In-Situ Remediation (ISR-MT3DMS^{TM}) Features: Reactions

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Introduction

- The core reaction framework in ISR-MT3DMS^{TM} was developed using the public domain reaction package from BioRedox (Carey et al., 1998)
- This package offers the user a very flexible framework with many options for simulating transformations involving chlorinated solvents, petroleum hydrocarbons, and some metals such as Cr(VI).
- The model links to a user-defined database with solute properties, and if needed, oxidation-reduction half-reaction equations.

Degradation Pathways

- ISR-MT3DMS^{TM} can model the degradation of parent species (e.g. 1,1,1-TCA, PCE/TCE, or 1,2-DCA) due to abiotic or biological mechanisms
- The model also has the option of simulating daughter product formation
  - The user defines the daughter products for each parent species
- In addition, the user may simulate halogen production (e.g. chloride accumulation), as a means of calibrating the degradation rate along a flowpath

Solute Classes

- There are four main classes of solutes in ISR-MT3DMS^{TM}:
  - Electron donors
  - Electron acceptors
  - General solutes which are not directly involved in coupled oxidation-reduction reactions
  - Halogens (e.g. chloride or bromide) included in molecules of other solutes such as chlorinated solvents
    - For example, this option allows the model to simulate the accumulation of chloride during chlorinated solvent degradation

Reaction Mechanisms

- There are up to four types of reaction mechanisms which may be specified for electron donors and general solutes:
  - Abiotic transformation (e.g. 1,1,1-TCA to 1,1-DCE)
  - Oxidation e.g. for electron donors such as BTEX or MTBE
  - Reduction reactions which may or may not be explicitly coupled with oxidation reactions
    - e.g. chlorinated solvents or Cr(VI)
  - Cometablism – where a solute degrades fortuitously in the presence of another substrate
    - For example, methane from the anaerobic zone may be transported to the fringes of the aerobic zone where it supports rapid methanotrophic cometabolism of TCE and other contaminants

Reaction Kinetics

- There are various options for reaction kinetics in ISR-MT3DMS^{TM}, including:
  - Instantaneous (e.g. BTEX or Fe(II) in the aerobic zone)
  - First-order kinetics
  - Modified monod kinetics to simulate the influence of substrate concentration on chlorinated solvent rates
  - Second-order kinetics

Redox Reactions

- Users have the option to simulate coupled oxidation-reduction (redox) reactions between one or more electron donors and acceptors
- When redox reactions are included, they are modeled sequentially. For example, the most preferred electron acceptor (oxygen) is used until depleted; then the next most preferred electron acceptor (e.g. nitrate) is used until depleted; and so on.
- The user specifies how many electron acceptors (i.e. redox zones) are to be simulated, and the order of preferred reactivity for each acceptor.

Redox Reactions

- Each electron donor and general solute may be specified to have reaction mechanisms, kinetic models, and daughter products/halogens that vary with each redox zone

- Also, metabolic by-products from electron acceptor reduction may be simulated, such as:
  - $Mn(IV)_{(s)} \rightarrow Mn(II)_{(aq)}$
  - $Fe(III)_{(s)} \rightarrow Fe(II)_{(aq)}$
  - $SO_4{}^{2-}{}_{(aq)} \rightarrow S^{2-}{}_{(aq)}$
  - $CO_{2\,(aq)} \rightarrow CH_{4\,(aq)}$

- Electron acceptors and metabolic by-products may be aqueous or mineral species, so simple mineral precipitation and dissolution reactions may be simulated

Redox Reactions

- Users also have the option to simulate:
  - Simple aerobic and anaerobic zones
  - Unlimited supply of electron acceptors like CO_2 in the methanogenic zone, so they don't have to be modeled as additional solutes
    - But CH_4 production can still be modeled if desired
  - Influence of magnetite on abiotic transformation of chlorinated solvents like TCE
  - Different reactivity of mineral species like amorphous and crystalline $Fe(III)_{(s)}$

Solute Properties Database

- User can easily change default properties or add solutes. Only the solute ID number is specified in the model input file – the model will then obtain properties directly from the database prior to running the simulation. Properties include:
  - Solute ID number and name
  - Solute phase (e.g. aqueous or mineral)
  - Molecular weight
  - Sorption coefficient(s)
  - Free-water diffusion coefficient

Redox Half-Reaction Database

- Default oxidation and reduction half-reaction properties, which the user can refine or add to
- The user also defines which half-reactions to be used for each electron donor and acceptor; model automatically calculates reaction stoichiometry
- Properties in the database include:
  - Half-reaction ID number and name
  - Solute ID number(s) (including metabolic by-products if simulated)
  - Number of electron equivalents transferred in each half reaction
  - For electron acceptor reduction half-reactions:
    - Stoichiometry of metabolic by-products (# moles produced)
    - Minimum concentration needed (e.g. 0.1 mg/L for oxygen)
    - Whether the EA has unlimited supply (e.g. CO_2 in the methanogenic zone)

Stimulation/Inhibition of Degradation Rates

- Users may also specify changes to degradation rates due to the presence of substrates or inhibitory compounds, such as:
  - Zero or slow degradation rate without a substrate, and higher rate when the substrate exceeds a minimum threshold concentration
    - For example – different rates depending on whether an oxidant is present
  - Zero degradation when an inhibitory compound is present within min/max, or above a min. concentration
    - For example – when concentrations are high enough to be toxic to microbes, or when native organic matter is preferentially oxidized in the presence of an oxidant

Ongoing Code Development

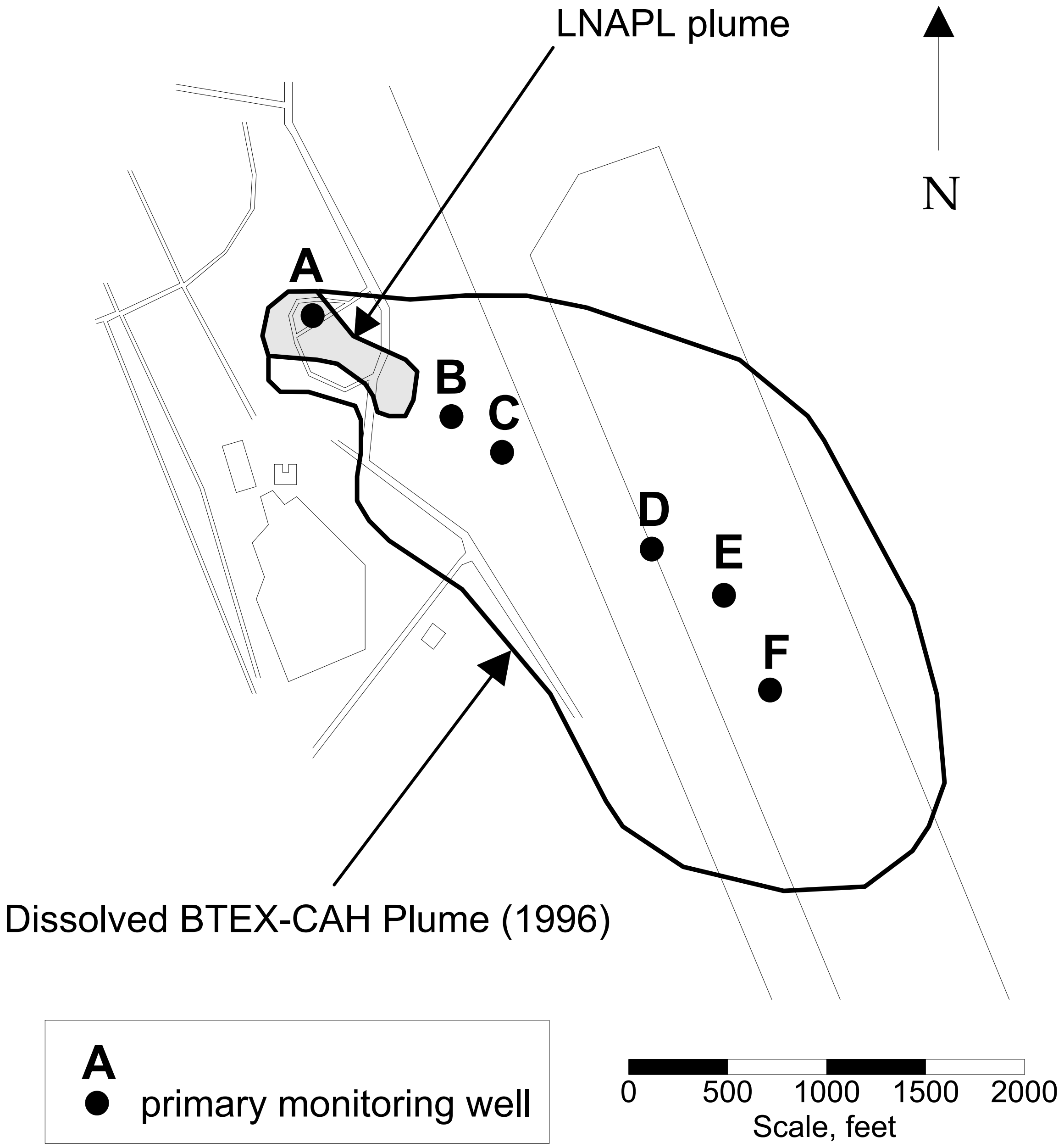
- Most of the options on the preceeding slides included reactions from the previously published BioRedox reaction package

