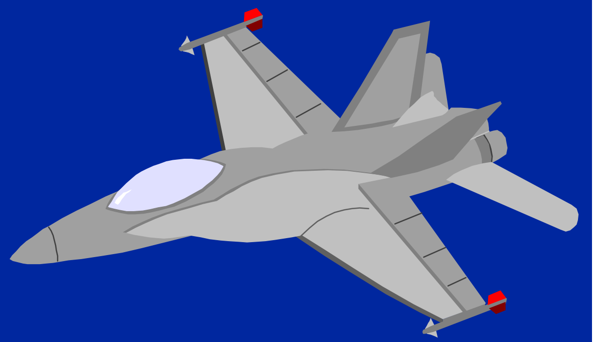
The BIOSCREEN Natural Attenuation Model

U.S. AIR FORCE

Charles J. Newell, Ph.D., P.E.
Groundwater Services, Inc.

Jan. 31, 2001

Team Members and Funding



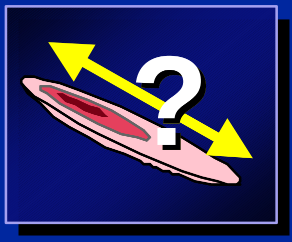
- **K. McCleod**
  GSI / Radian

- **Jim Gonzales, Ross Miller**
  AFCEE Tech Transfer Division

Funded by AFCEE Tech Transfer Division

Talk Outline

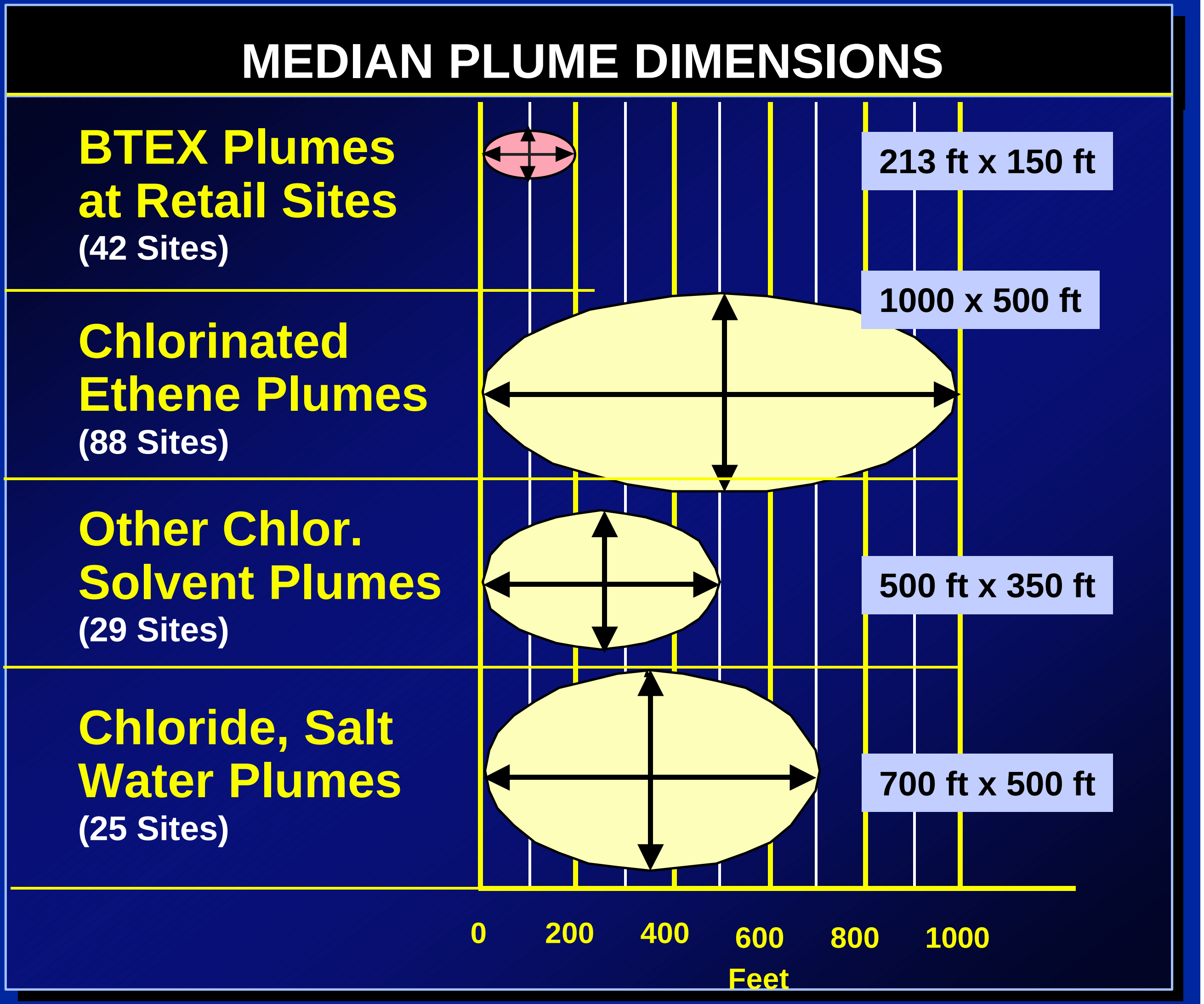
- *INTRODUCTION*
- *BIOSCREEN Natural Attenuation Model*
- *BIOCHLOR Natural Attenuation Model*
- *BIOPLUME III Natural Attenuation Model*



BTEX Plumes vs. Other Plumes

Data from HGDB Hydrogeologic Database

(Newell et al., 1990; API, 1989)



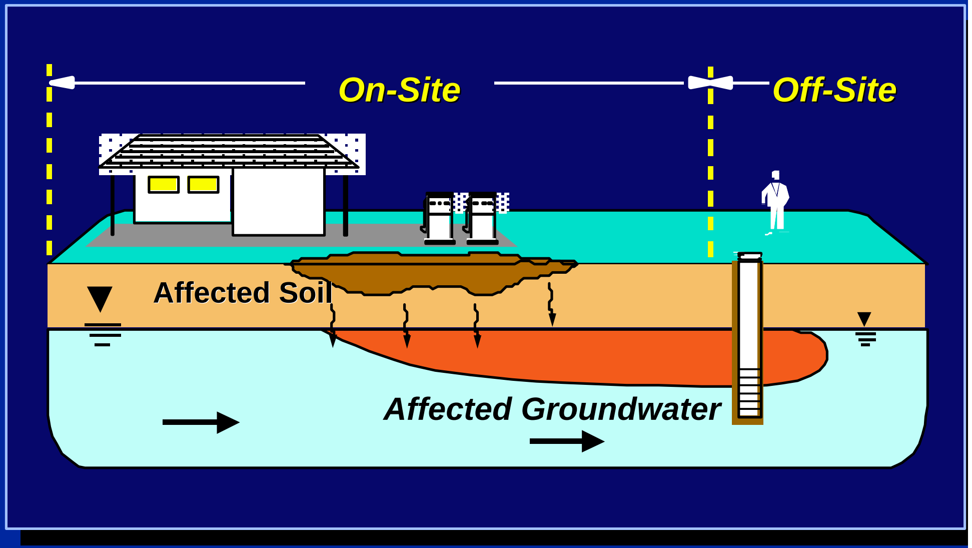
BIOSCREEN Processes

Key Concept:

- Applies to Most Types of Sites Except Some of Biodeg.

Key Processes:

- Advection
- Dispersion
- Adsorption
- Biodegradation

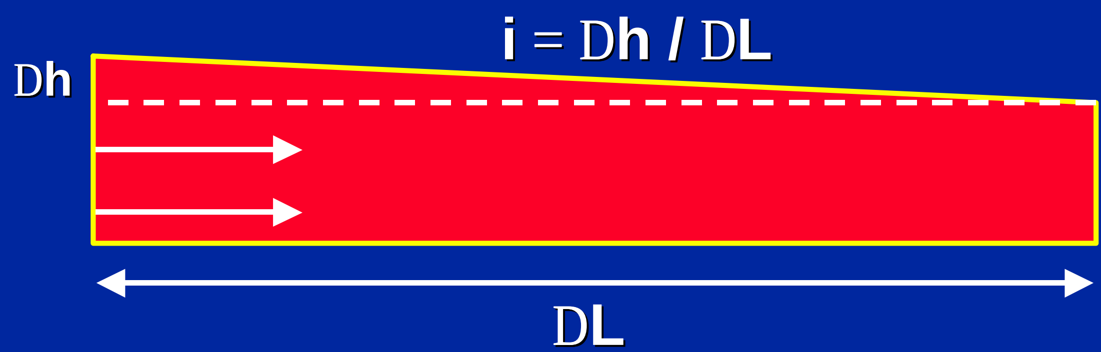


Advective Transport

"Advection" refers to the bulk motion of a fluid.

$$V_d = K\ i$$

$$V_s = \frac{K\,i}{n}$$



V_d = Darcy velocity (cm/s, ft/d, etc.)

V_s = Seepage velocity [cm/s, ft/d, etc.]

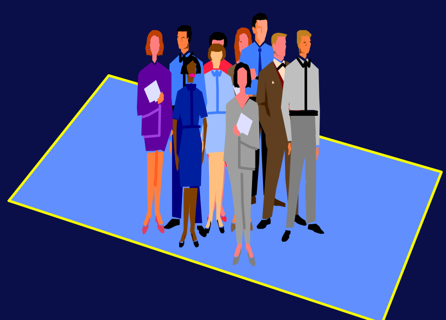
K = hydraulic conductivity [cm/s, ft/d, etc.]

i = hydraulic gradient [cm/cm, ft/ft, etc.]

n = effective soil porosity (dim)

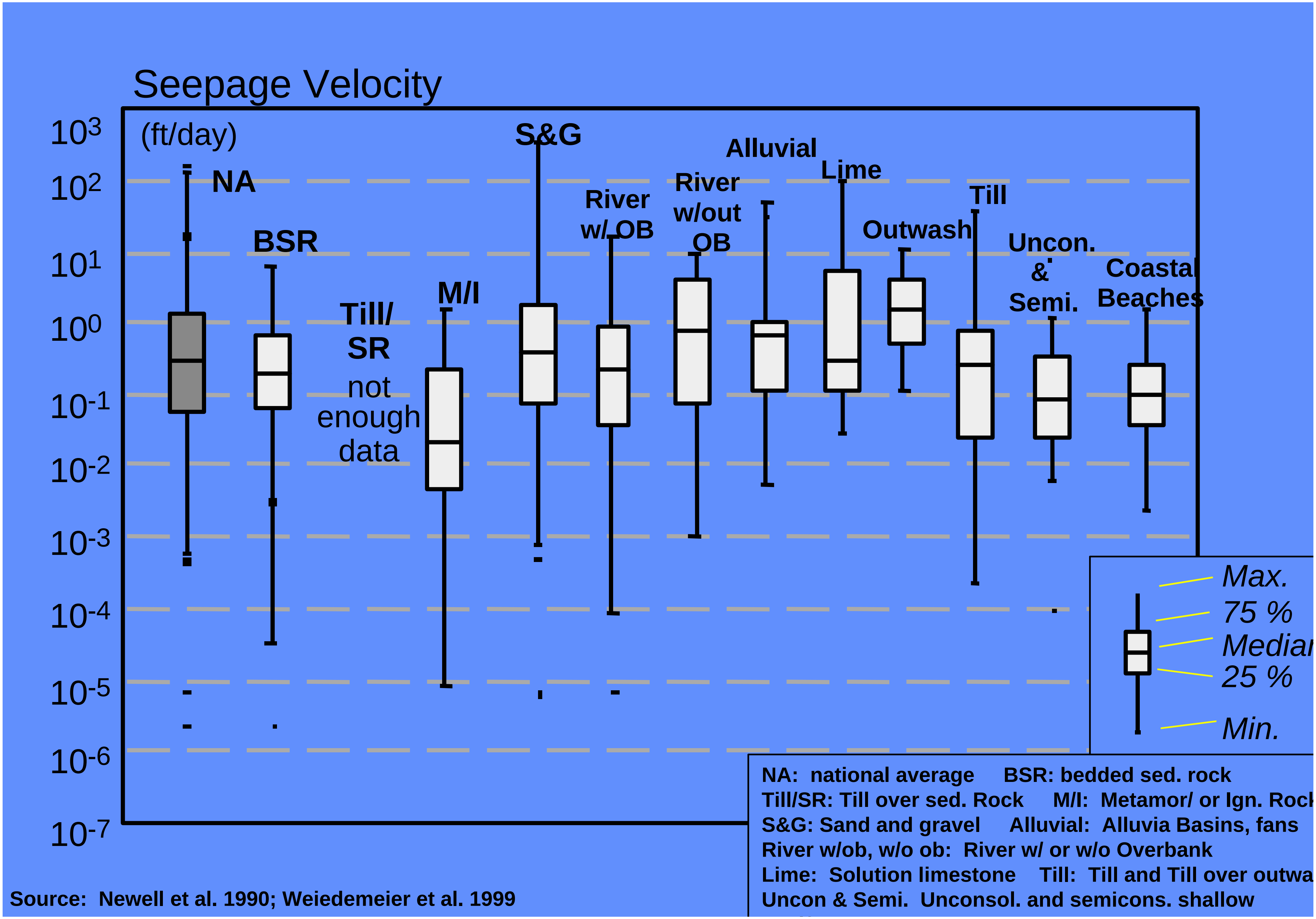
Parameters for Advection

Parameter	Measure?	Estimate?
• Hydraulic Conduct.	Slug, Pump Test	*5 x 10^{-3} cm/sec (HGDB National Median)*
• Hydraulic Gradient	Pot. Map	*0.006 ft/ft (HGDB National Median)*
• Effect. Porosity	*Lab Test*	*ASTM: 0.38* *Others: 0.25*



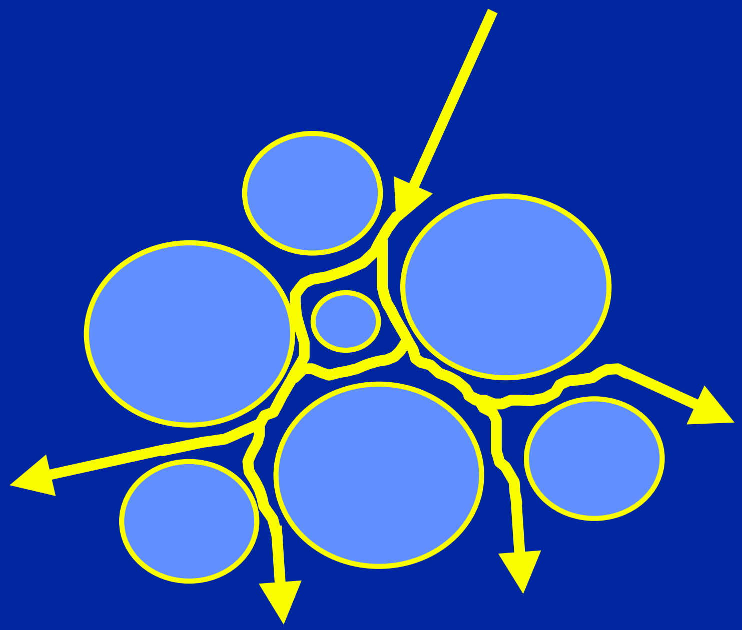
HGDB National Median
Seepage Velocity:

25%: 30 ft/yr
Median: 88 ft/yr
75%: 400 ft/yr


Seepage Velocity
(ft/day)
10³
10²
10¹
10⁰
10⁻¹
10⁻²
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
NA
BSR
Till/
SR
not
enough
data
M/I
S&G
River
w/ OB
River
w/out
OB
Alluvial
Lime
Outwash
Till
Uncon.
&
Semi.
Coastal
Beaches
Max.
75 %
Median
25 %
Min.
NA: national average
BSR: bedded sed. rock
Till/SR: Till over sed. Rock
M/I: Metamor/ or Ign. Rock
S&G: Sand and gravel
Alluvial: Alluvia Basins, fans
River w/ob, w/o ob: River w/ or w/o Overbank
Lime: Solution limestone
Till: Till and Till over outwa
Uncon & Semi. Unconsol. and semicons. shallow
Source: Newell et al. 1990; Weiedemeier et al. 1999

Dispersion

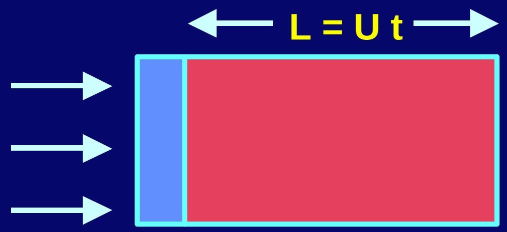
"Dispersion" refers to the in-situ micro-scale mixing that results as a fluid flows through a porous medium.



