LECTURE 13

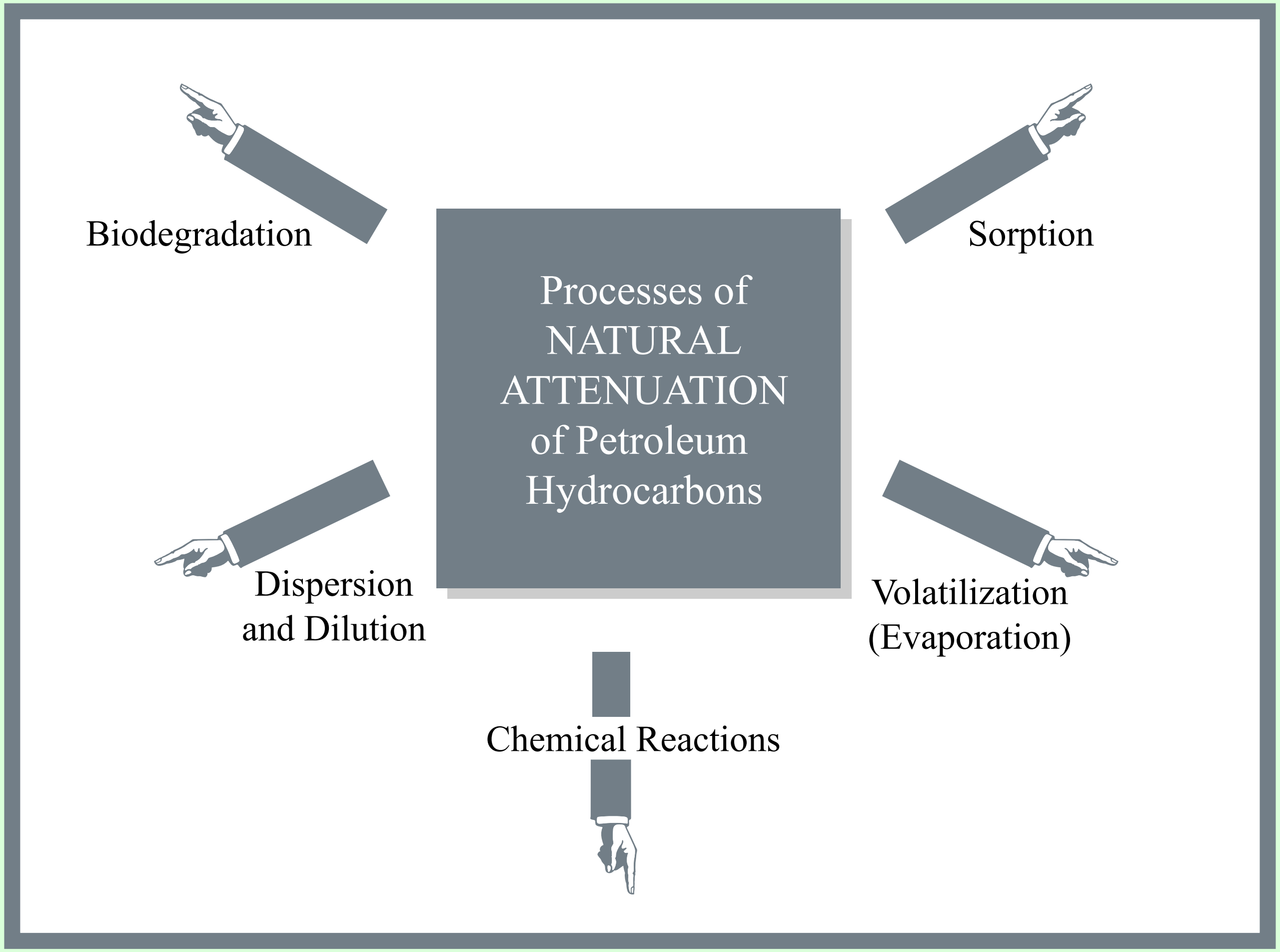
MONITORED NATURAL ATTENUATION

Monitored Natural Attenuation

As defined by U.S. EPA:

reliance on natural processes to achieve site-specific remedial objectives

Source: Pope, D. F., and J. N. Jones, 1999. Monitored Natural Attenuation of Chlorinated Solvents. U.S. EPA Remedial Technology Fact Sheet. Report Number EPA/600/F-98/022. Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C. May 1999. (http://www.epa.gov/ada/download/fact/chl-solv.pdf).

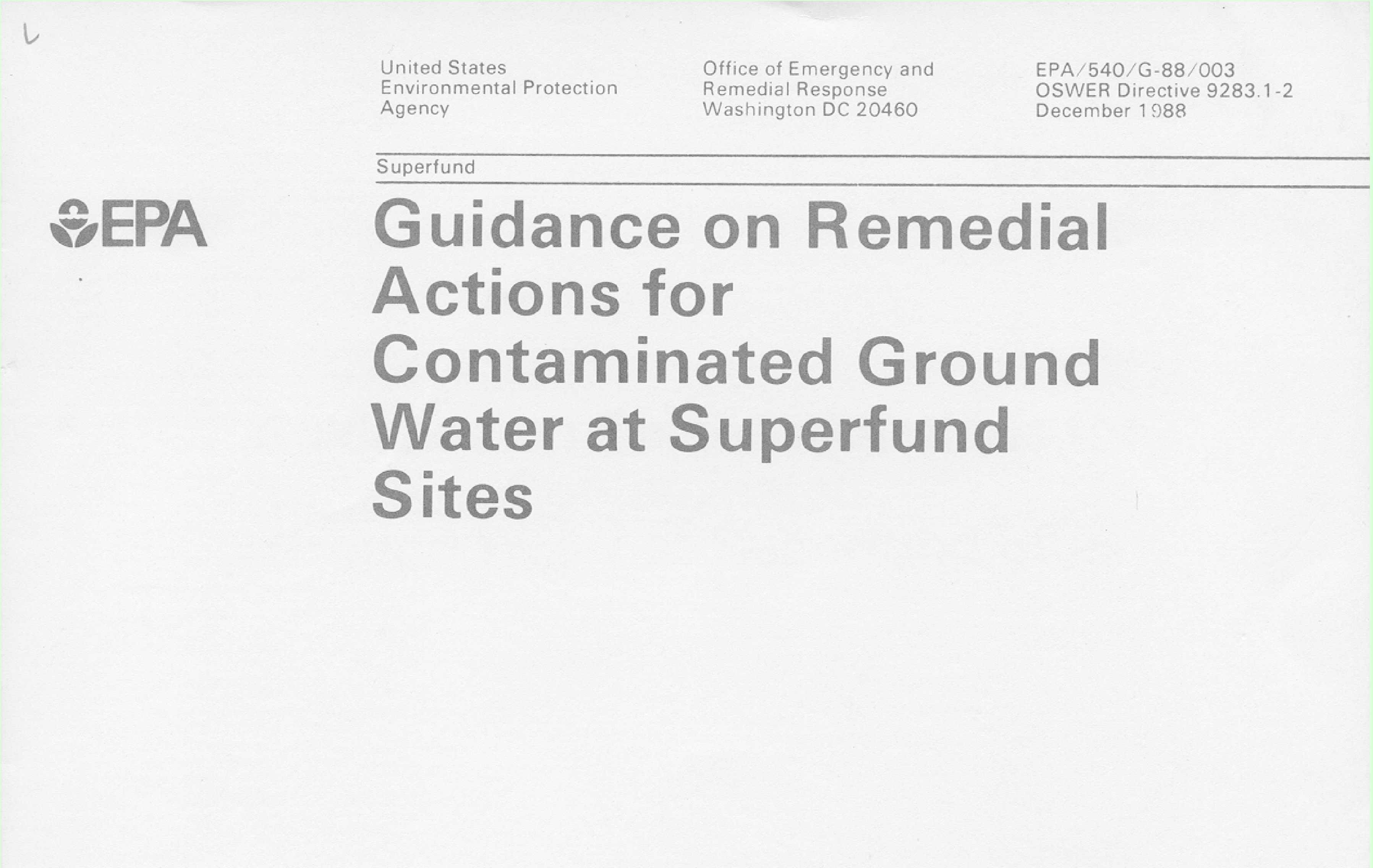

Processes of NATURAL ATTENUATION of Petroleum Hydrocarbons
Biodegradation
Sorption
Dispersion and Dilution
Volatilization (Evaporation)
Chemical Reactions

Historical development of MNA

Historical development

- 1985 – Always a remedial alternative: EPA says it was used in Superfund as early as 1985
- 1988 – Guidance on Remedial Actions for Contaminated Ground Water at Superfund Sites discusses natural attenuation, but mostly as a comparison standard for active remediation. Natural attenuation is not encouraged
- Began to be more commonplace with recognition of intractability of DNAPL cleanups and inadequacy of pump and treat technology
- Simultaneously, there was increasing recognition that in situ processes were containing or cleaning up contamination
- 1993-94 – Two key studies by National Research Council:
    - *In Situ Bioremediation – When does it work?* – 1993 study discusses intrinsic bioremediation
    - *Alternatives for Ground Water Cleanup* – 1994
- 1995 – Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater
    - Prepared by Air Force Center for Environmental Excellence working with U.S. EPA research laboratory
    - Defines procedure to show intrinsic remediation is occurring
- September 1996 – EPA Symposium on Natural Attenuation of Chlorinated Organics in Ground Water
- November 1996 – Draft Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater (Final in Sept. 1998)
- December 1997 – OSWER Policy Directive: Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites
- Sept.-Dec. 1998 – EPA Seminars on Monitored Natural Attenuation in nine cities around the US

1988 Guidance on Ground Water



United States
Environmental Protection
Agency

Office of Emergency and
Remedial Response
Washington DC 20460

EPA/540/G-88/003
OSWER Directive 9283.1-2
December 1988

Superfund

EPA

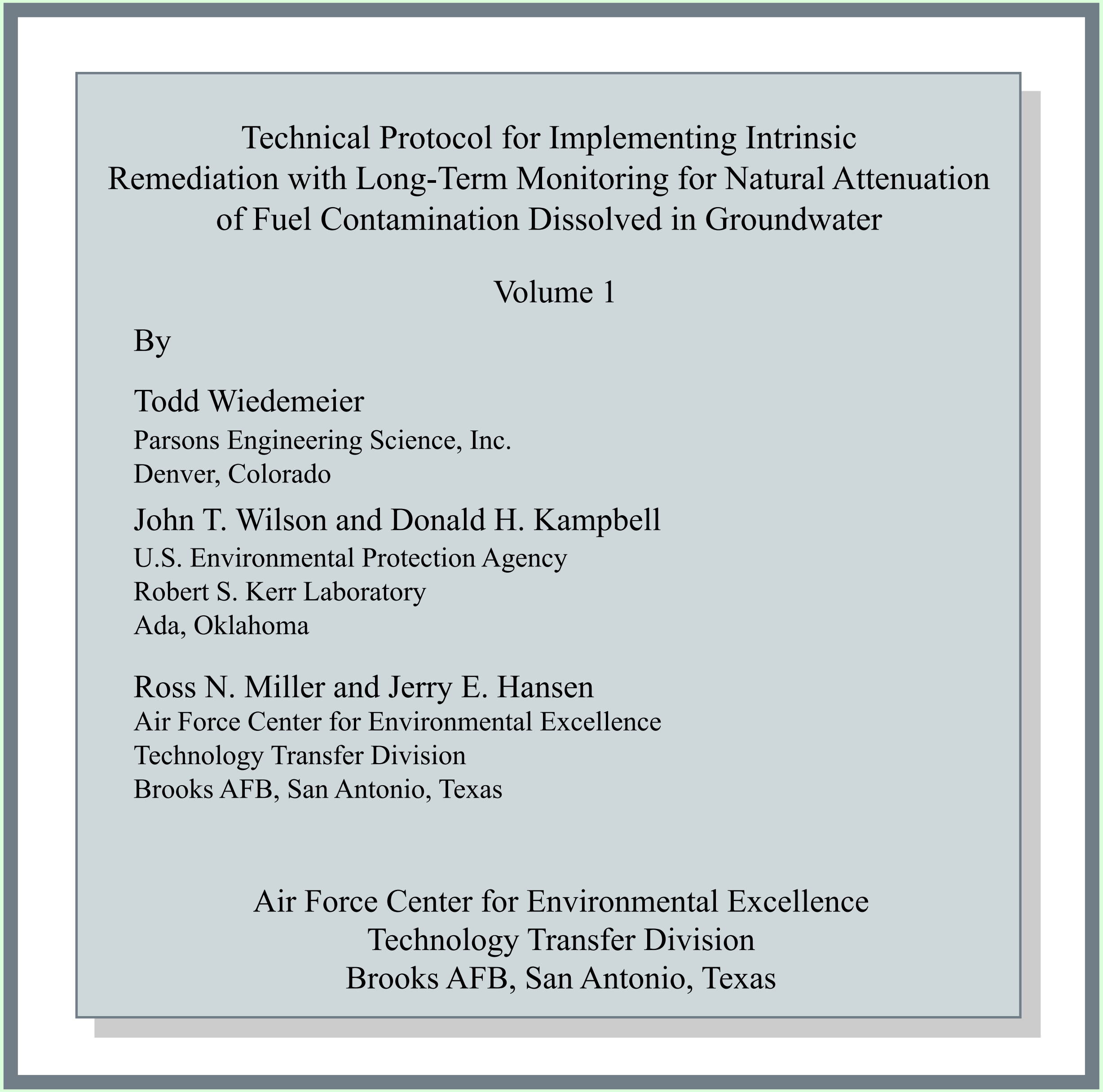
Guidance on Remedial Actions for Contaminated Ground Water at Superfund Sites

1993 and 1994 – NRC Studies

"In Situ Bioremediation. When does it work?" National Research Council.

"Alternatives for Ground Water Cleanup." National Research Council.

