Fate and Transport Models Under Development by ORD

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Outline

- A Few Words on Models
  - Conceptualization
  - Types of Solutions
  - Parameter Values
  - Calibration
- The Hydrocarbon Spill Screening Model (HSSM) and extensions
- Capture Zone Modeling with Region 9
- Transport in Product
- Surface Water Spill Modeling

Introduction

- Model = Representation and quantification of site knowledge
  - Conceptual model
    - Generic knowledge of fate and transport AND site-specific data
  - Release history
  - Site data
  - Application and testing of a computer code
    - Matches conceptualization of site
  - Results
  - Interpretation of results
- Modeling = Idealization

Conceptual Models

- Source type and history
  - Soil vs water table contamination
  - Release date
  - Release volume and composition
    - (how well known?)
- Geometric configuration
  - Stratigraphy
  - Hydrologic boundaries
  - Transport pathways
    - (how well known?)
- More …

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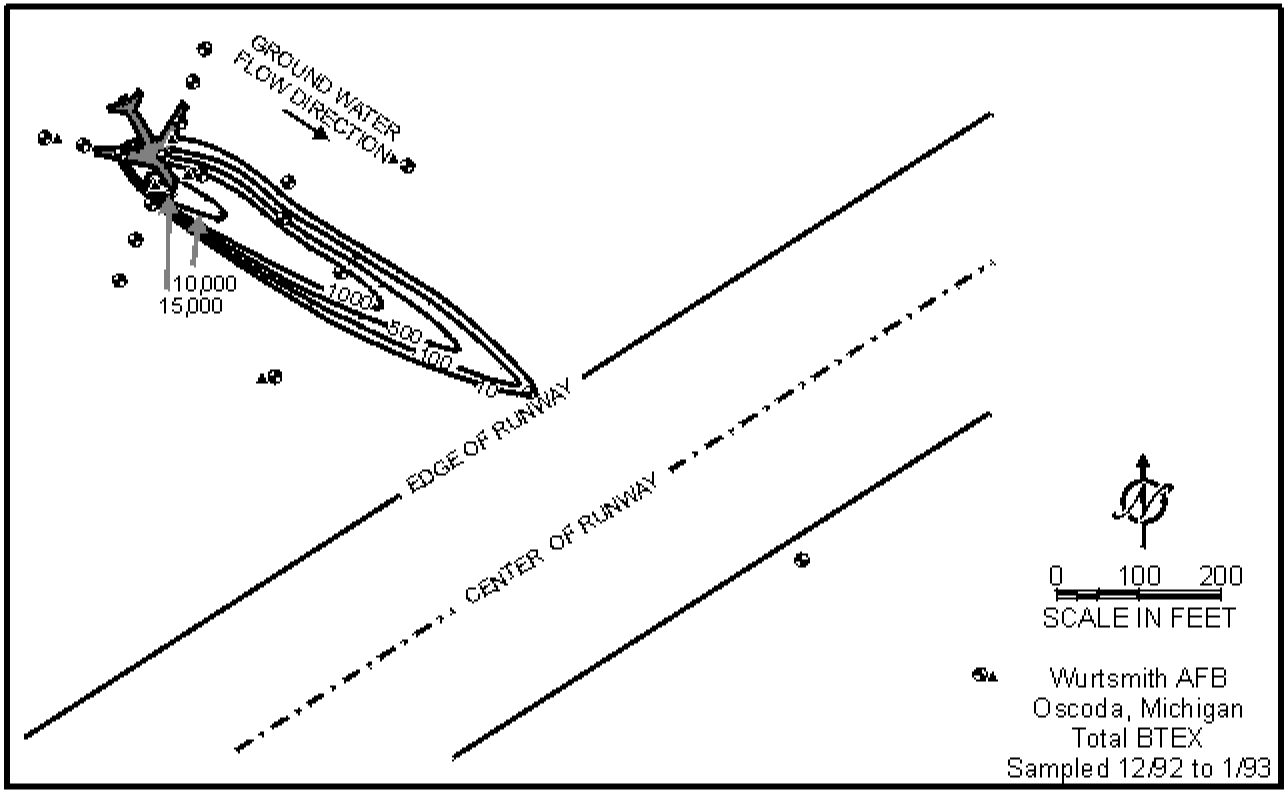
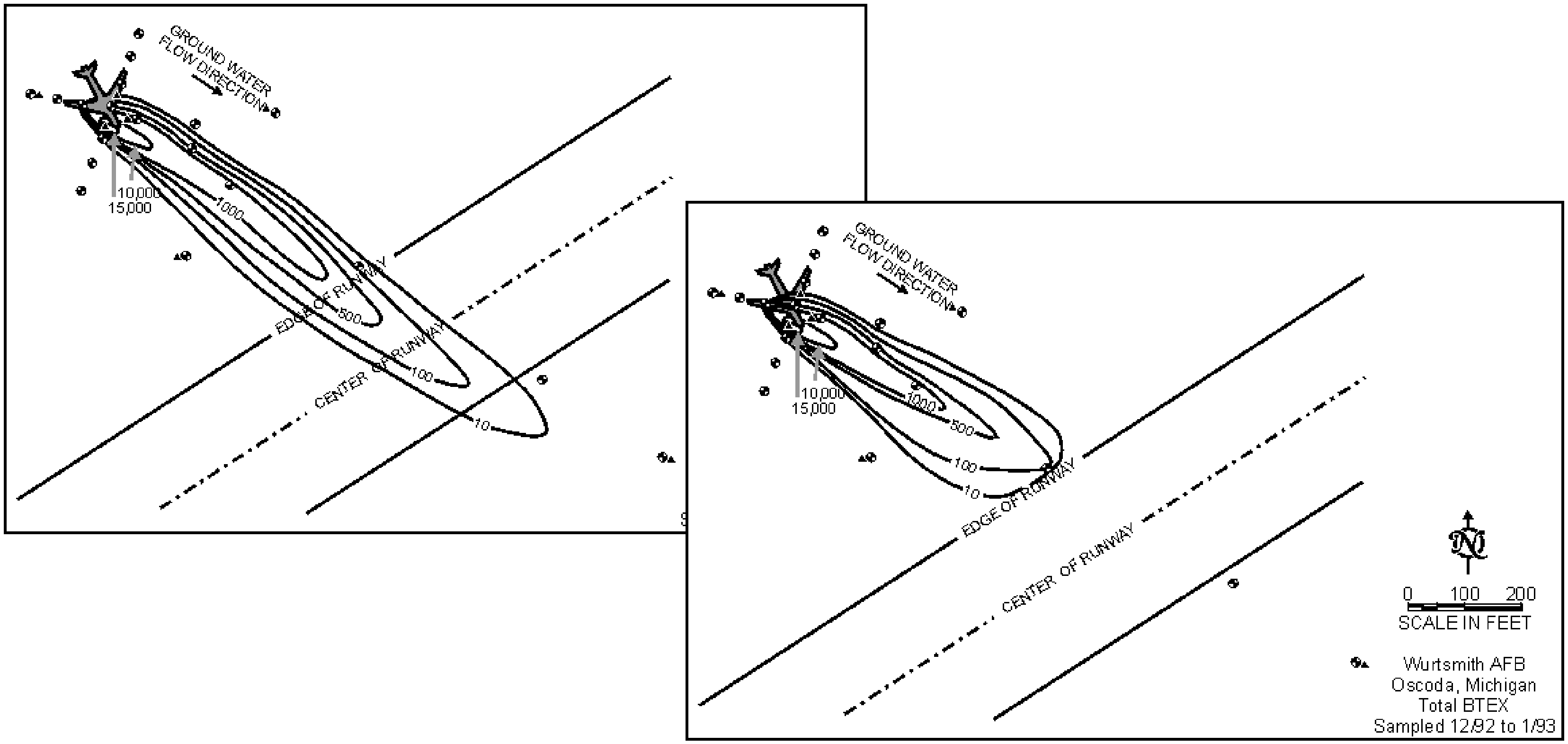
Data Interpretation: Wurtsmith AFB Total BTEX



Why Not These?



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Types of Computer Models

- Two Major Types:
  - Analytical
  - Numerical (Finite Difference/Finite Element)
- Others
  - Semi-analytical
  - Random Walk/Particle Tracking
  - Analytic Elements for Ground Water Flow
  - Hybrid Types

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Critical Assumptions of Analytical Solutions

- All analytical solutions of the transport equation share the assumptions:
  - Steady ground water flow
  - One-dimensional ground water flow
  - Uniform ground water flow
  - 2nd and 3rd transport dimensions are by dispersion only
  - Homogeneous (uniform) aquifer
    - No grid, all parameters unchanging

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Numerical

- Description
  - Gridded Domain
  - Solution by mathematical/computer approximations
  - More time/effort than analytical
  - Include more capabilities
- Used for
  - complex geologies, pumping wells, interactions with surface waters
  - Not common for LUST sites

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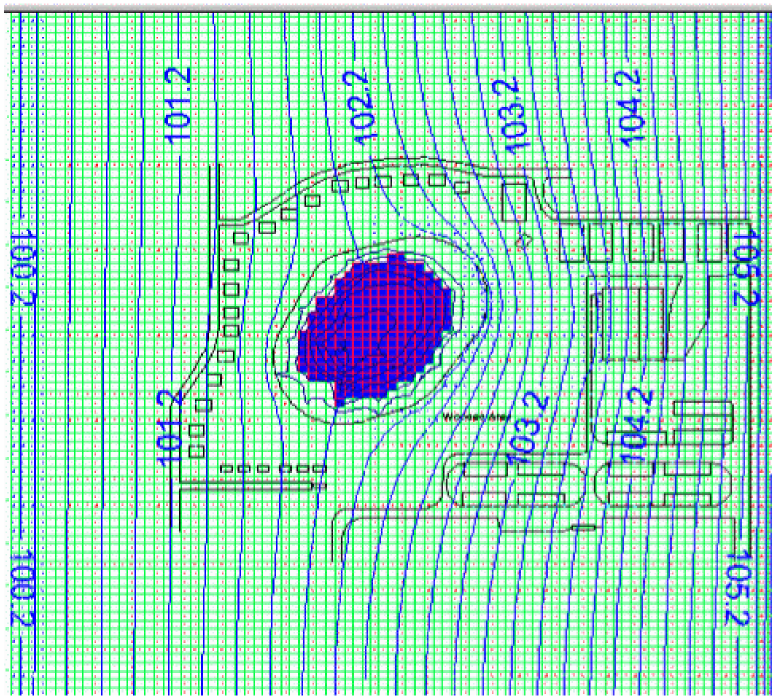
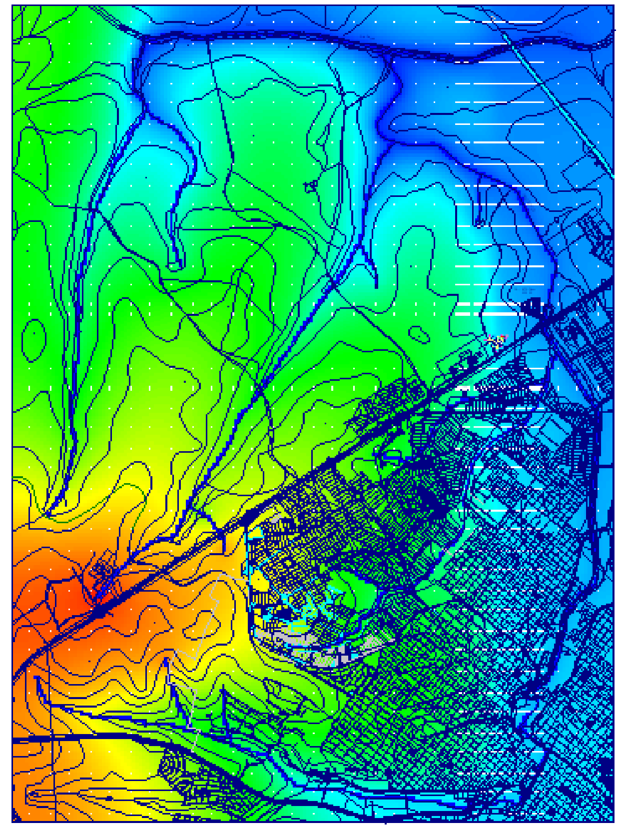
Numerical