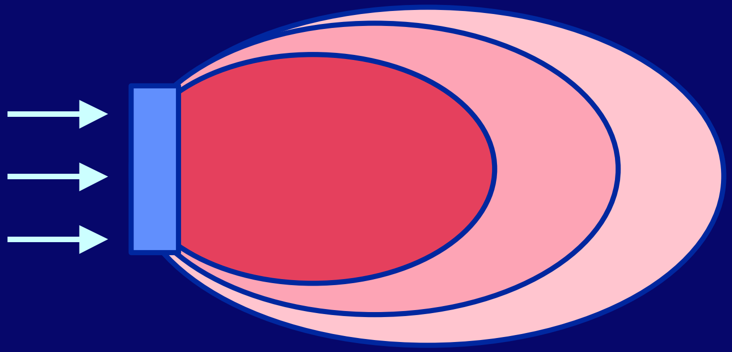
Hydrodynamic Dispersion

The extent of spreading, or mixing, caused by dispersion is characterized by a "dispersion coefficient," D [ft^2/d, cm^2/s, etc.],

where { width of spreading in direction i } → Is related to the seepage velocity and "dispersivity"



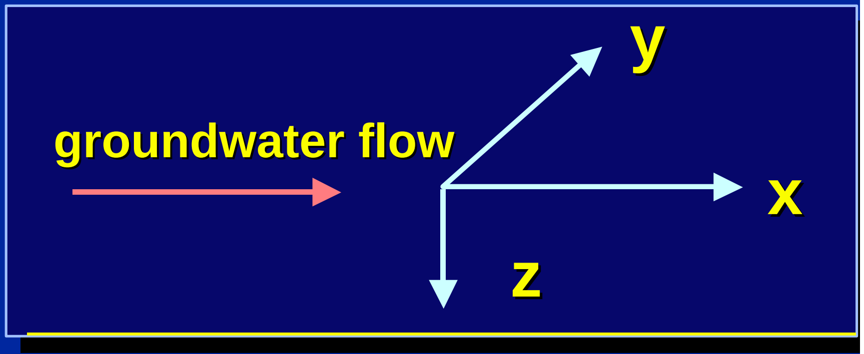
Transport at time t without dispersion



Transport at time t with dispersion

Dispersivities in Three Directions

Dispersion coefficients are typically expressed as the product of a "dispersivity" and the groundwater velocity vs:

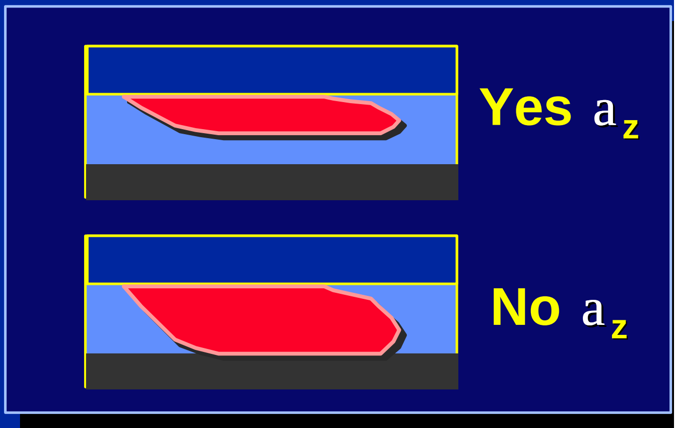


a_x = longitudinal (x-direction) dispersivity

a_y = transverse (y-direction) dispersivity

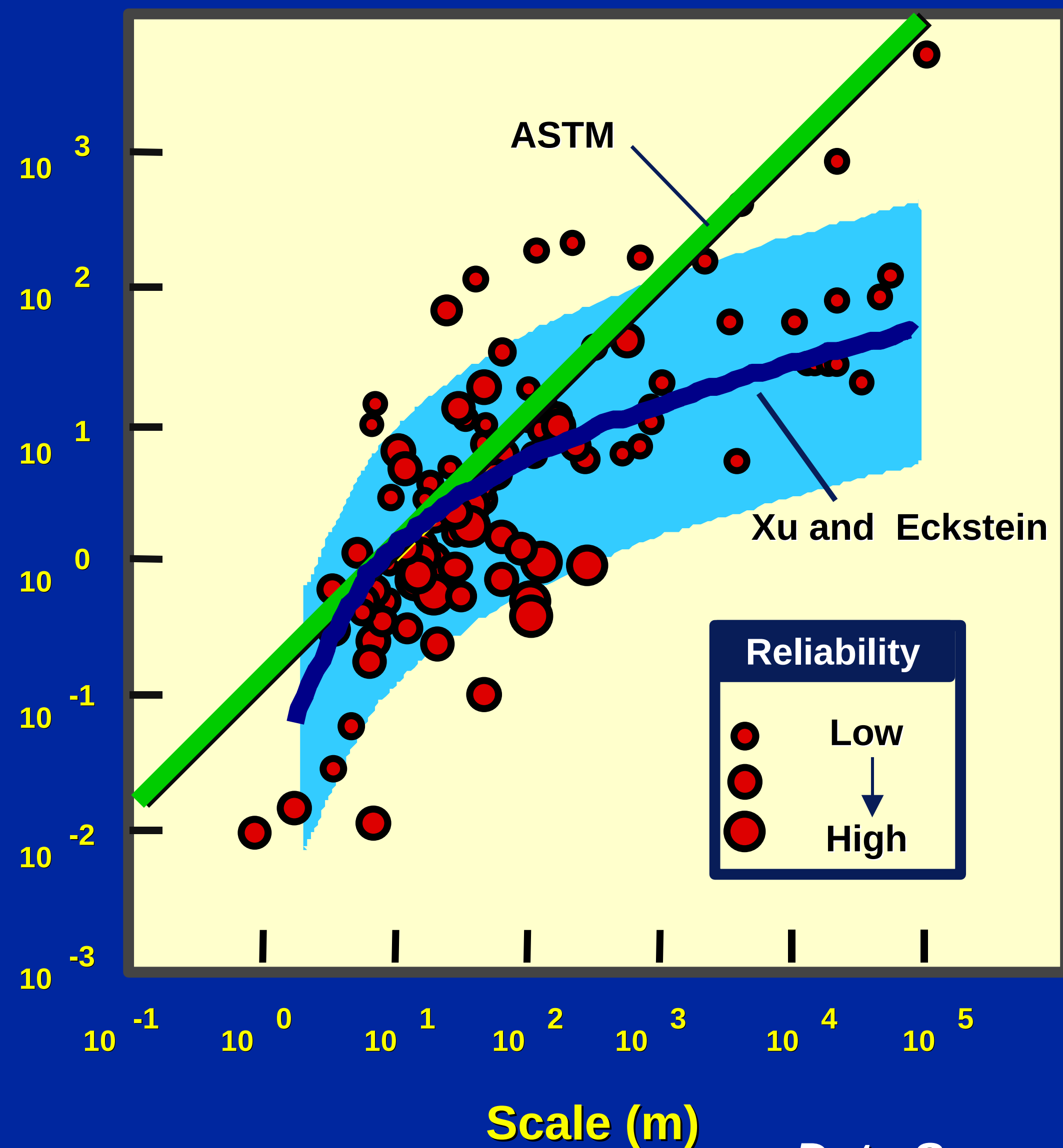
a_z = vertical (z-direction) dispersivity

(Note: If plume extends throughout vertical extent of the saturated zone, there is no vertical dispersion and a_z is a very low number.)



REQUIRED DATA: a_x, a_y, a_z **[ft, m, cm, etc.]**

Estimating Dispersivity



Dispersivity is correlated to "scale"

Dispersivity is NOT strongly correlated to permeability, aquifer material, grain size, other geologic factors

Data Source: Gelhar et al., 1992

Hydrodynamic Dispersion

Rules of Thumb are usually used to estimate the dispersivities - and are based on size of plume, not geology

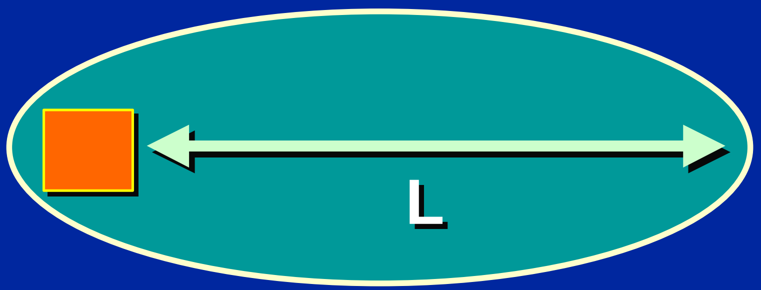
$a_x = L/10$

$a_x = 0.83[\log(L)]^{2.414}$ (Xu/Eckstein relationship)

$a_Y = a_x/3$ or $a_x/10$

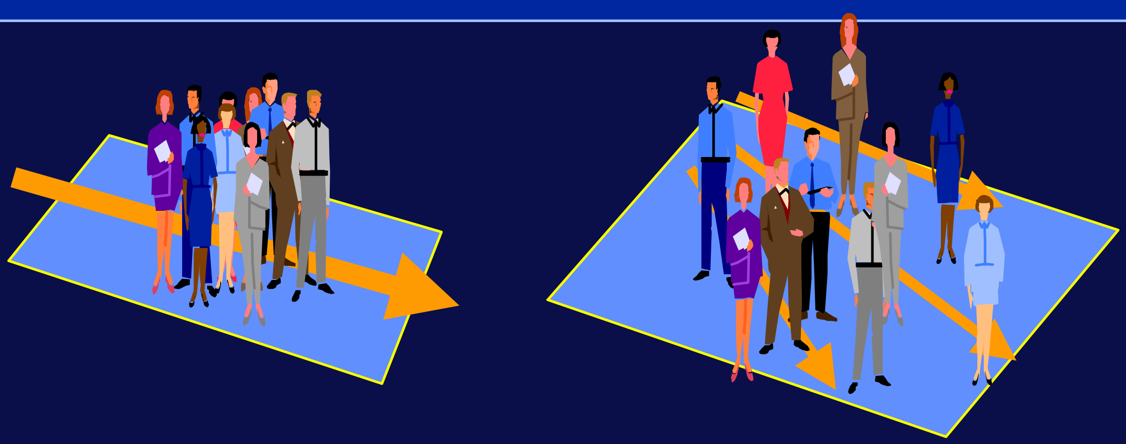
$a_z = a_Y/10$

L = distance away from source



Parameters for Dispersion

Parameter	Measure?	Estimate?
• Longitudinal Dispersivity	*no*	ROT / 10- 70 ft
• Transverse Dispersivity	*no*	10% of Long.D.
• Vertical Dispersivity	*no*	10^{-99} or 10% of Trans. D.



Very Rough ROT:

Dispersion not important if plume < 1000 ft long

Groundwater Transport Processes

Sorption Effects

Due to sorption to naturally occurring carbon on the aquifer matrix, dissolved hydrocarbons move at a slower speed than that of the bulk groundwater movement.

$$V_{hc} = \frac{V_s}{R}$$

$$R = 1 + \frac{k_d \, r_s}{n}$$

V_{hc} = contaminant velocity [cm/s, ft/d, etc.]

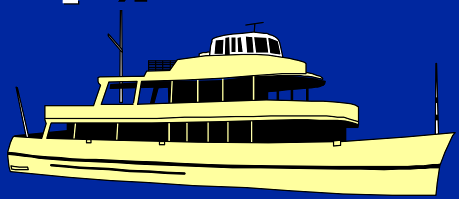
V_s = groundwater seepage velocity [cm/s, ft/d, etc.]

R = retardation factor

k_d = soil-water distribution coefficient [(mg/kg-soil)/(mg/l-H_2O)]

r_s = soil bulk density [g_{dry}-soil/cm^3-soil]

n = effective soil porosity [l-H_2O/l-soil]



Where Does k_d Come From?

- Estimation of distribution coefficient (k_d) for organic chemicals.

$$k_d = K_{oc} \times f_{oc}$$

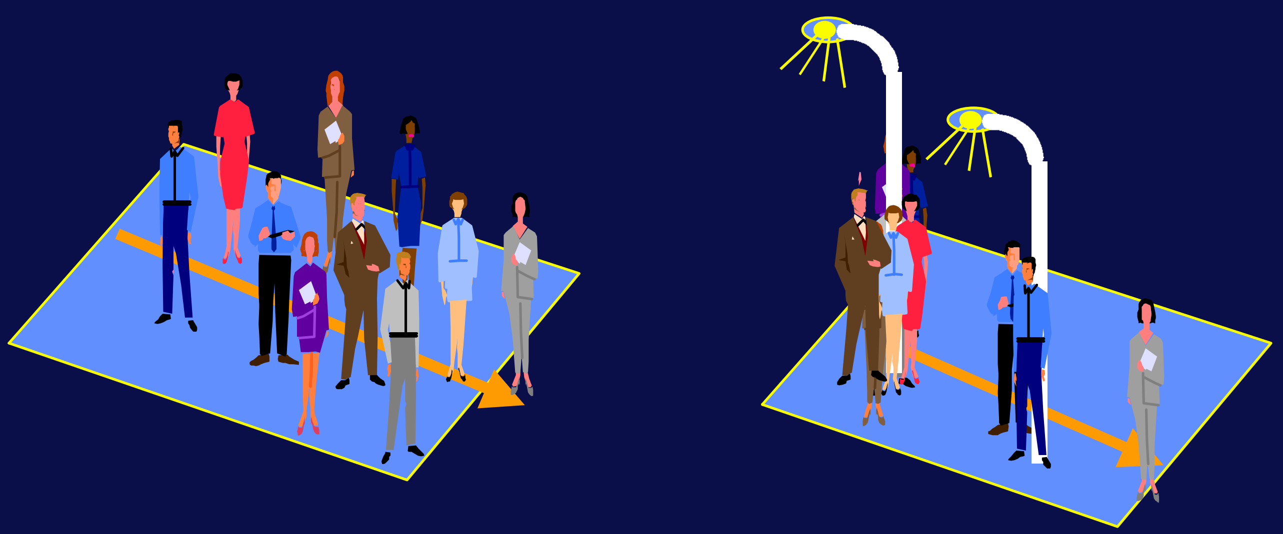
$$k_d = \frac{C_s}{C_w}$$

k_d = soil-water distribution coefficient ([mg/kg-soil]/[mg/l-H_2O])
f_{oc} = fraction of organic carbon in soil (unitless)
K_{oc} = organic carbon partition coefficient (mg/mg/mg/l)

- estimated using regression equations
- obtained from the literature, reference books, chemical databases

Parameters for Adsorption

Parameter	Measure?	Estimate?
Bulk Density (r_b), Porosity	~~Not typical~~ **Soil sample** (clean part of water-bearing zone)	r_b: 1.7 g/cm^3
Fraction organic carbon (foc)		ROT: 0.001 g/g
Partition Coefficient (koc)	No	Book value: 1-500 L/kg



ROT for Typical R Values:

BTEX: 1.2 -2.0

Solvents: 1.5 -5.0

Groundwater Transport Processes

Biodegradation

Indigenous micro-organisms are capable of degrading most fuel-range petroleum hydrocarbons. These organisms are typically found at cell densities of 10^4 - 10^6 cells/g-soil (based on plate counts).