1995 – AFCEE Technical Protocol



Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater

Volume 1

By

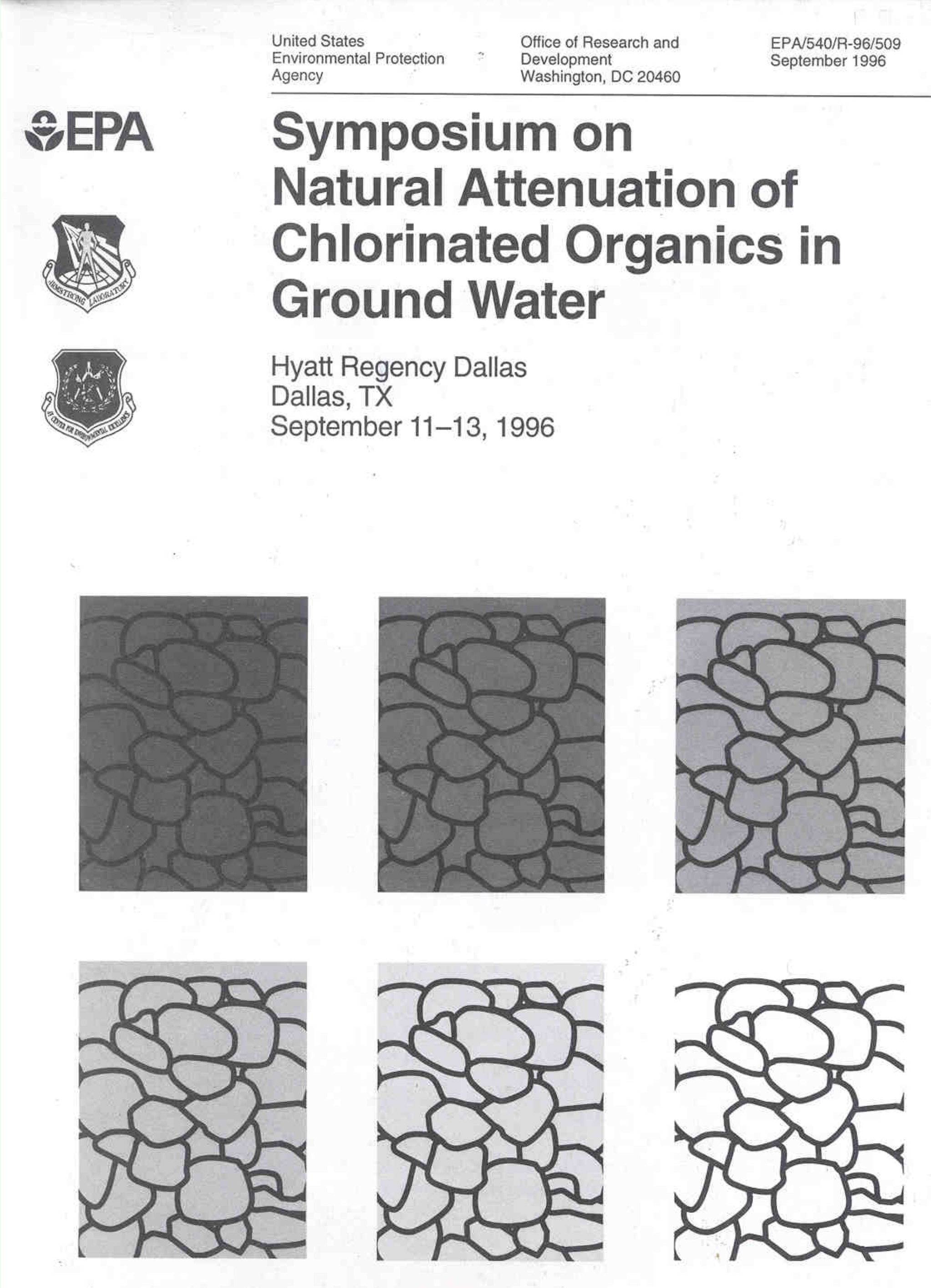
Todd Wiedemeier
Parsons Engineering Science, Inc.
Denver, Colorado

John T. Wilson and Donald H. Kampbell
U.S. Environmental Protection Agency
Robert S. Kerr Laboratory
Ada, Oklahoma

Ross N. Miller and Jerry E. Hansen
Air Force Center for Environmental Excellence
Technology Transfer Division
Brooks AFB, San Antonio, Texas

Air Force Center for Environmental Excellence
Technology Transfer Division
Brooks AFB, San Antonio, Texas

1996 – EPA Symposium on Natural Attenuation



United States
Environmental Protection
Agency

Office of Research and
Development
Washington, DC 20460

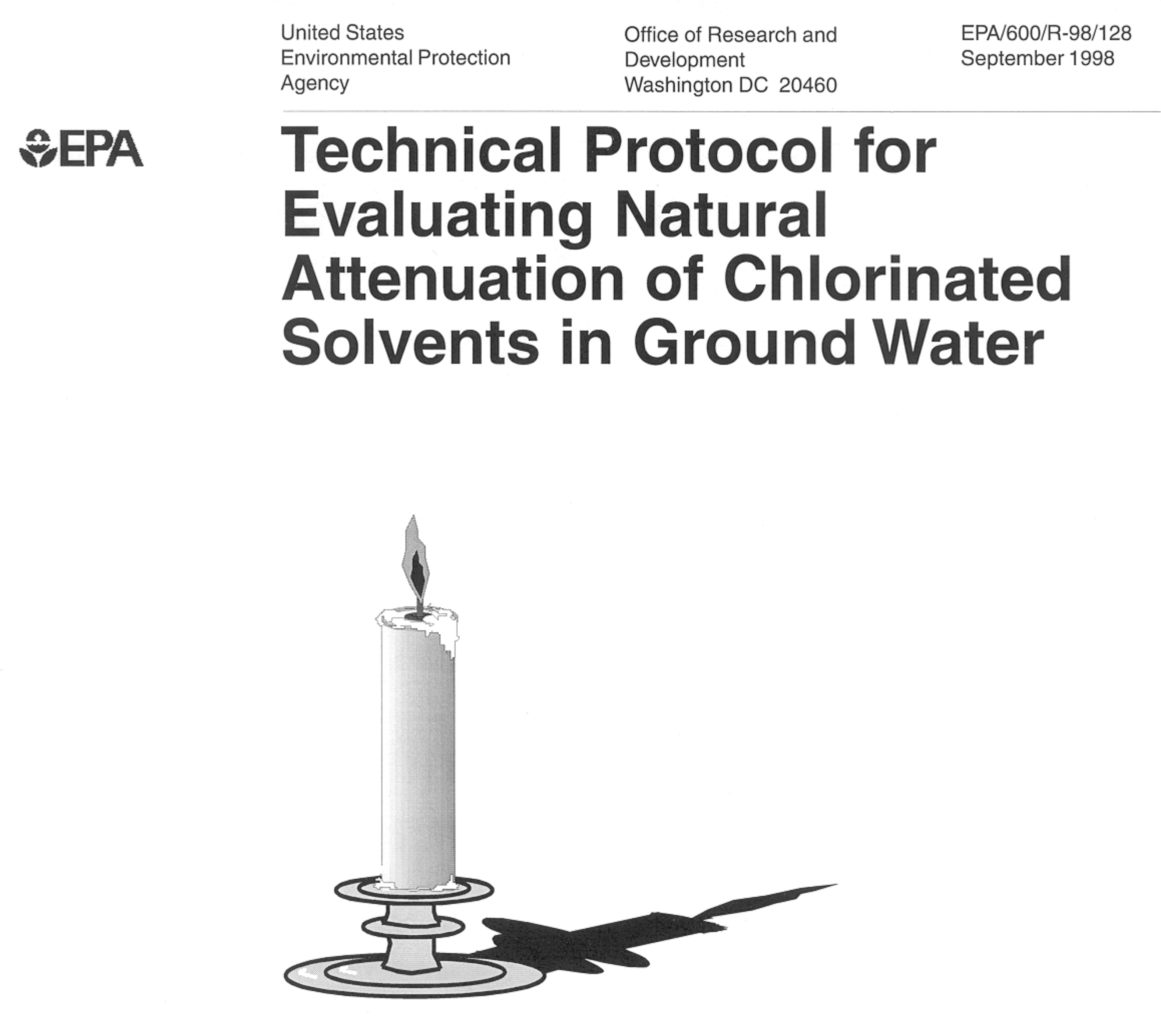
EPA/540/R-96/509
September 1996

EPA

Symposium on Natural Attenuation of Chlorinated Organics in Ground Water

Hyatt Regency Dallas
Dallas, TX
September 11–13, 1996

1996 – Draft Technical Protocol



United States
Environmental Protection
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Office of Research and
Development
Washington DC 20460

EPA/600/R-98/128
September 1998

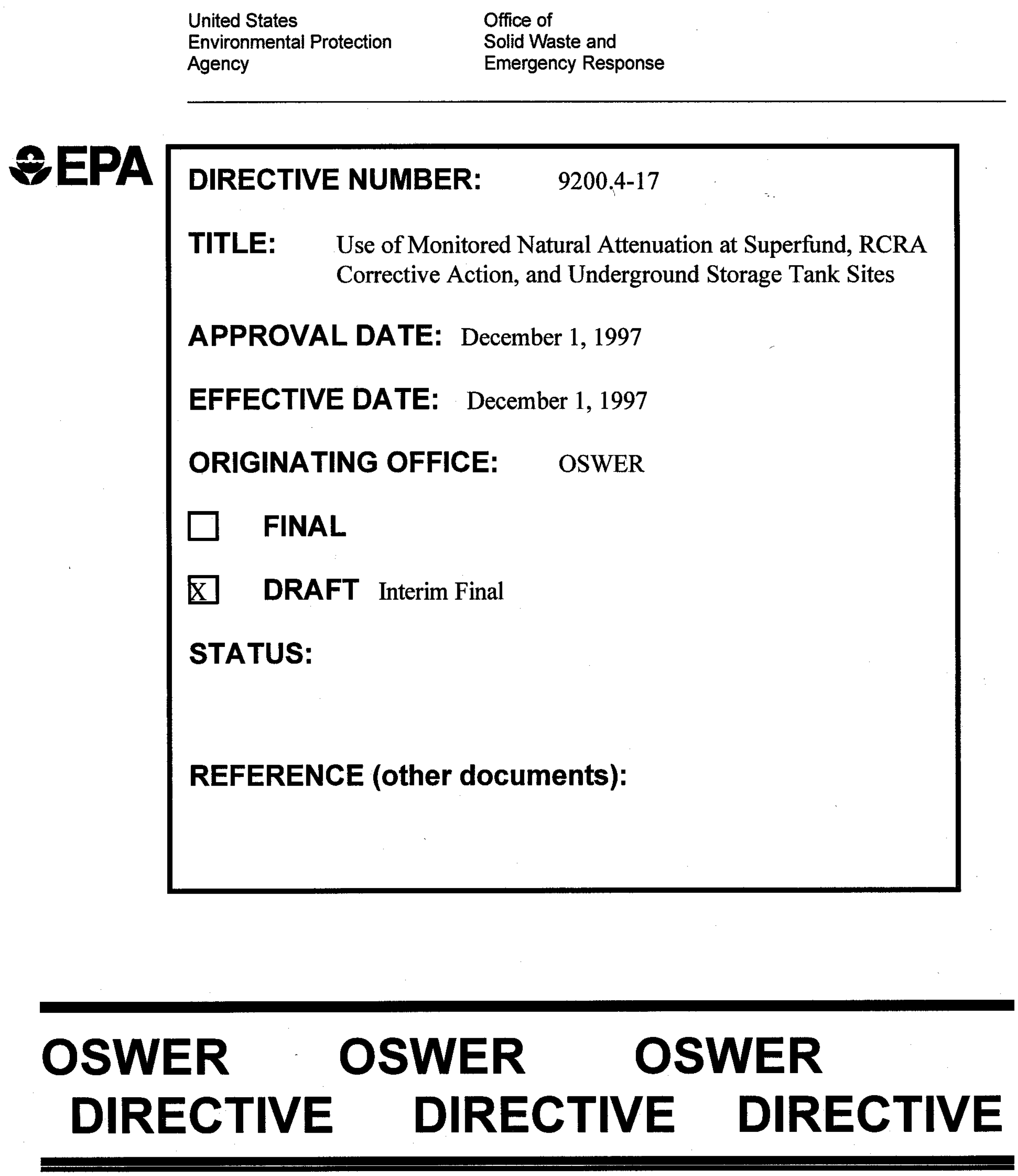
EPA

Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water

Nov. 1996 – Draft

Sept. 1998 - Final

1997 – MNA Policy Directive



United States
Environmental Protection
Agency

Office of
Solid Waste and
Emergency Response

EPA

DIRECTIVE NUMBER: 9200.4-17

TITLE: Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites

APPROVAL DATE: December 1, 1997

EFFECTIVE DATE: December 1, 1997

ORIGINATING OFFICE: OSWER

☐ **FINAL**

☒ **DRAFT** Interim Final

STATUS:

REFERENCE (other documents):

OSWER DIRECTIVE OSWER DIRECTIVE OSWER DIRECTIVE

1998 – MNA Seminars

United States
Environmental Protection
Agency

Office of Research and
Development
Washington, DC 20460

EPA/625/K-98/001
September 1998

EPA

Seminars

Monitored Natural Attenuation for Ground Water

September 2–3, 1998—Philadelphia, PA

September 14–15, 1998—Denver, CO

September 16–17, 1998—Chicago, IL

October 14–15, 1998—Kansas City, MO

November 2–3, 1998—Dallas, TX

November 16–17, 1998—Atlanta, GA

December 2–3, 1998—Seattle, WA

December 8–9, 1998—Boston, MA

December 14–15, 1998—San Francisco, CA

Definition of MNA (continued)

May be physical, chemical or biological

Act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or ground water

Processes include:

  biodegradation

  dispersion

  dilution

  sorption

  volatilization

  chemical or biological stabilization, transformation, or destruction

Source: Pope, D. F., and J. N. Jones, 1999. Monitored Natural Attenuation of Chlorinated Solvents. U.S. EPA Remedial Technology Fact Sheet. Report Number EPA/600/F-98/022. Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C. May 1999. (http://www.epa.gov/ada/download/fact/chl-solv.pdf).

