



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

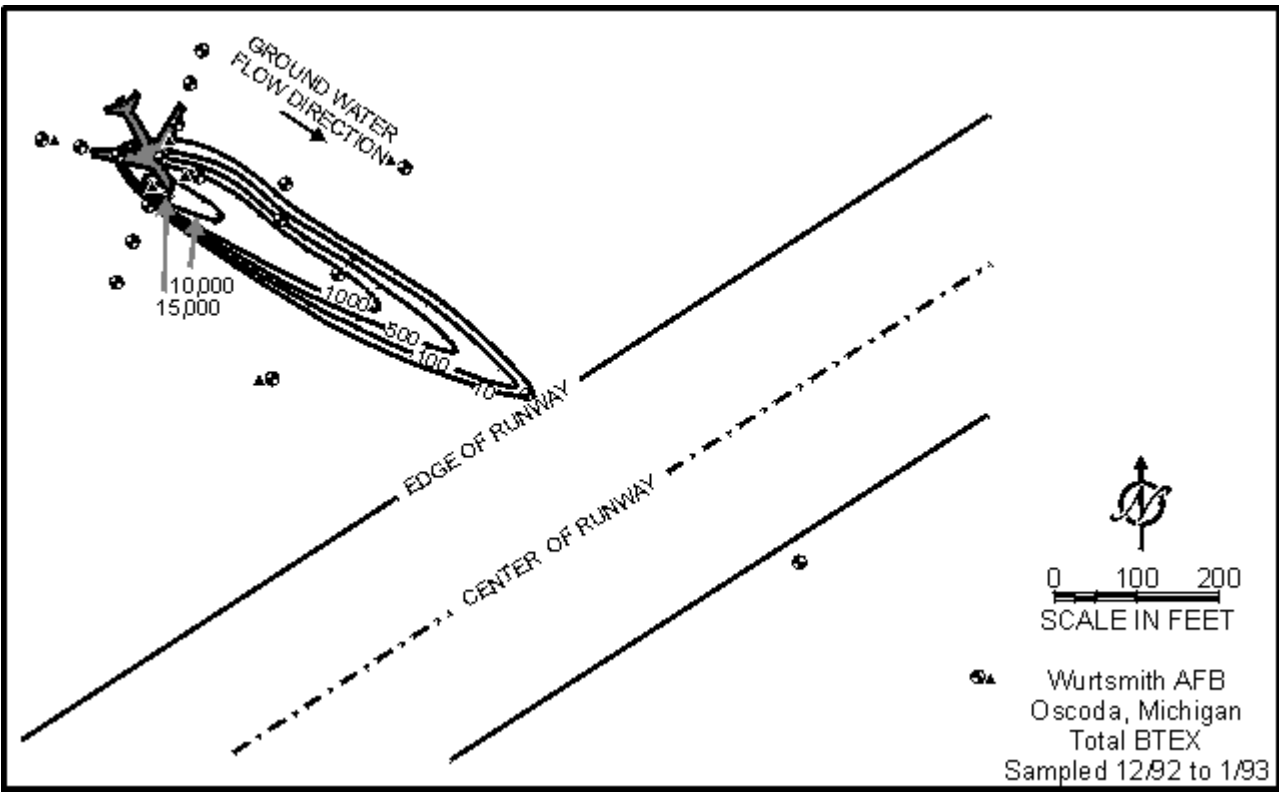
- Model = Representation and quantification of site knowledge
 - Conceptual model
 - Generic knowledge of fate and transport AND site-specific data
 - Release history
 - Site data
 - Application and testing of a computer code
 - Matches conceptualization of site
 - Results
 - Interpretation of results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

Conceptual Models

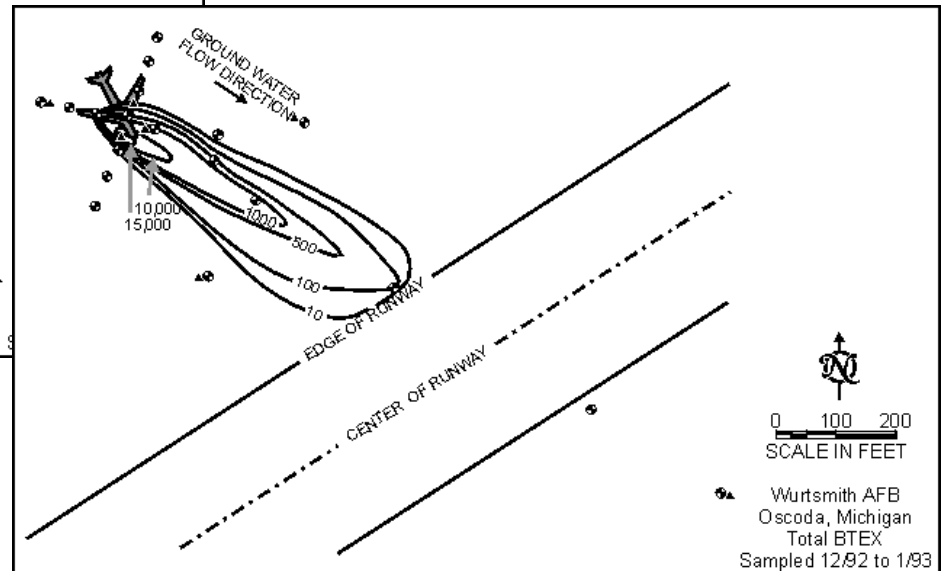
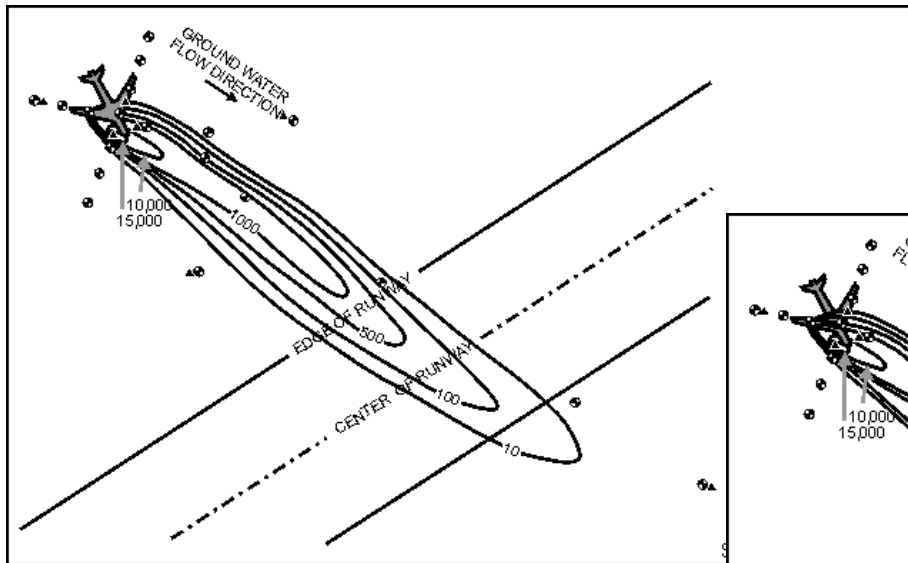
- Source type and history
 - Soil vs water table contamination
 - Release date
 - Release volume and composition
 - (how well known?)
- Geometric configuration
 - Stratigraphy
 - Hydrologic boundaries
 - Transport pathways
 - (how well known?)
- More ...