For example, for the aerobic reaction:

$$C_6H_6 + 15/2\ O_2 \text{ --> } 6\ CO_2 + 3\ H_2O$$

Here, the hydrocarbon acts as an electron donor, an energy source and a source of carbon for growth of new bacteria cells.

First Order Decay Model

- Simplification of M-M Model
- Fewer parameters required
- Mathematically simple
- Assumptions: $C << K_s$, X is constant

$$\text{Rate} = \frac{-k_s X C}{K_s + C}$$

→

$$\text{Rate} = -l C$$

Biodegradation: First Order Decay

Most hydrocarbon degradation reactions are treated as being "first-order" reactions:

{ rate of disappearance } is proportional to { concentration of hydrocarbon }

$$\text{rate} = -\lambda C$$

λ is a called a "rate constant."

First-Order Decay Model

$$\frac{dC}{dt} = -\lambda C$$

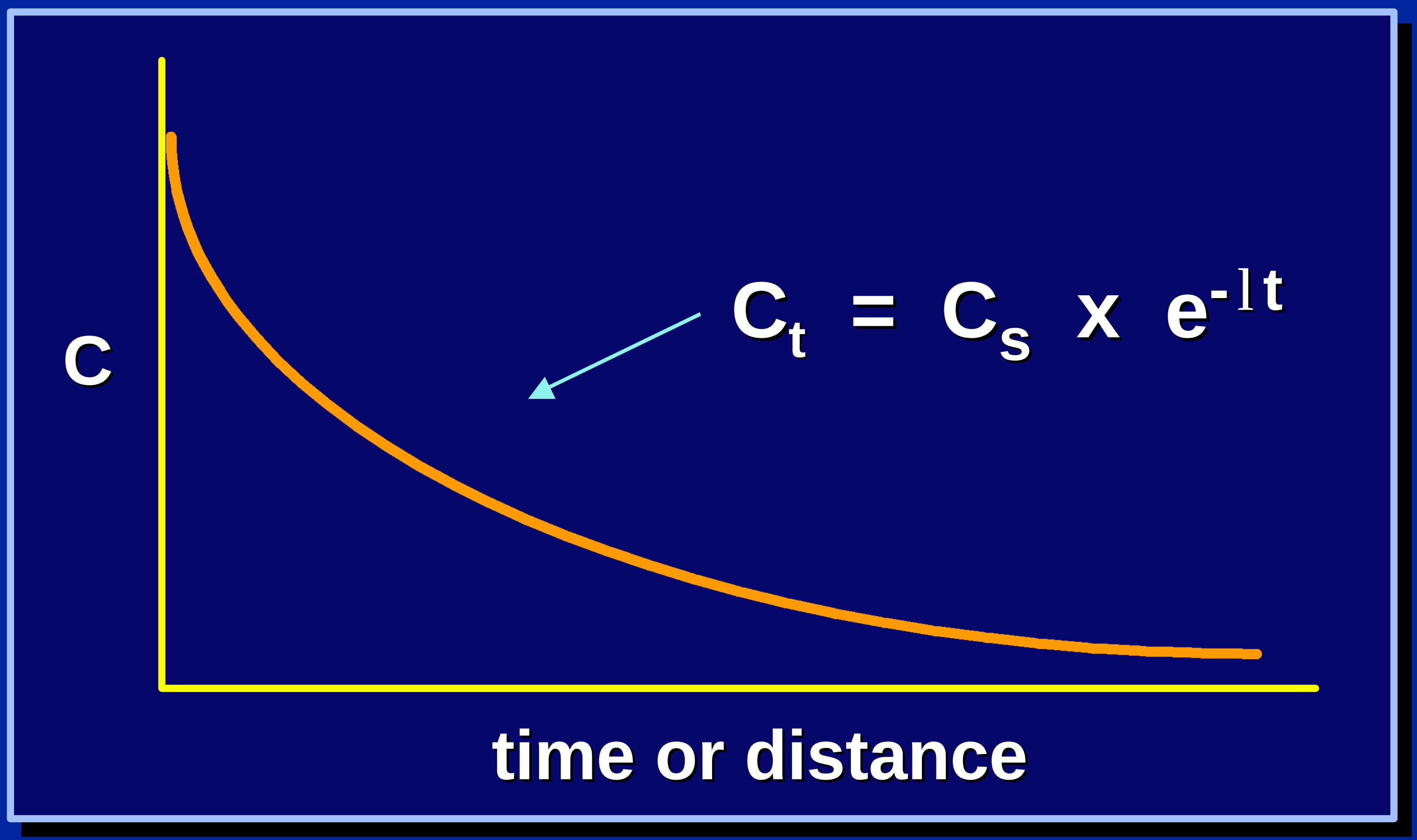
$$C_{(t)} = C_o e^{(-\lambda t)}$$

$C_{(t)}$ = concentration at time t (mg/L)

C_o = initial concentration (mg/L)

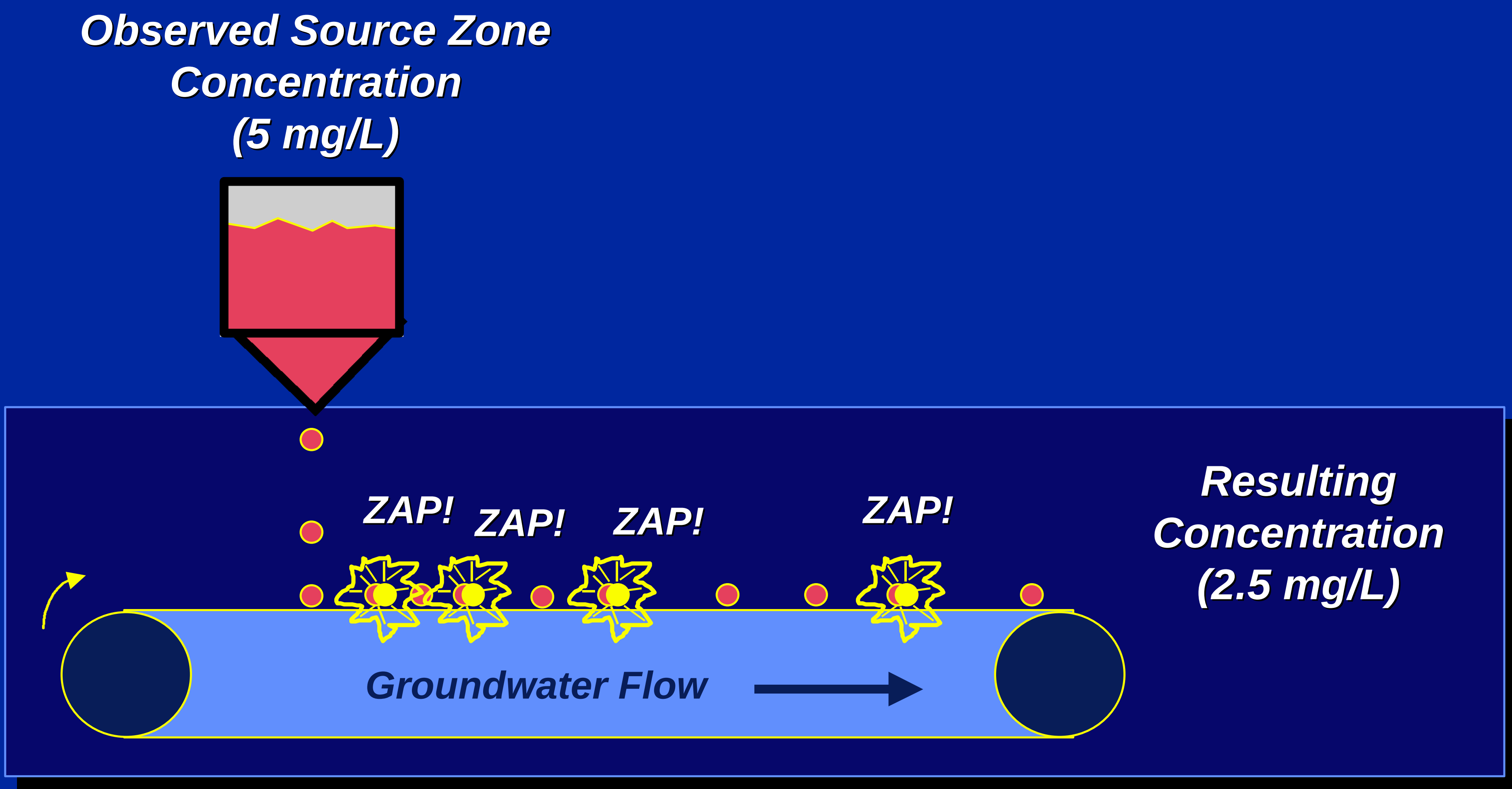
λ = first order decay rate constant (l / t)

First Order Decay Model



First Order Decay Biodegradation

Conceptual Model



Biodegradation Half-Life

The half life of a chemical is defined as the time it takes for the first order reaction to transform half of the initial mass of the chemical. If C(t)/Co is replaced with 0.5, then:

$t_{half} = -(\ln 0.5)/l$ or $t_{half} =$ **0.693/ l**

t_{half} = half life of the chemical (days). Example:

l = 1.386/yr	t_{half} = 0.5 yrs
and	
l = 2.77/yr	t_{half} = 0.25 yrs

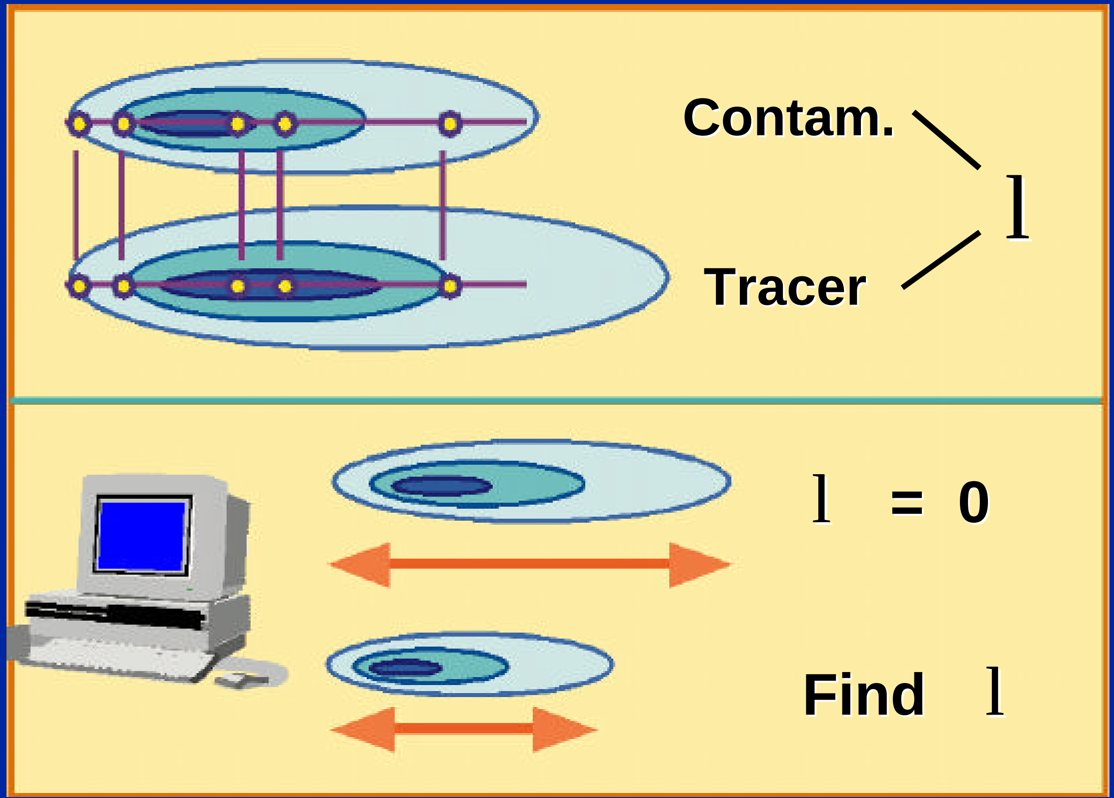
Parameters for Biodegradation

Parameter	**Measure?**	**Estimate?**
• First Order Decay Rate Constant (l)	Calibrate to site data	Literature values