Elements of Natural Attenuation

MNA is not:

- No-action alternative
- Presumptive or default remedy

MNA must be:

- Evaluated along with other alternatives
- Selected only is it meets remediation objectives
- Work in reasonable time frame (30 years)
- Used very cautiously as sole remedy

Components of MNA

Required components of MNA:

- Source control
- Performance monitoring

Prerequisite for MNA:

- Site-specific characterization data and analysis

Demonstrating efficacy of MNA

1. Historical chemical data showing clear trend of decreasing mass or concentration.
2. Hydrogeologic or geochemical data that indirectly demonstrate natural attenuation processes
3. Field or microcosm studies that directly demonstrate natural attenuation processes

Aerobic biodegradation of fuel hydrocarbons

Oxygen used as electron acceptor

$2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$

Indicators of biodegradation:

- Reduction in dissolved oxygen
  (3 mg DO needed to metabolize 1 mg of benzene)
- Reduction in hydrocarbon concentration

Biodegradation sequence

Order of aerobic biodegradation:

- Ethyl benzene
- Toluene
- Benzene
- Xylene

Denitrification

Nitrate is electron acceptor

$6NO_3^- + 6H^+ + C_6H_6 \rightarrow 6CO_2\uparrow + 6H_2O + 3N_2\uparrow$

Actually occurs in multiple steps mediated by different bacteria:

$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow NH_4^+ \rightarrow N_2$

Denitrification

Indicators of biodegradation:

- Reduction in nitrate
- Reduction in hydrocarbon concentration
- Presence of denitrifying bacteria
- Reducing conditions (dissolved oxygen < 1 mg/L)

Iron reduction

Insoluble iron(III) (ferric iron) is electron acceptor

Reduced to soluble iron(II) (ferrous iron)

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

Iron reduction

Indicators of iron biodegradation:

- Increase in dissolved iron
- Reduction in hydrocarbon concentration
- Low or no dissolved oxygen

Sulfate reduction

Sulfate is electron acceptor

Sulfate reduction to sulfide

$$30H^+ + 15SO_4^{2-} + 4C_6H_6 \rightarrow 24CO_2 + 15H_2S + 12H_2O$$

Methanogenesis (Methane fermentation)

Not a redox reaction – fermentation reaction

Occurs only in highly anaerobic conditions

$4C_6H_6 + 18H_2O \rightarrow 9CO_2 + 15CH_4$

Methanogenesis

Indicators of methanogenesis:

- Increase in methane and carbon dioxide
- Reduction in hydrocarbon concentration
- Very low or no dissolved oxygen
- Presence of methanogenic bacteria

Carbon dioxide neutralization

All hydrocarbon degradation processes create CO_2

$CO_2 + H_2O \rightarrow H_2CO_3$ (carbonic acid)

$H_2CO_3 + CaCO_3 \rightarrow Ca^{2+} + 2HCO^{3-}$

CO_2 neutralization increases alkalinity

8 mg alk produced per mg benzene degraded

Analytical protocol

Ground water:

- Total hydrocarbons – confirm HC decrease
- Aromatic hydrocarbons – confirm BTEX decrease
- Oxygen – confirm utilization, redox state
- Nitrate – confirm utilization
- Iron(II) – confirm production
- Sulfate – confirm utilization
- Methane – confirm methanogenesis

Analytical protocol

Ground water:

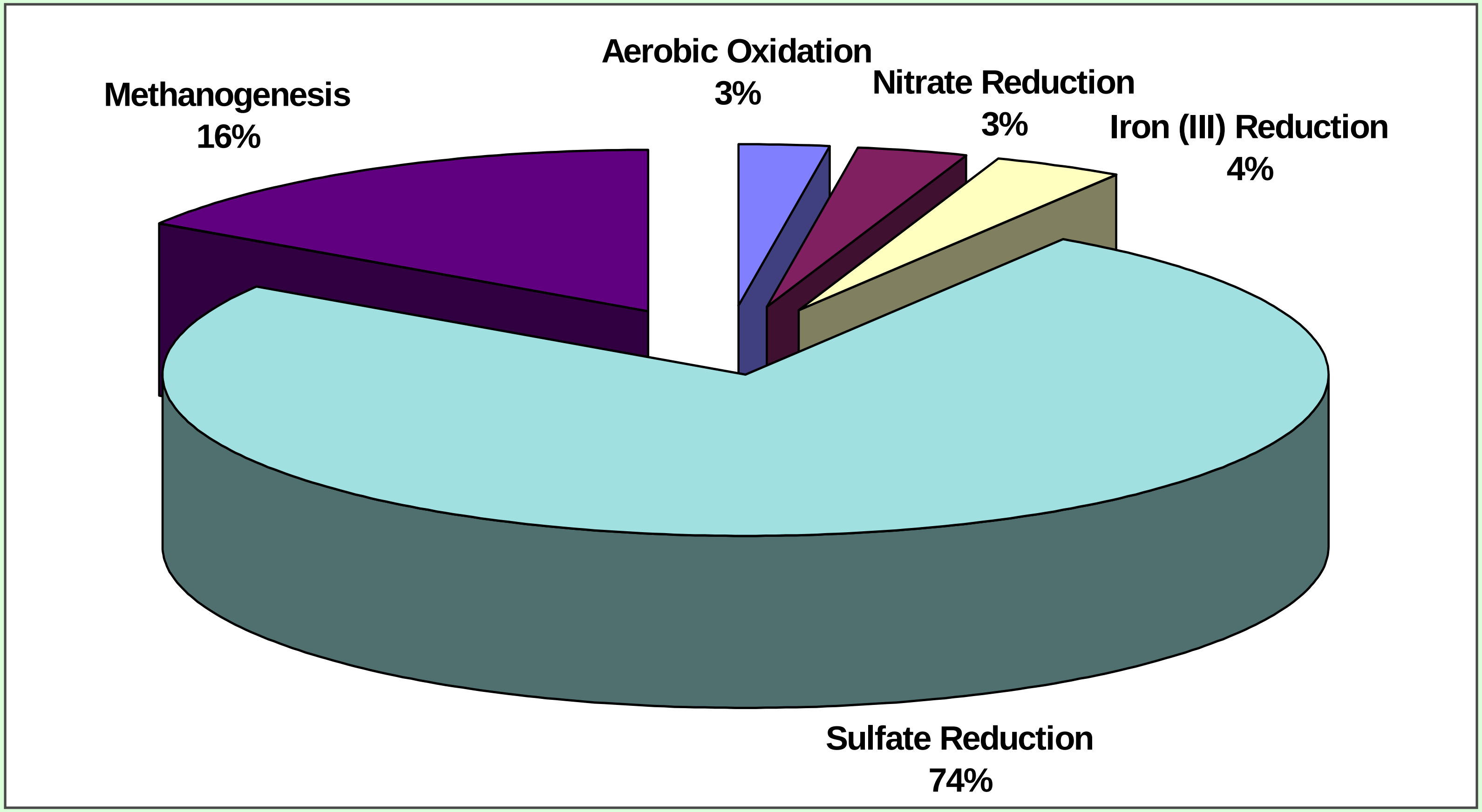
- Alkalinity – confirm CO_2 production and neutralization
- Oxidation-reduction potential – confirm geochemical environment
- pH, temperature, conductivity, chloride – confirmation of single ground-water system

Analytical protocol

Biological:

- Field dehydrogenase test – confirm presence of aerobic bacteria
- Volatile fatty acids – biodegradation byproduct of complex organic compounds
- Microcosm studies – confirm biodegradation is occurring

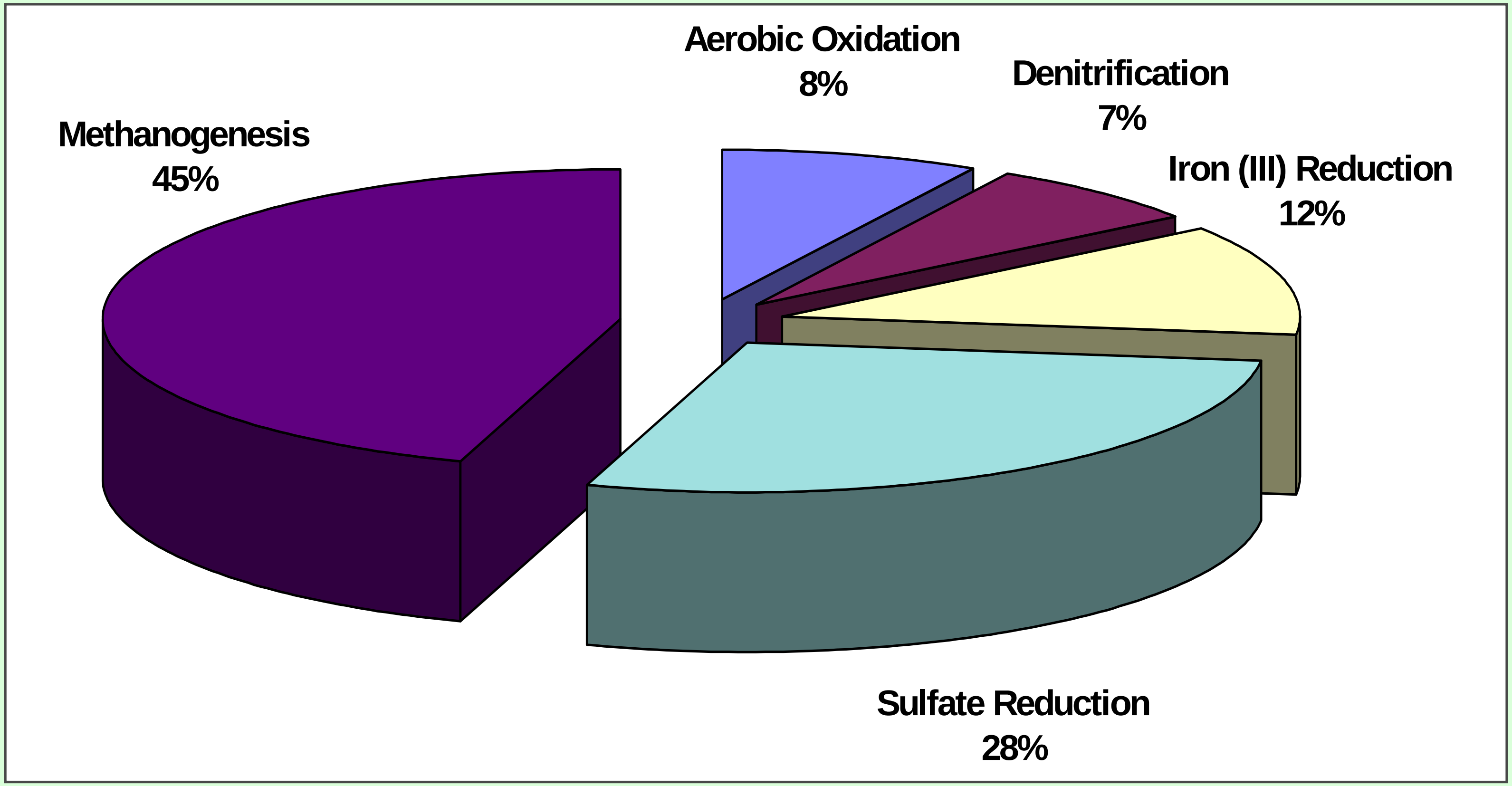
Average Relative Contribution of BTEX Biodegradation Processes in Site Ground Water at 42 sites



Source: http://www.afcee.brooks.af.mil/er/ert/download/natattenfuels.ppt

Average Relative Contribution of BTEX Biodegradation Processes in Site Ground Water at 42 sites

(Excluding five sites with >200 mg/L Sulfate Reduction Capacity)



Treatability Study Results (continued)

BTEX assimilative capacity averaged 64 mg/L

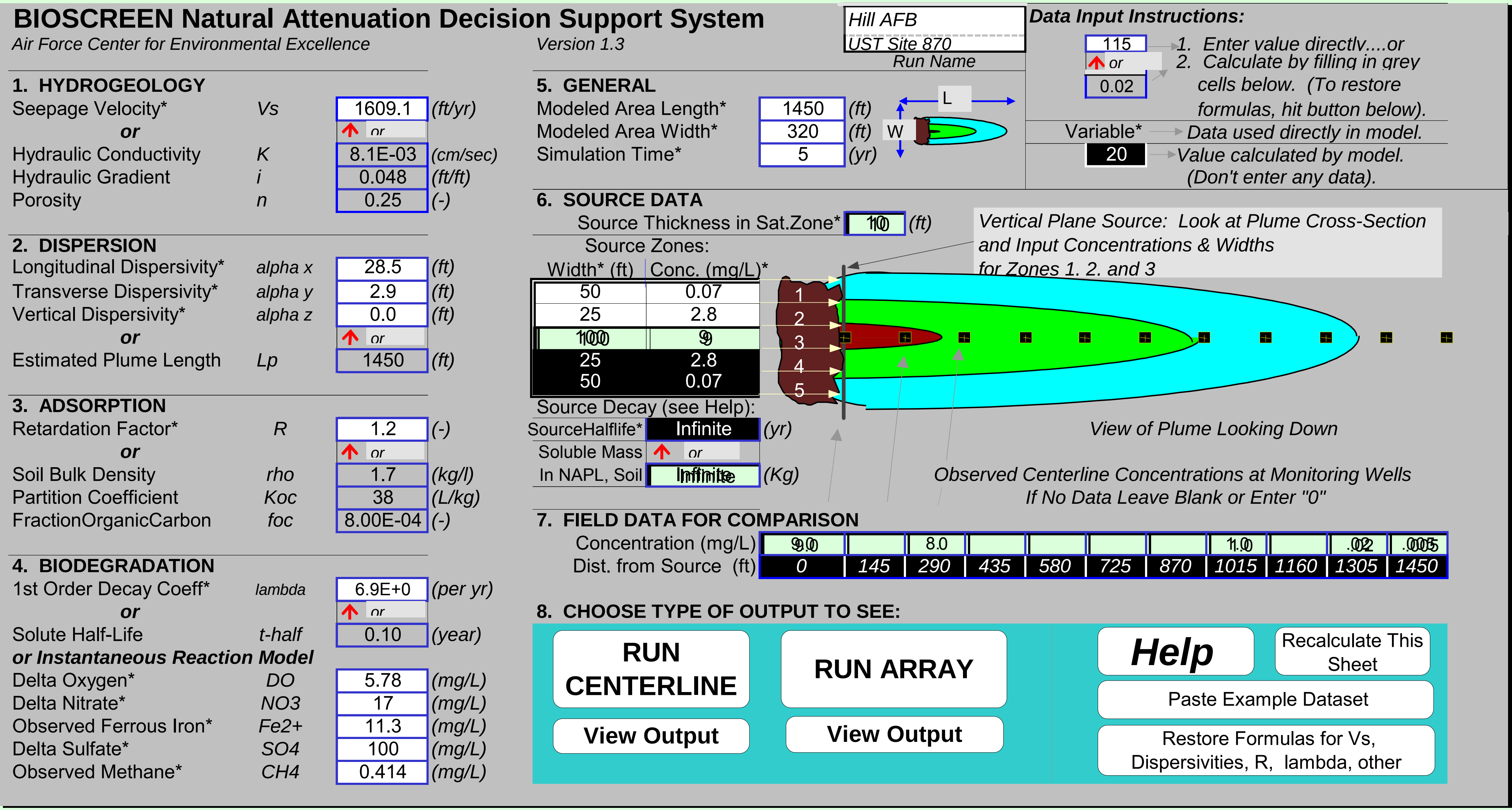
Field-scale biodegradation half-lives:

  Range = 9 days to 9.5 years

  Mean = 1 year.