- New features currently being evaluated for ISR-MT3DMS^{TM} include:
  - Second order oxidation (ISCO)
  - Branched decay chains (radionuclides)
  - Rate-limited desorption

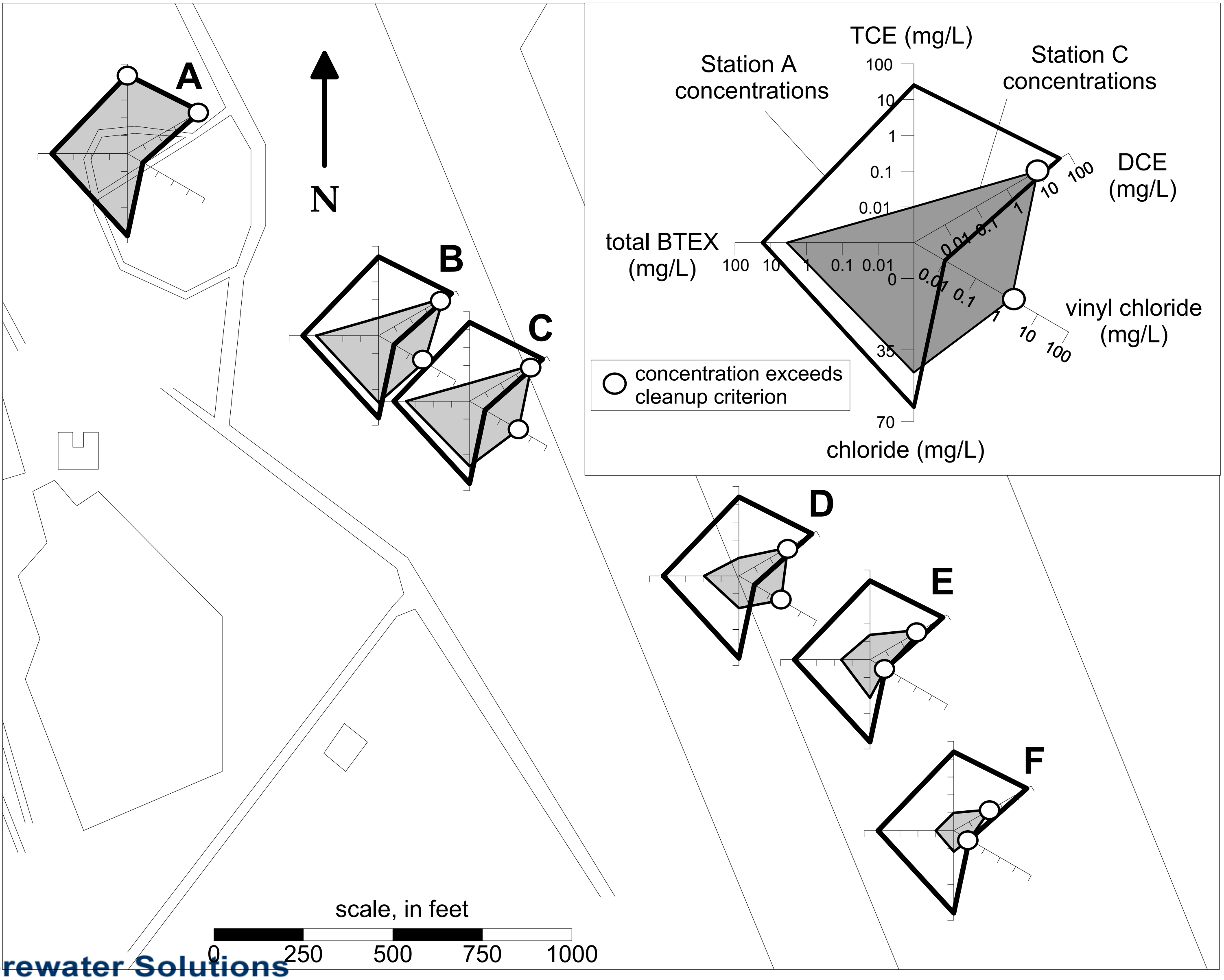
- Note that all of the reaction options specified in this document are available in the local domains where diffusion-dominated transport is simulated. This will facilitate modeling of benefits and limitations with enhanced attenuation in silt/clay layers.

Case Study: Plattsburgh Air Force Base, New York

Site Map


LNAPL plume
N
A
B
C
D
E
F
Dissolved BTEX-CAH Plume (1996)
A
● primary monitoring well
0
500
1000
1500
2000
Scale, feet

Radial Diagram Map: VOCs (1995)



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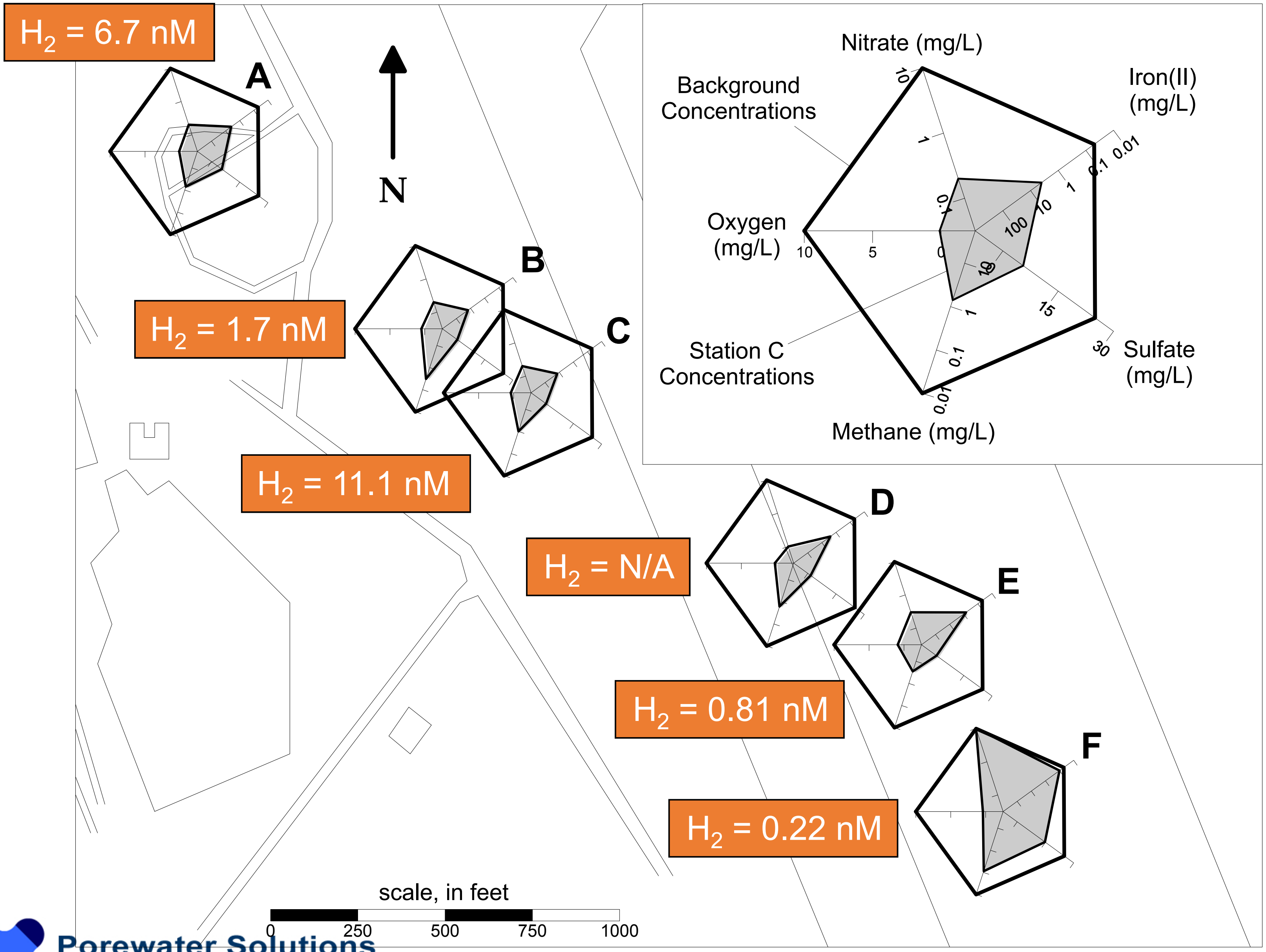
Radial Diagram Map: Redox Indicators (1995)