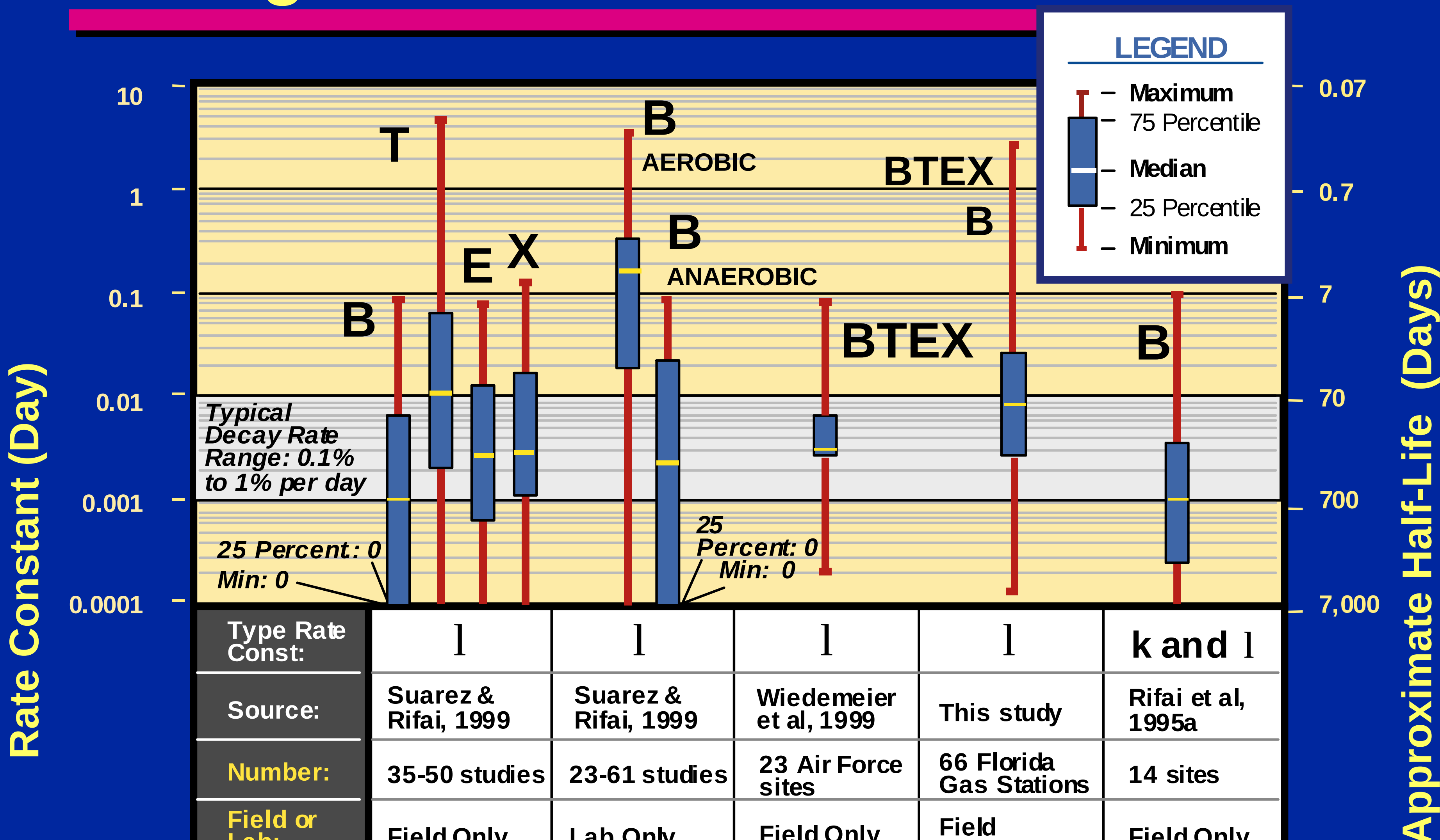
Type of Rate: Biodegradation Rate Constant (lambda - l)

Represents:
Biodegradation rate of dissolved constituents. Used to estimate how far a plume will migrate.

It <u>should not</u> be used to estimate the time required to reach a remediation goal.



Biodegradation Rate Constants

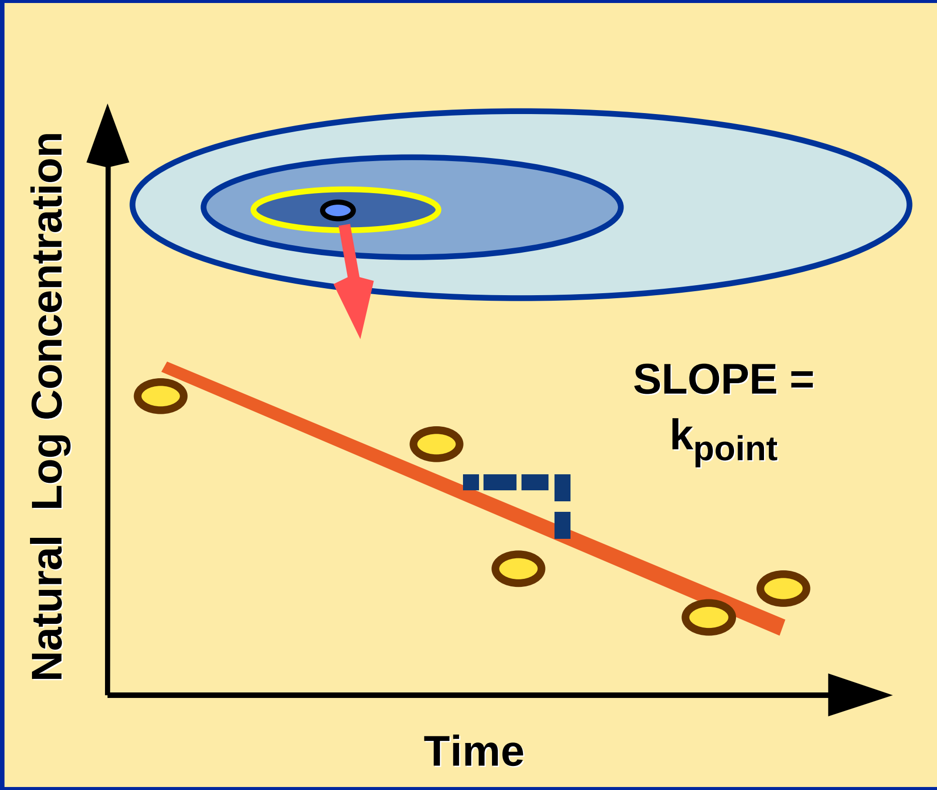


Type Rate Const:	λ	λ	λ	λ	k and λ
Source:	Suarez & Rifai, 1999	Suarez & Rifai, 1999	Wiedemeier et al, 1999	This study	Rifai et al, 1995a
Number:	35-50 studies	23-61 studies	23 Air Force sites	66 Florida Gas Stations	14 sites
Field or Lab:	Field Only	Lab Only	Field Only	Field	Field Only
Consti-tuents:	B, T, E, X	Benzene	BTEX	Benzene and BTEX	Benzene

Type of Rate: Point Decay Rate (k_{point}) Constant

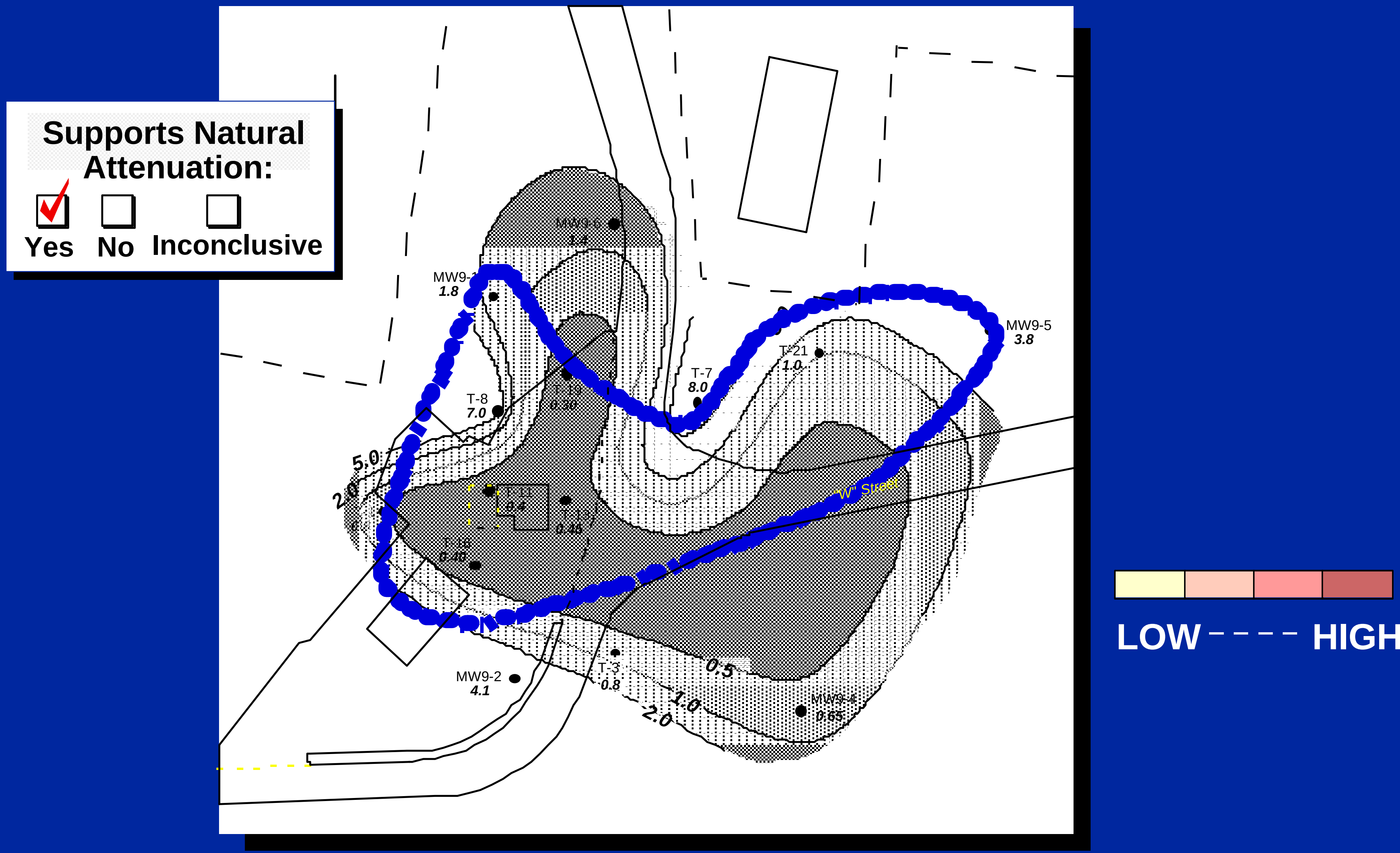
Represents:
Primarily change in source strength over time (also called k_{source}).

It <u>should not</u> be used to describe biodegration in models!



Keesler Air Force Base

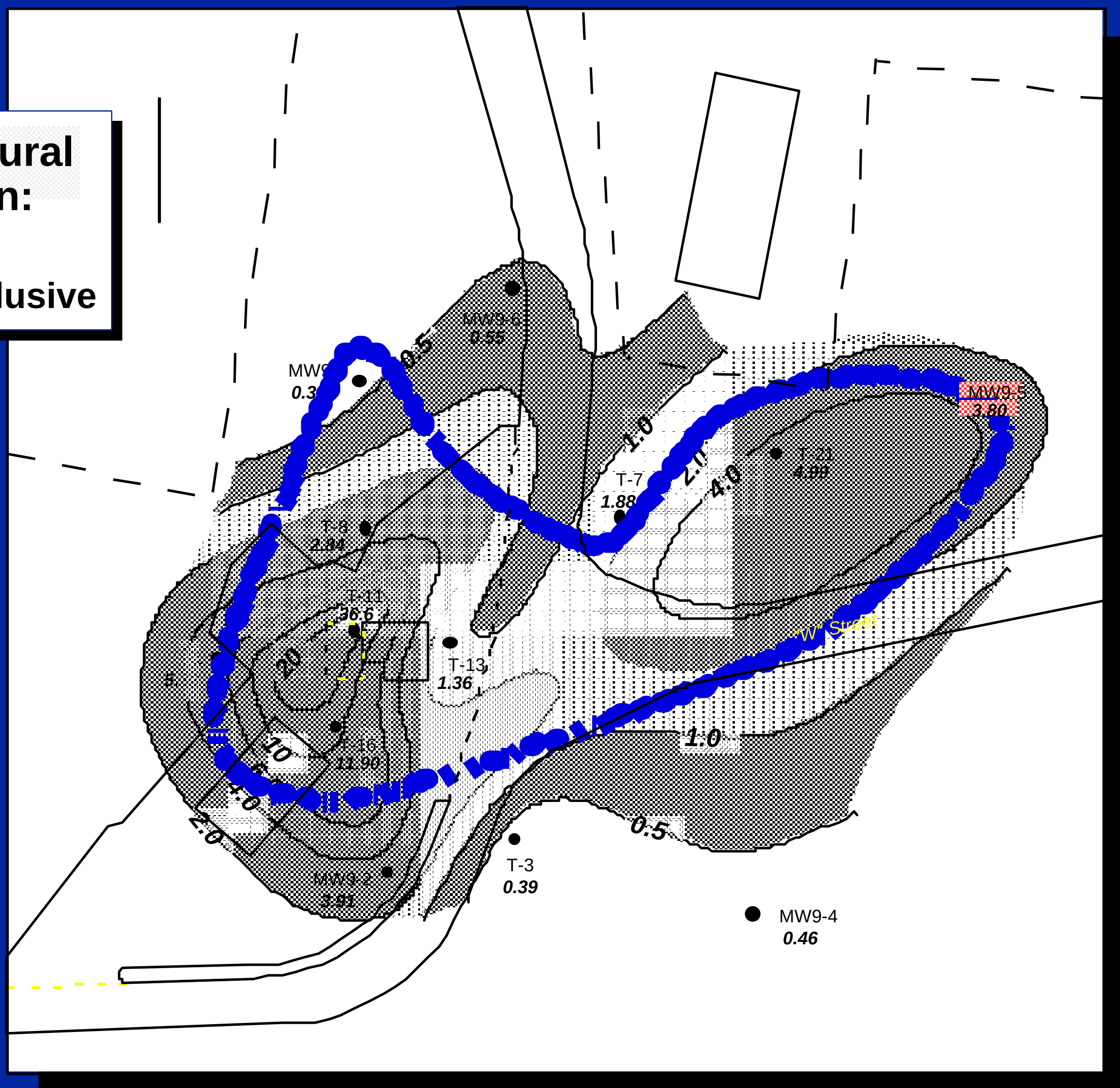
Dissolved Oxygen in Groundwater (mg/L)



Dissolved Ferrous Iron in Groundwater (mg/L)

Supports Natural Attenuation:

☑ Yes ☐ No ☐ Inconclusive

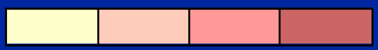


LOW - - - - HIGH

Sulfate in Groundwater (mg/L)

Supports Natural Attenuation:

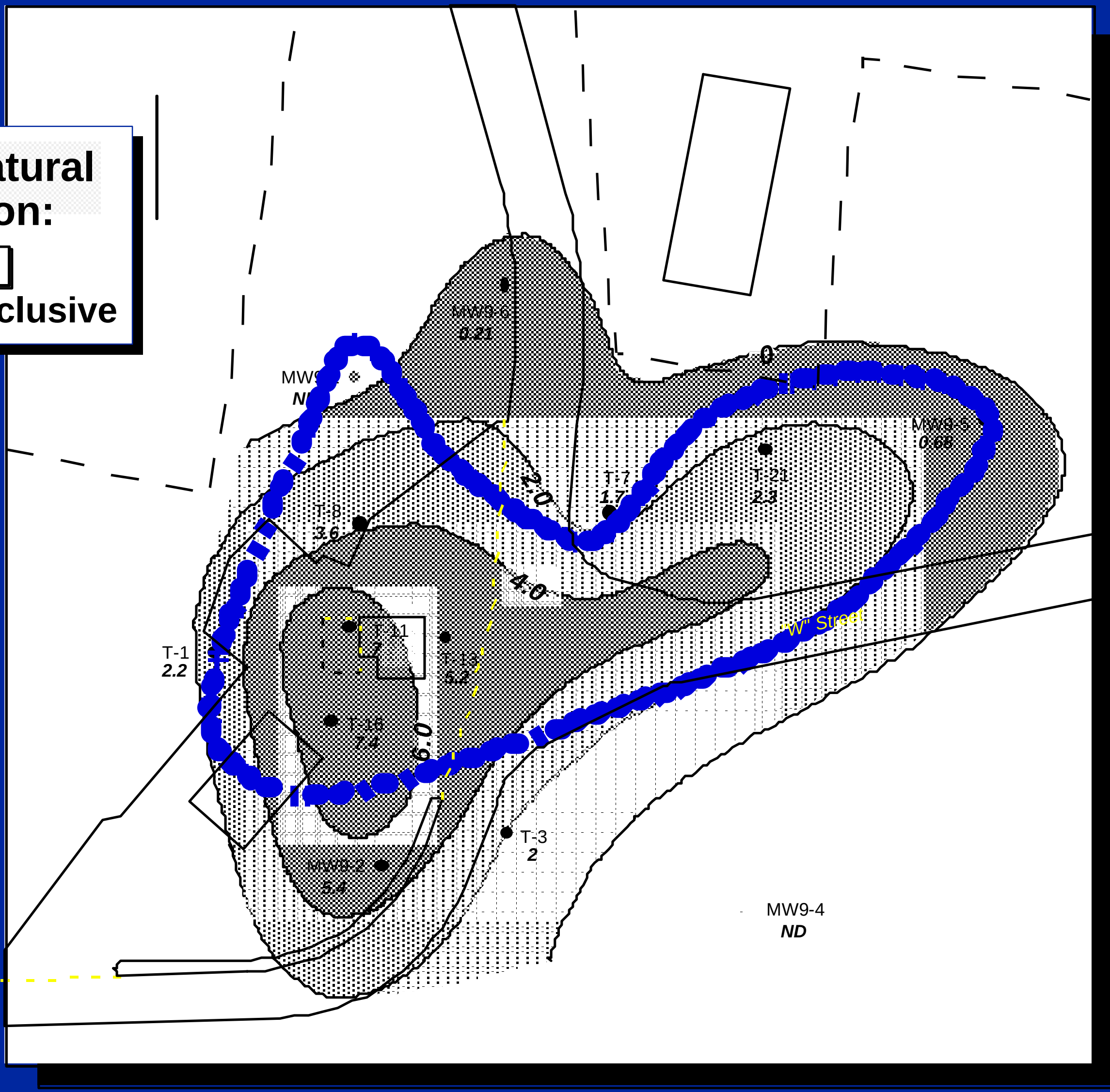
☑ Yes ☐ No ☐ Inconclusive

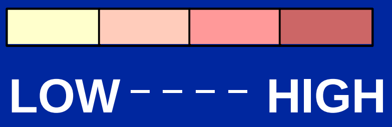


Methane in Groundwater (mg/L)

Supports Natural Attenuation:

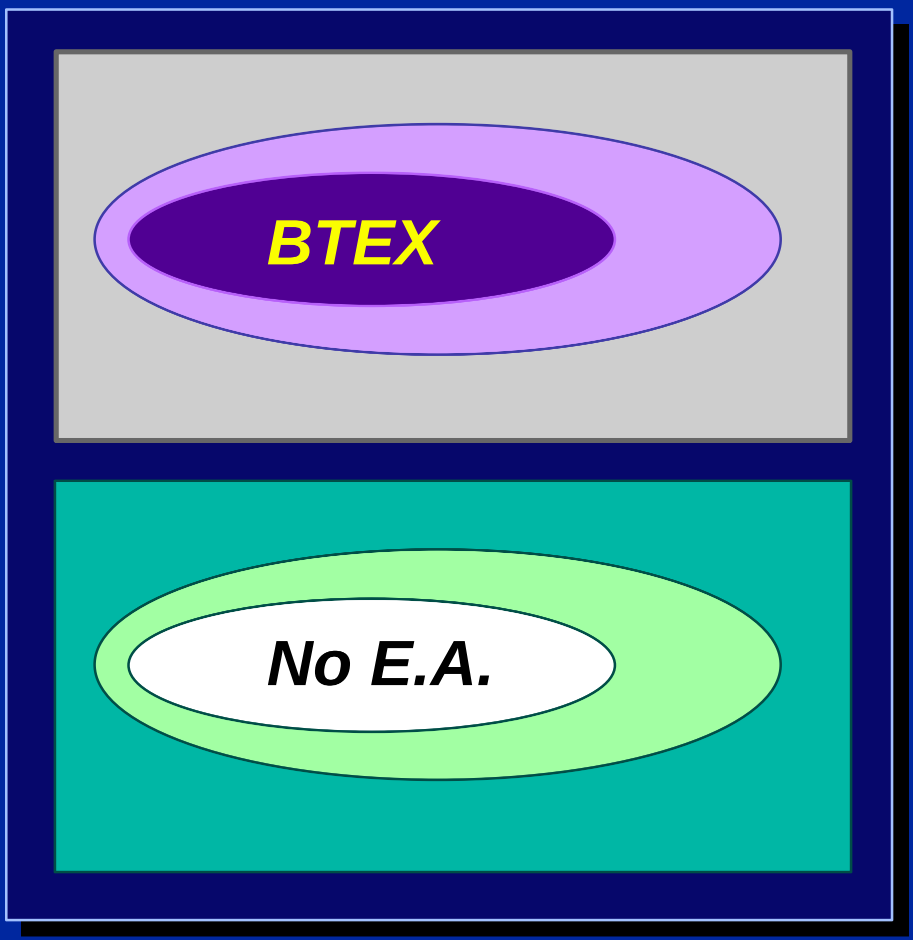
☑ Yes ☐ No ☐ Inconclusive





Electron Acceptor	Type of Reaction	Metabolic By-Product	Redox Potential (pH =7 in volts)	Reaction Preference
Oxygen	Aerobic	CO_2	+ 820	Most Preferred
Nitrate	Anaerobic	N_2, CO_2	+ 740	
Ferric Iron (solid)	Anaerobic	Ferrous Iron (dissolved)	- 50	
Sulfate	Anaerobic	H_2S	- 220	
Carbon Dioxide	Anaerobic	Methane	- 240	Least Preferred

Instantaneous Reaction Model



Hydrocarbon
+ Electron Acceptor =

Electron Acceptor Only, or
Hydrocarbon Only

Instantaneous or Electron-Acceptor-Limited Reaction

The microbial reaction is assumed to occur much faster than the time required to replenish the electron acceptor by groundwater flow.

Only holds for Fuel Sites (BTEX plumes)!

Electron Acceptor or By-Product	Utilization Factor * (Mass E. Acceptor / By-Prod. Consumed per Mass Dissolved Hydrocarbon Degraded)
Oxygen	3.14 gm/gm
Nitrate	4.9 gm/gm
Ferrous Iron	21.8 gm/gm
Sulfate	4.6 gm/gm
Methane	0.78 gm/gm

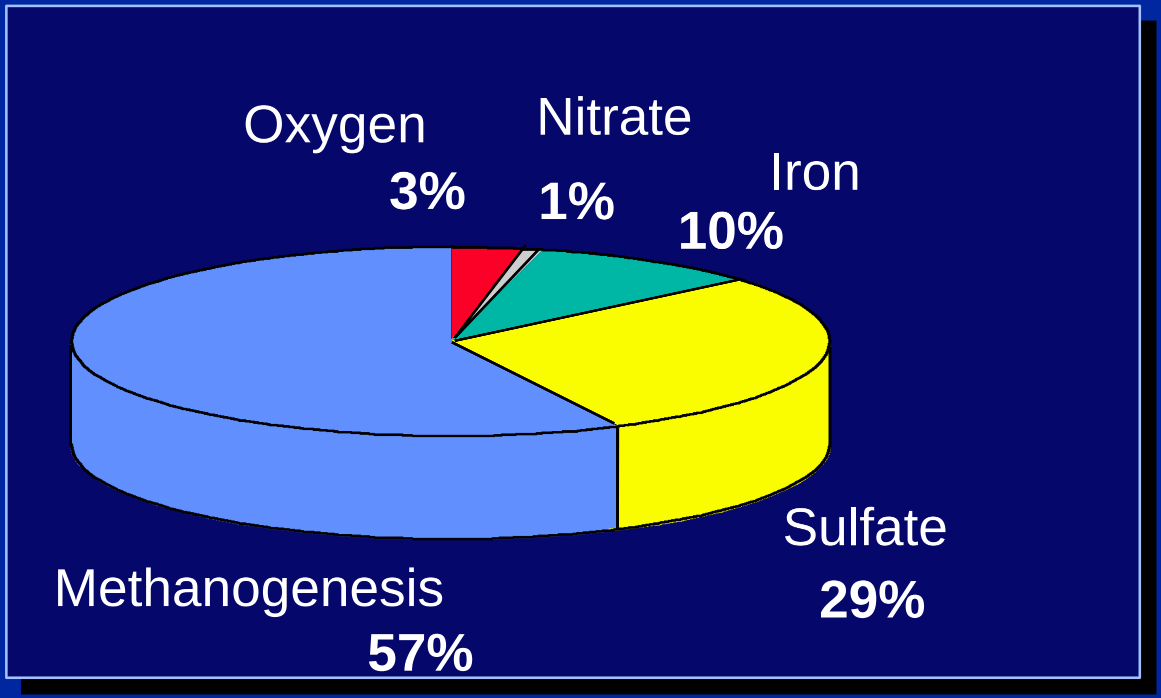
* Based on BTEX

Biodegradation Capacity: 16.7 mg/L

CONCENTRATIONS (mg/L)	D.O.	NO_3	Iron	SO_4	CH_4
Background	2	0.7	0.5	26.2	0
Source	0.4	0	36.6	3.8	7.4
Utilization Factor	*3.14*	*4.9*	*21.8*	*4.6*	*0.78*
BIODEG. CAPAC.	0.5	0.1	1.7	4.9	9.5