Microsoft Excel
Worksheet

BIOSCREEN



BIOSCREEN Natural Attenuation Decision Support System

Air Force Center for Environmental Excellence

Version 1.3

Hill AFB
UST Site 870
Run Name

Data Input Instructions:

115	*1. Enter value directly....or*
or	*2. Calculate by filling in grey*
0.02	*cells below. (To restore formulas, hit button below).*
Variable*	*Data used directly in model.*
20	*Value calculated by model. (Don't enter any data).*

1. HYDROGEOLOGY

Seepage Velocity*	*Vs*	1609.1	*(ft/yr)*
or		or	
Hydraulic Conductivity	*K*	8.1E-03	*(cm/sec)*
Hydraulic Gradient	*i*	0.048	*(ft/ft)*
Porosity	*n*	0.25	*(-)*

2. DISPERSION

Longitudinal Dispersivity*	*alpha x*	28.5	*(ft)*
Transverse Dispersivity*	*alpha y*	2.9	*(ft)*
Vertical Dispersivity*	*alpha z*	0.0	*(ft)*
or		or	
Estimated Plume Length	*Lp*	1450	*(ft)*

3. ADSORPTION

Retardation Factor*	*R*	1.2	*(-)*
or		or	
Soil Bulk Density	*rho*	1.7	*(kg/l)*
Partition Coefficient	*Koc*	38	*(L/kg)*
FractionOrganicCarbon	*foc*	8.00E-04	*(-)*

4. BIODEGRADATION

1st Order Decay Coeff*	*lambda*	6.9E+0	*(per yr)*
or		or	
Solute Half-Life	*t-half*	0.10	*(year)*
or Instantaneous Reaction Model			
Delta Oxygen*	*DO*	5.78	*(mg/L)*
Delta Nitrate*	*NO3*	17	*(mg/L)*
Observed Ferrous Iron*	*Fe2+*	11.3	*(mg/L)*
Delta Sulfate*	*SO4*	100	*(mg/L)*
Observed Methane*	*CH4*	0.414	*(mg/L)*

5. GENERAL

Modeled Area Length*	1450	*(ft)*
Modeled Area Width*	320	*(ft)*
Simulation Time*	5	*(yr)*

6. SOURCE DATA

Source Thickness in Sat.Zone* 10 *(ft)*

Source Zones:

Width* (ft)	Conc. (mg/L)*
50	0.07
25	2.8
100	9
25	2.8
50	0.07

Vertical Plane Source: Look at Plume Cross-Section and Input Concentrations & Widths for Zones 1, 2, and 3

View of Plume Looking Down

Source Decay (see Help):

SourceHalflife*	Infinite	*(yr)*
Soluble Mass	or	
In NAPL, Soil	Infinite	*(Kg)*

Observed Centerline Concentrations at Monitoring Wells
If No Data Leave Blank or Enter "0"

7. FIELD DATA FOR COMPARISON

Concentration (mg/L)	9.0		8.0					1.0		.02	.005
Dist. from Source (ft)	0	145	290	435	580	725	870	1015	1160	1305	1450

8. CHOOSE TYPE OF OUTPUT TO SEE:

Anaerobic transformation of carbon tetrachloride

$$\mathrm{CCl_4} \rightarrow \mathrm{CHCl_3} \rightarrow \mathrm{CH_2Cl_2} \rightarrow \mathrm{CH_3Cl}$$

$$\downarrow$$

$$\mathrm{CO_2} + \mathrm{H_2O} + \mathrm{Cl^-}$$

Redox conditions:

- Denitrification $\mathrm{CCl_4} \rightarrow \mathrm{CHCl_3}$
- Sulfate reduction $\mathrm{CCl_4} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} + \mathrm{Cl^-}$

Abiotic degradation of TCA

$CH_3CCl_3 \rightarrow CH_2CCl_2 + CH_3COOH \rightarrow CO_2 + H_2O + Cl^-$

1,1,1-TCA → 1,1-DCE + Acetic acid → mineralization

Redox conditions:

All redox conditions

Anaerobic dechlorination of TCA

$CH_3CCl_3 \rightarrow CH_3CHCl_2 \rightarrow CH_3CH_2Cl \rightarrow CO_2 + H_2O + Cl^-$

1,1,1-TCA → 1,1-DCA → Chloroethane → mineralization

Redox conditions:

- Sulfate reduction   1,1,1-TCA → 1,1-DCA
- Methanogenesis   1,1,1-TCA → mineralization

Anaerobic degradation of PCE & TCE

$CCl_2{=}CCl_2 \rightarrow CHCl{=}CCl_2 \rightarrow CHCl{=}CHCl \rightarrow$
$CH_2{=}CHCl \rightarrow CH_2CH_2 \rightarrow CH_3CH_3$

PCE → TCE → cis-1,2-DCE →
vinyl chloride → ethene → ethane?

Redox conditions:

Sulfate reduction PCE → DCE, TCE → DCE
Methanogenesis PCE → ethene, TCE → ethene

Analytical protocol

Ground water:

- Same as for hydrocarbons, plus:
- Methane – to confirm methanogenesis
- Chlorinated VOCs – materials degraded and degradation products
  - Distinguish cis-1,2-DCE and trans-1,2-DCE
- Degradation byproducts: CO_2, ethane, ethene, chloride

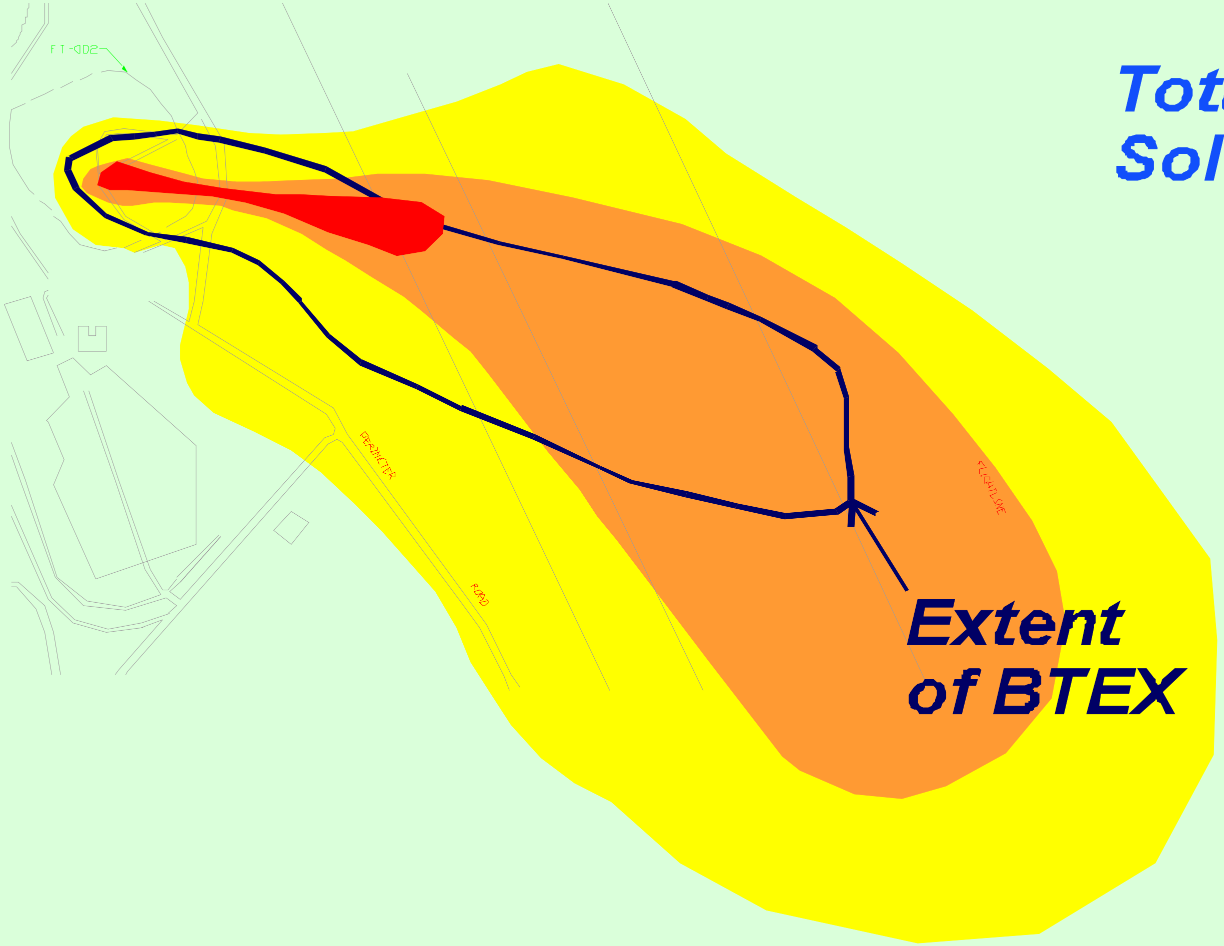
Analytical protocols

Ground water:

Dissolved hydrogen – distinguishes strength of dechlorination and redox state:

Electron acceptor	**H_2 concentration (ng/L)**
Denitrification	< 0.1
Iron reduction	0.2 to 0.8
Sulfate reduction	1 to 4
Reductive dechlorination	> 1
Methanogenesis	5 to 20