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Common Sources of Model Inputs Used at Leaking Underground Storage Tank Sites

- Hydraulic Conductivity (slug tests)
- Porosity (literature)
- Dispersivity (estimates)
- Retardation Factor
  - Koc (literature)
  - Foc (measurement/estimate)
- Biodegradation Rate (usually literature)
- + all these vary in space

- Forcing Function:
  - Release – normally unkown
    - Mass
    - Timing
    - Composition

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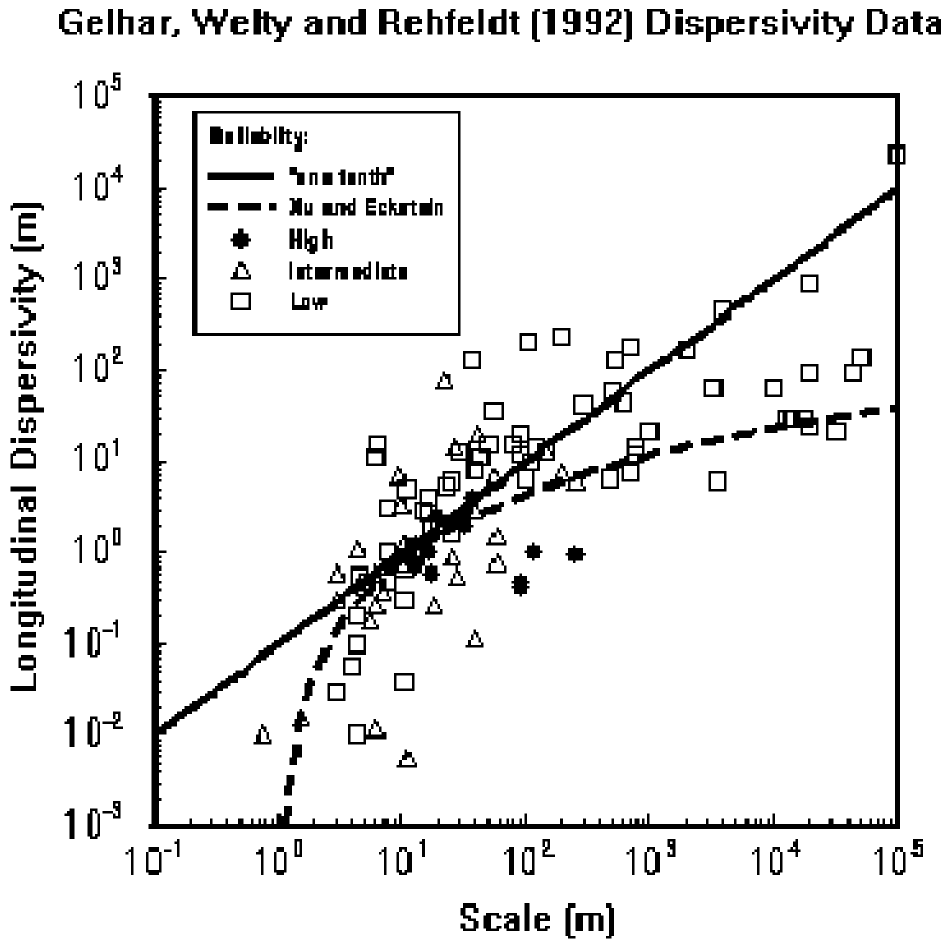
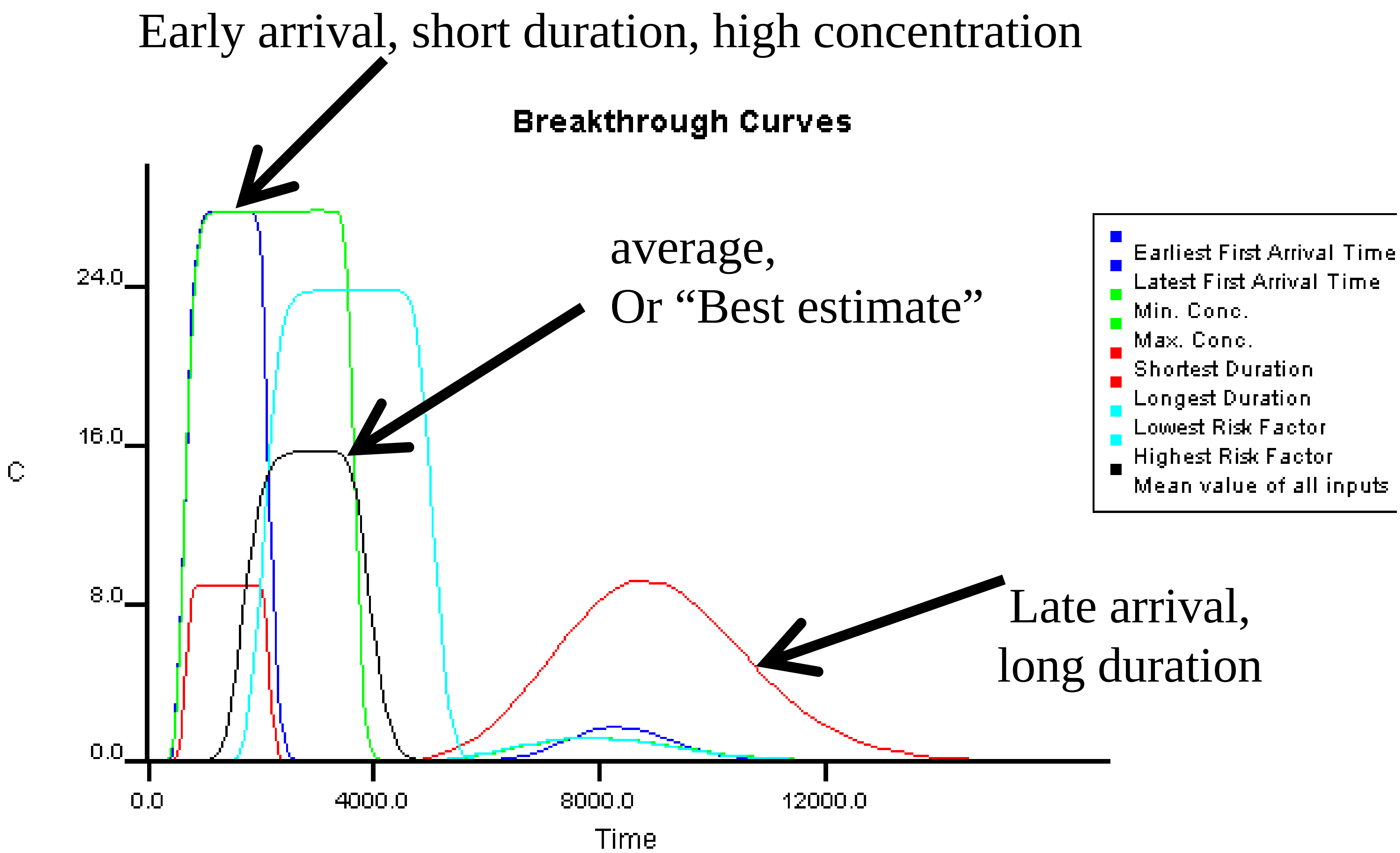
Dispersivity Data (Gelhar, 1992)