H_2 = 6.7 nM

H_2 = 1.7 nM

H_2 = 11.1 nM

H_2 = N/A

H_2 = 0.81 nM

H_2 = 0.22 nM

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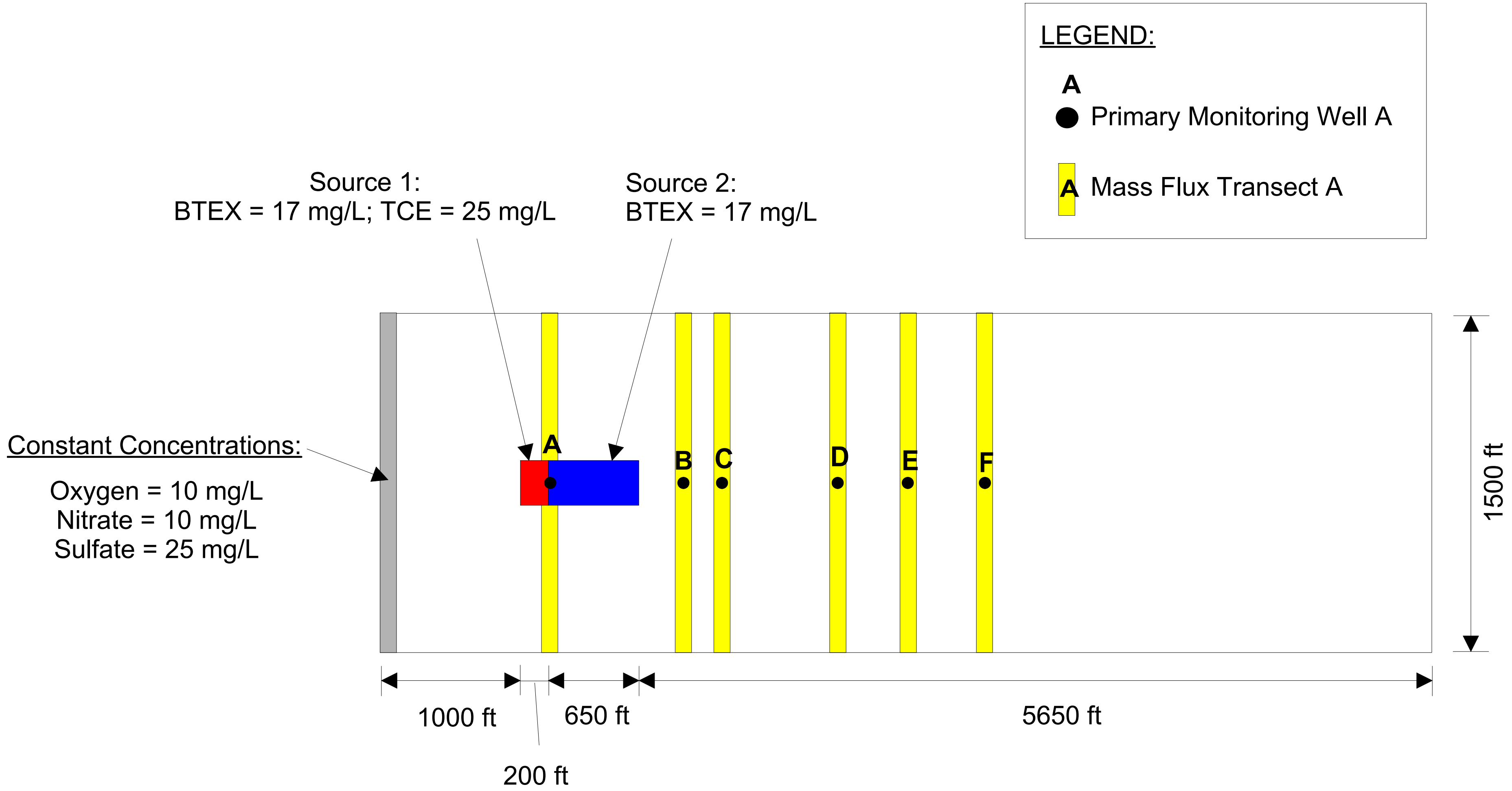
Transport Model Domain and Boundary Conditions



LEGEND:

- ● A Primary Monitoring Well A
- 🟨 A Mass Flux Transect A

Source 1:
BTEX = 17 mg/L; TCE = 25 mg/L

Source 2:
BTEX = 17 mg/L

Constant Concentrations:

Oxygen = 10 mg/L
Nitrate = 10 mg/L
Sulfate = 25 mg/L

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Example – Plattsburgh AFB

Redox Zone:	CH_4	SO_4	Fe^{3+}	NO_3	O_2
BTEX	🟦 0.6	🟦 0.6	🟦 0.6	🟦 0.6	⬛ INST.
TCE	0.2	0.3	1		▨ 0.25
DCE	2	2	2		▨ 0.25 🟦 0.2
VC	0.2		🟦 0.02/0.2*		▨ 0.25 🟦 0.2
Fe^{2+}					⬛ INST.
CH_4	🟦 2	🟦 2	🟦 2	🟦 2	🟦 0.2

LEGEND:

	Mechanism	***Kinetics***
⬛	Oxidation	Instantaneous
🟦	Oxidation	First-Order
▨	CH_4 Co-metabolism	First-Order
🟥	Dehalogenation	First-Order
	No Degradation	n/a

Carey (2007)