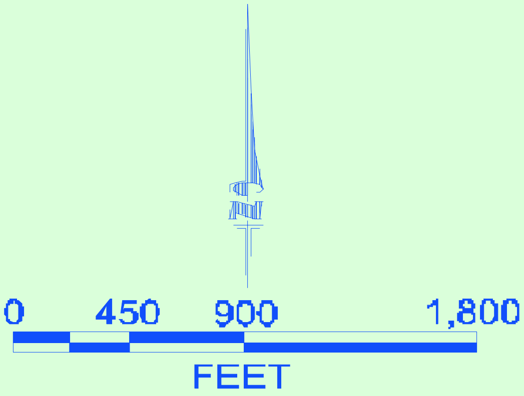
Extent of Chlorinated Solvents and BTEX



Extent of BTEX

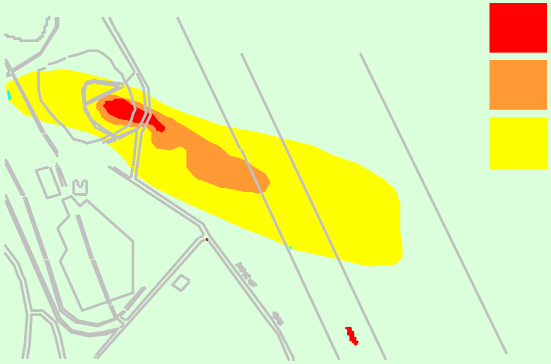
Total Chlorinated Solvent Concentration

- 🟥 > 10,000 µg/L
- 🟧 1,000 - 10,000 µg/L
- 🟨 ND - 1,000 µg/L



BTEX and Electron Acceptors

Total BTEX

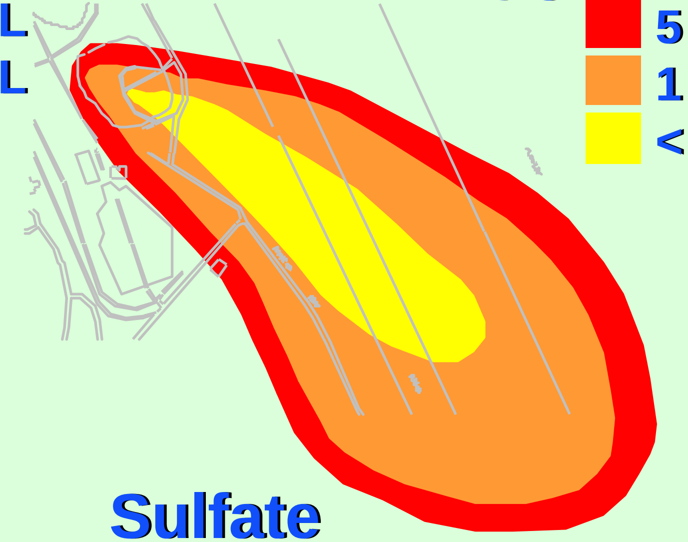


🟥 4,000 - 6,000 µg/L

🟧 2,000 - 4,000 µg/L

🟨 0 - 2,000 µg/L

Dissolved Oxygen

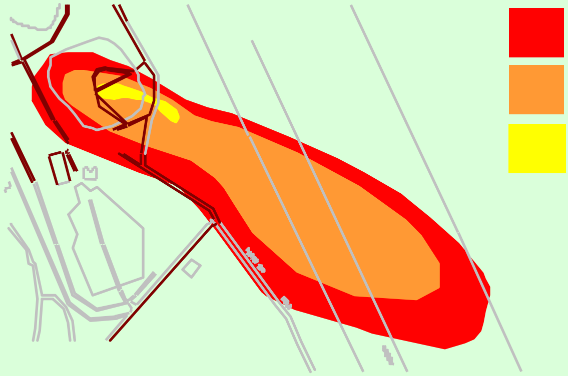


🟥 5 - 10 mg/L

🟧 1 - 5 mg/L

🟨 < 1 mg/L

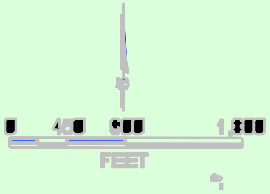
Nitrate



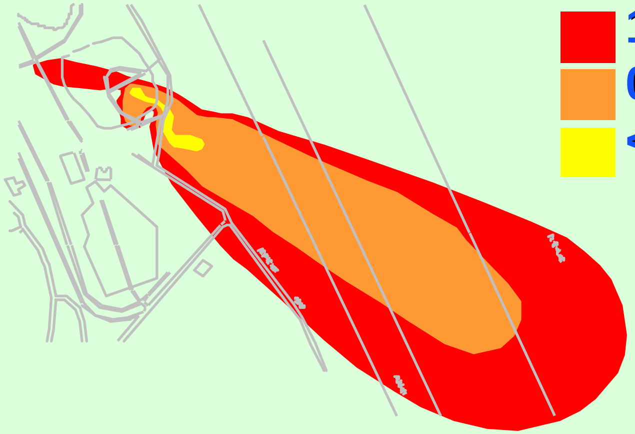
🟥 2 - 4 mg/L

🟧 0.05 - 2 mg/L

🟨 < 0.05 mg/L



Sulfate



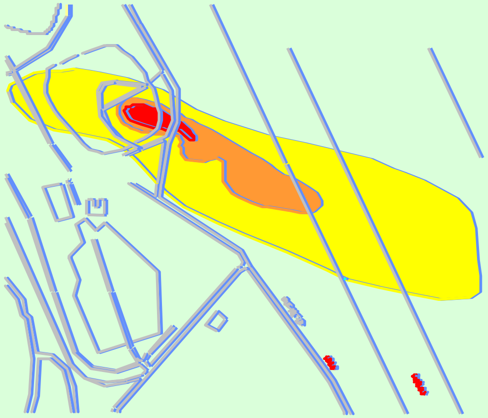
🟥 10 - 20 mg/L

🟧 0.05 - 10 mg/L

🟨 < 0.05 mg/L

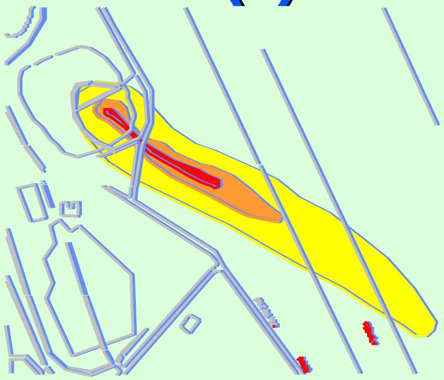
BTEX and Metabolic Byproducts

Total BTEX



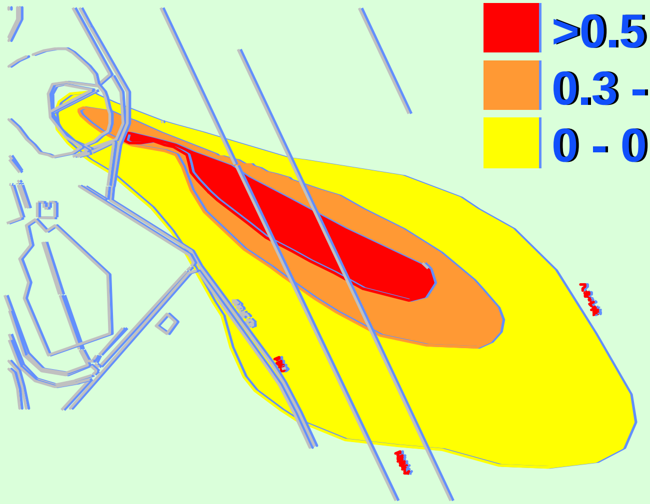
🟥 4,000 - 6,000 µg/L
🟧 2,000 - 4,000 µg/L
🟨 0 - 2,000 µg/L

Iron (II)



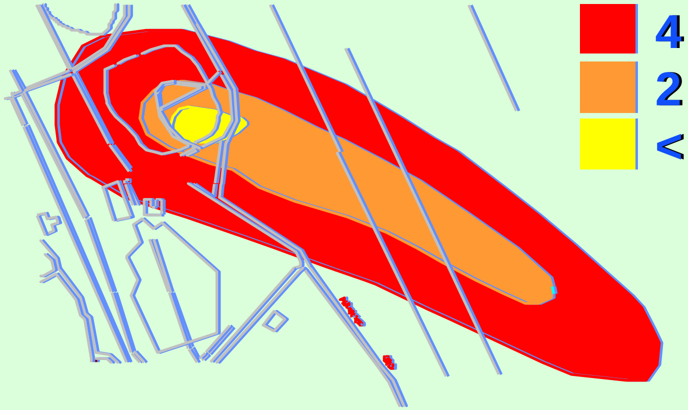
🟥 10 - 11 mg/L
🟧 5 - 10 mg/L
🟨 0.05 - 5 mg/L

Methane

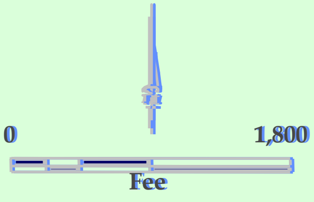


🟥 >0.5 mg/L
🟧 0.3 - 0.5 mg/L
🟨 0 - 0.3 mg/L

pe

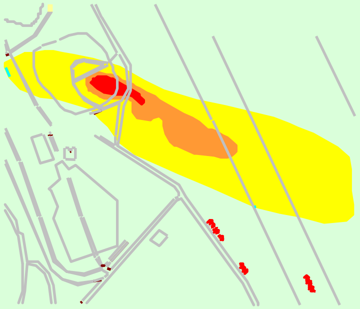


🟥 4 - 7
🟧 2 - 4
🟨 < 2



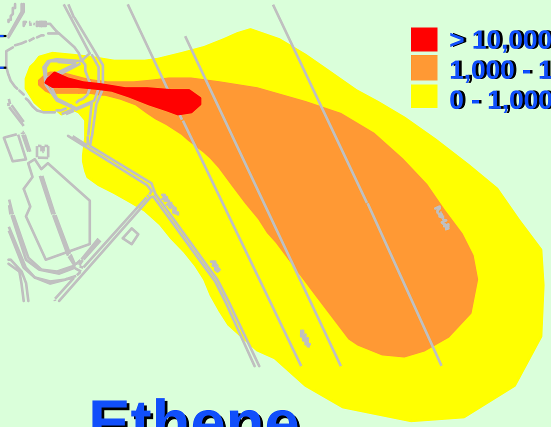
Chlorinated Solvents and Byproducts

Total BTEX



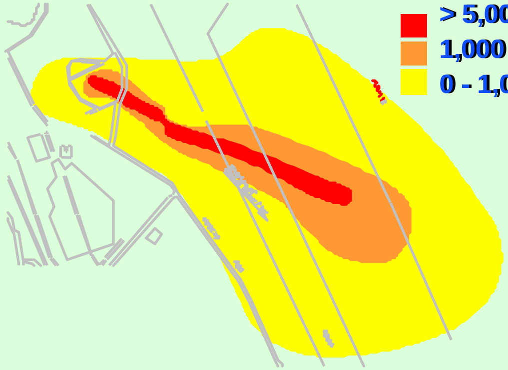
🟥 4,000 - 6,000 µg/L
🟧 2,000 - 4,000 µg/L
🟨 0 - 2,000 µg/L

Trichloroethene



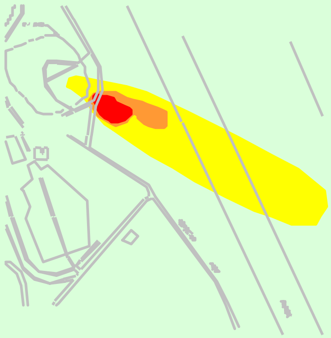
🟥 > 10,000 µg/L
🟧 1,000 - 10,000 µg/L
🟨 0 - 1,000 µg/L

Dichloroethene



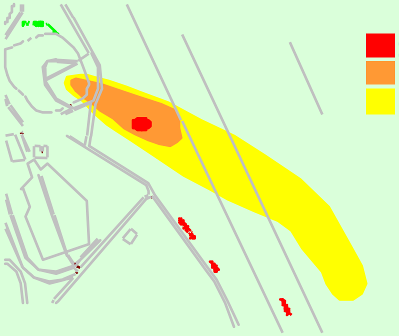
🟥 > 5,000 µg/L
🟧 1,000 - 5,000 µg/L
🟨 0 - 1,000 µg/L

Vinyl Chloride



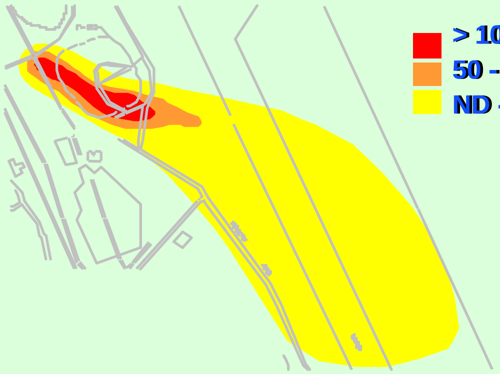
🟥 > 1,000 µg/L
🟧 500 - 1,000 µg/L
🟨 ND - 500 µg/L