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Data Interpretation: Wurtsmith AFB Total BTEX



Why Not These?



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

Critical Assumptions of Analytical Solutions

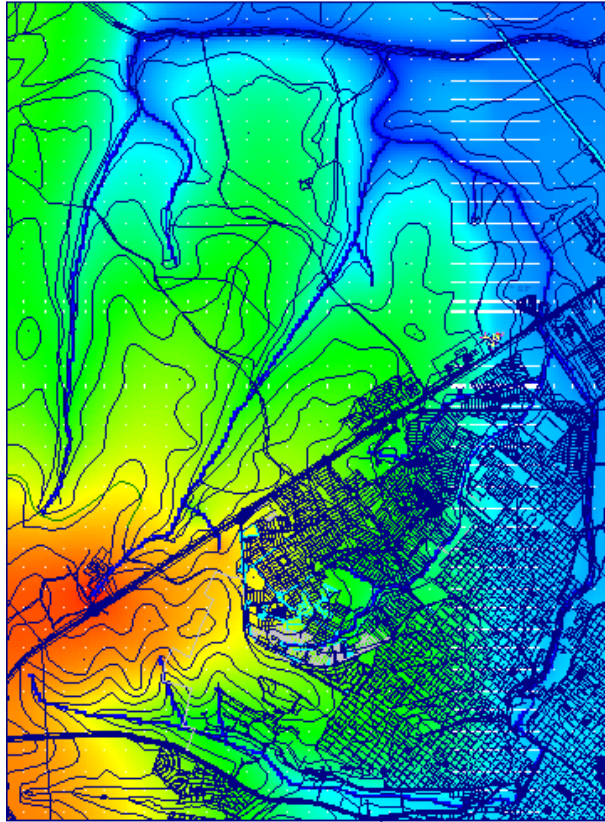
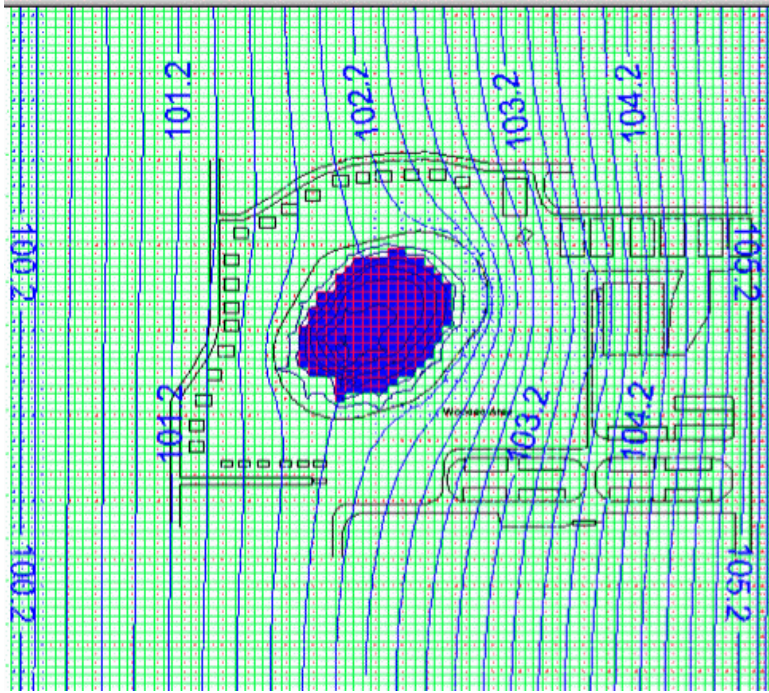
- **All** analytical solutions of the **transport** equation share the assumptions:
 - Steady **ground water** flow
 - One-dimensional **ground water** flow
 - Uniform **ground water** flow
 - 2nd and 3rd **transport** dimensions are by dispersion only
 - Homogeneous (uniform) aquifer
 - No grid, all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