http://www.epa.gov/athens/onsite

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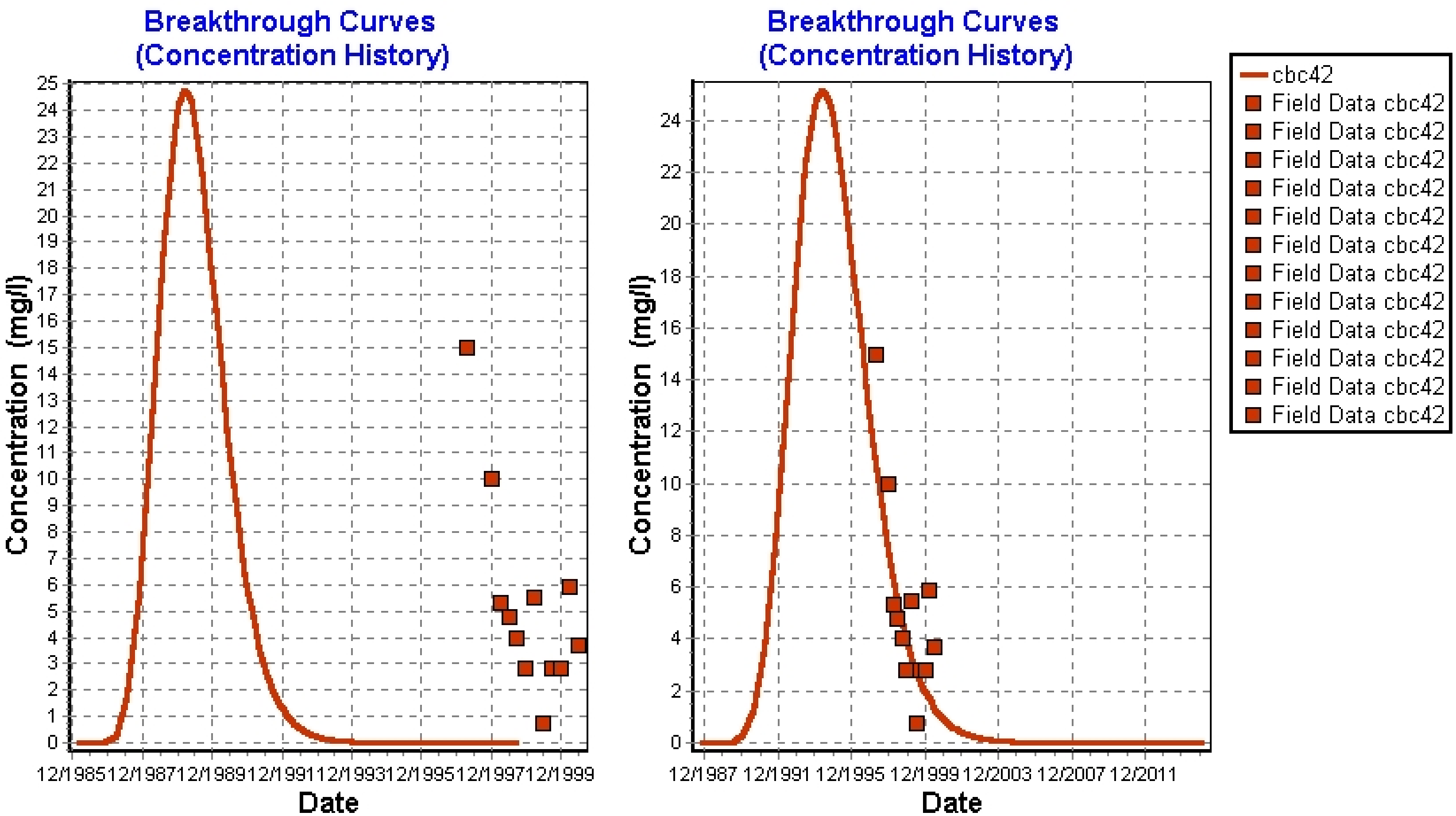
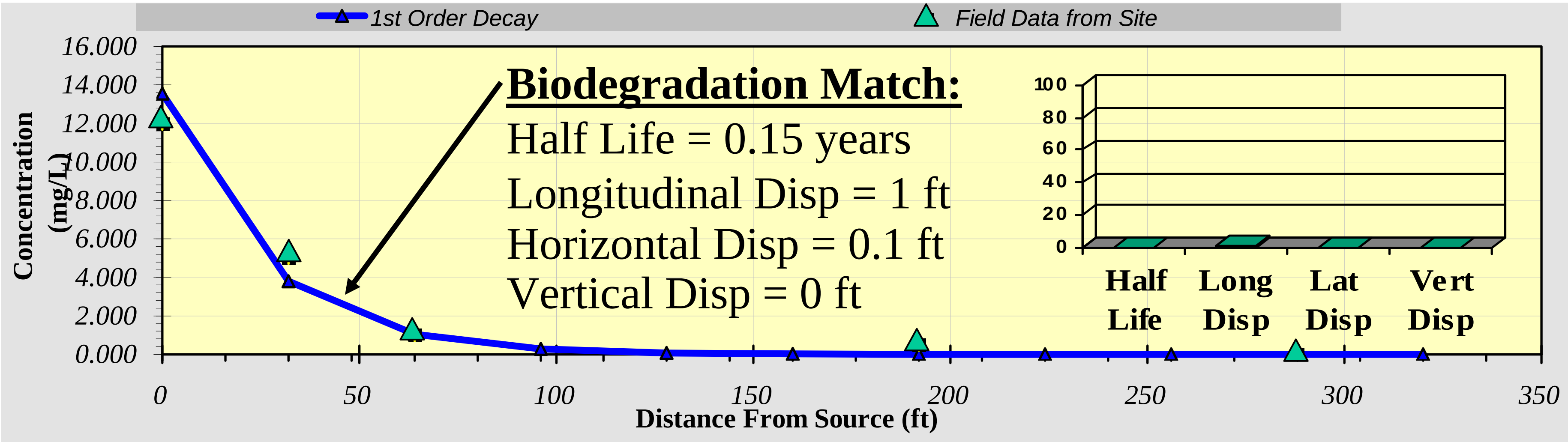
Calibration: Match model results to the site

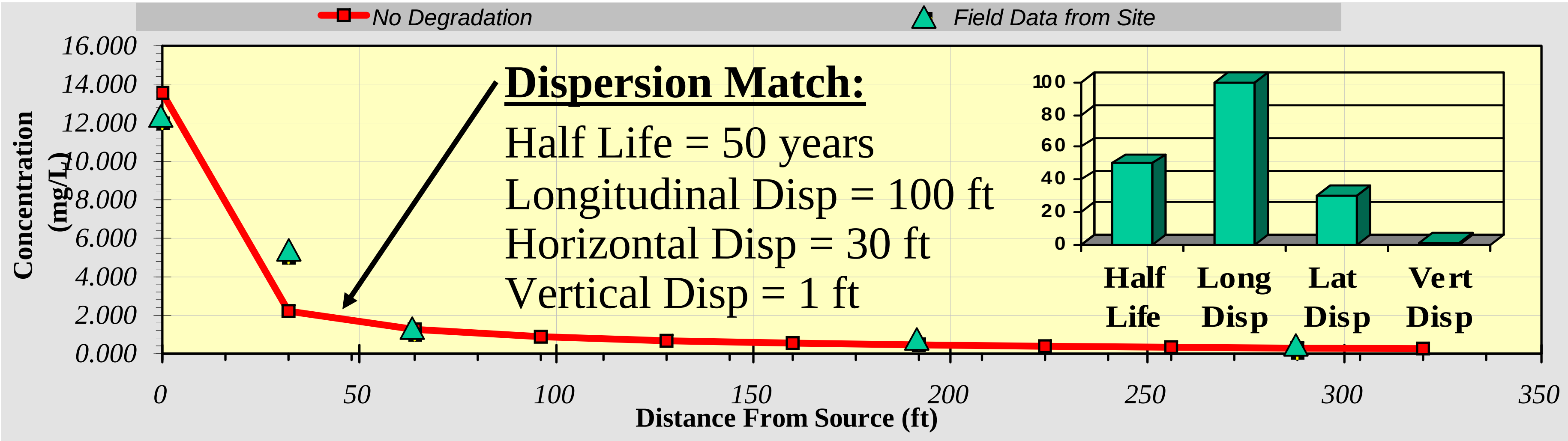
- Parameters (hydraulic conductivity, porosity, etc.) are:
  - Variable – differ throughout aquifer
  - Uncertain – measurements are not perfect
- Calibration is adjustment of the model inputs and boundaries to match observed outputs
  - ground water levels
  - concentrations

Left = average est. hydraulic conductivity
Right = fitted



Reasonable Values of Calibration Parameters?





Model Prediction

- Calibration
  - forced match to existing data (interpolation)
    - Model reproduces ***observations***
  - Does this show the model is predictive?
    - no
- What's Needed For Prediction?
  - Unforced match to data collected outside calibration set (extrapolation)
    - 1) calibrate
    - 2) match additional data
    - 3) predict
    - 4) iterate to improve

Conclusions: Things to Think About

- Use of Models (not all parameters measured, release usually unknown, computer codes with idealizations)
  - Uncalibrated
    - Guesses in accordance with scientific principles
      - Use in site assessments where subsequent data will show if good guesses or not
  - Calibrated
    - Force fitted to data
      - Overcomes uncertainty in parameters and model form
      - Belief in predictions might be built from repeated demonstrations

Models

- "Models as a substitute for site characterization"?
  - Use of a generically-parameterized, uncalibrated, simplified model for vapor intrusion assessment in Colorado. Sometimes overpredict, sometimes underpredict
- …moving away from the prevailing view of models as "truth-generating machines"
  - Bruce Beck, 2009, Grand Challenges of the Future for Environmental Modeling, NSF.

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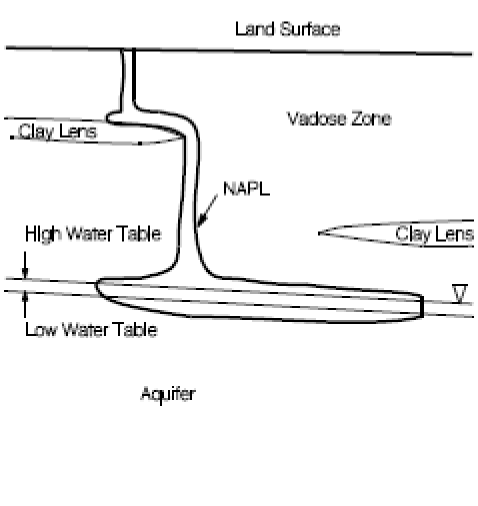
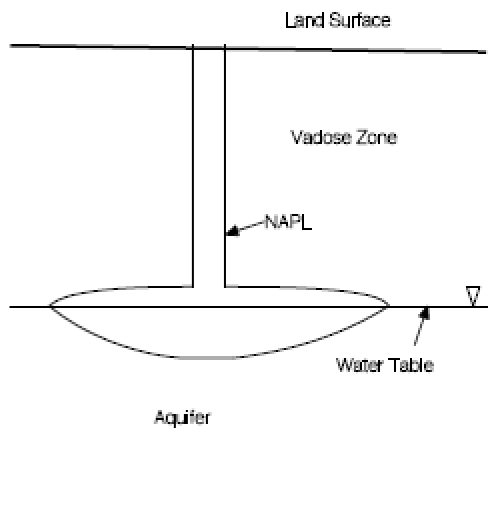
The Hydrocarbon Spill Screening Model

- HSSM (1994/95)
  - Four regimes:
    - Release of gasoline
    - Gasoline transport to water table
    - Spreading on water table and dissolution to aquifer
    - Transport in aquifer to receptor
  - Solution via semi-analytical approaches
    - Full numeric multiphase, multicomponent models are very compute intensive.

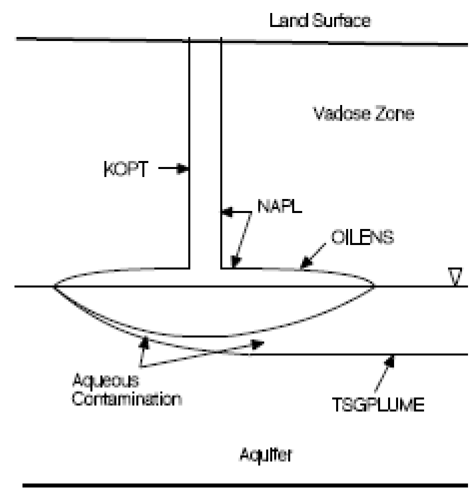
HSSM



Release Scenario



Simplified Scenario



Simulation Codes

Weaver, J.W., R.J. Charbeneau, J.D. Tauxe, B.K. Lien, and J.B. Provost, 1994, The Hydrocarbon Spill Screening Model (HSSM) Volume 1: User's Guide, US EPA, EPA/600/R-94/039a.
Charbeneau, R.J., J.W. Weaver, and B.K. Lien, 1995, The Hydrocarbon Spill Screening Model (HSSM) Volume 2: Theoretical Background and Source Codes, US EPA, EPA/600/R-94/039b.