Ethene

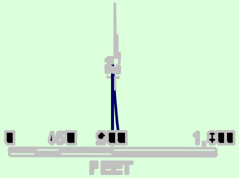


🟥 > 500 µg/L
🟧 100 - 500 µg/L
🟨 ND - 100 µg/L

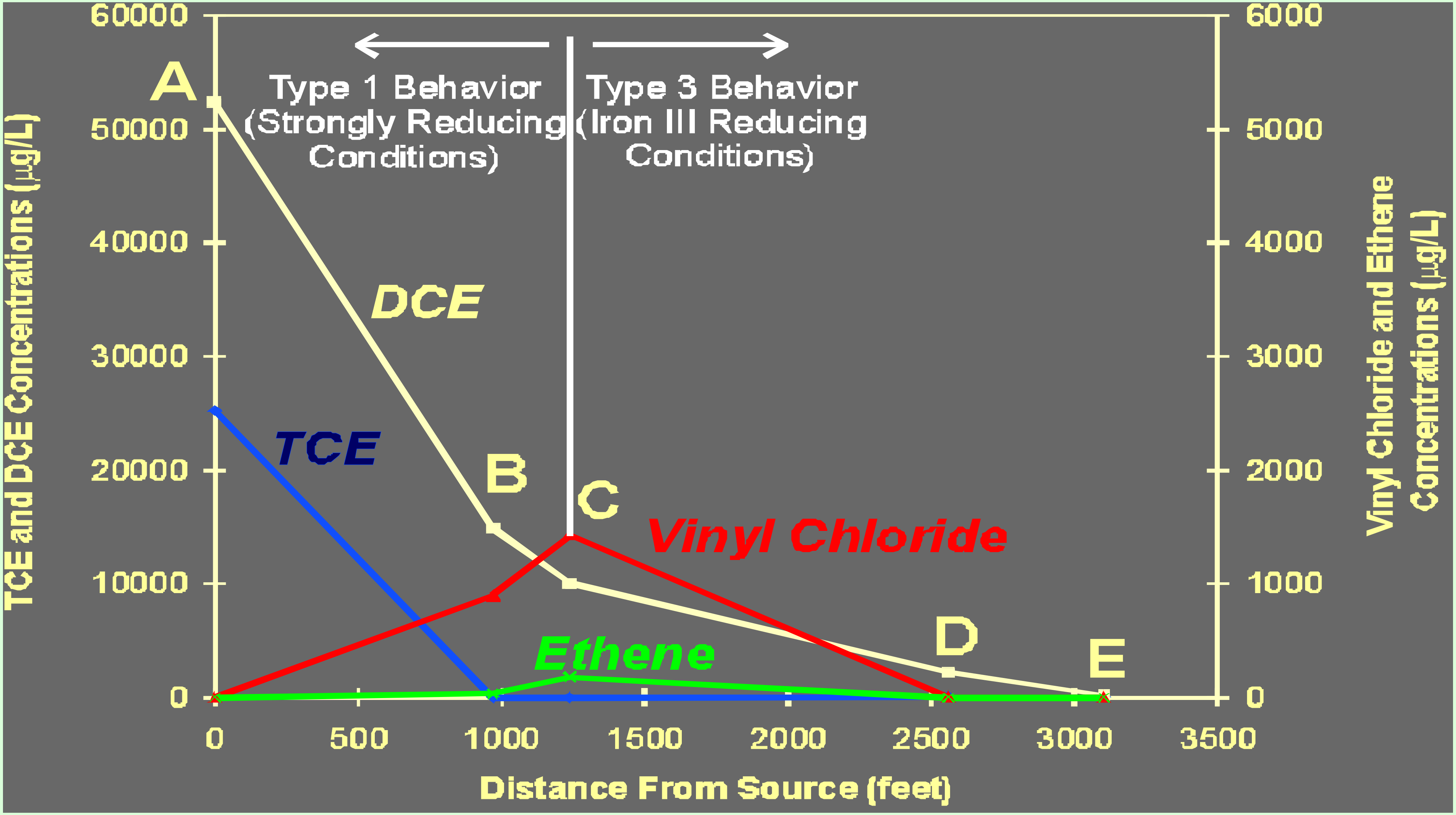
Chloride



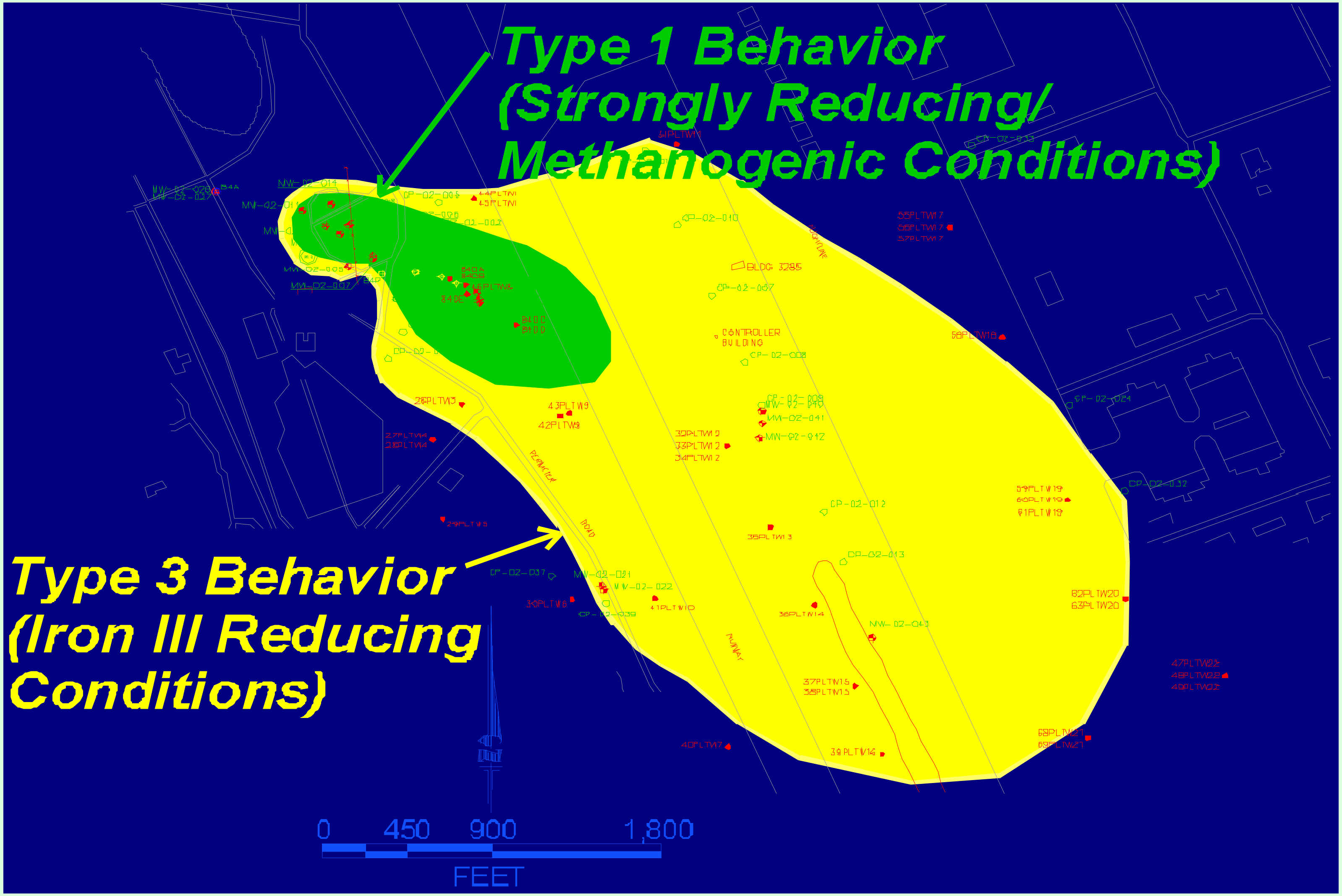
🟥 > 100 mg/L
🟧 50 - 100 mg/L
🟨 ND - 50 mg/L



Plot of TCE, DCE, VC, and Ethene versus Distance Downgradient

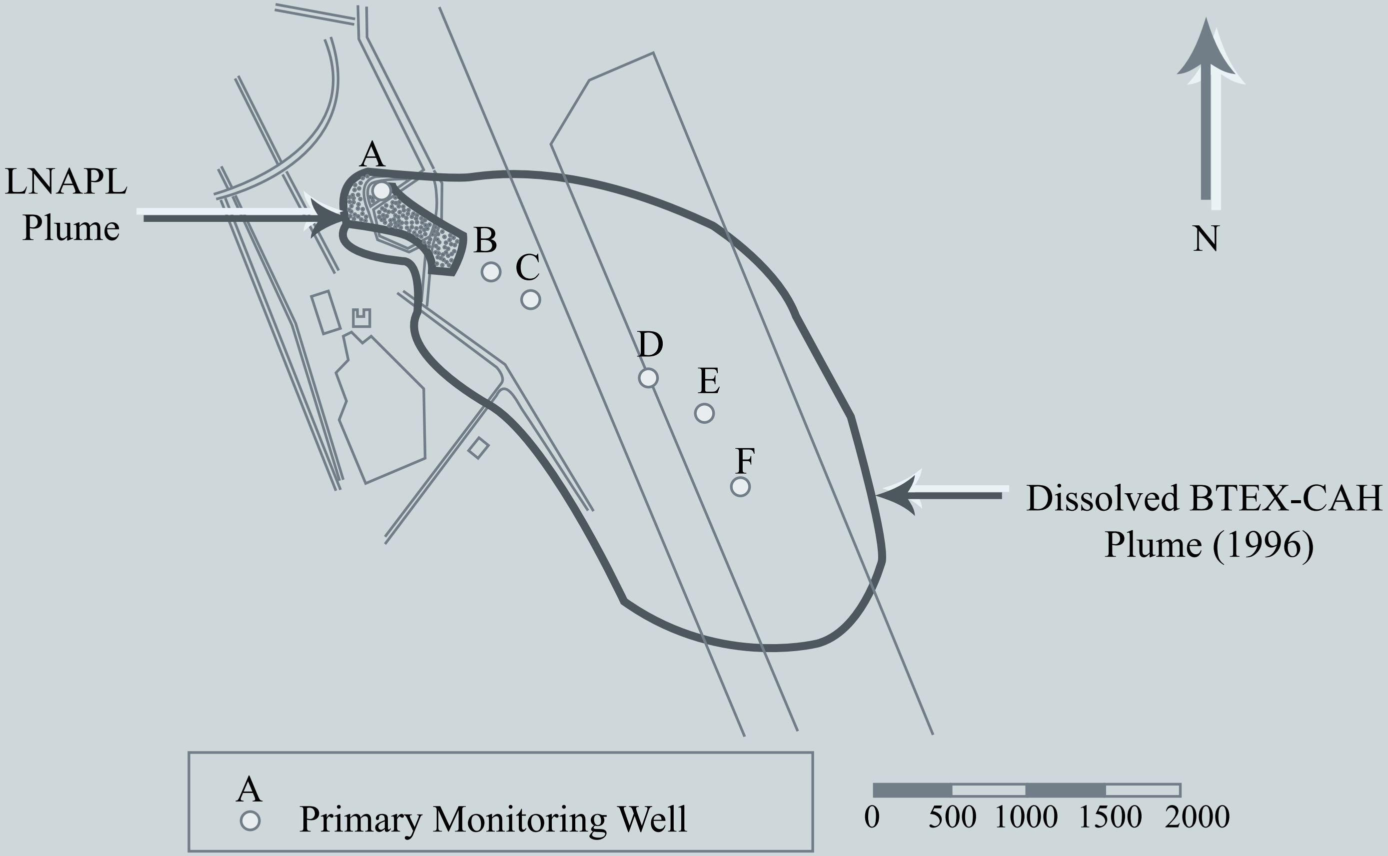


Plume Classification

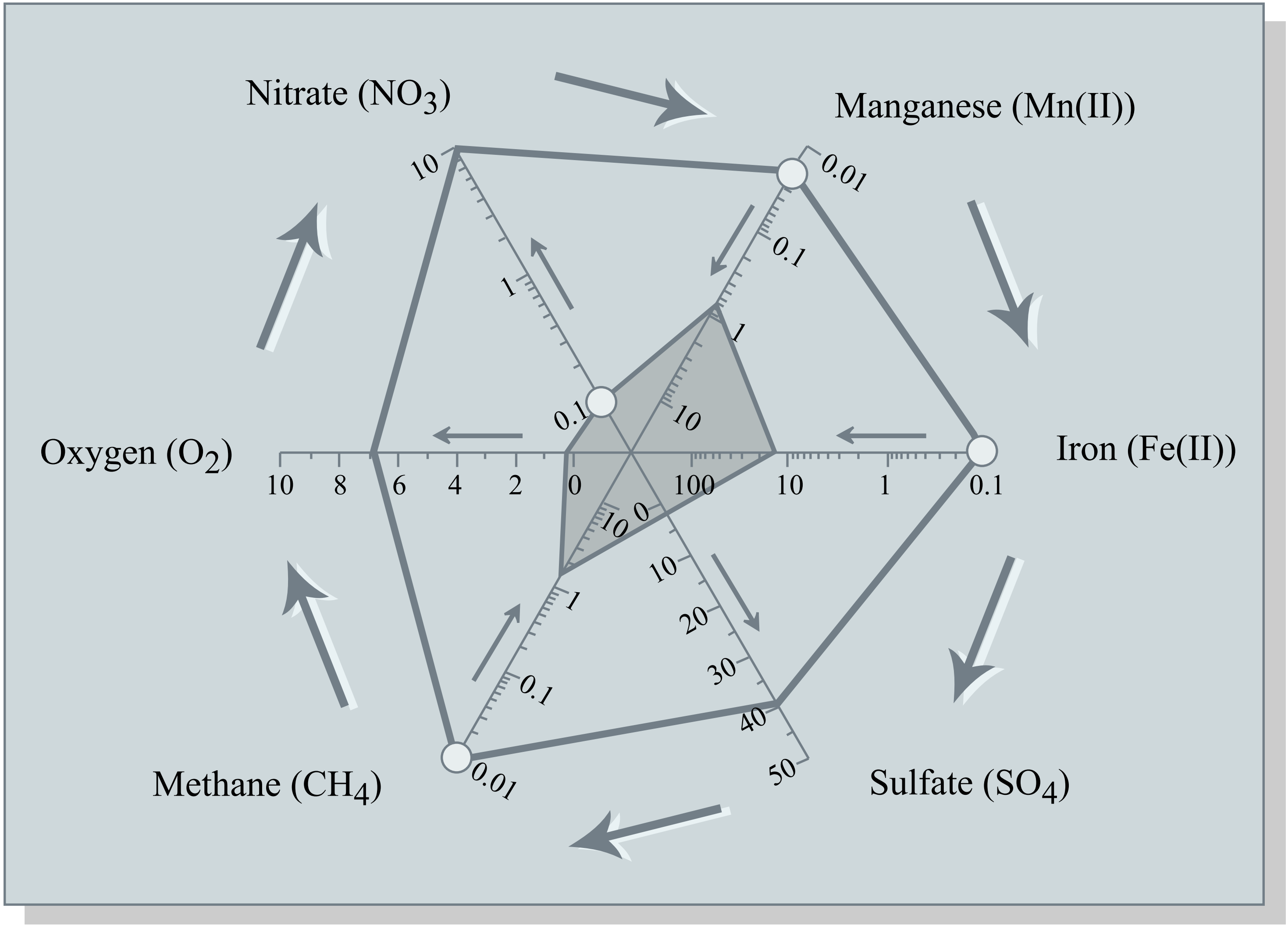


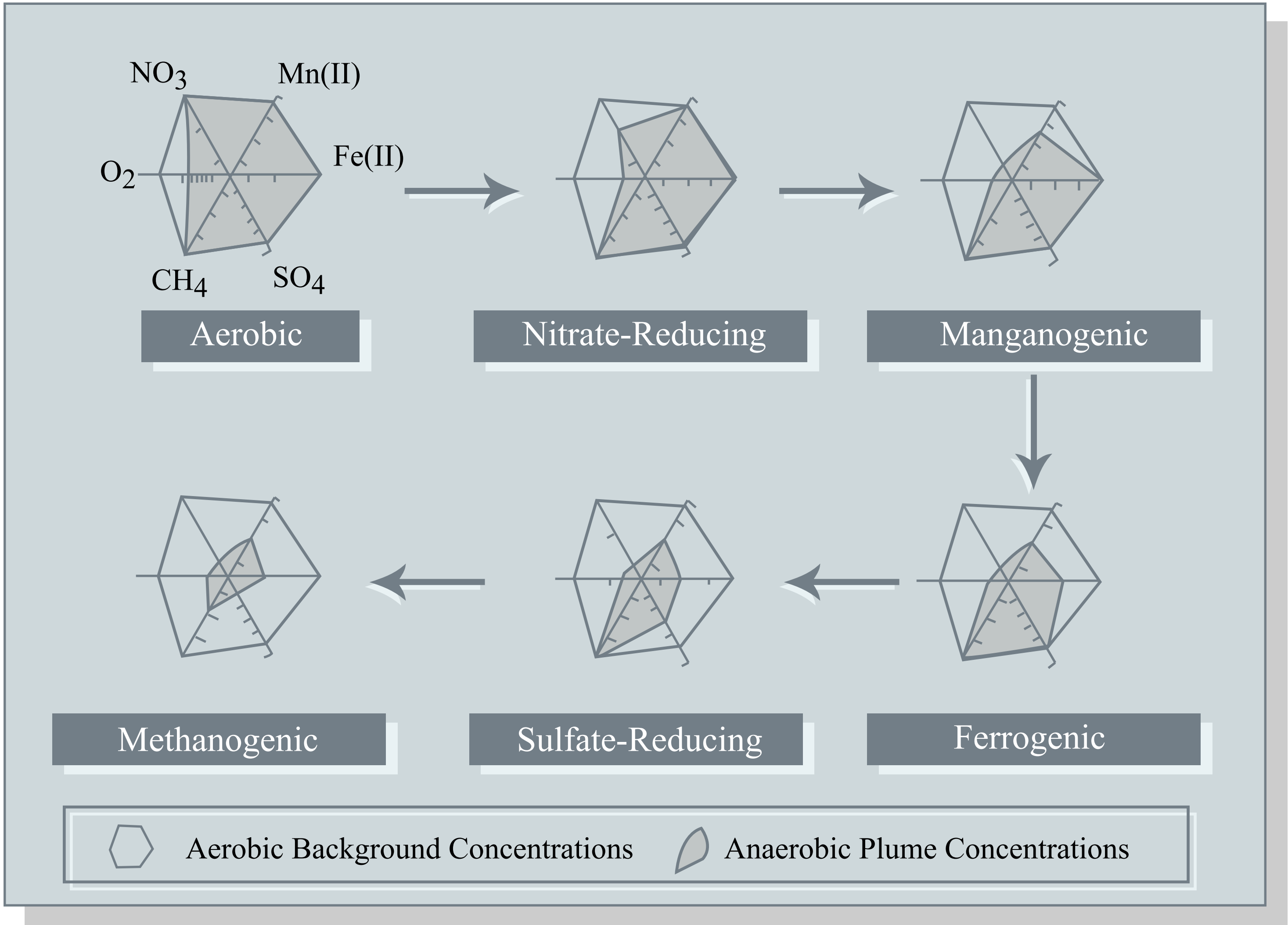
Type 1 Behavior (Strongly Reducing/ Methanogenic Conditions)