Contribution to Biodegradation Capacity

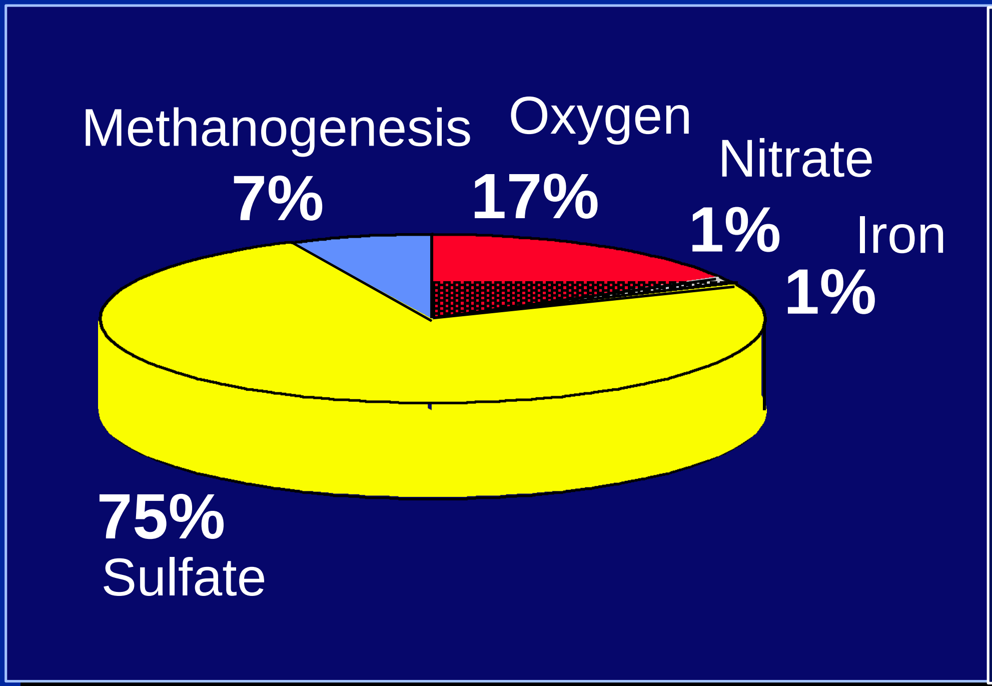
SWMU 66
KEESLER AFB, MISSISSIPPI



TOTAL BC: 16.7 mg/L

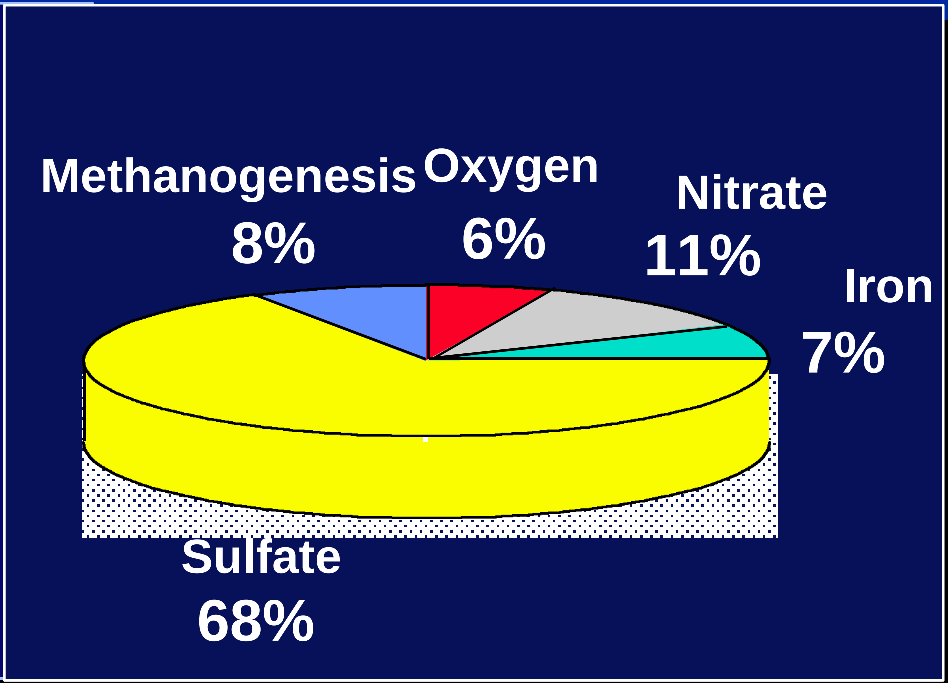
Contribution to Biodegradation Capacity

Bldg. 735,
GRISSOM AFB, INDIANA



TOTAL BC: 17.4 mg/L

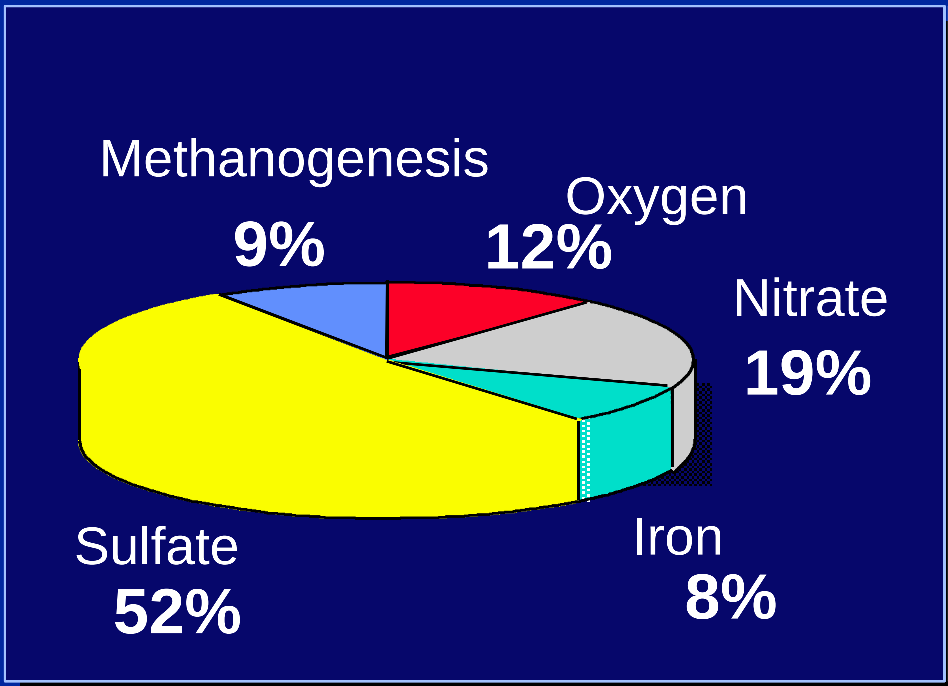
POL Site,
HILL AFB, UTAH



TOTAL BC: 31.6 mg/L

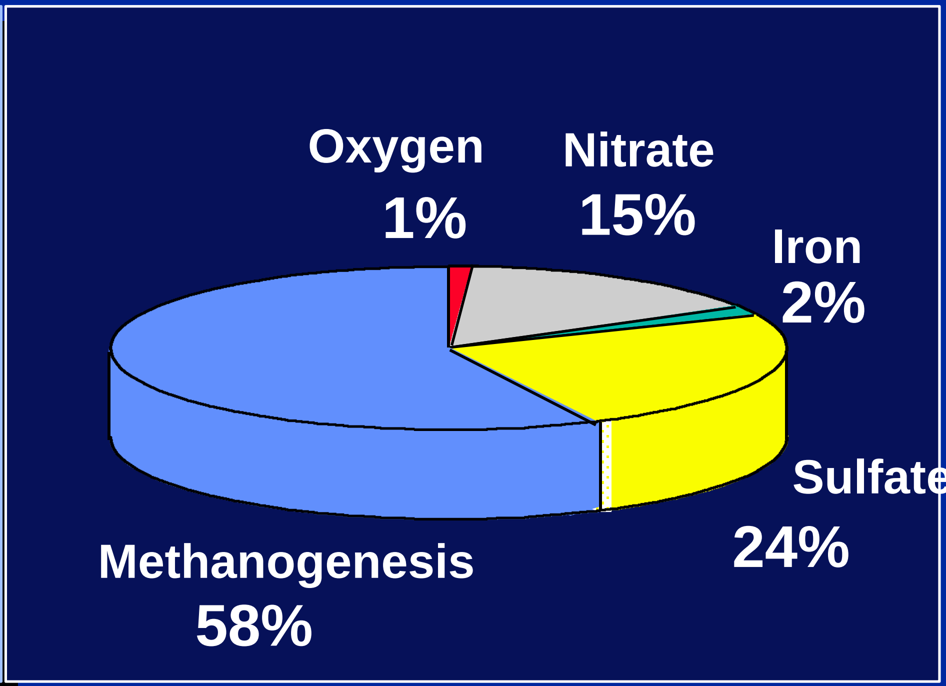
Contribution to Biodegradation Capacity

Site ST-41,
ELMENDORF AFB, ALASKA



TOTAL BC: 23.3 mg/L

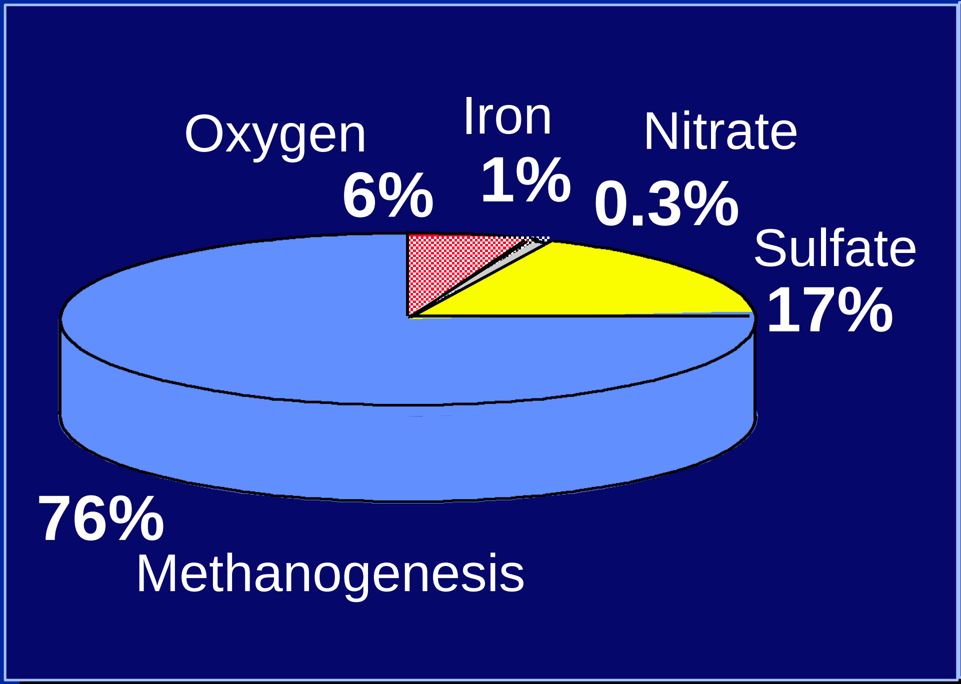
Hangar 10 Site,
ELMENDORF AFB, ALASKA



TOTAL BC: 20.6 mg/L

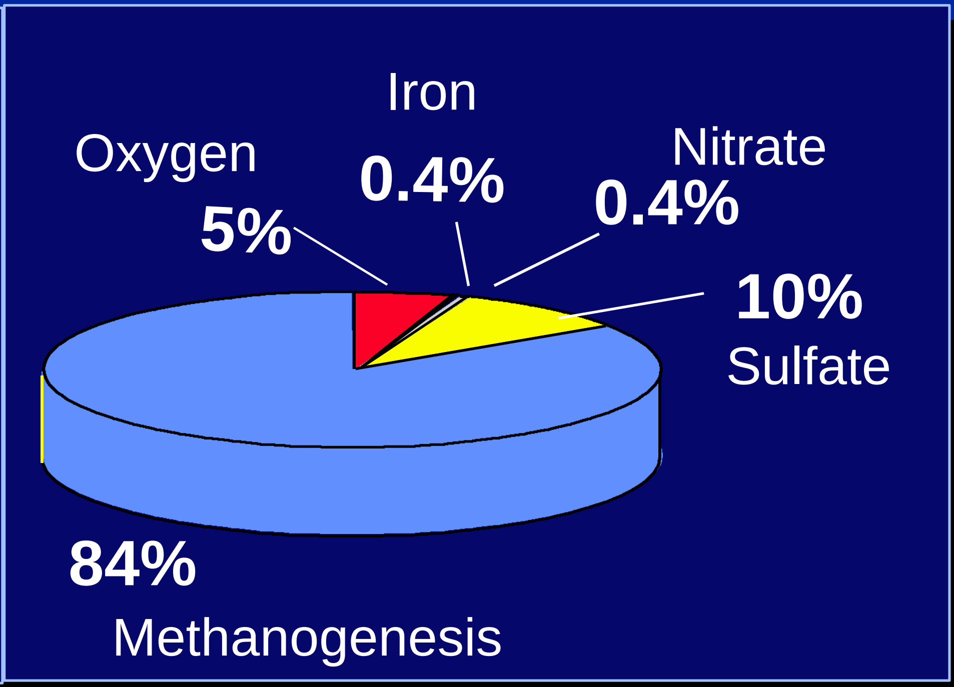
Contribution to Biodegradation Capacity

POL B,
TYNDALL AFB, FLORIDA



TOTAL BC: 7.7 mg/L

Site ST-29,
PATRICK AFB, FLORIDA

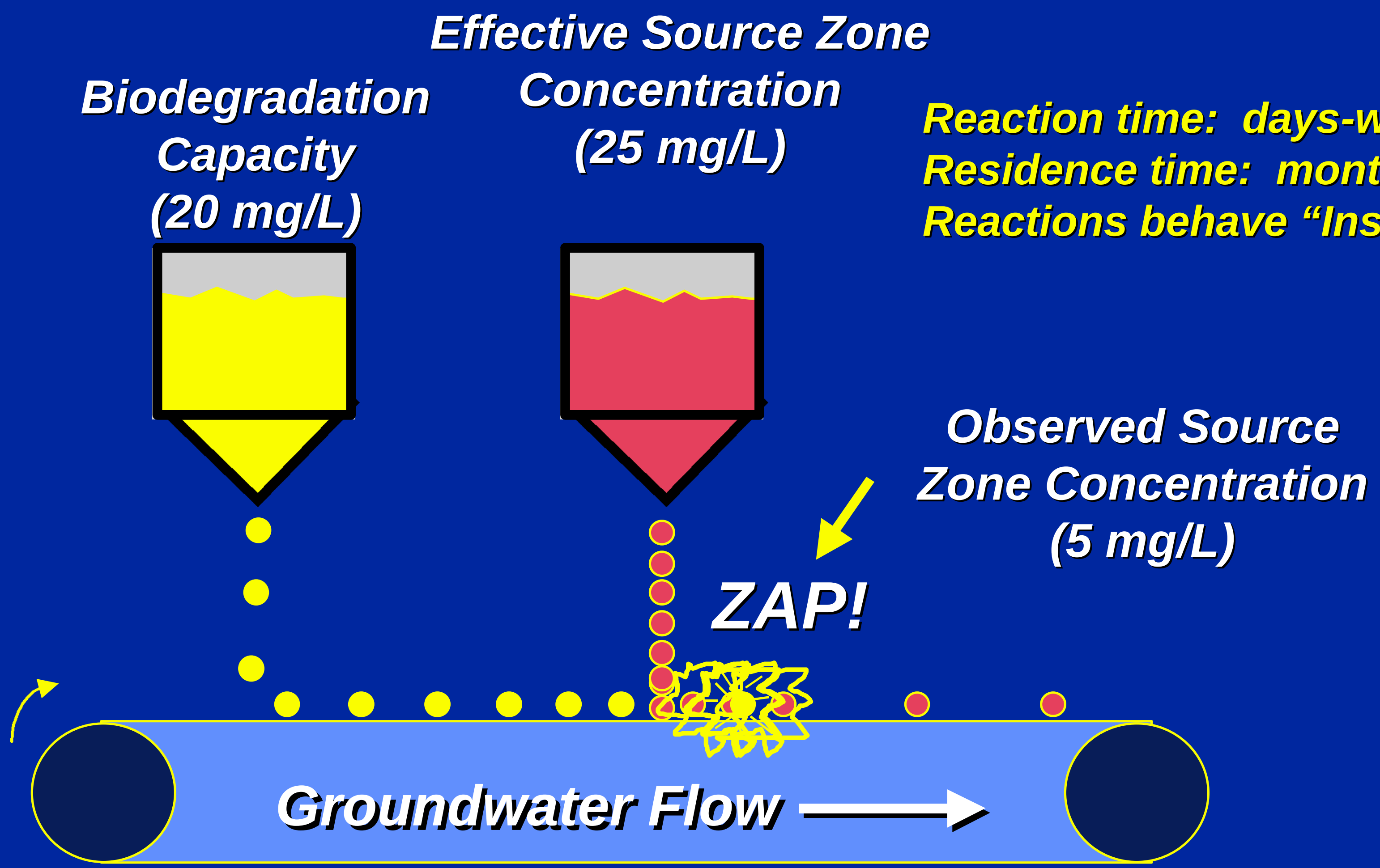


TOTAL BC: 23.1 mg/L

Electron-Acceptor-Limited Biodegradation

Conceptual Model

Reaction time: days-weeks
Residence time: months/years
Reactions behave "Instantaneous"



Biodegradation Capacity

Options:

1. Measure in Field

2. Use Typical Values from BIOSCREEN Manual or Literature

Range of Biodegradation Capacity:

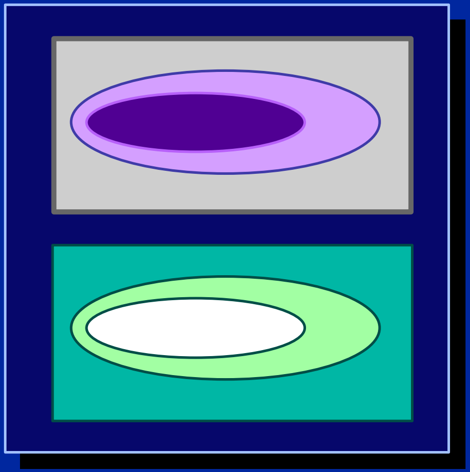
26 Air Force Sites: 7 to 70 mg/L

Median 26 Sites = 28.5 mg/L

Median 6 sites Florida = 16.6 mg/L

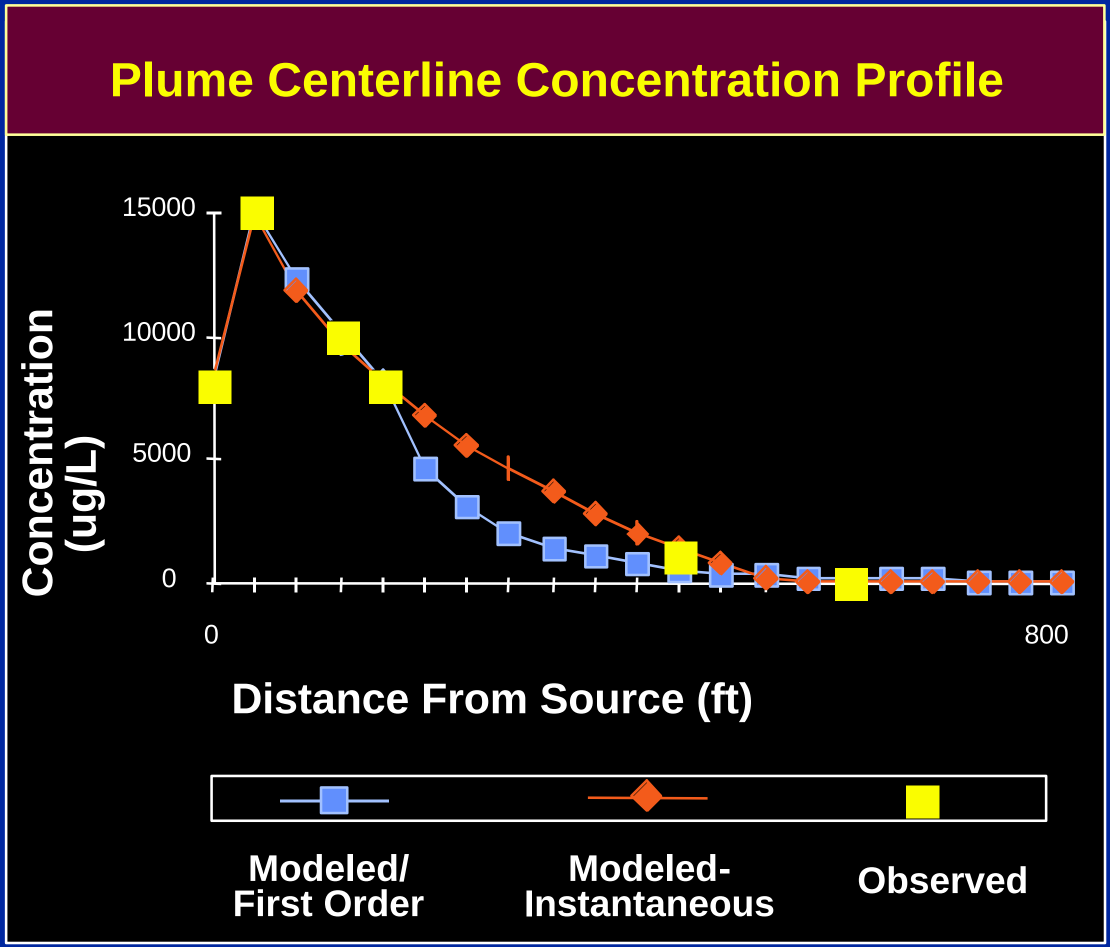
Instantaneous Reaction Model: *Summary*

- Assumes microbial kinetics relatively fast
- “Fast” related to residence time in plume
- Transport limited by availability of electron acceptors
- Accounts for electron acceptor reactions in source zone