HSSM

- Reasonably simulates the impact of the gasoline as a separate phase (NAPL), given the complexity of the phenomena.
  - Chronic releases add gasoline to the subsurface continually
  - Duration of contaminant loading depends on partitioning out of the gasoline (NAPL)

Biggest HSSM Limitation

- The HSSM code for aquifer transport is a semi-analytical solution requiring the assumption of:
  - Homogeneous aquifer
  - One-dimensional, uniform ground water flow
  - Lateral transport by dispersion only

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HSSM Expansion

- Link HSSM with MODFLOW/MT3D
- Extend for reactive transport accounting for electron acceptors/donors
- Special treatment of ethanol and methane generation

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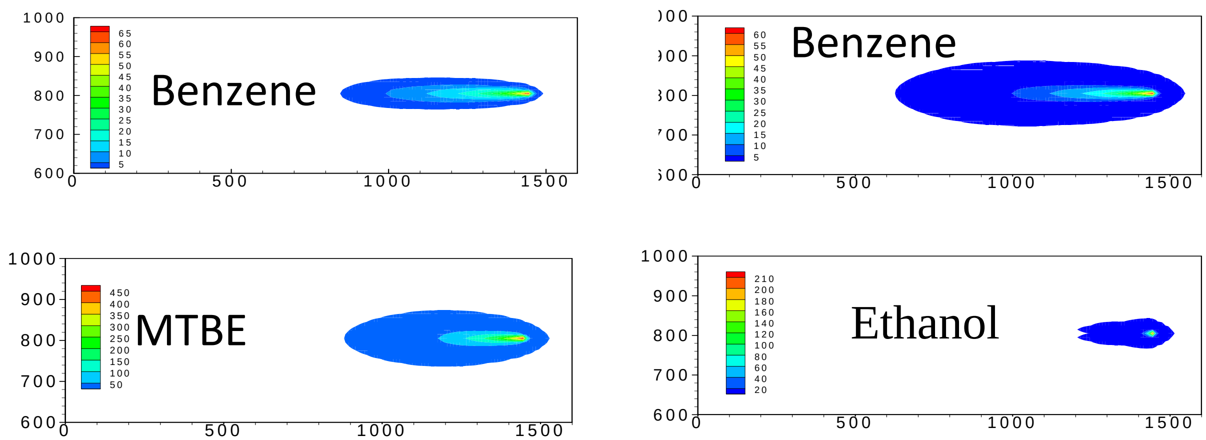
Modeled RFG (w MTBE) vs E10



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R9 Contaminant Transport/Capture Zone Modeling

- A RARE (Regional Applied Research Effort) Project
  - Simple (analytical) transport models used for LUST sites require restrictive assumptions—excluding
    - Wells, irregular geometry/boundaries, transients
    - Most exclude gasoline phase (NAPL)
  - Complex numerical models find little use at LUST sites. Why?
    - Lots of sites with minimal impact
    - Perceived complexity and cost
    - Limited modeling budget
    - Limited budget for characterizing model params.

R9 RARE

- Hierarchy of approaches
  - 1) Analytical/semi analytical models
    - Analytical ground water flow
      - Bear and Jacobs (1965)
        - » Flow to a single well in a uniform flow
        - » Fully penetrating well
      - Javendel (1978)
        - » Multiple wells, restricted placement
    - Transport from LUST source(s)
      - Analytical solution for source release from a smear zone (gasoline, NAPL) composed of a series of compartments
    - Uncertainty analysis:
      - Parameter measurements are imprecise
      - Some parameters are not measured (dispersivity) or un-knowable (release date)
      - Heterogeneity is not fully characterized
    - Small (2003) Managing the Risks of Exposure to Methyl Tertiary Butyl Ether (MTBE) Contamination in Ground Water at Leaking Underground Storage Tank (LUST) Sites, Univ. of California, 2003.

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R9 RARE

- Why include gasoline as NAPL, when it would be simpler to specify a ground water concentration at the source?
  - Duration, duration, duration
  - Effects due to partitioning from the gasoline
    - Multicomponent effects
      - Ethanol + benzene

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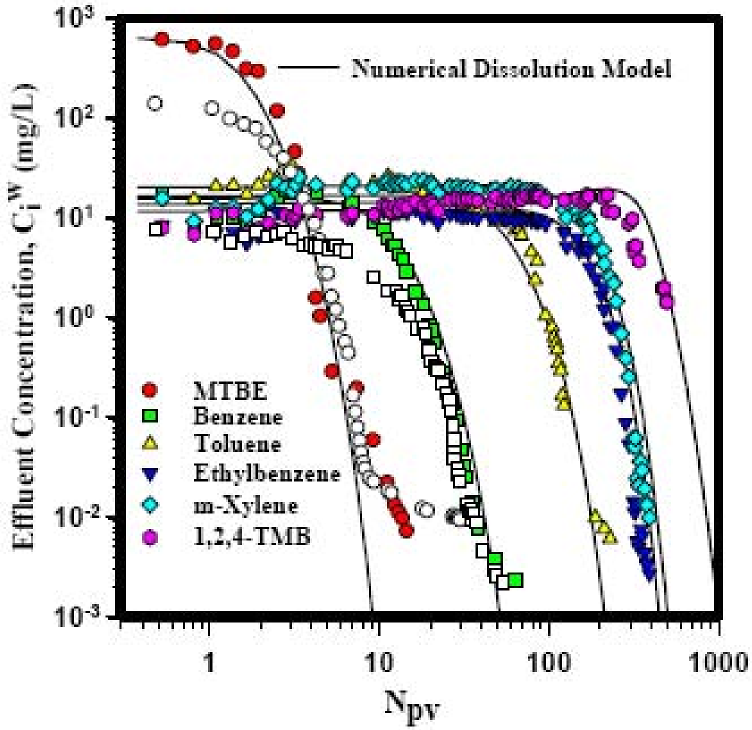


Figure 4. Dissolution curves for MTBE, BTEX and 1,2,4-TMB from a model NAPL mixture in soil. Filled symbols – two weeks aged (Experiment 4a). Open symbols – seven months aged (Experiment 4b). Pe=20.

Rixey, W. G., S. Joshi, 2000, Dissolution of MTBE from a Residually Trapped Gasoline Source: A Summary of Research Results, American Petroleum Institute, Technical Bulletin 13

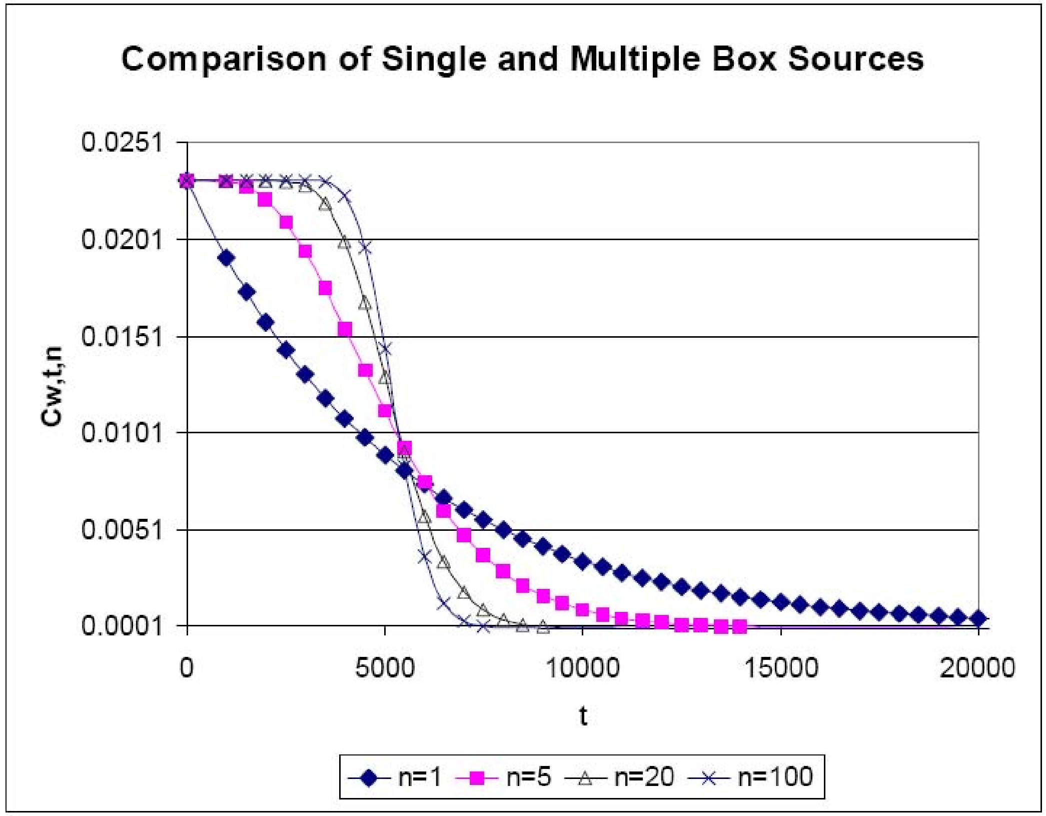
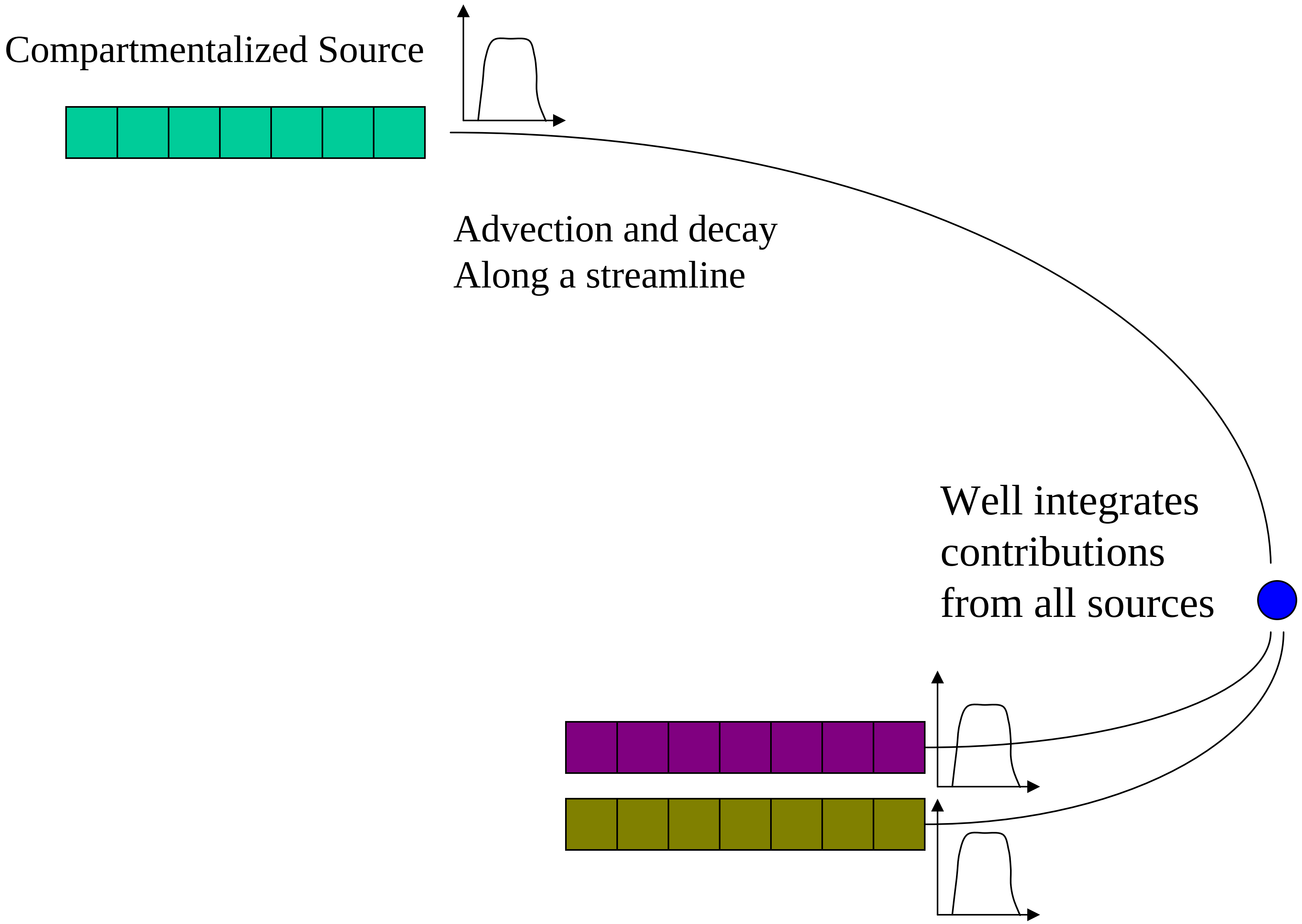