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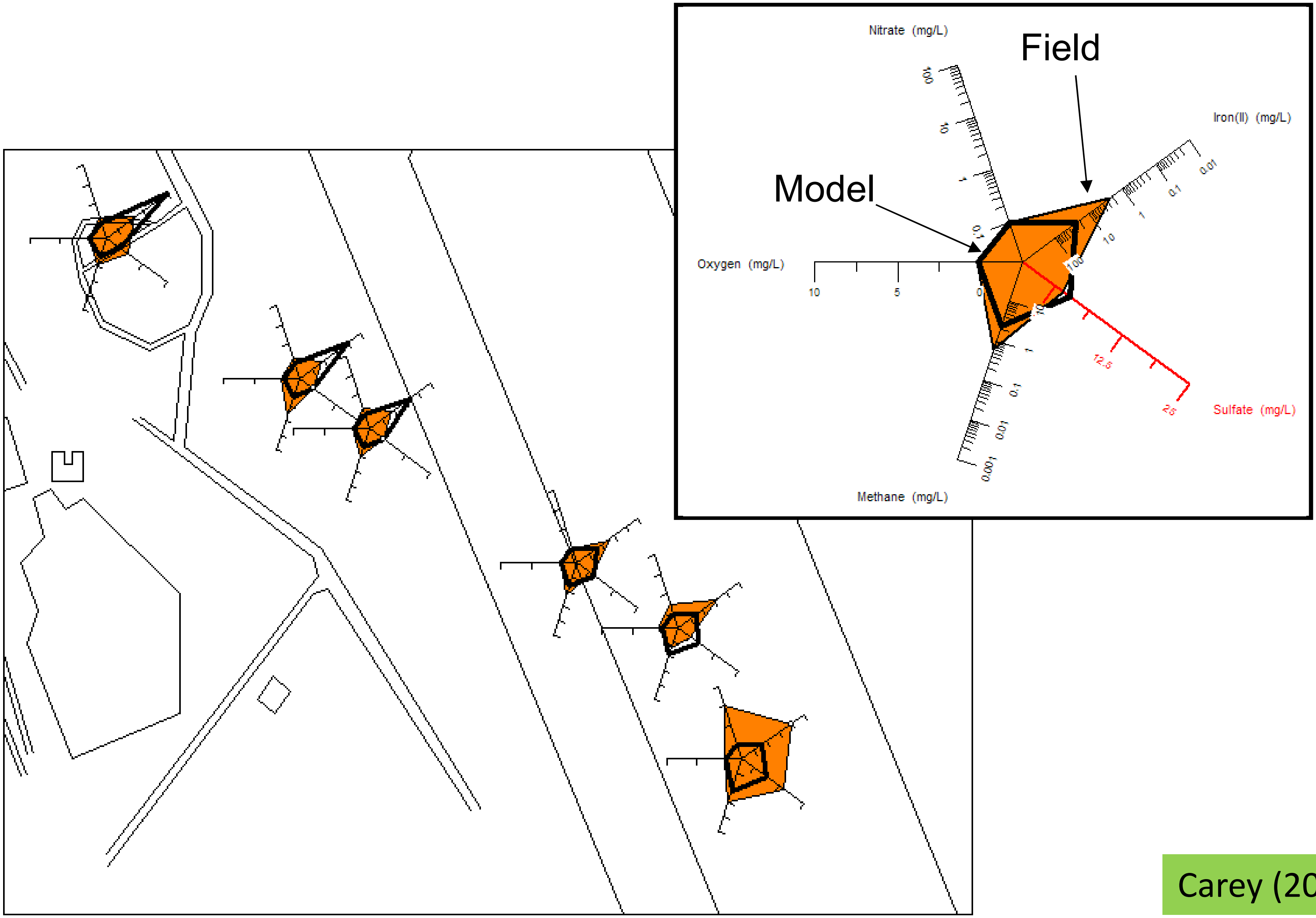
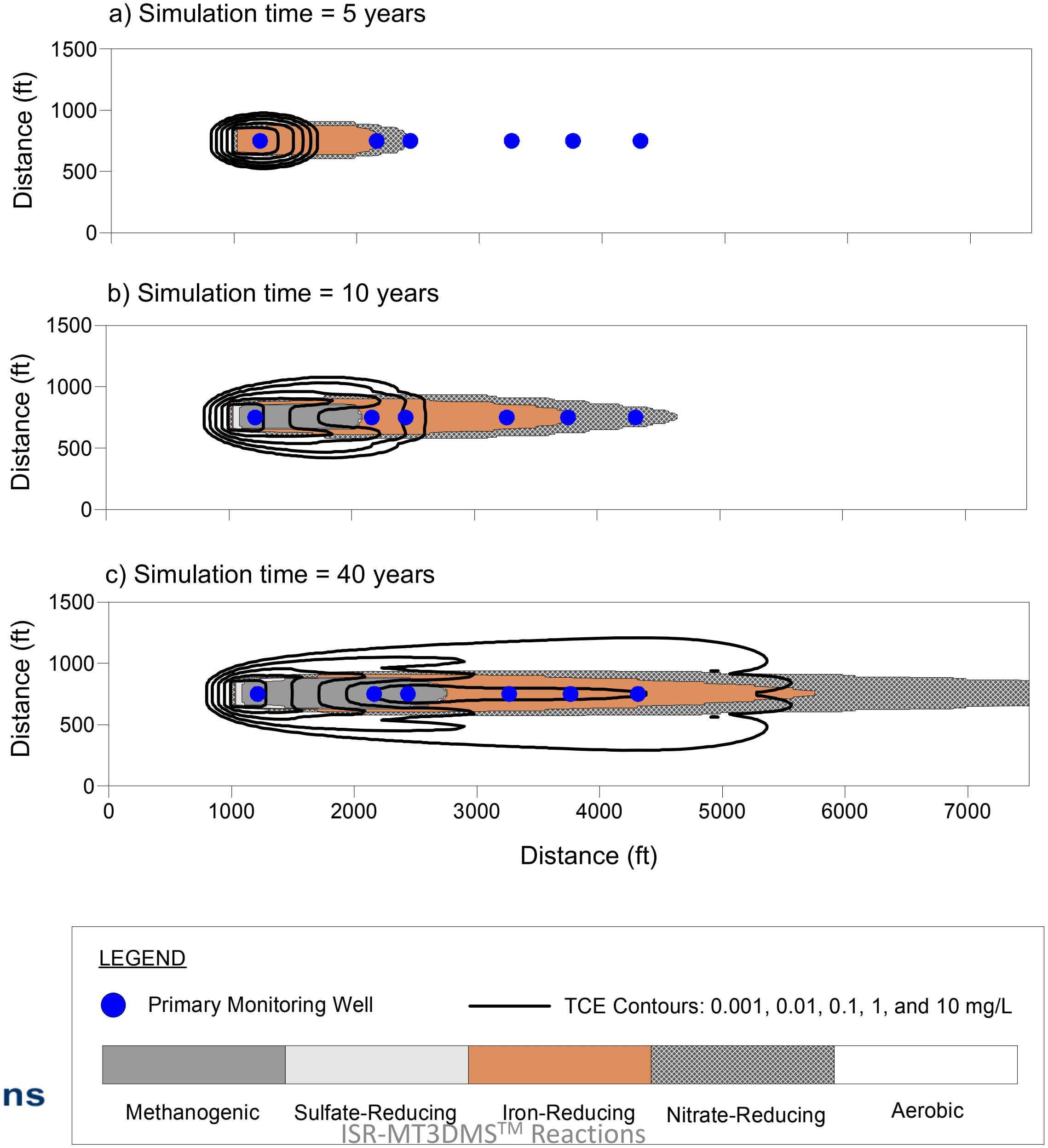
Model vs. Field Concentrations: Redox Indicators



Carey (2007)

Simulated TCE and Redox Zones Distributions over Time



a) Simulation time = 5 years

b) Simulation time = 10 years

c) Simulation time = 40 years

Carey (2007)

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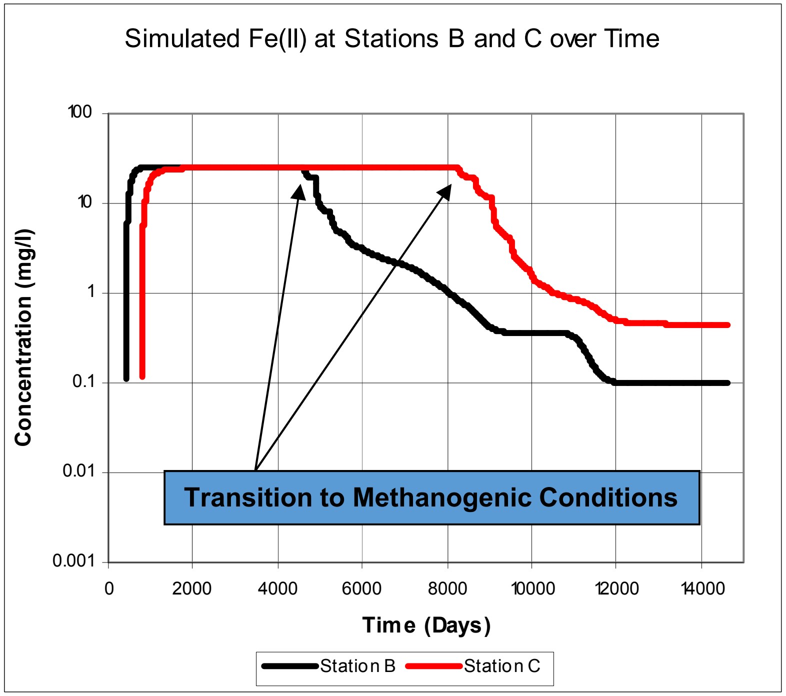
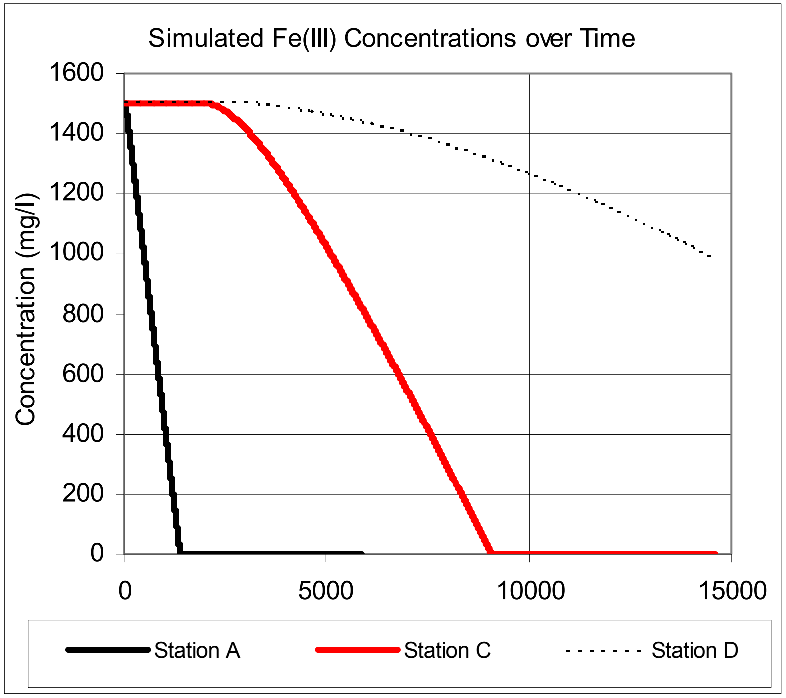
Simulated Iron Concentrations