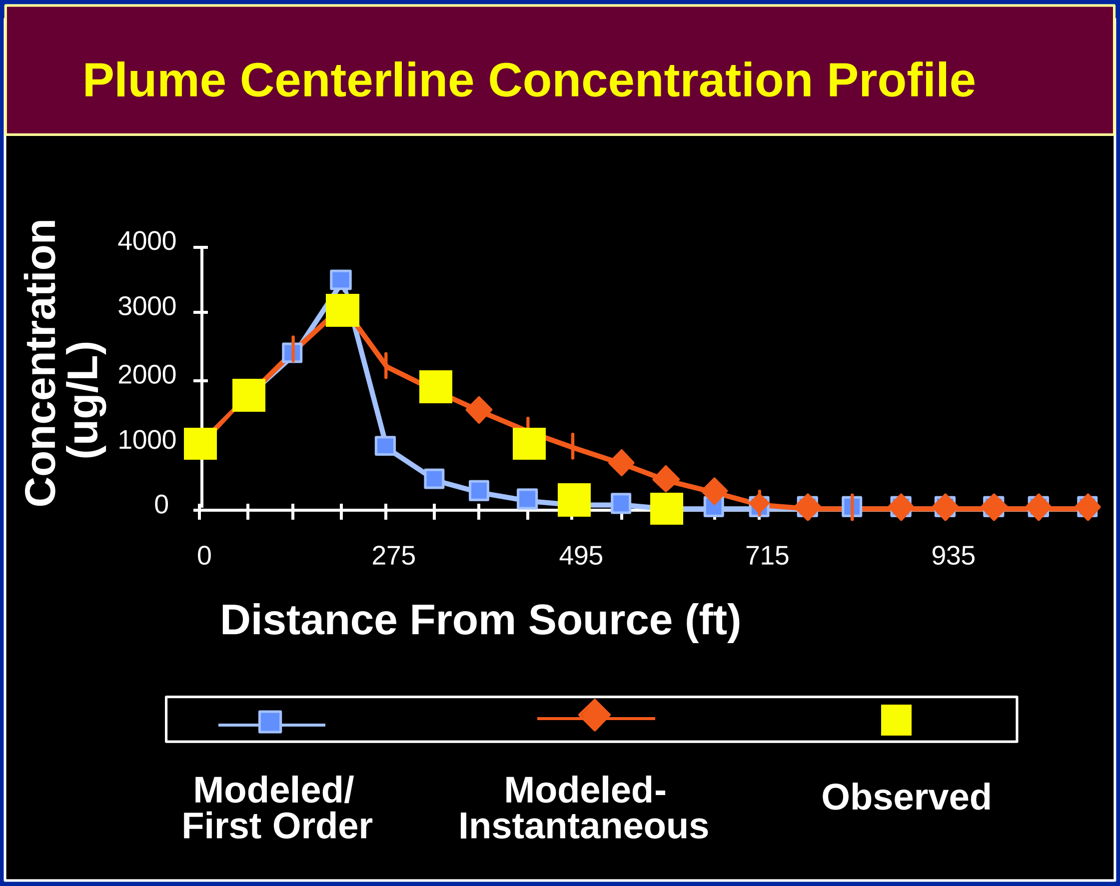
BIOSCREEN Modeling Results

POL Site / Hill AFB



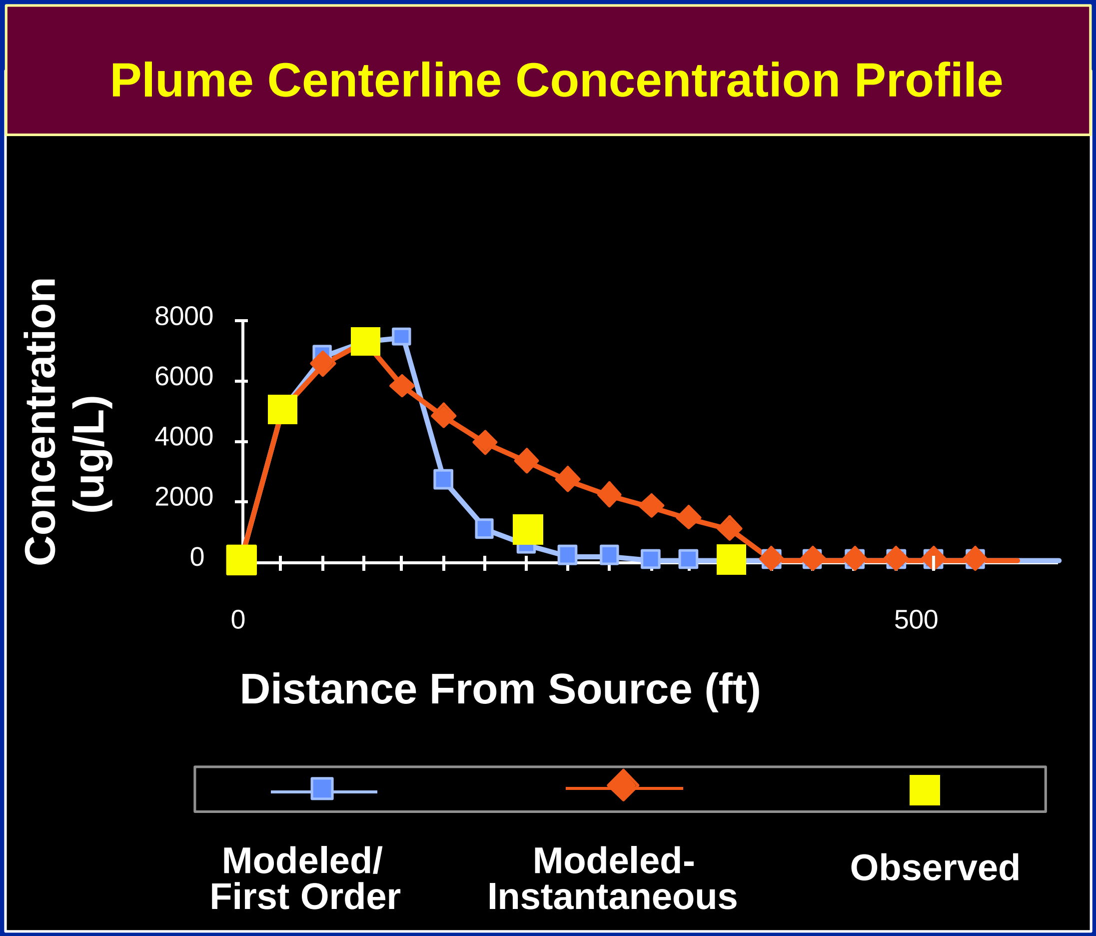
BIOSCREEN Modeling Results

ST-41 Site / Elmendorf AFB



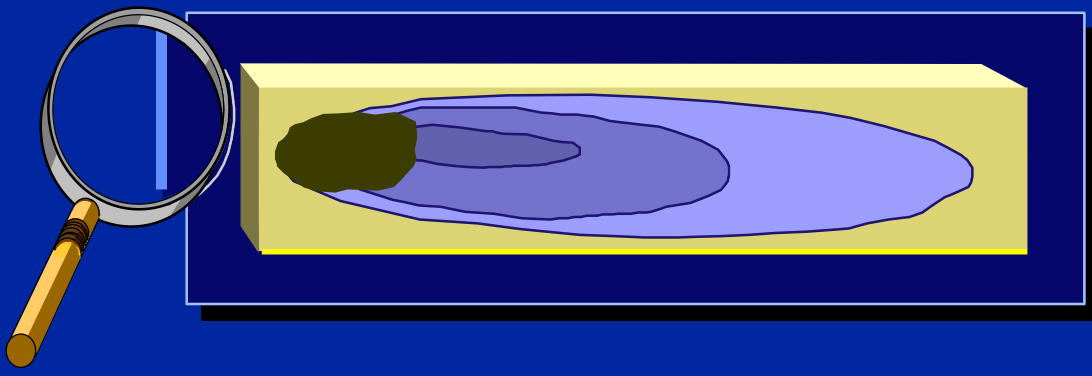
BIOSCREEN Modeling Results

ST-29 Site / Patrick AFB



Modeling Natural Attenuation with

BIOSCREEN



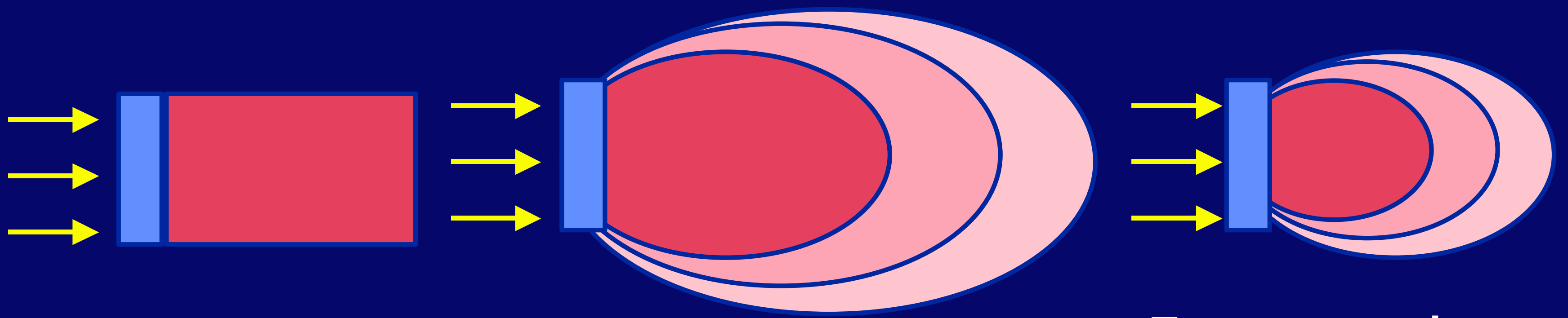
GROUNDWATER SERVICES, INC.

Groundwater Transport Processes

Groundwater Transport Modeling

All groundwater transport models are based on the advective-dispersive-reactive equations.

{ rate of change in HC conc. at any point } = { net rate of advective transport to that point } + { net rate of dispersive transport to that point } - { net rate of degradation at that point }



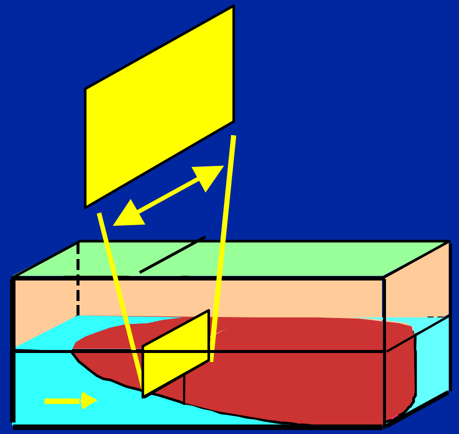
Transport at time t advection only

Transport at time t with dispersion

Transport at time *t* with dispersion & degradation

Types of Fate and Transport Models

- 1-D vs. 2-D vs. 3-D Advection
- 1-D vs. 2-D vs. 3-D Dispersion
- Deterministic vs. Statistical
- Numerical vs. Analytical
- Transient vs. Steady State
- Constant Source vs. Changing Source



(BIOSCREEN Features)

Transport: Groundwater in Source Zone → Groundwater at Receptor

Concentration at Downgradient Distance x Away from Source

$$\text{Conc}(x) = \exp\left\{\frac{x}{2\,\alpha_x}\left[1-\left(1+\frac{4\,\lambda\,\alpha_x}{Vs/R}\right)^{1/2}\right]\right\}\operatorname{erf}\left[\frac{S_w}{4\sqrt{\alpha_y\,x}}\right]\operatorname{erf}\left[\frac{S_d}{4\sqrt{\alpha_z\,x}}\right]$$

- *First-Order Decay Constant*
- *Groundwater Source Width and Depth*
- *Longitudinal Dispersivity*
- *Retardation Factor*
- *Error Function*
- *Transverse Dispersivity*
- *Vertical Dispersivity*