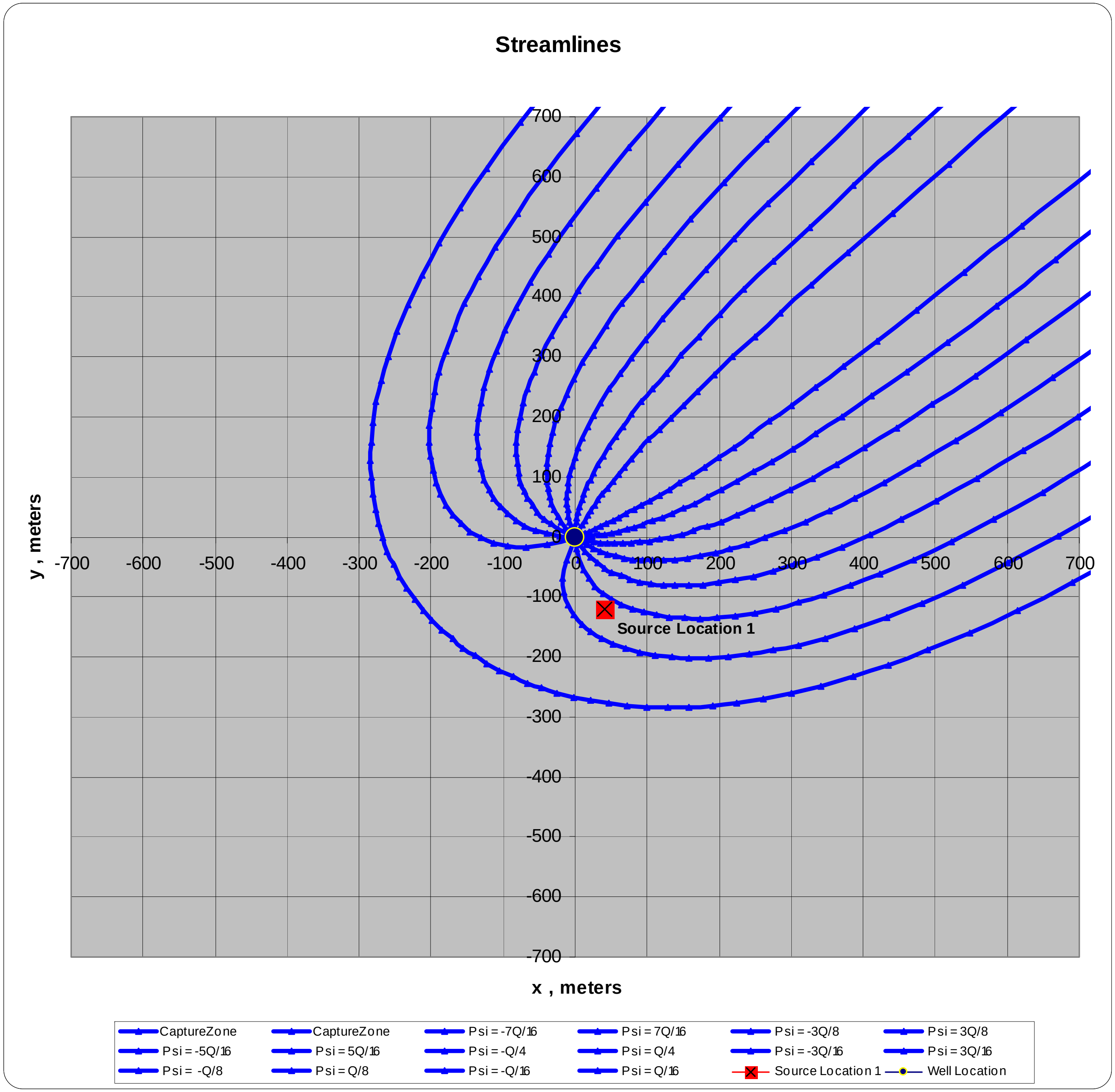
Figure 5. Concentration versus time at the downgradient face of the LUSTimpact source model illustrating the transition from a single continuously stirred tank reactor (CSTR) where n=1, to a plug flow reactor (PFR), or step function as the number of source boxes in series is increased.

Small, Matthew, 2003, Managing the Risks of Exposure to Methyl Tertiary Butyl Ether (MTBE) Contamination in Ground Water at Leaking Underground Storage Tank (LUST) Sites, Univ. California Berkeley, Dissertation

R9 RARE

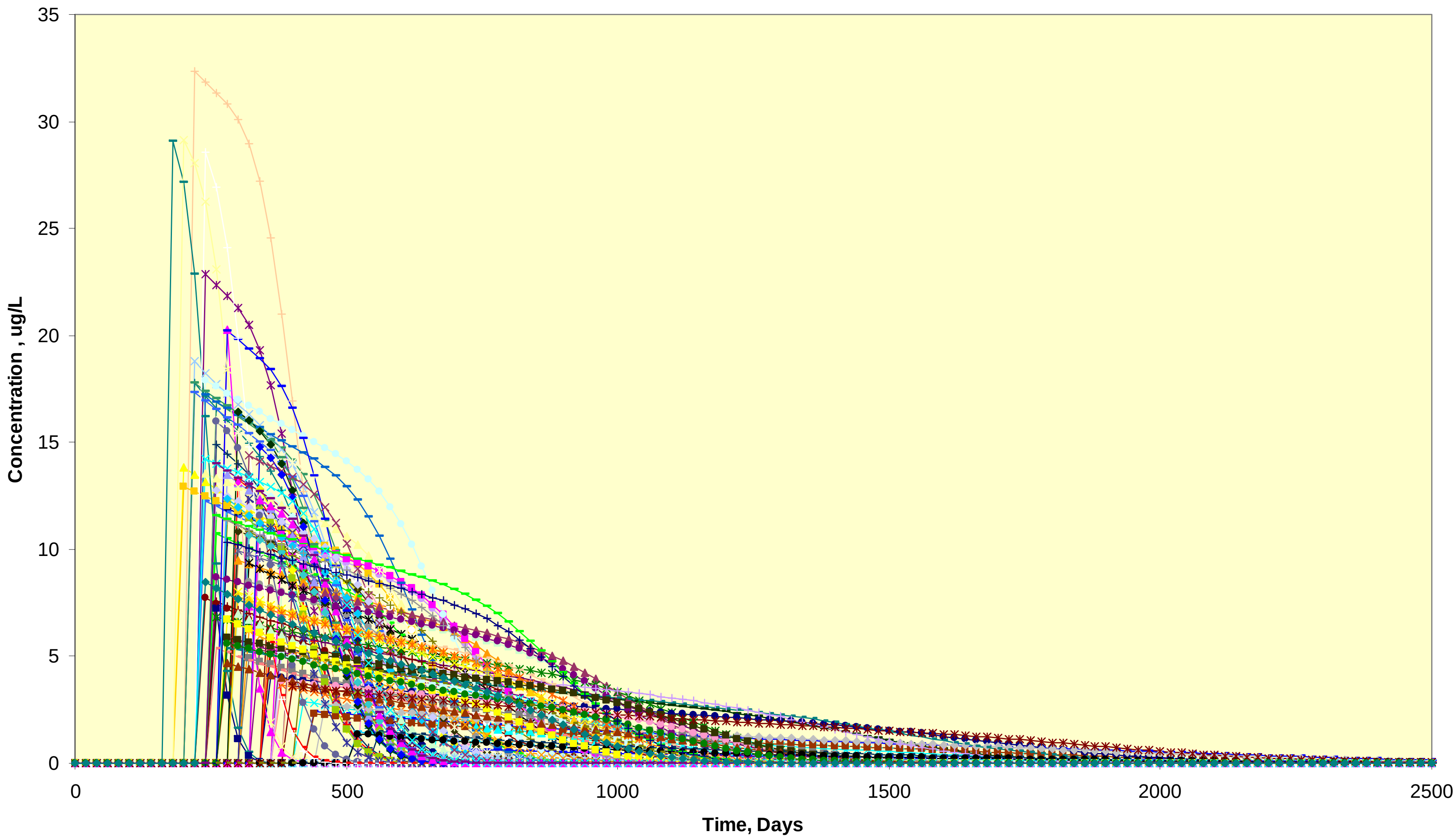
- With variation in parameters, e.g.:
  - Hydraulic conductivity 10 m/d to 100 m/d
  - Flow direction -65º to 65º
  - Gasoline Volume 300 gal to 500 gal
  - Gasoline Saturation 0.1 to 0.2
  - Benzene 3% by volume
  - Etc. (many use value +/- 10%)
- Results from three cases: 1 source, 4 sources, 6 sources, 100 simulations each.