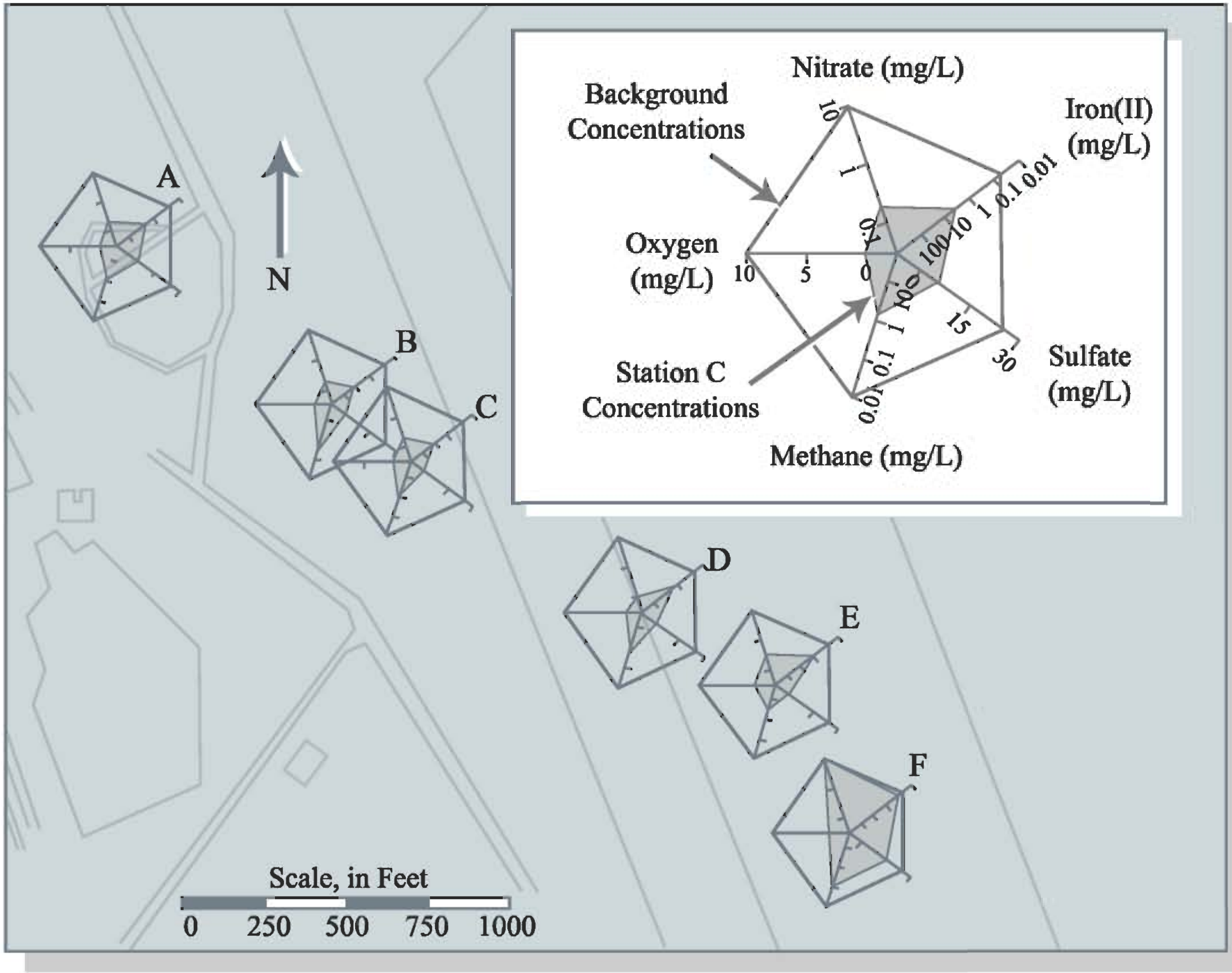
Type 3 Behavior (Iron III Reducing Conditions)



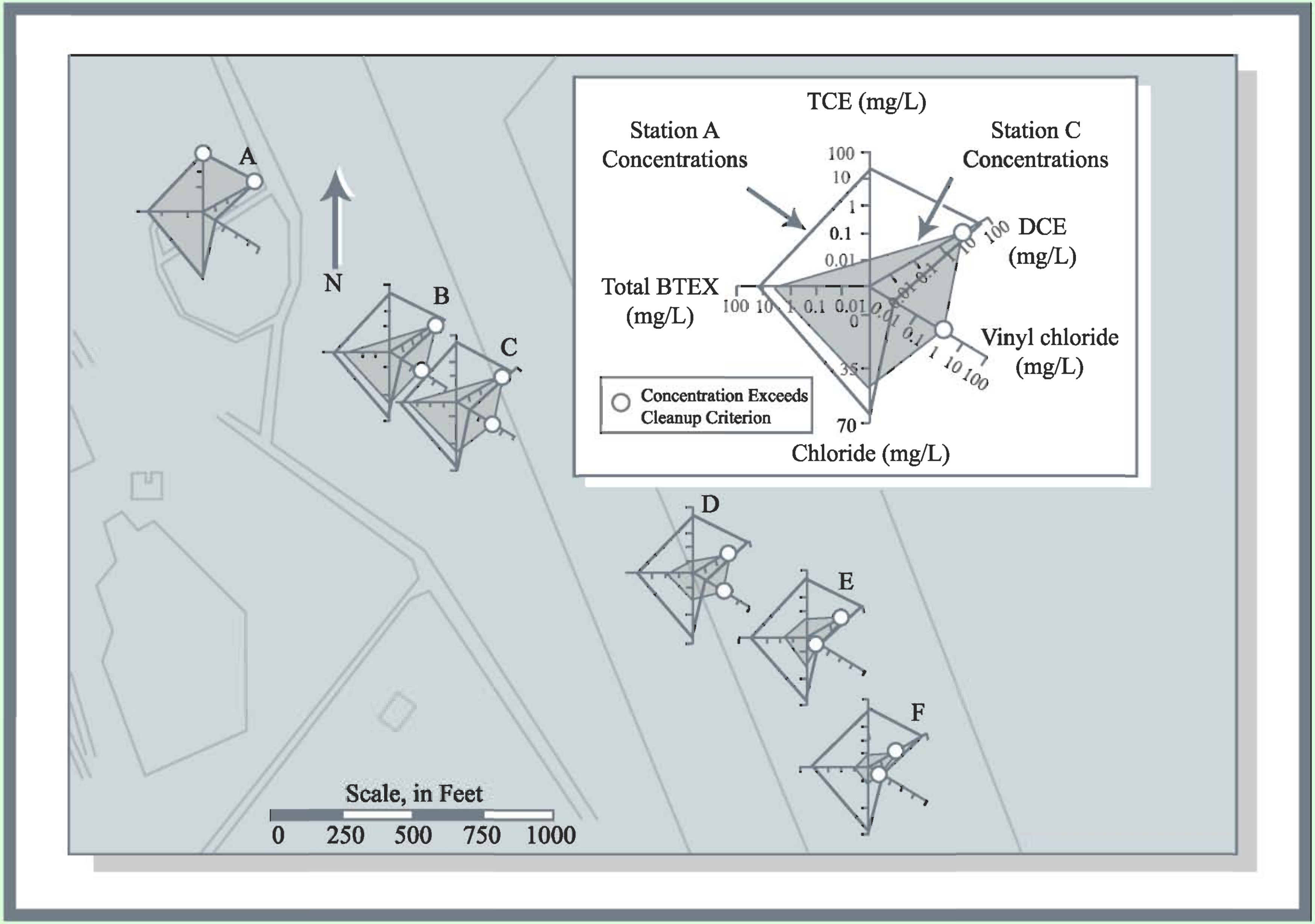
Adapted from: Carey, G. R., P. J. V. Geel, T. H. Wiedemeier, and E. A. McBean. "A Modified Radial Diagram Approach for Evaluating Natural Attenuation Trends for Chlorinated Solvents and Inorganic Redox Indicators." *Ground Water Monitoring & Remediation* 23, no. 4 (Fall 2003): 75-84.


Nitrate (NO_3)
Manganese (Mn(II))
Oxygen (O_2)
Iron (Fe(II))
Methane (CH_4)
Sulfate (SO_4)
10
1
0.1
0.01
0.1
1
10
10
8
6
4
2
0
100
10
1
0.1
0
10
1
0.1
0.01
0
10
20
30
40
50


NO3
Mn(II)
O2
Fe(II)
CH4
SO4
Aerobic
Nitrate-Reducing
Manganogenic
Ferrogenic
Sulfate-Reducing
Methanogenic
Aerobic Background Concentrations
Anaerobic Plume Concentrations

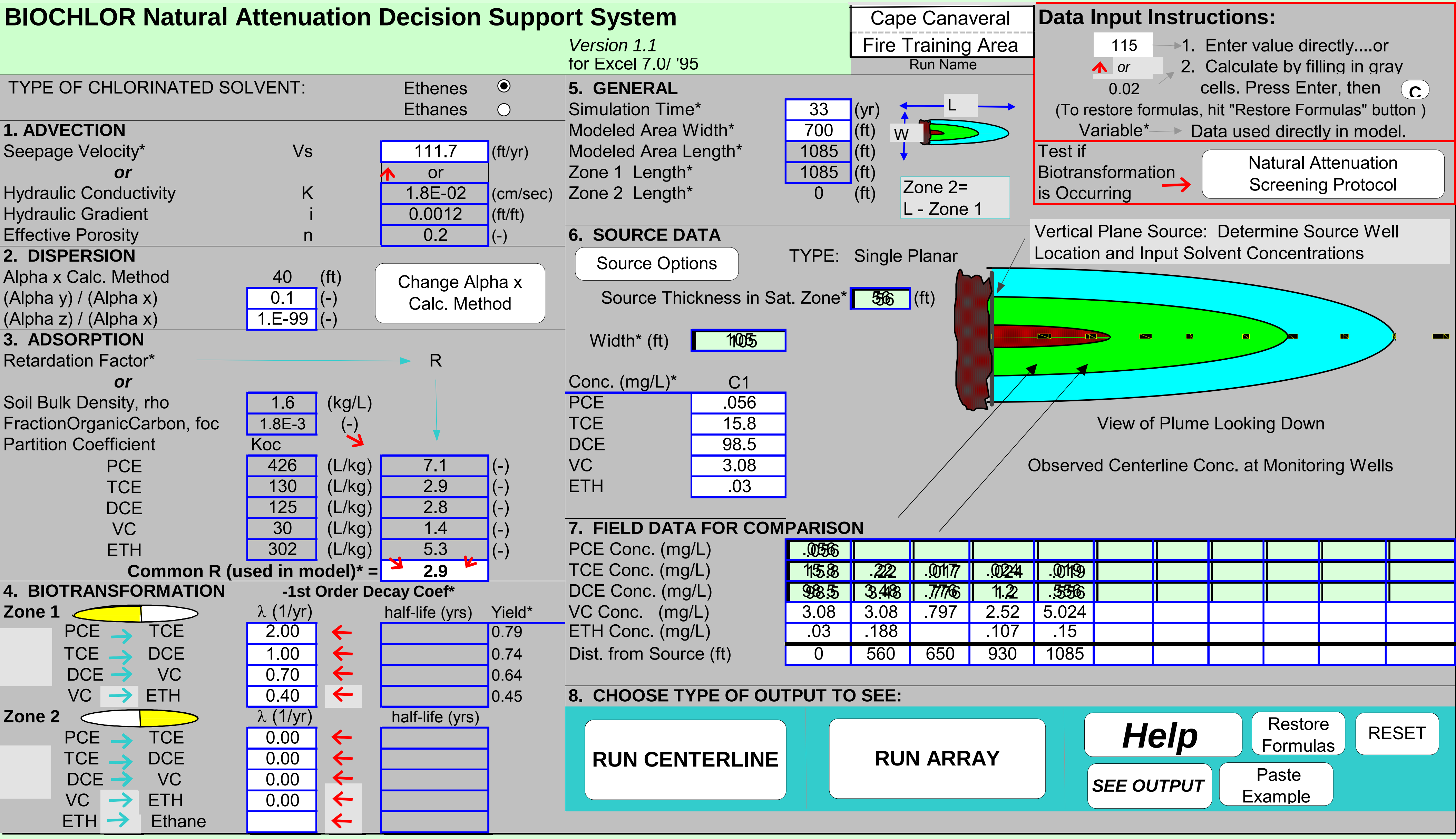


A
B
C
D
E
F
N
Nitrate (mg/L)
Iron(II) (mg/L)
Background Concentrations
Oxygen (mg/L)
Sulfate (mg/L)
Station C Concentrations
Methane (mg/L)
10
1
0.1
0.01
0.1
1
10
100
10
5
0
15
30
100
10
1
0.1
0.01
Scale, in Feet
0
250
500
750
1000


A
B
C
D
E
F
N
TCE (mg/L)
Station A Concentrations
Station C Concentrations
100
10
1
0.1
0.01
DCE (mg/L)
Total BTEX (mg/L)
100 10 1 0.1 0.01
0
0.01 0.1 1 10 100
Vinyl chloride (mg/L)
35
70
Chloride (mg/L)
○ Concentration Exceeds Cleanup Criterion
Scale, in Feet
0 250 500 750 1000

Microsoft Excel Worksheet

BIOCHLOR



BIOCHLOR Natural Attenuation Decision Support System

Version 1.1
for Excel 7.0/ '95

Cape Canaveral
Fire Training Area
Run Name

Data Input Instructions:

115 → 1. Enter value directly....or
or 2. Calculate by filling in gray
0.02 cells. Press Enter, then C
(To restore formulas, hit "Restore Formulas" button)
Variable* → Data used directly in model.