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

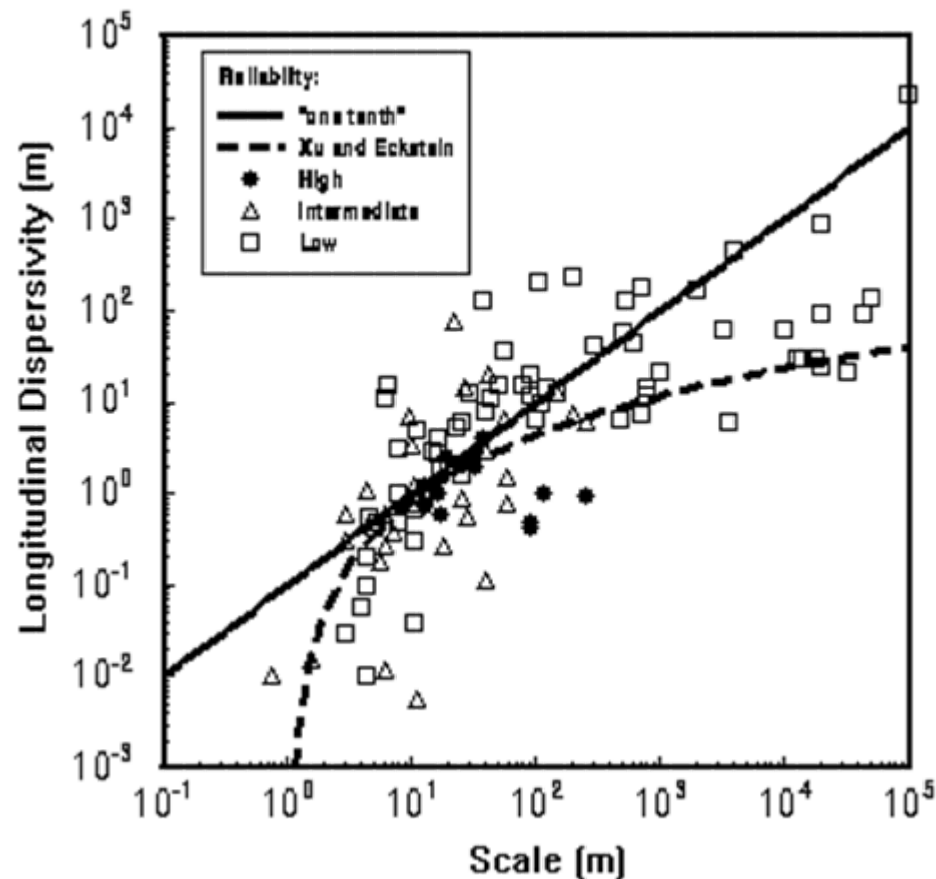


Common Sources of Model Inputs Used at Leaking Underground Storage Tank Sites

- 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 unknown
 - Mass
 - Timing
 - Composition

Dispersivity Data (Gelhar, 1992)

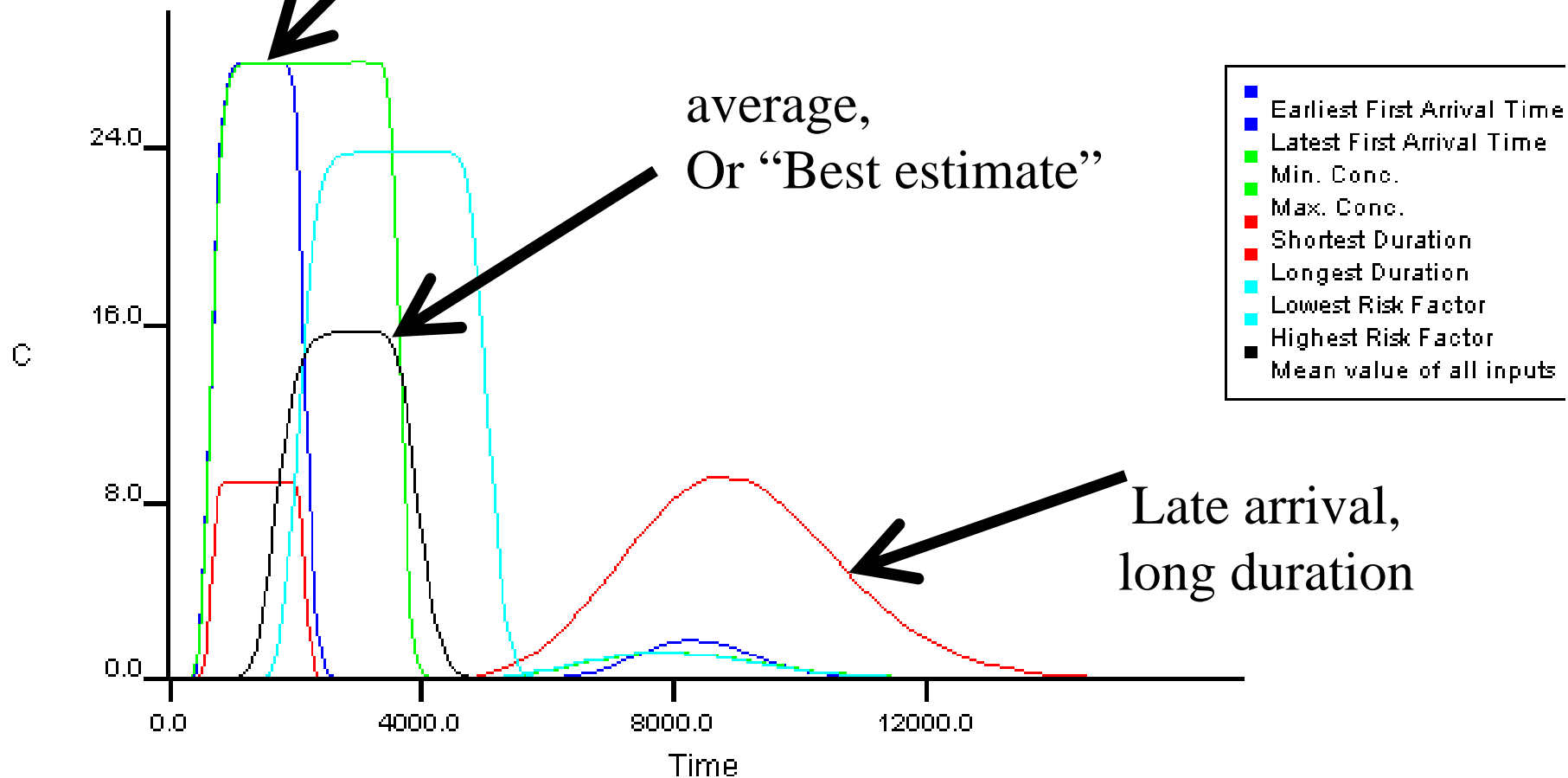
Gelhar, Welty and Rehfeldt (1992) Dispersivity Data