a) Simulated Fe(II) vs. time at Stations B and C



Transition to Methanogenic Conditions

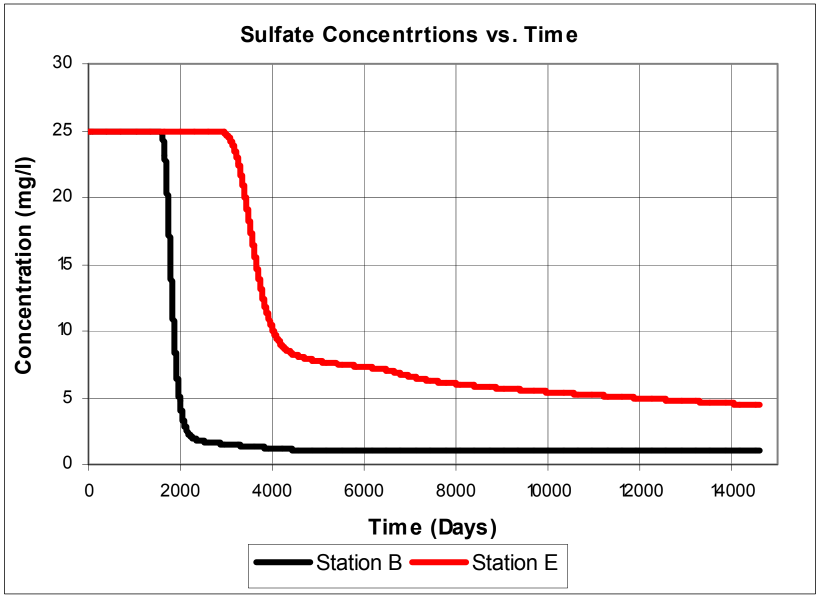
b) Simulated Fe(III) vs. time at Stations A, C, and D



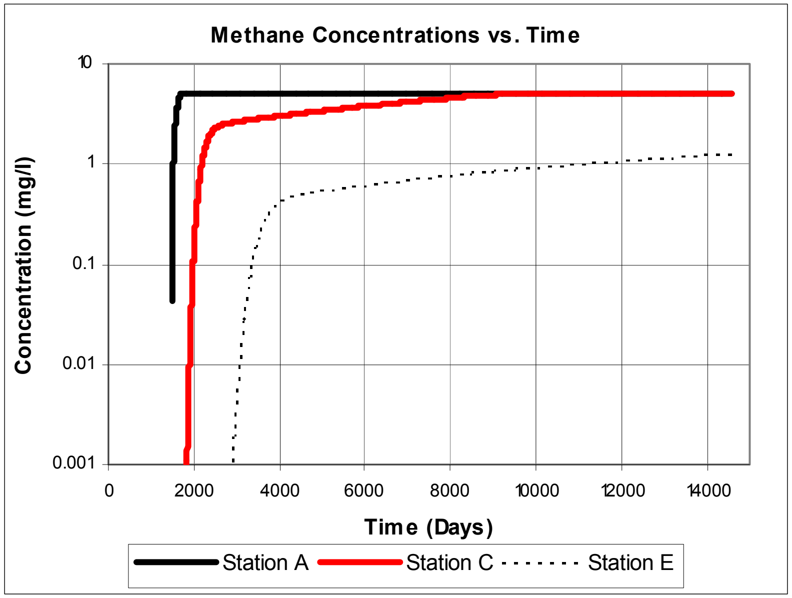
Carey (2007)

Simulated Sulfate and Methane Concentrations

a) Simulated Sulfate vs. time at Stations B and E

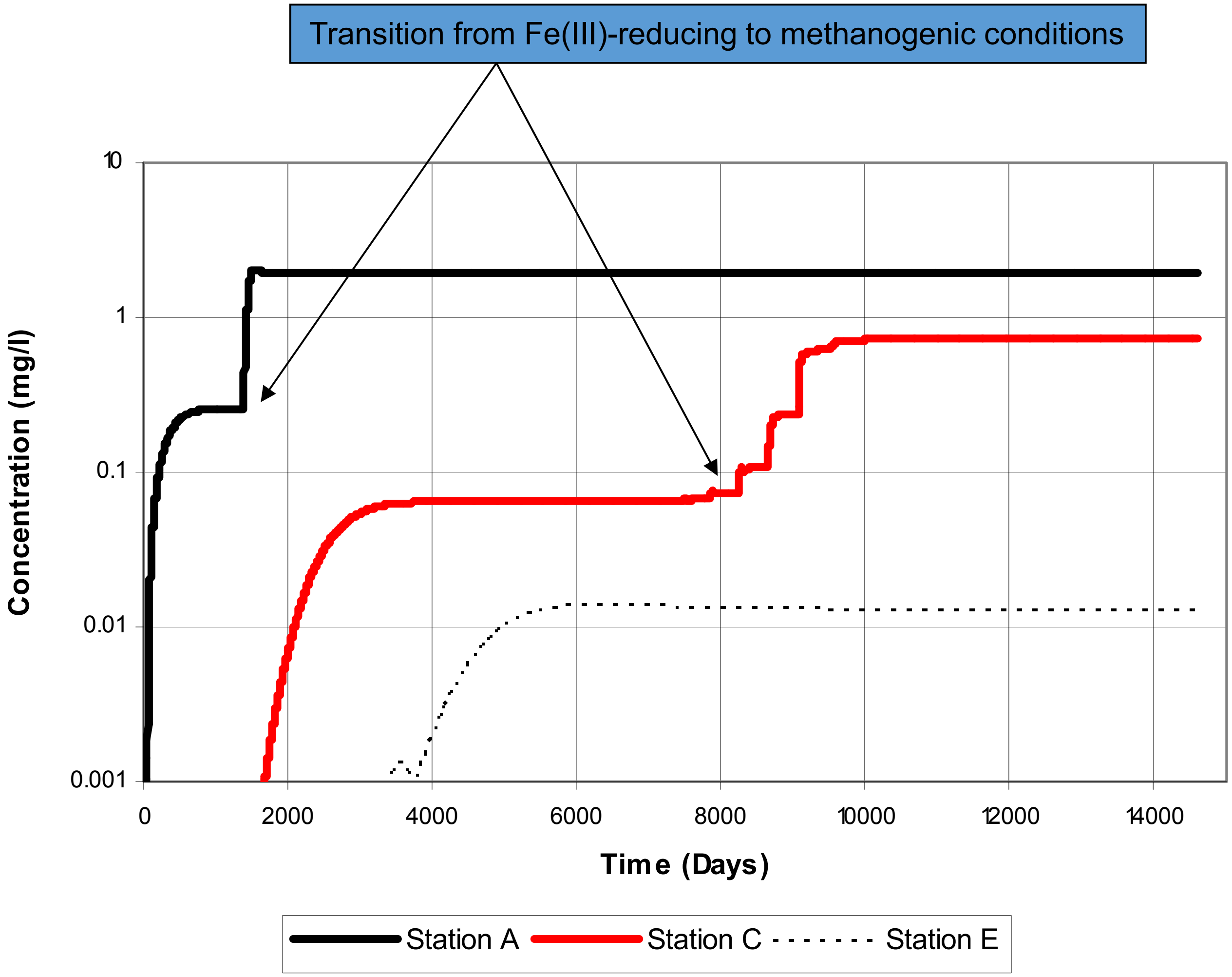


b) Simulated Methane vs. time at Stations A, C, and E



Carey (2007)