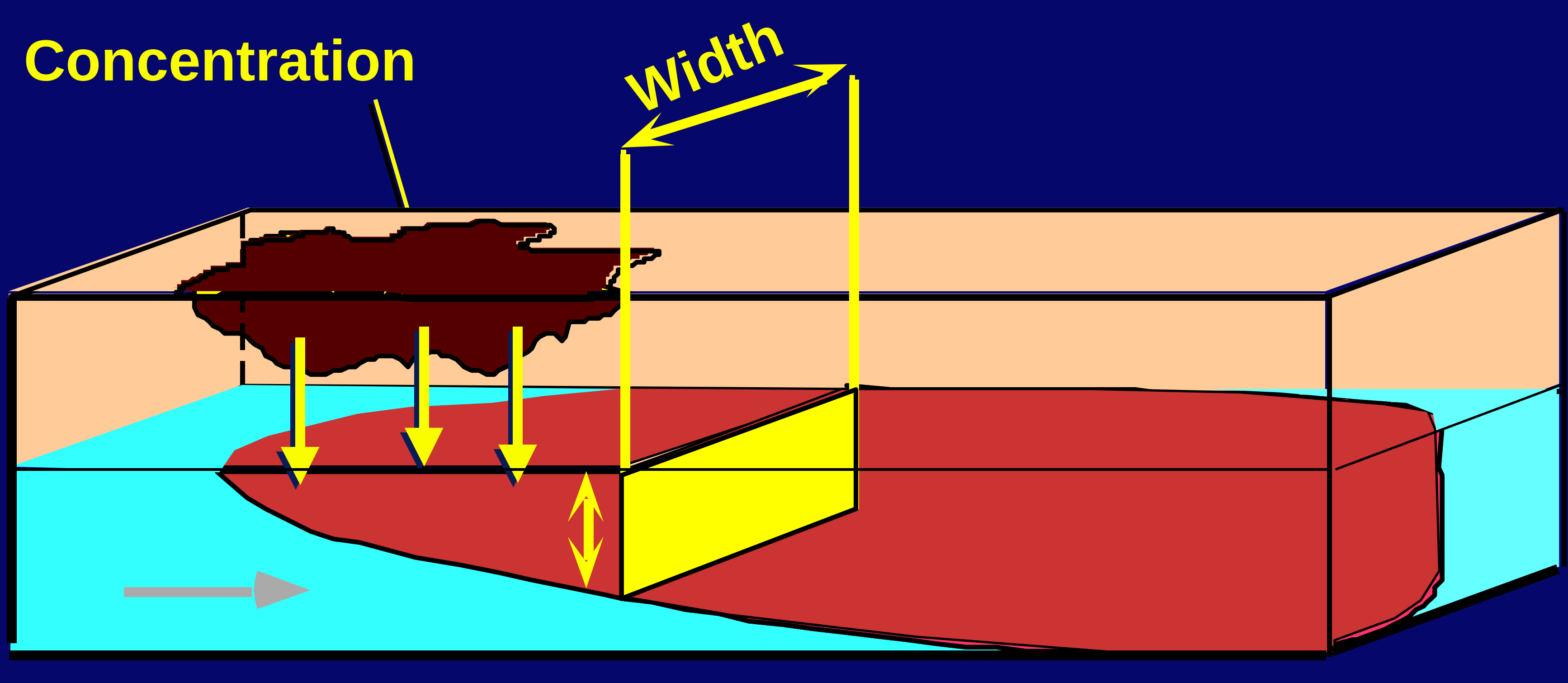
Groundwater Seepage Velocity

$$Vs = \frac{K\,i}{n}$$

- *Hydraulic Conductivity*
- *Hydraulic Gradient*
- *Effective Porosity*

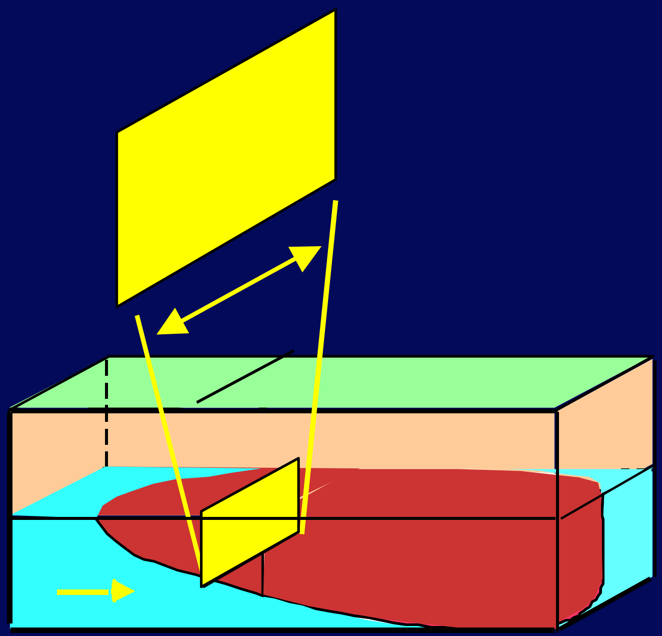
Source Term Configuration

Location: Downstream of Affected Soil Zone



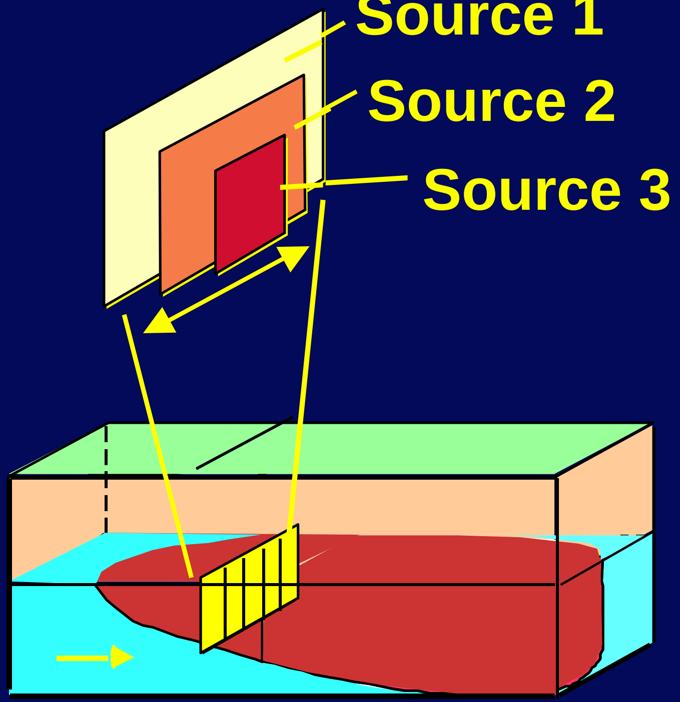
BIOSCREEN Model: *Other Features*

- **Single Vertical Plane Source**



- **Superimposed Sources**

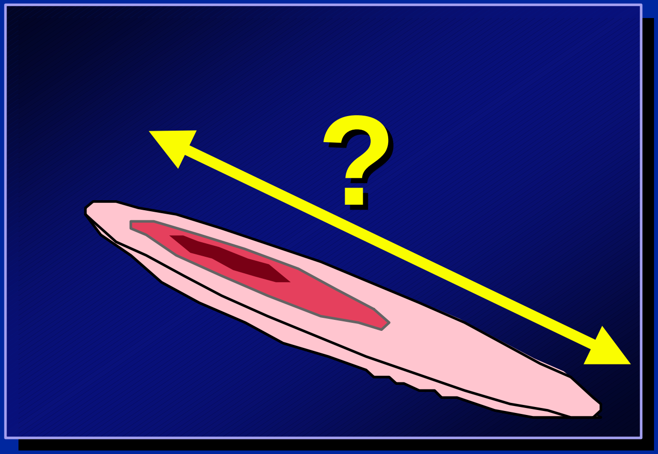
(Connor et al., 1995)



How Are Models Used Demonstrate Natural Attenuation?

Three Viewpoints:

- **ASTM RNA Standard**
- **EPA Directive**
- **NRC Report**



ASTM Lines of Evidence for RNA

NRC Data Type	ASTM LINES OF EVIDENCE		Notes
1 Measured Loss	Primary	■ COC data to define plume as shrinking, stable, or expanding.	■ Key evidence for NA ■ Need historical data
2 Evidence of Bio Processes	Secondary	■ Geochemical indicators of naturally-occurring biodegradation. ■ Estimates of attenuation rates.	■ ASTM says not needed most UST retail releases ■ Different rates can be confusing
3 Modeling, lab studies, other calcs	Optional (for fuel sites)	■ Microbiological studies. ■ GW solute transport modeling. ■ Estimates of assimilative capacity.	■ May not be optional for non-UST retail sites (EPA quote) ■ Lab studies done very infrequently

KEY POINT: Follow a weight of evidence approach, applying secondary and optional lines of evidence as appropriate.

EPA MNA Directive: Lines of Evidence

	Line of Evidence	*Approach*
1	*Historical Trends*	■ *Show "clear and meaningful" trend of decreasing contaminant mass and/or concentration vs. time*
2	*Indirect Hydrogeologic/ Geochemical Data*	■ *Shows the type of natural attenuation processes active at a site, and the rate which such processes will reduce contaminant concentrations to required levels.*
3	*Direct Microbial Evidence*	■ *Directly demonstrates occurrence of a particular attenuation process*

KEY POINT: **Probably need both #1 and #2 lines of evidence.**

Computer Models In EPA MNA Directive

.....a computer model may be helpful for understanding and visualizing current site conditions or for predictive simulations of potential future conditions. Computer models, which simulate sit processes mathematically, should in turn be based upon sound conceptual site models to provide meaningful information. Computer models typically require a lot of data, and the quality o the output from computer models is directly related to the quality of the input data. Because of the complexity of natural systems, models necessarily rely on simplifying assumptions that may or may not accurately represent the dynamics of the natural system Calibration and sensitivity analyses are important steps in appropriate use of models. Even so, the results of computer models should be carefully interpreted and continuously verified with adequate field data.

National Research Council MNA Report

Requirements	Approach			
1 *Evaluate "Footprints" of NA Processes*	■ *Identify trends in footprint concentrations* ■ *Possibly do mass balances of footprints*			
2 *Analyze Site Data*	*Recommended level of analysis:*	Biodegrades Under Most Conditions (e.g., BTEX)	Biodegrades Under Limited Conditions (e.g., solvents)	Mobile and Degrades Slowly (e.g., MTBE)
	Simple flow, uniform geochemistry, AND low concs	*GS*	*MB*	*MB + SM*
	Simple flow, small-scale physical or chemical heterog., AND med. To high concs.	*MB*	*MB + SM*	*CM*
	Strongly transient flow, large-scale physical or chemical heterog., OR high concs.	*MB or SM*	*CM*	*CM*

- *Graphical and statistical analysis= GS*
- *Mass budgeting to track fate of contaminants = MB*
- *Simple Modeling= SM*
- *Compreh. Modeling= CM*

Computer Models In NRC Report

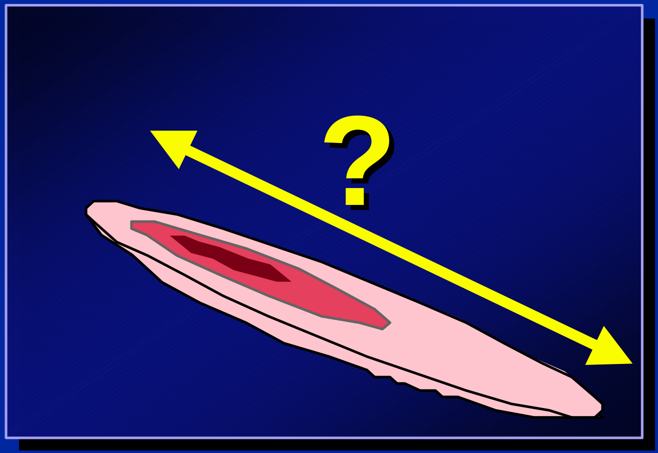
Models are the "…highest level of analysis for natural attenuation site data…"

"For sites at which degradation products are straightforward and hydrogeology is relatively simple, a budget analysis combined with simple solute transport modeling often is adequate. On the other hand, as biochemical or hydrogeological characteristics become more complex, analysis of the site requires the rigor of comprehensive models."

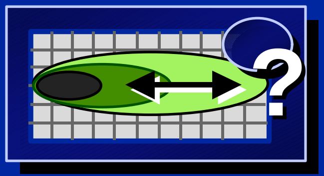
What Goes Into an MNA Report?

Combined Viewpoint:

- **Concentration vs. Time Data**
- **"Footprint" Data**
- **Modeling Results**



Third L.O.E.: How are Models Used to Demonstrate MNA?



Method 1.

Use model to show plume is shrinking or stable

Step 1

Calibrate model to existing monitoring data.

Step 2

Increase time to 100 years in the future.

Step 3

See if plume gets larger.

Method 2.
Use model to link biodegradation to footprints

For BTEX plumes:

Model with Electron Acceptor Limited Biodegradation and Fit Model to Site Data

For Chlorinated Solvent plumes:

Model with Sequential Reductive Dechlorination to Generate Daughter Product, Match to Site Data

Why Use Models?

- Method for Predicting Something Precisely ? **No**

- System to Organize Site Data . . . . **Yes**
- Tool to Help Understand Site Processes . **Yes**
- Additional Line of Evidence . . . . **Yes**
- Screen for Applicability of MNA . . . . **Yes**

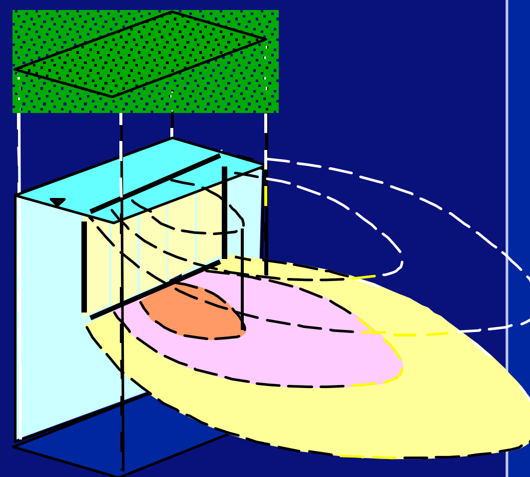
Model Selection Guidelines

Model Type	Capabilities	Data Needs	Complexity
Hand Calcs:	Advection Only	Simple	 “Gilligan
Analytical (BIOSCREEN BIOCHLOR):	Uniform flow Simple source Key NA Processes	Moderate	 “Skipper
Numerical Model (BIOPLUMEIII):	Complex flow Complex sources Pumping	High	 The “Professor

Natural Attenuation Models

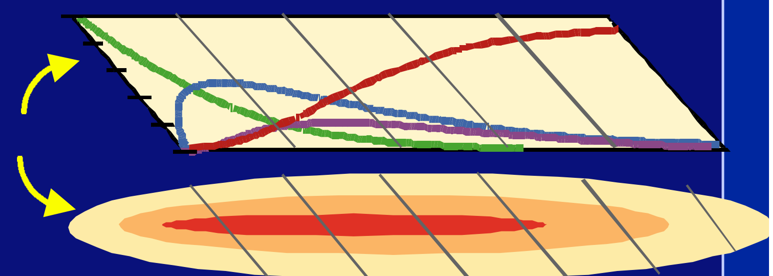
Fuel Sites

- **BIOSCREEN** *(analytical, two decay options, source decay term)*
- **BIOPLUME III** *(numerical, electron acceptors)*



Solvent Sites

- **BIOCHLOR** *(analytical, sequential reductive dechlorination)*
- **RT3D** *(complex numerical model)*



Where to Get BIOSCREEN

EPA Center for Subsurface Modeling Support (R. S. Kerr Lab)

- **Web:**
  http://www.epa.gov/ada/bioscreen.html
- **Phone**
  (405) 436 8718

Natural Attenuation Tools

Line of Evidence	Excel	Mapping SW, CAD	MAROS	Fate 5	Seq-uence	BIO-SCREEN	BIO-CHLOR	BIOPLUMEIII RT3D	BIOSOURCE
Primary									
■ Plotting C vs. T	3*	3*	3						
■ Mann-Kendall, Mann-Whitney Stats	3*		3						
Secondary									
■ Plotting geochemical indicators	3*	3*			3				
■ Estimation of attenuation rates	3*			3		3	3	3	
Optional									
■ GW solute model						3	3		
■ Soil-to-GW leachate model									
■ Calculation of Time to Natural Attenuate						3*			3
■ Assimilative capacity calc.								3	
Cost	$ 200	varies	Free	$ 250	$495	Free	Free	Free	Free

3 * = not built-in

Where to Get Natural Attenuation Software Tools

- **Primary Line of Evidence**

  - MAROS *(www.gsi-net.com)*

- **Secondary Line of Evidence**

  - SEQUENCE *(www.rovers.com - see innovations)* ($495)
  - Fate V *(www.gsi-net.com)* ($295)

- **Models**

  - BIOSCREEN *(www.epa.gov/ada/models.html)* (free)
  - BIOPLUME III *(www.epa.gov/ada/models.html)* (free)
  - BIOCHLOR *(www.epa.gov/ada/models.html)* (free)
  - RT3D *(http://terrassa.pnl.gov:2080/bioprocess/rt3d.ht)* (free)