Early arrival, short duration, high concentration

Breakthrough Curves

average,
Or “Best estimate”

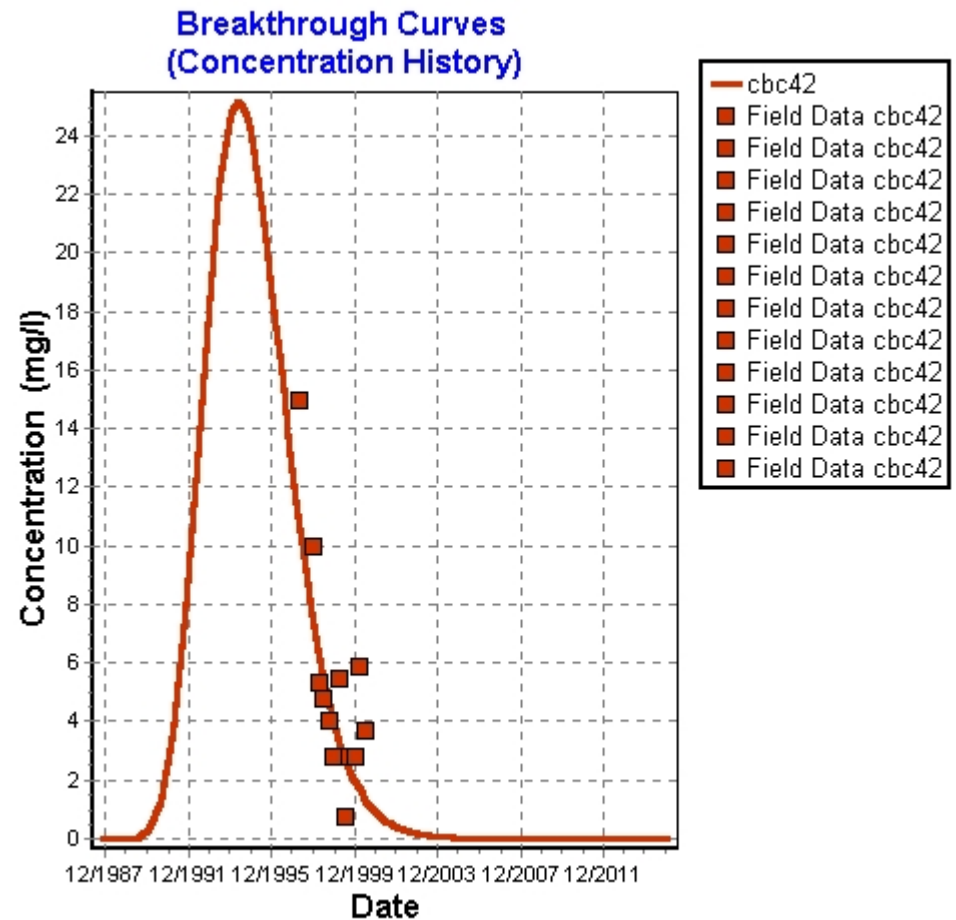


<http://www.epa.gov/athens/onsite>

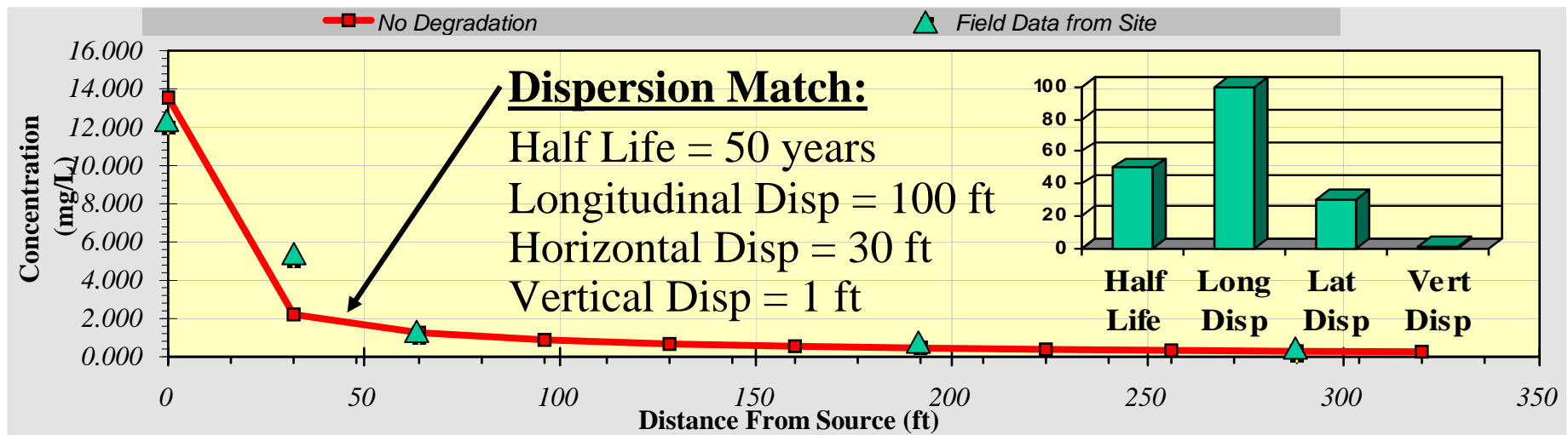
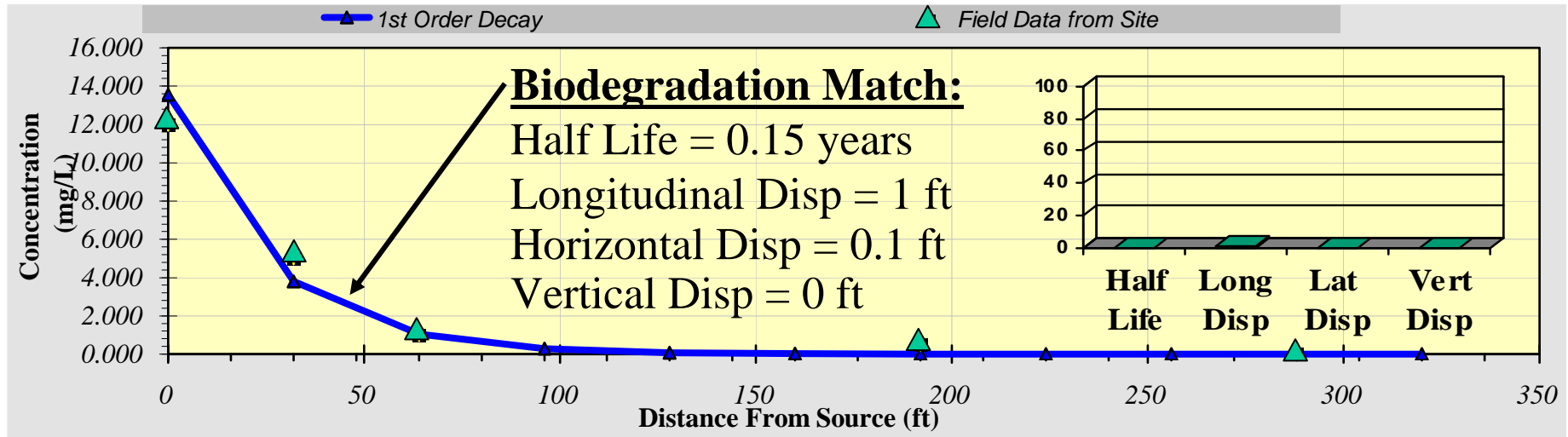
Calibration: Match model results to the site