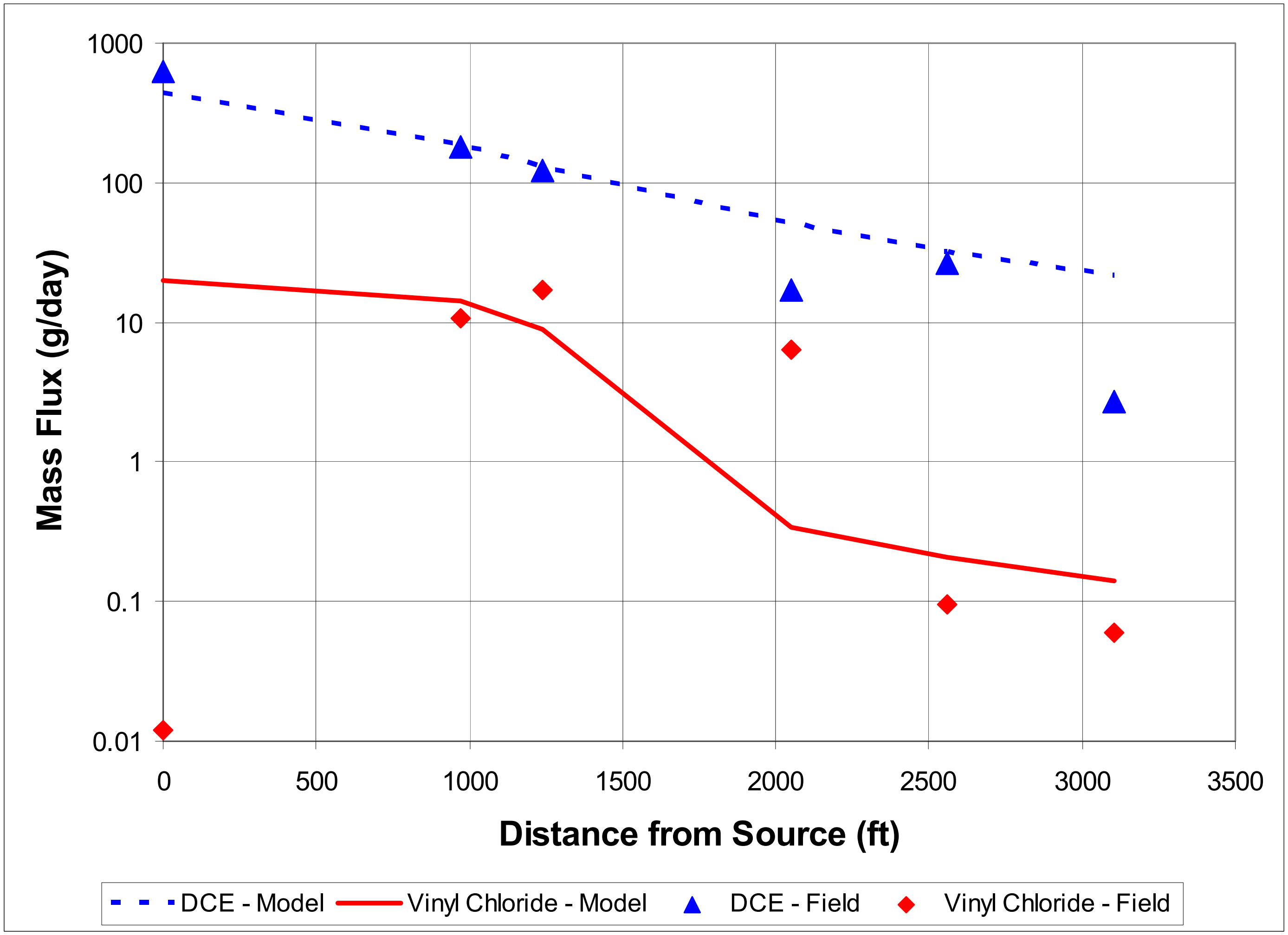
Simulated Vinyl Chloride Concentrations



Transition from Fe(III)-reducing to methanogenic conditions

Carey (2007)

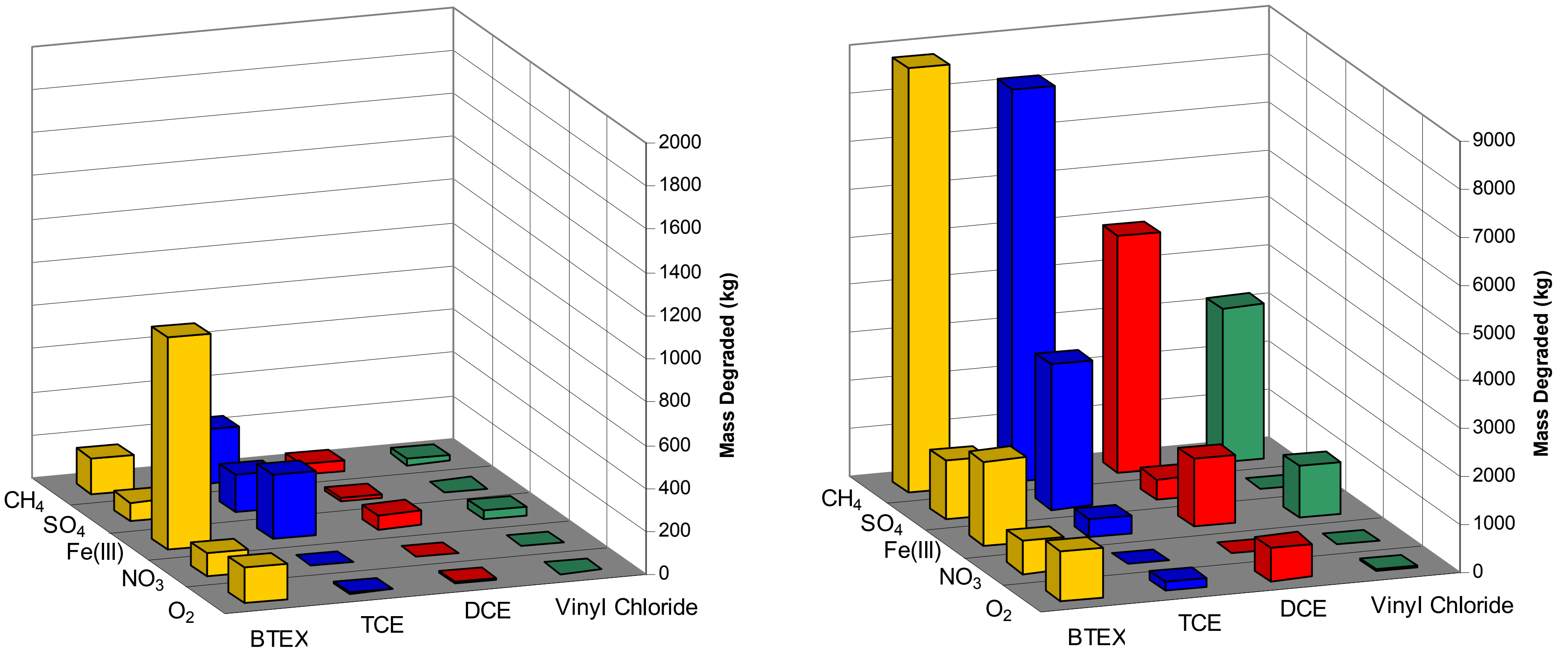
Mass Flux Comparison: Model vs. Field (t = 40 years)



Note – field-estimated mass flux is based on concentrations at key monitoring wells along plume centerline, and assumption that main plume width is equal to source width of 200 feet.

Carey (2007)

Simulated Biodegradation Mass Balance (t=30 years)


a) Simulated Mass Degraded by Redox Zone (t = 5 years)