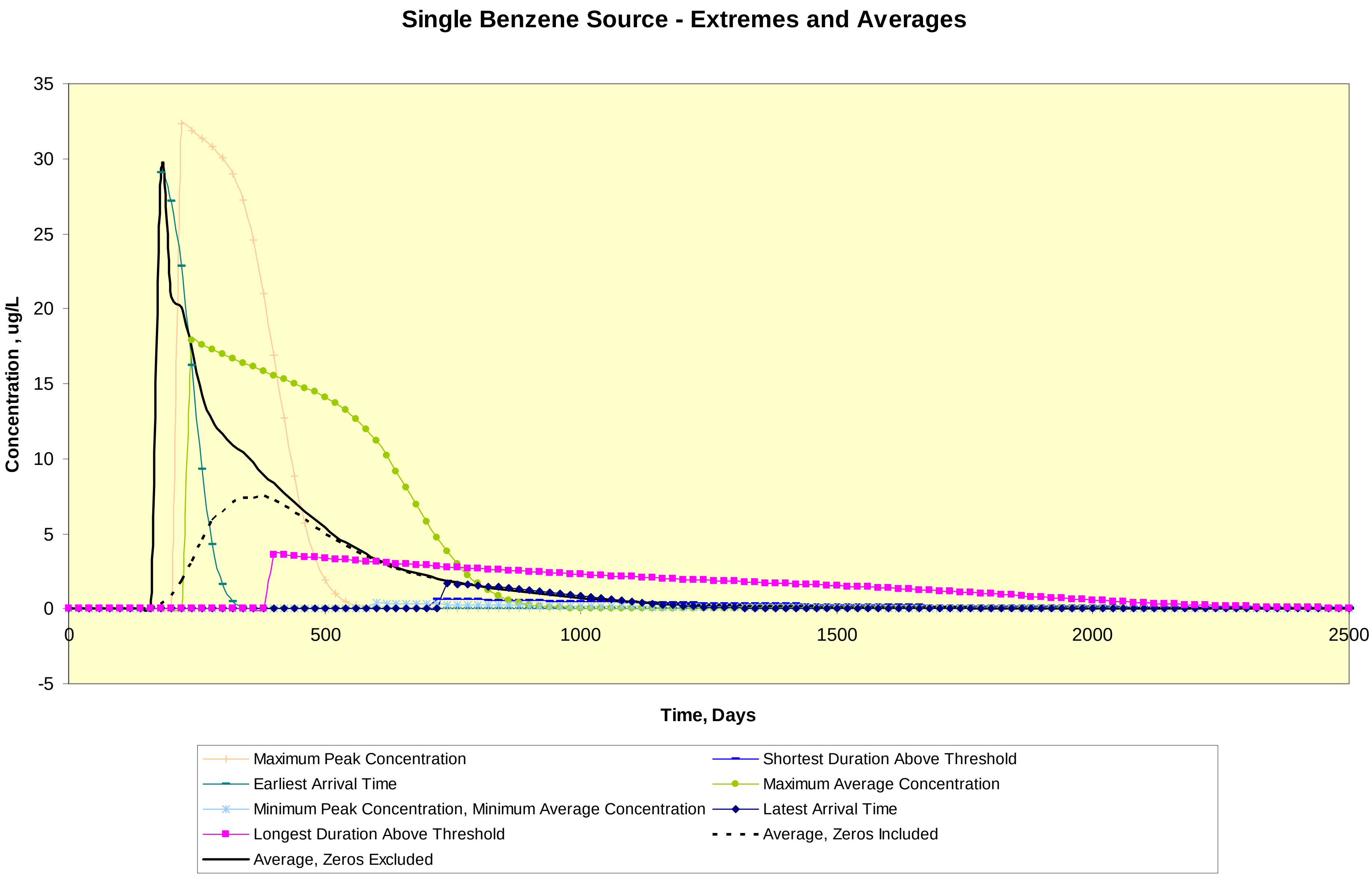

Compartmentalized Source
Advection and decay
Along a streamline
Well integrates
contributions
from all sources

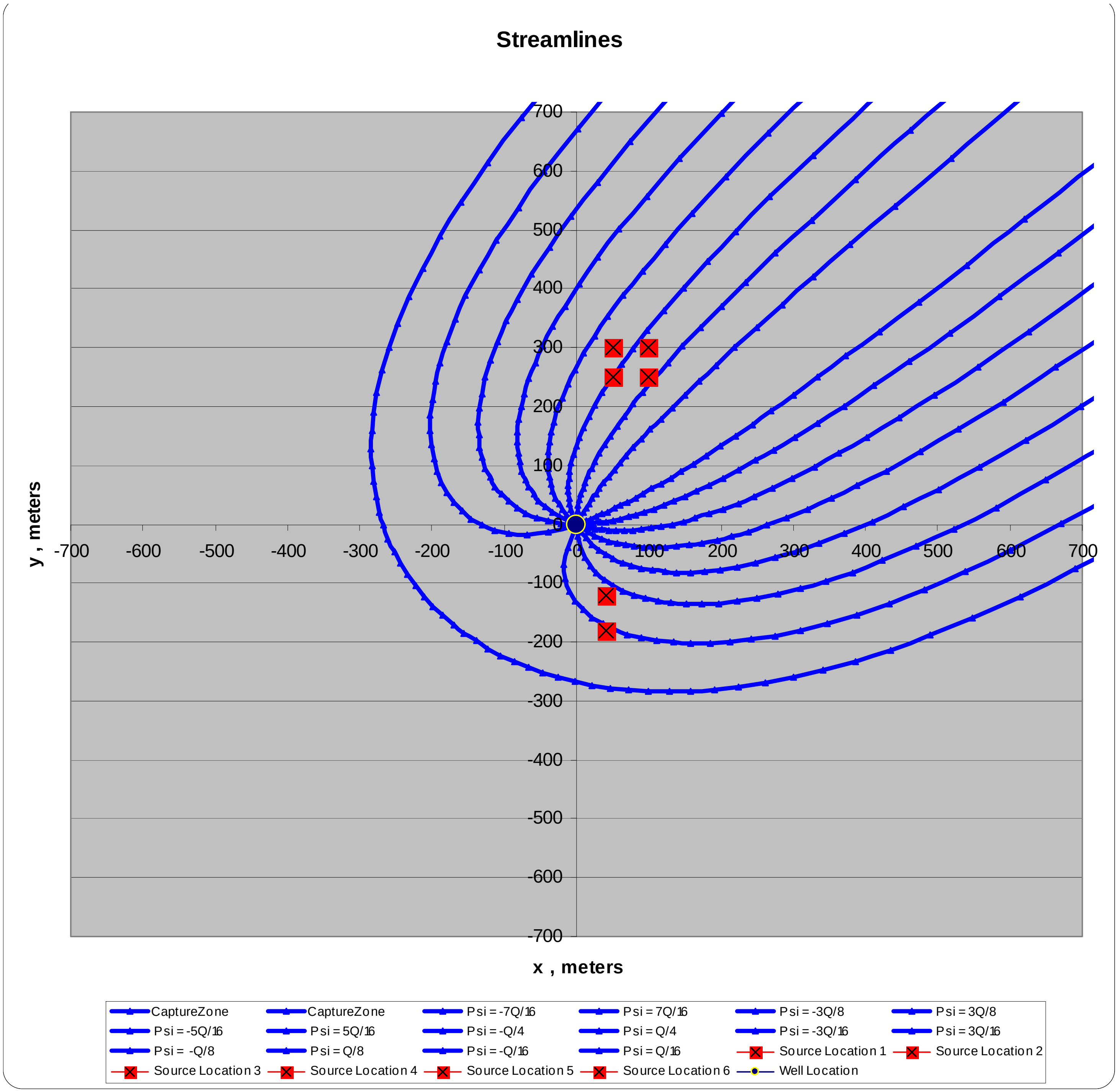


Streamlines
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
-700
-600
-500
-400
-300
-200
-100
0
100
200
300
400
500
600
700
Source Location 1
y , meters
x , meters
CaptureZone
CaptureZone
Psi = -7Q/16
Psi = 7Q/16
Psi = -3Q/8
Psi = 3Q/8
Psi = -5Q/16
Psi = 5Q/16
Psi = -Q/4
Psi = Q/4
Psi = -3Q/16
Psi = 3Q/16
Psi = -Q/8
Psi = Q/8
Psi = -Q/16
Psi = Q/16
Source Location 1
Well Location