- 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

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

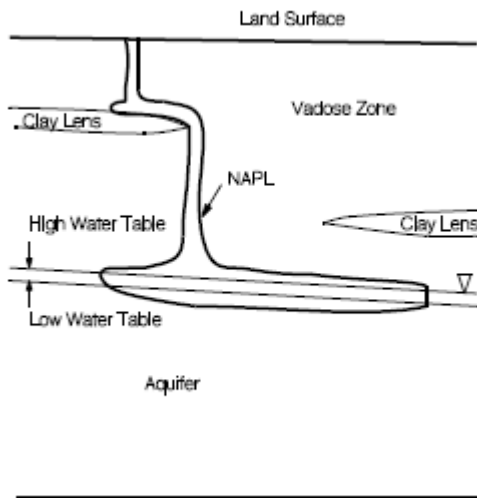
Models

- “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.

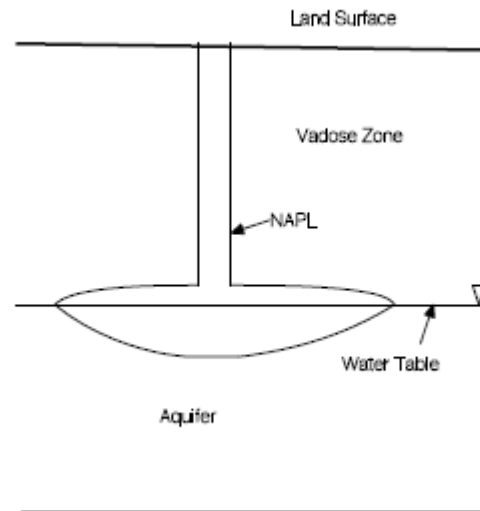
The Hydrocarbon Spill Screening Model

- 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.

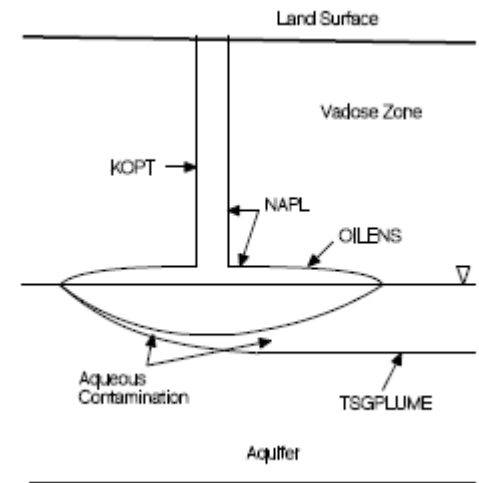
HSSM



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)

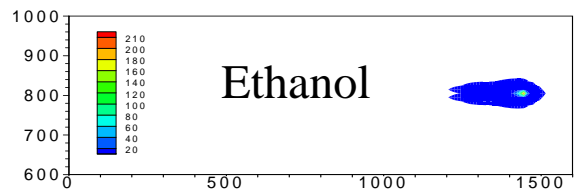
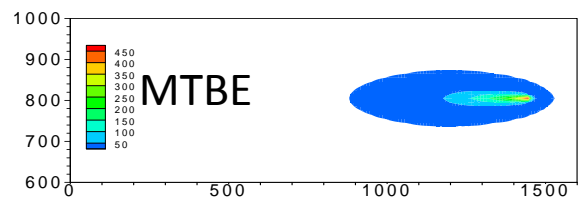
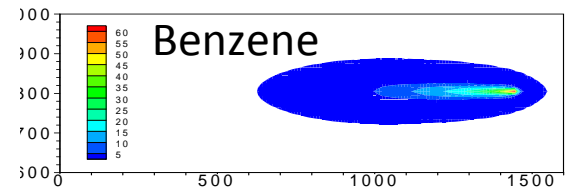
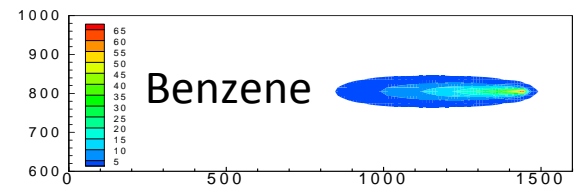
Biggest HSSM Limitation

- 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

HSSM Expansion

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

Modeled RFG (w MTBE) vs E10



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.