Test if Biotransformation is Occurring → Natural Attenuation Screening Protocol

TYPE OF CHLORINATED SOLVENT: Ethenes ● Ethanes ○

1. ADVECTION

Seepage Velocity*	Vs	111.7	(ft/yr)
or		or	
Hydraulic Conductivity	K	1.8E-02	(cm/sec)
Hydraulic Gradient	i	0.0012	(ft/ft)
Effective Porosity	n	0.2	(-)

2. DISPERSION

Alpha x Calc. Method	40	(ft)
(Alpha y) / (Alpha x)	0.1	(-)
(Alpha z) / (Alpha x)	1.E-99	(-)

Change Alpha x Calc. Method

3. ADSORPTION

Retardation Factor* → R

or

Soil Bulk Density, rho	1.6	(kg/L)		
FractionOrganicCarbon, foc	1.8E-3	(-)		
Partition Coefficient	Koc			
PCE	426	(L/kg)	7.1	(-)
TCE	130	(L/kg)	2.9	(-)
DCE	125	(L/kg)	2.8	(-)
VC	30	(L/kg)	1.4	(-)
ETH	302	(L/kg)	5.3	(-)

Common R (used in model)* = 2.9

4. BIOTRANSFORMATION **-1st Order Decay Coef***

Zone 1

	λ (1/yr)	half-life (yrs)	Yield*
PCE → TCE	2.00		0.79
TCE → DCE	1.00		0.74
DCE → VC	0.70		0.64
VC → ETH	0.40		0.45

Zone 2

	λ (1/yr)	half-life (yrs)
PCE → TCE	0.00	
TCE → DCE	0.00	
DCE → VC	0.00	
VC → ETH	0.00	
ETH → Ethane		

5. GENERAL

Simulation Time*	33	(yr)
Modeled Area Width*	700	(ft)
Modeled Area Length*	1085	(ft)
Zone 1 Length*	1085	(ft)
Zone 2 Length*	0	(ft)

L W

Zone 2= L - Zone 1

6. SOURCE DATA

Source Options TYPE: Single Planar

Source Thickness in Sat. Zone* 56 (ft)

Width* (ft) 105

Conc. (mg/L)*	C1
PCE	.056
TCE	15.8
DCE	98.5
VC	3.08
ETH	.03

Vertical Plane Source: Determine Source Well Location and Input Solvent Concentrations

View of Plume Looking Down

Observed Centerline Conc. at Monitoring Wells

7. FIELD DATA FOR COMPARISON

PCE Conc. (mg/L)	.056											
TCE Conc. (mg/L)	15.8	.22	.017	.024	.019							
DCE Conc. (mg/L)	98.5	3.48	.776	1.2	.556							
VC Conc. (mg/L)	3.08	3.08	.797	2.52	5.024							
ETH Conc. (mg/L)	.03	.188		.107	.15							
Dist. from Source (ft)	0	560	650	930	1085							

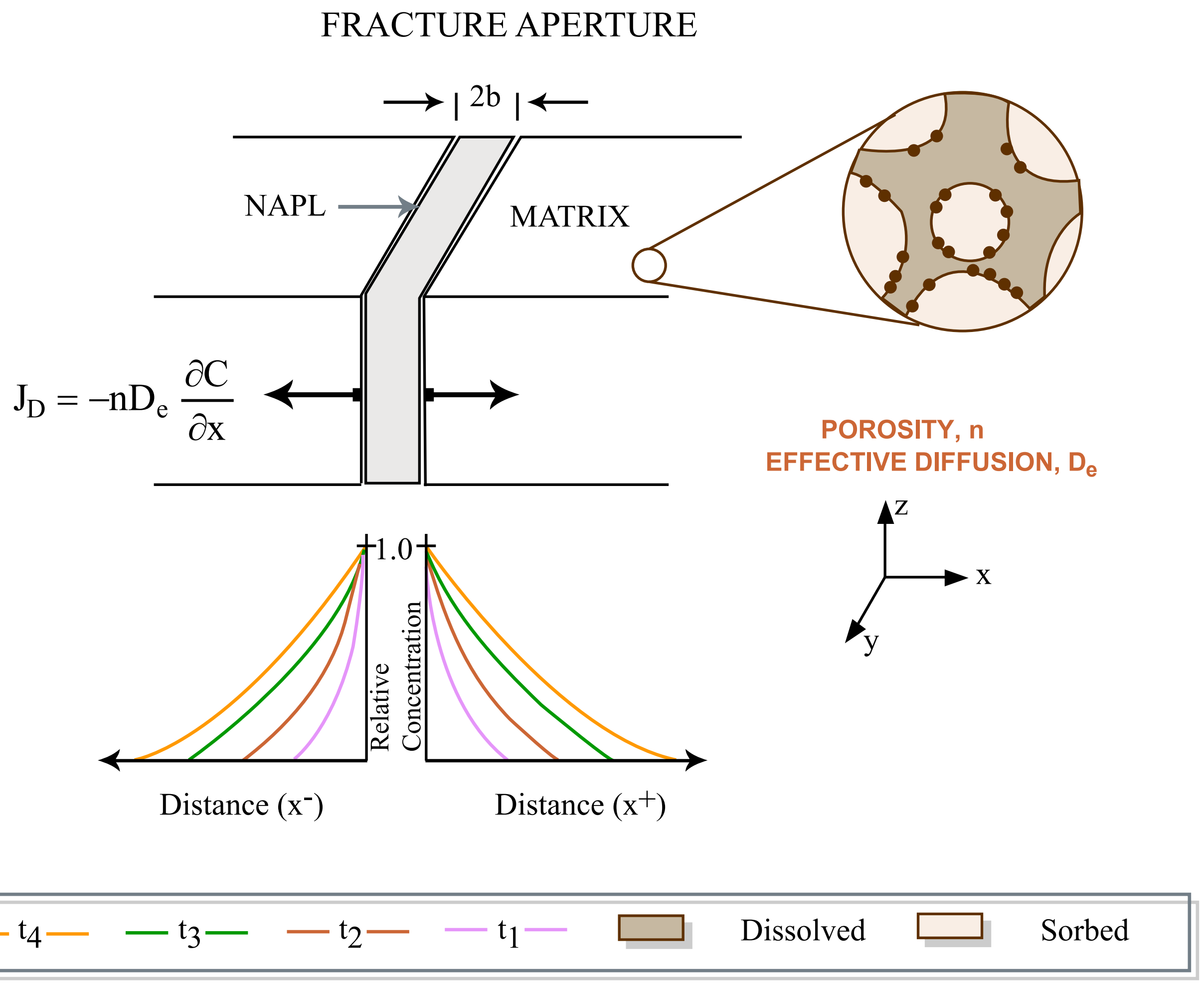
8. CHOOSE TYPE OF OUTPUT TO SEE:

Diffusive disappearance

Parker, B. L., R. W. Gillham and J. A. Cherry, 1994. "Diffusive Disappearance of Immiscible-Phase Organic Liquids in Fractured Geologic Media." *Ground Water*, Vol. 32, No. 5, Pp. 805-820. September/October 1994.

See Figure 1 of:

Parker, B. L., R. W. Gillham and J. A. Cherry, 1994. "Diffusive Disappearance of Immiscible-Phase Organic Liquids in Fractured Geologic Media." *Ground Water*, Vol. 32, No. 5, Pp. 805-820. September/October 1994.


FRACTURE APERTURE
2b
NAPL
MATRIX
$J_D = -nD_e \frac{\partial C}{\partial x}$
POROSITY, n
EFFECTIVE DIFFUSION, D_e
z
x
y
1.0
Relative Concentration
Distance (x^-)
Distance (x^+)
t_4
t_3
t_2
t_1
Dissolved
Sorbed

$$J_D = -nD_e \frac{\partial C}{\partial x}$$

$$\frac{\partial C}{\partial t} = \frac{D_e}{R} \frac{\partial^2 C}{\partial x^2}$$

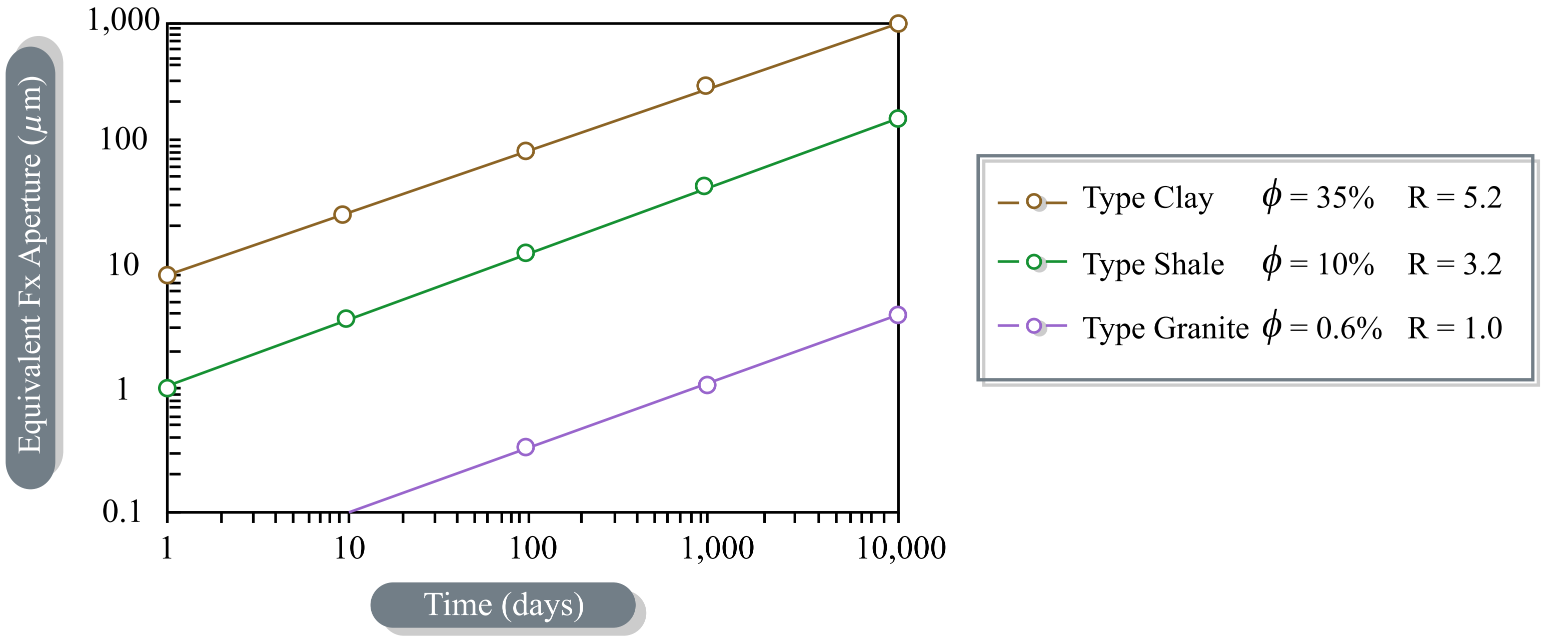
Assume $C(x = 0, t) = S_w$

and $C(x, t = 0) = 0$

$$J_D(0, t) = -nS_W \left(\frac{RD_e}{\pi t} \right)^{1/2}$$

Integrate over time to get mass leaving fracture :

$$M_t = nS_w \frac{4}{\sqrt{\pi}} \left(RD_e t \right)^{1/2}$$



Comparison of TCE mass loss rates for three geologic media expressed in terms of equivalent immiscible-phase fracture aperture and time for NAPL disappearance: type-clay R= 5.2, type-sandstone/shale R = 3.2, and type-granite R= 1. Parameter values provided in the next slide.

Image adapted from: Parker, B. L., R. W. Gillhamand J. A. Cherry, 1994. "Diffusive Disappearance of Immiscible-Phase Organic Liquids in Fractured Geologic Media." *Ground Water*, Vol. 32, No. 5. Pp. 805-820. September/October 1994.

Geologic media parameters for three type-fractured geologic media used for comparison of TCE mass loss rates due to diffusion and sorption to matrix solids presented in figure: type-clay, type-shale/sandstone, and type-granite.

Parameter	**Clay**	**Type-geologic media Shale/sandstone**	**Granite**
Porosity: ϕ	0.35	0.10	0.006
Bulk density: ρ_b (g/cm^3)	1.6	2.4	2.63
Fraction organic carbon: f_{oc}	0.01	0.002	0
Apparent tortuosity: τ	0.33	0.10	0.06
		Combined parameters: TCE & geologic media	
Effective diffusion coefficient: D_e (cm^2/s)	3.3E-06	1.0E-06	6.0E-06
Retardation factor: R	5.2	3.2	1

Image adapted from: Parker, B. L., R. W. Gillhamand J. A. Cherry, 1994. "Diffusive Disappearance of Immiscible-Phase Organic Liquids in Fractured Geologic Media." *Ground Water*, Vol. 32, No. 5. Pp. 805-820. September/October 1994.