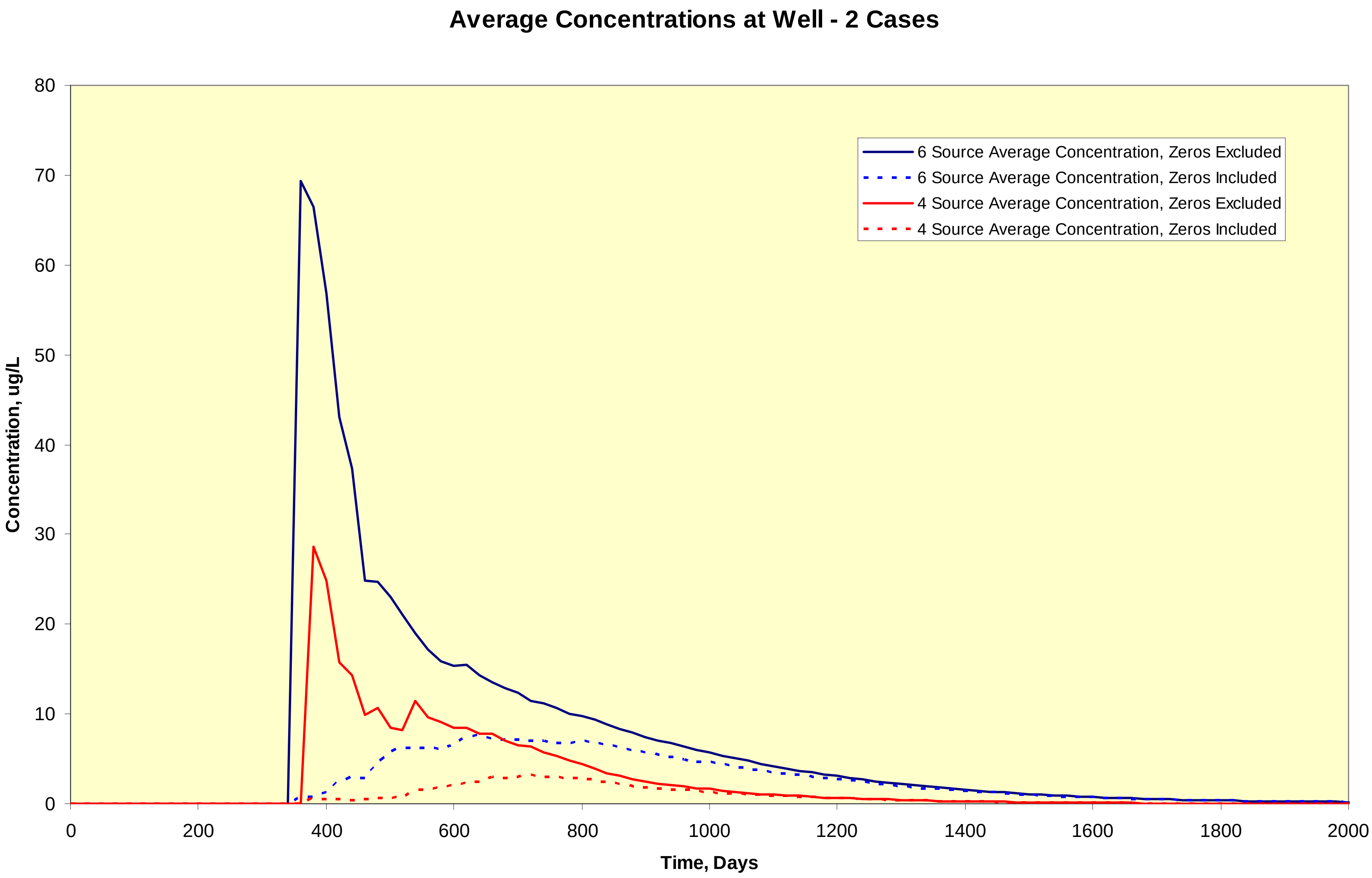
Single Benzene Source - All Simulations




Single Benzene Source - Extremes and Averages
Concentration , ug/L
35
30
25
20
15
10
5
0
-5
0
500
1000
1500
2000
2500
Time, Days
Maximum Peak Concentration
Earliest Arrival Time
Minimum Peak Concentration, Minimum Average Concentration
Longest Duration Above Threshold
Average, Zeros Excluded
Shortest Duration Above Threshold
Maximum Average Concentration
Latest Arrival Time
Average, Zeros Included



Streamlines
y , meters
x , meters
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
-700
-600
-500
-400
-300
-200
-100
0
100
200
300
400
500
600
700
CaptureZone
CaptureZone
Psi = -7Q/16
Psi = 7Q/16
Psi = -3Q/8
Psi = 3Q/8
Psi = -5Q/16
Psi = 5Q/16
Psi = -Q/4
Psi = Q/4
Psi = -3Q/16
Psi = 3Q/16
Psi = -Q/8
Psi = Q/8
Psi = -Q/16
Psi = Q/16
Source Location 1
Source Location 2
Source Location 3
Source Location 4
Source Location 5
Source Location 6
Well Location


Average Concentrations at Well - 2 Cases
Concentration, ug/L
Time, Days
6 Source Average Concentration, Zeros Excluded
6 Source Average Concentration, Zeros Included
4 Source Average Concentration, Zeros Excluded
4 Source Average Concentration, Zeros Included
0
10
20
30
40
50
60
70
80
0
200
400
600
800
1000
1200
1400
1600
1800
2000

R9 RARE

- Upper Tier:
  - Numerical Ground Water model(s)
    - Java Aquifer Solver
      - – Irregular domain ground water flow code
  - Numerical Transport Codes
    - Combined object-oriented (Java) numerical gasoline (NAPL) leaching/volatilization with aquifer transport
      - – to assess
        - » source duration combined with aquifer transport
        - » Spatial variation in gasoline composition
        - » Vapor intrusion

$$\eta B(S_w, S_o)\frac{\partial C_w}{\partial t} = -q_{w-g}\frac{\partial C_w}{\partial x} + \frac{\partial}{\partial x}\left[S_w D_w \frac{\partial C_w}{\partial x}\right] - F_{vol} - F_{d-gw}$$

$$B = \left(S_{w-aq} + S_o K_o + \frac{\rho_b}{\eta} K_{oc}\, f_{oc}\right)$$

The beauty of this formulation is that the presence of the gasoline phase is directly incorporated into the transport equation for water

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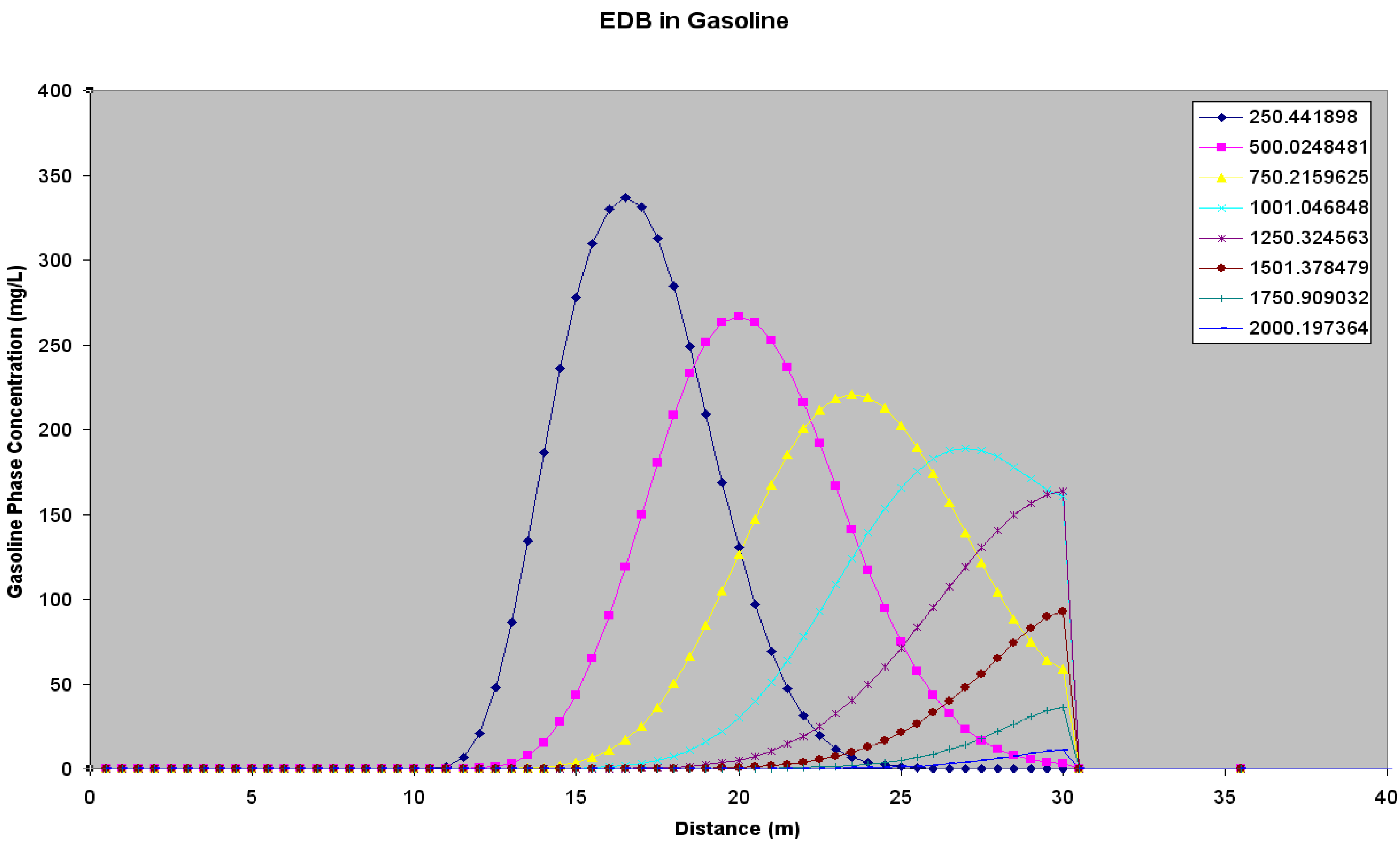
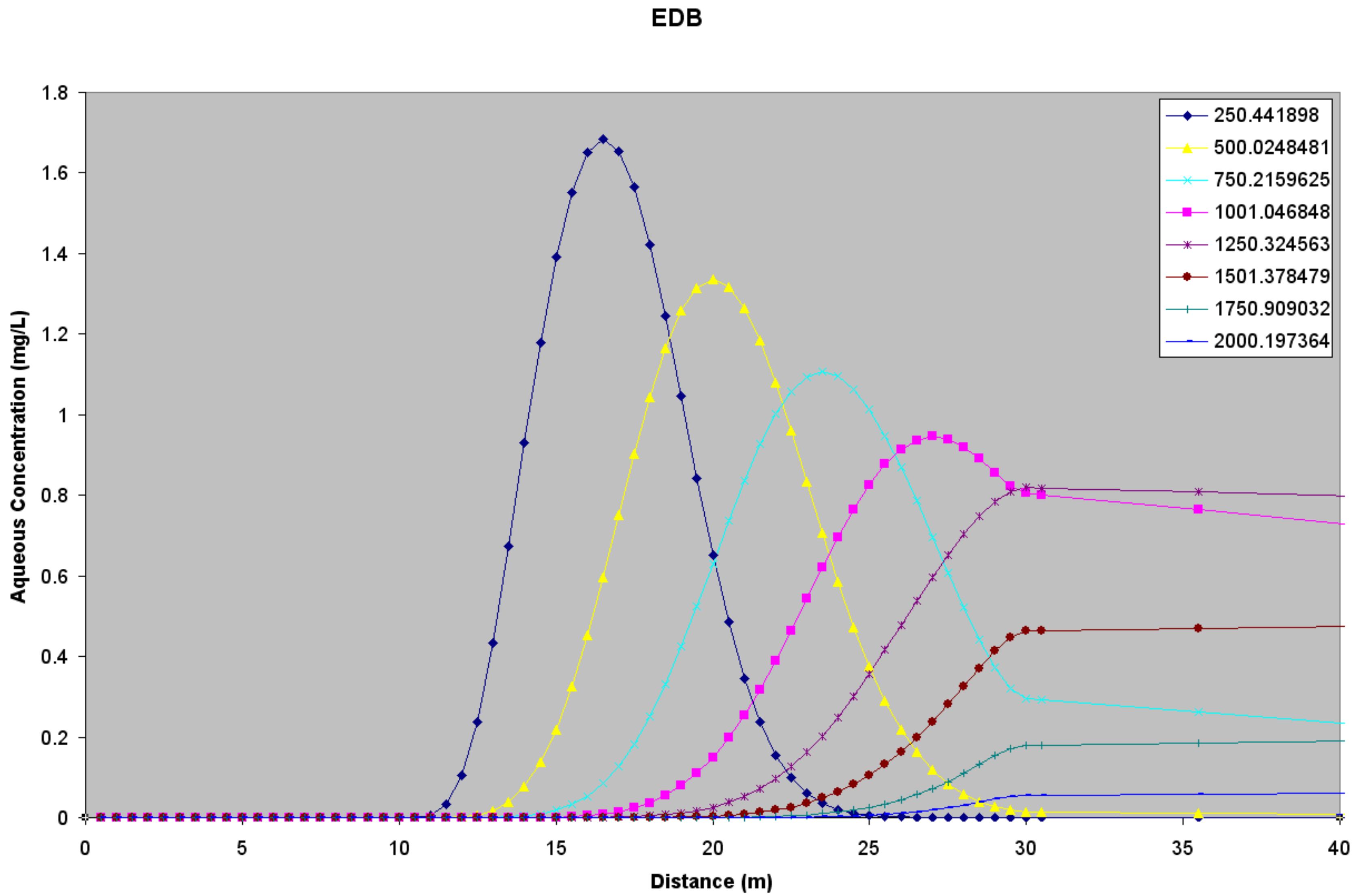
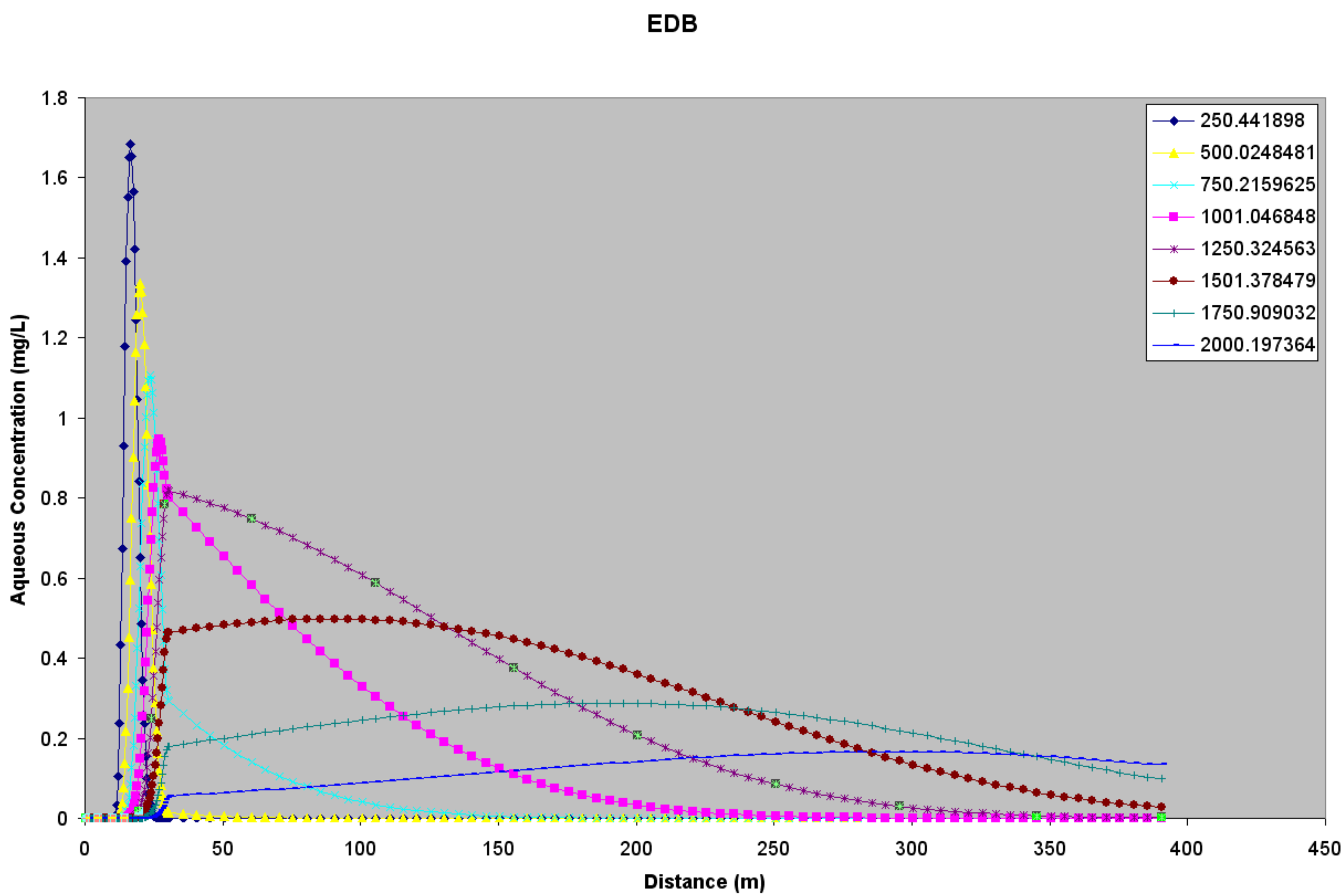
Example