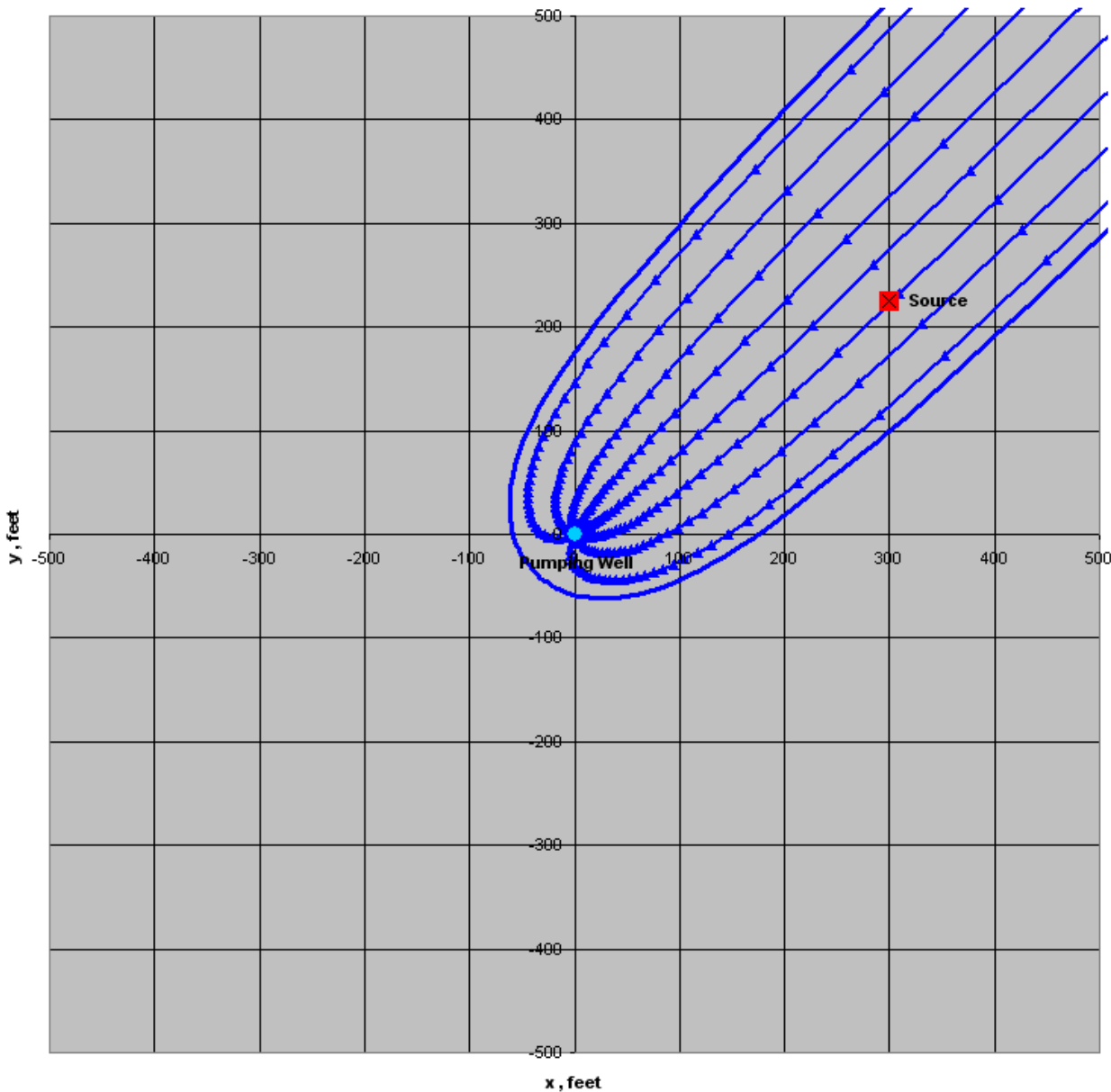
R9 RARE

- 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
 - Javandel (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 (Small, 2003)
 - Uncertainty analysis:
 - Parameter measurements are imprecise
 - Some parameters are not measured (dispersivity) or un-knowable (release date)
 - Heterogeneity is not fully characterized

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Capture Zone and Streamlines for Single Pumping Well

Chart Area



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

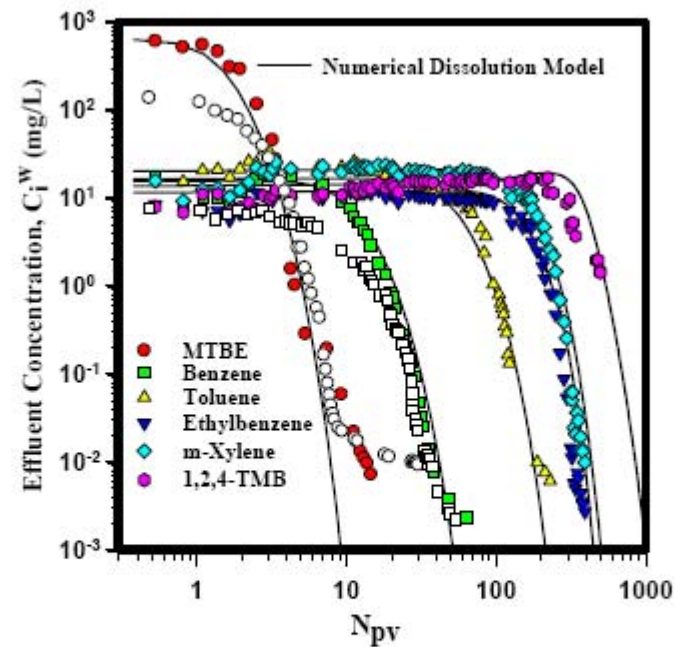


Figure 4. Dissolution curves for MTBE, BTEX and 1,2,4-TMB from a model NAPL mixture in soil. Filled symbols – two weeks aged (Experiment 4a). Open symbols – seven months aged (Experiment 4b). $Pe=20$.