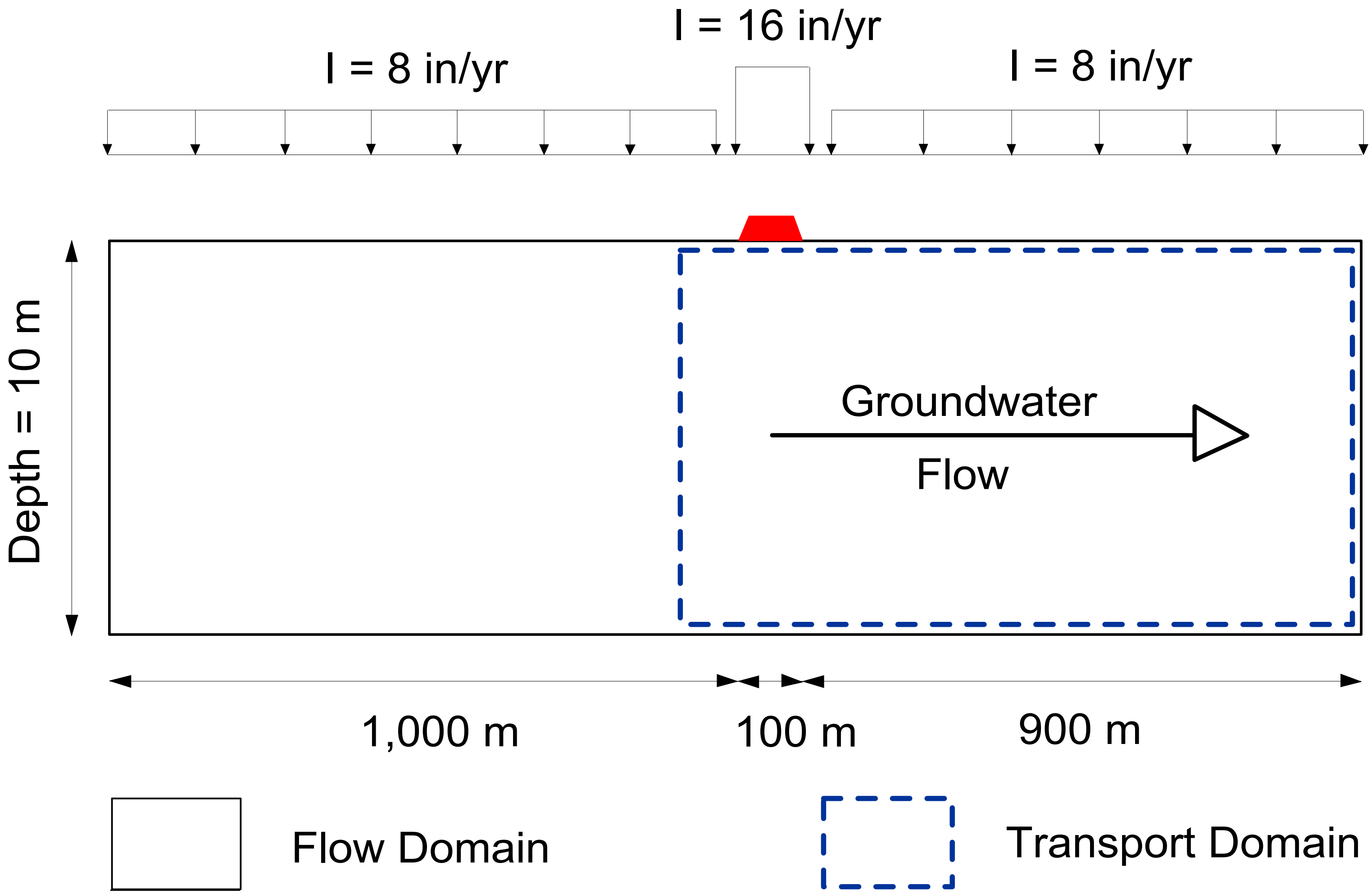
b) Simulated Mass Degraded by Redox Zone (t = 40 years)

Redox Zone Legend: O_2 = aerobic; NO_3 = nitrate-reducing;
Fe(III) = iron-reducing; SO_4 = sulfate-reducing;
CH_4 = methanogenic.

Carey (2007)

Case Study:
Vejen Landfill, Denmark

Example – Vejen Landfill, Denmark



Carey (2001)

Solute Properties

Solute	***Molecular Weight (g/mol)***	***K_{oc} (mL/g)***	***Units of Concentration***	***Boundary and Initial Conditions***			
				C_{IN}	***C_{RCH}***	***C_{LF}***	***C(x,t=0)***
TOC	12	0	mg/L	0	0	(a)	0
PCE	166	364	ug/L	0	0	250	0
TCE	131.5	126	ug/L	0	0	250	0
DCE	97	49	ug/L	0	0	250	0
Vinyl Chloride	62.5	57	ug/L	0	0	250	0
Oxygen	32	0	mg/L	7	7	0	7
Nitrate	62	0	mg/L	25	25	0	25
Ferric Hydroxide	55.85	N/A	mg/g	N/A	N/A	N/A	5
Sulfate	96.1	0	mg/L	40	40	400	40

(a) $C = 14000e^{-0.26t}$, $t \le 10$ years; $C = 1040$ mg/L, $t > 10$ years

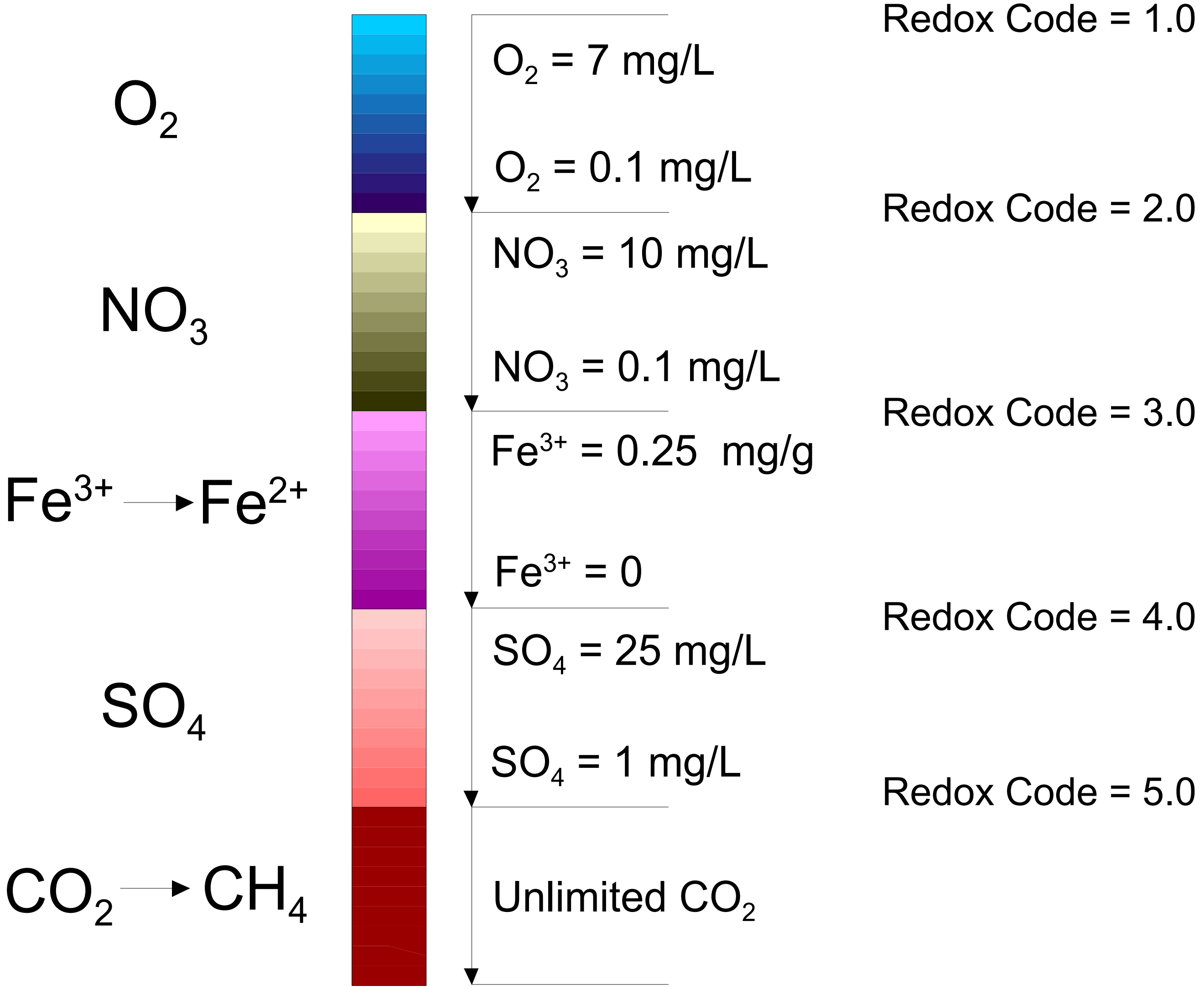
Carey (2001)

Solute Reactions

Solute	***Type***	***Half-Reaction***
TOC	Oxidation	$CH_2O + H_2O \text{-->} CO_2 + 4H^+ + 4e^-$
Vinyl Chloride	Oxidation	$CH_2CHCl + 2H_2O \text{-->} CH_3COOH + 3H^+ + 3e^-$
Oxygen	Reduction	$O_2 + 4H^+ + 4e^- \text{-->} 2H_2O$
Nitrate	Reduction	$NO3^- + 6H^+ + 5e^- \text{-->} 0.5N_2(g) + 3H_2O$
Ferric Hydroxide	Reduction	$Fe(OH)_3(s) + 3H^+ + e^- \text{-->} Fe^{2+} + 3H2O$
Sulfate	Reduction	$SO_4^{2-} + 9H^+ + 8e^- \text{-->} HS^- + 4H_2O$