- Gasoline from 10 to 30 meters in 400 meter domain
- Containiminant at 425 mg/L in gasoline from 10 to 15 m
- Transport through within gasoline and aquifer for 2000 days



EDB in Gasoline
Gasoline Phase Concentration (mg/L)
Distance (m)
0
50
100
150
200
250
300
350
400
0
5
10
15
20
25
30
35
40
250.441898
500.0248481
750.2159625
1001.046848
1250.324563
1501.378479
1750.909032
2000.197364


EDB
Aqueous Concentration (mg/L)
Distance (m)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
0
5
10
15
20
25
30
35
40
250.441898
500.0248481
750.2159625
1001.046848
1250.324563
1501.378479
1750.909032
2000.197364



EDB
Aqueous Concentration (mg/L)
Distance (m)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
0
50
100
150
200
250
300
350
400
450
250.441898
500.0248481
750.2159625
1001.046848
1250.324563
1501.378479
1750.909032
2000.197364

R9

- Numerical model
  - Extremely flexible in adding additional transport phenomena (equations)
  - Gasoline composition affects character of aquifer transport
  - Adaptable to a streamline modeling approach (using capture zones)
  - Alternately, adaptable to 2 and 3 dimensions

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Surface Water Spills

- Rockford, Ill, June 2009
- Train derailment, fire, two tank cars of denatured ethanol spill
- Flow to ditch, creek, Kishwaukee River, Rock River
- 75,000 fish killed

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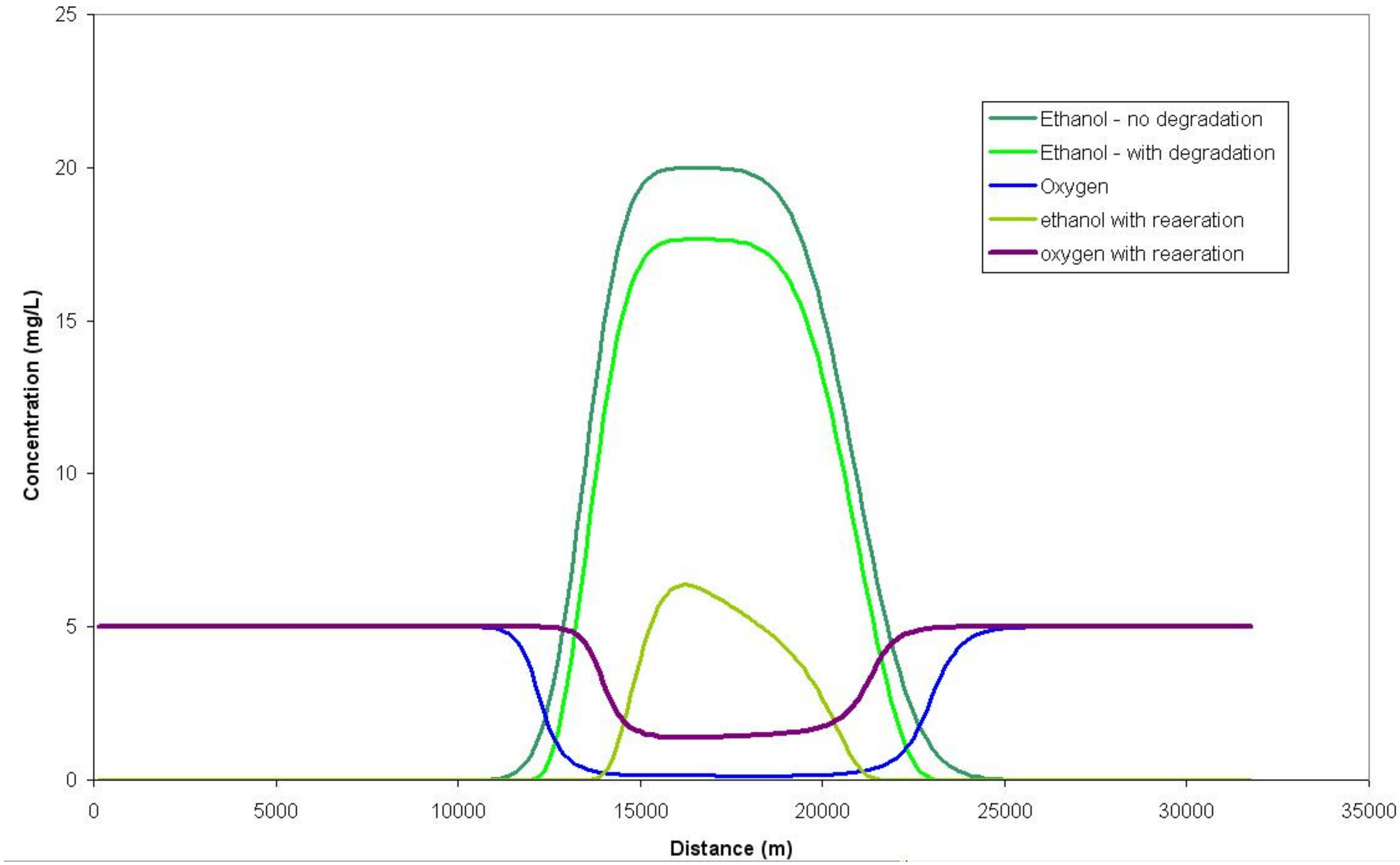
Reactive Transport for Ethanol/BTEX and oxygen

- Ethanol degrades aerobically in the presence of oxygen
- Approximately 2 g of O_2 required to mineralize 1 g of ethanol
- Oxygen is supplied from
  - Ambient dissolved oxygen concentration in water
  - Re-aeration from the atmosphere
  - Oxygenated inflows

Test Problem to Illustrate Appropriate Stoichiometry Example Profile 5 hrs After Release



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Next Steps

- Assembling data for Rockford, Ill spill
- Increased efficiency in the model is needed in order to simulated 100+ river miles
- Linkage with bioaccumulation/toxicity model to estimate fish kill due to ethanol + hydrocarbon toxicity
- Others

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National Exposure Research Laboratory

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  - Leigh DeHaven, US EPA, O.E.M.
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  - Matt Small, US EPA, R9
  - Matt Tonkin, SSP&A, Bethesda MD.

- Although this work was reviewed by EPA and approved for presentation, it may not necessarily reflect official Agency policy.

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