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

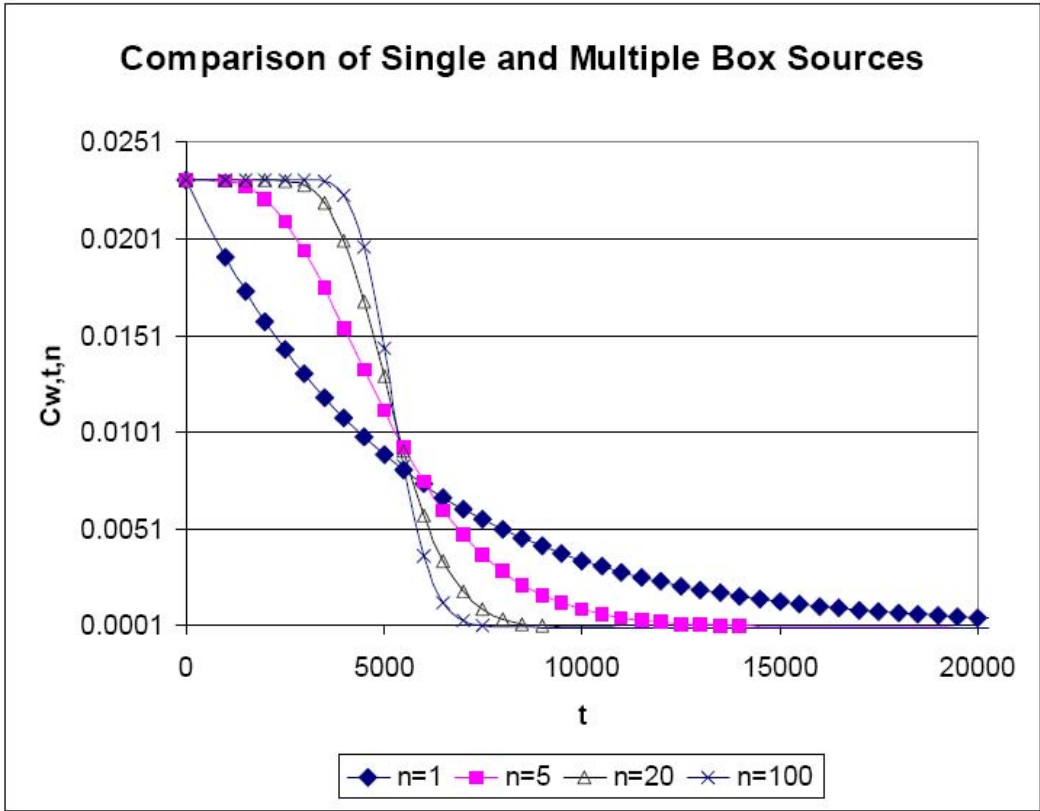


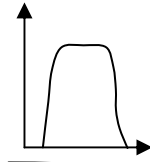
Figure 5. Concentration versus time at the downgradient face of the LUSTimpact source model illustrating the transition from a single continuously stirred tank reactor (CSTR) where $n=1$, to a plug flow reactor (PFR), or step function as the number of source boxes in series is increased.

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

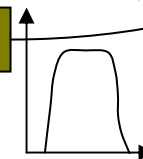
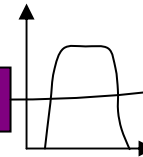
- With variation in parameters, e.g.:
 - Hydraulic conductivity 10 m/d to 100 m/d
 - Flow direction -65° to 65°
 - Gasoline Volume 300 gal to 500 gal
 - Gasoline Saturation 0.1 to 0.2
 - Etc. (many use value +/- 10%)