Carey (2001)

Redox Zone Visualization



O_2

NO_3

$Fe^{3+} \rightarrow Fe^{2+}$

SO_4

$CO_2 \rightarrow CH_4$

O_2 = 7 mg/L

O_2 = 0.1 mg/L

NO_3 = 10 mg/L

NO_3 = 0.1 mg/L

Fe^{3+} = 0.25 mg/g

Fe^{3+} = 0

SO_4 = 25 mg/L

SO_4 = 1 mg/L

Unlimited CO_2

Redox Code = 1.0

Redox Code = 2.0

Redox Code = 3.0

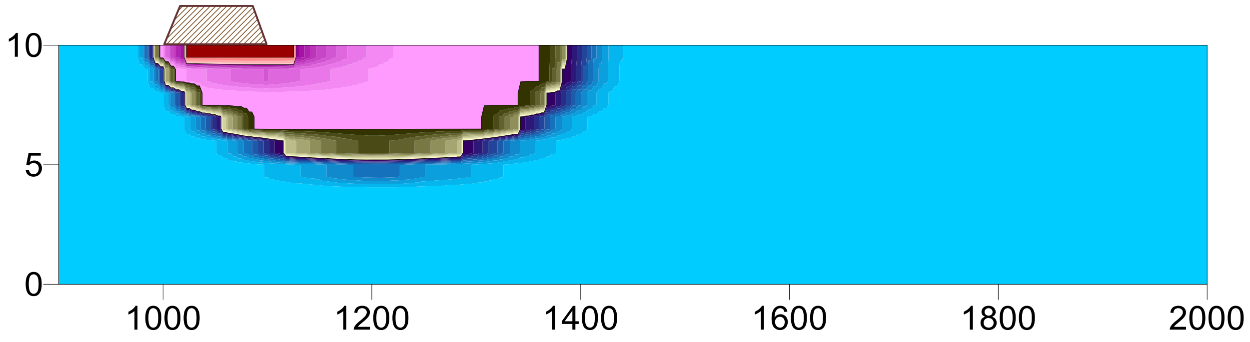
Redox Code = 4.0

Redox Code = 5.0

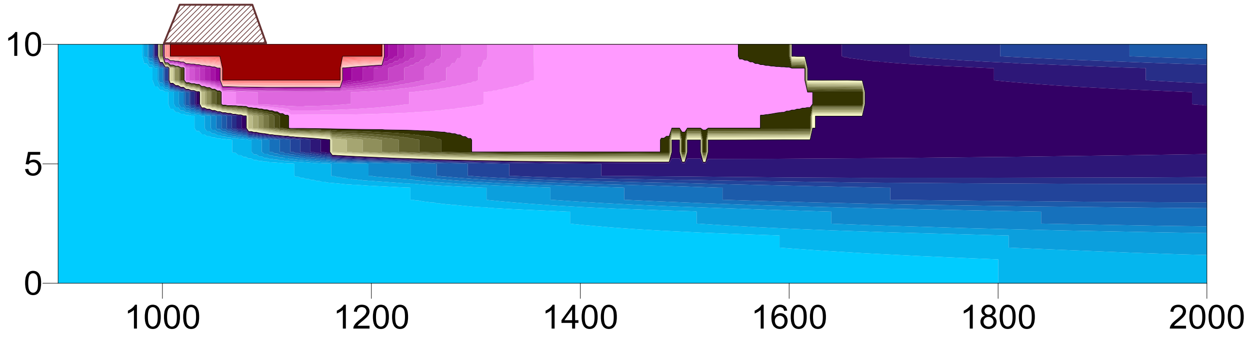
Carey (2001)

Transient Bioattenuation Capacity

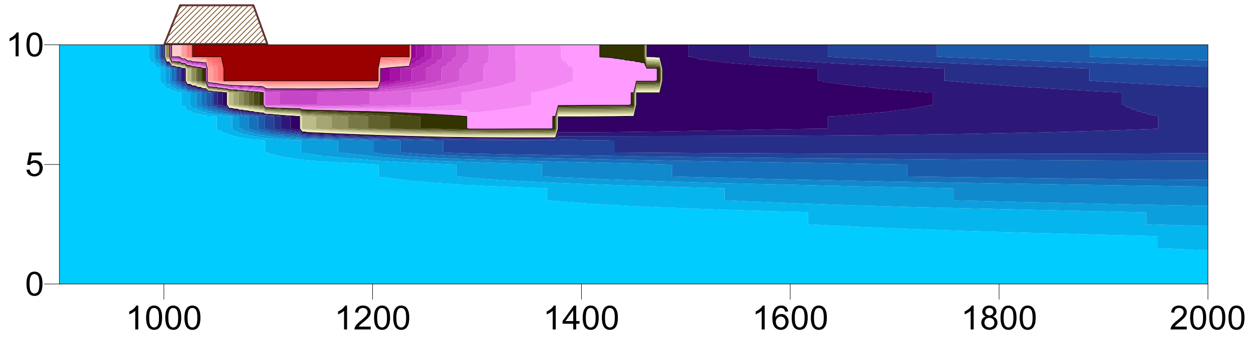
t =1 year



t = 5 years



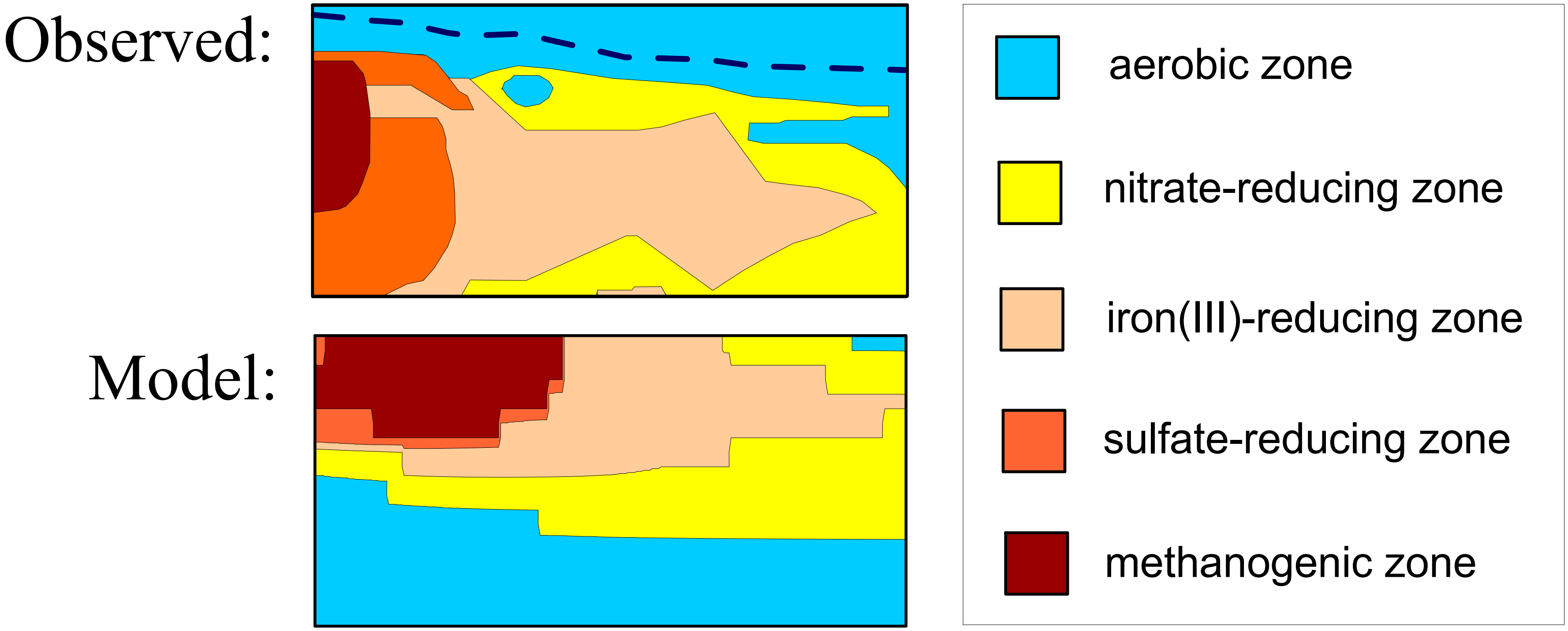
t = 15 years



Carey (2001)

Example – Vejen Landfill, Denmark

Vertical dispersivity = 0.008 m
rate = 7.6e-3 per day
TOC degrades when TOC > 0.1 mg/L



Carey (2001)