Compartmentalized Source

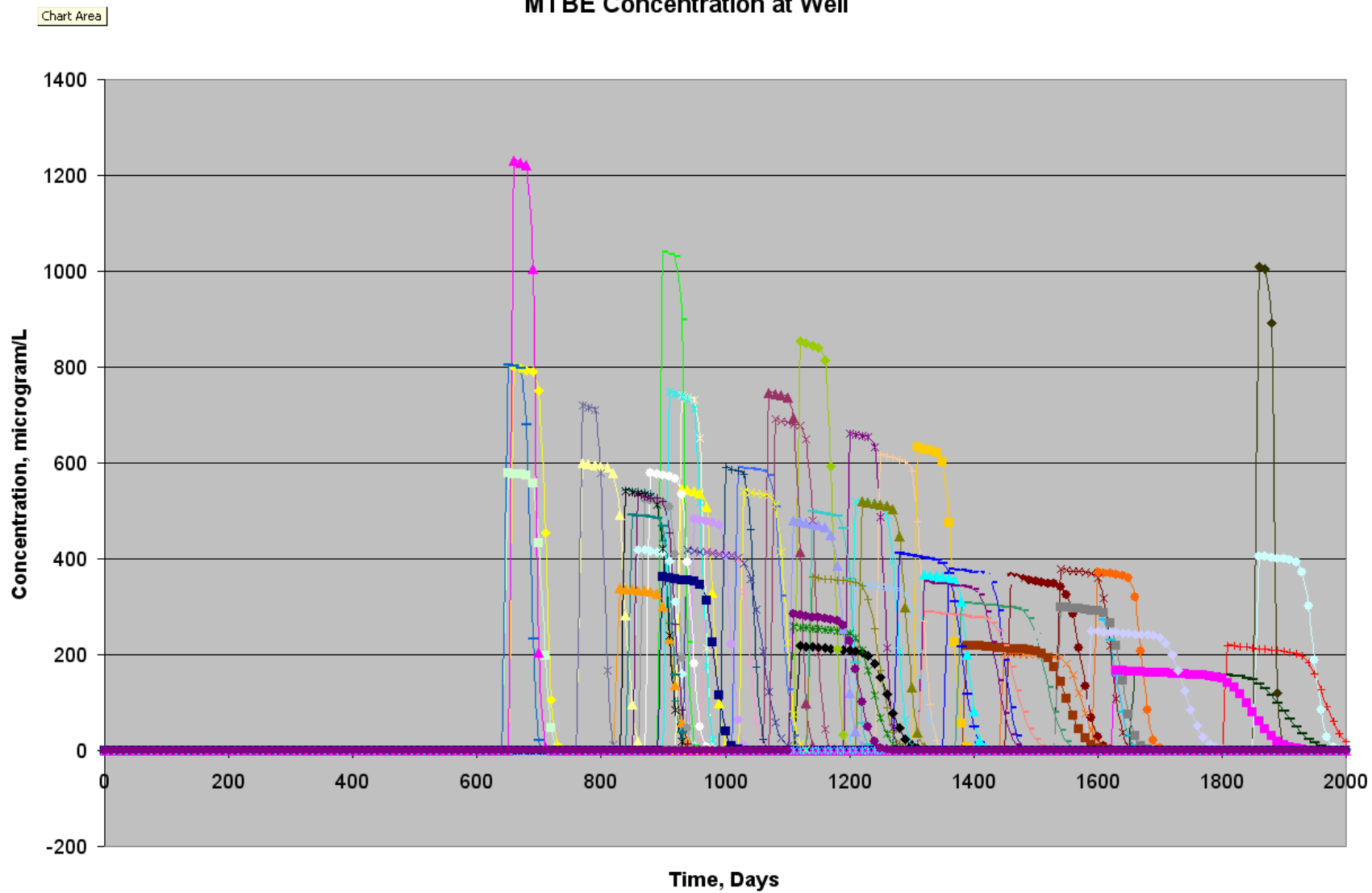


Advection and decay
Along a streamline

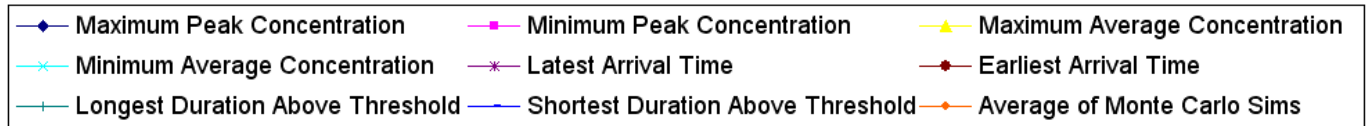
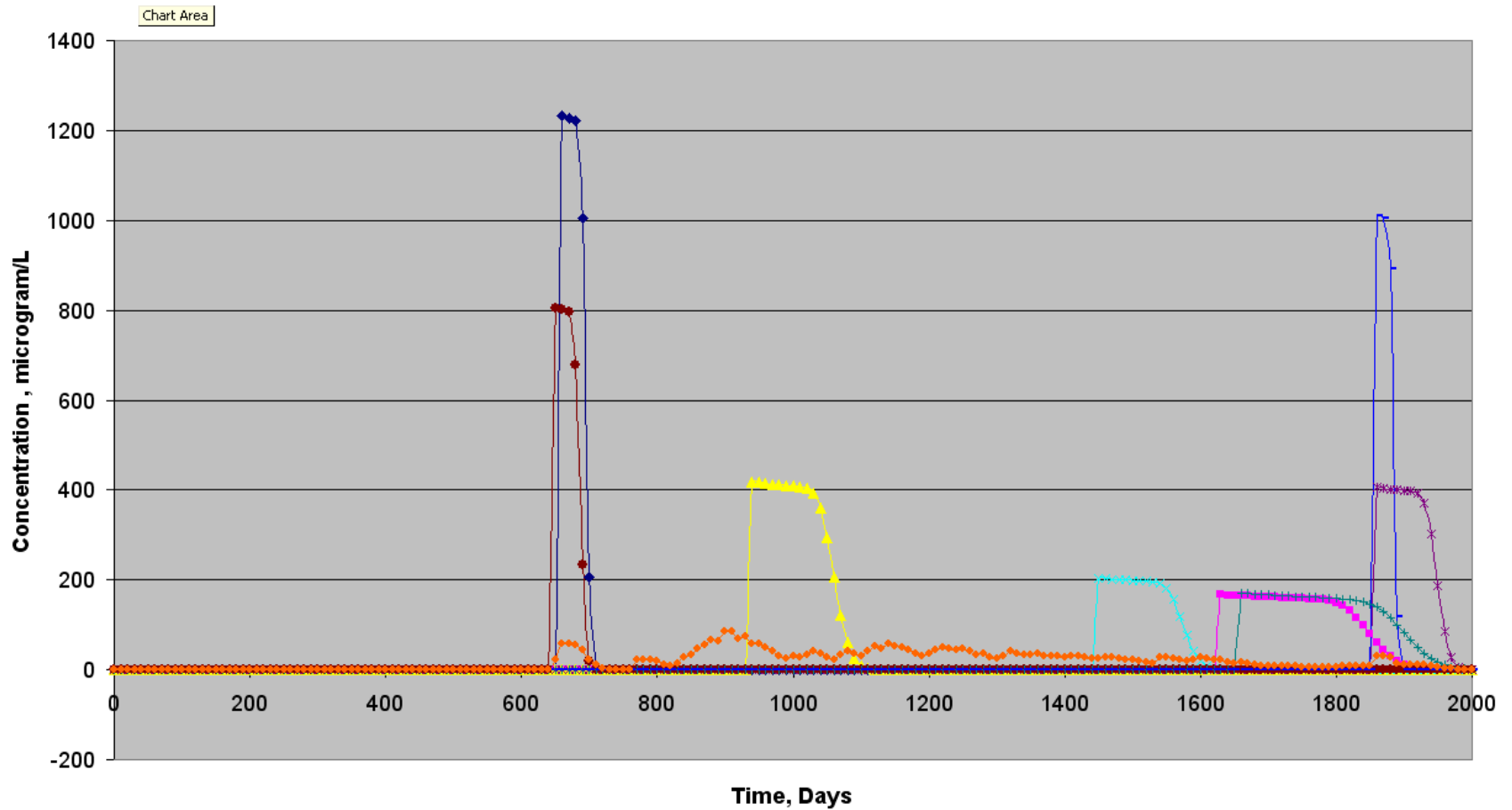
Well integrates
contributions
from all sources



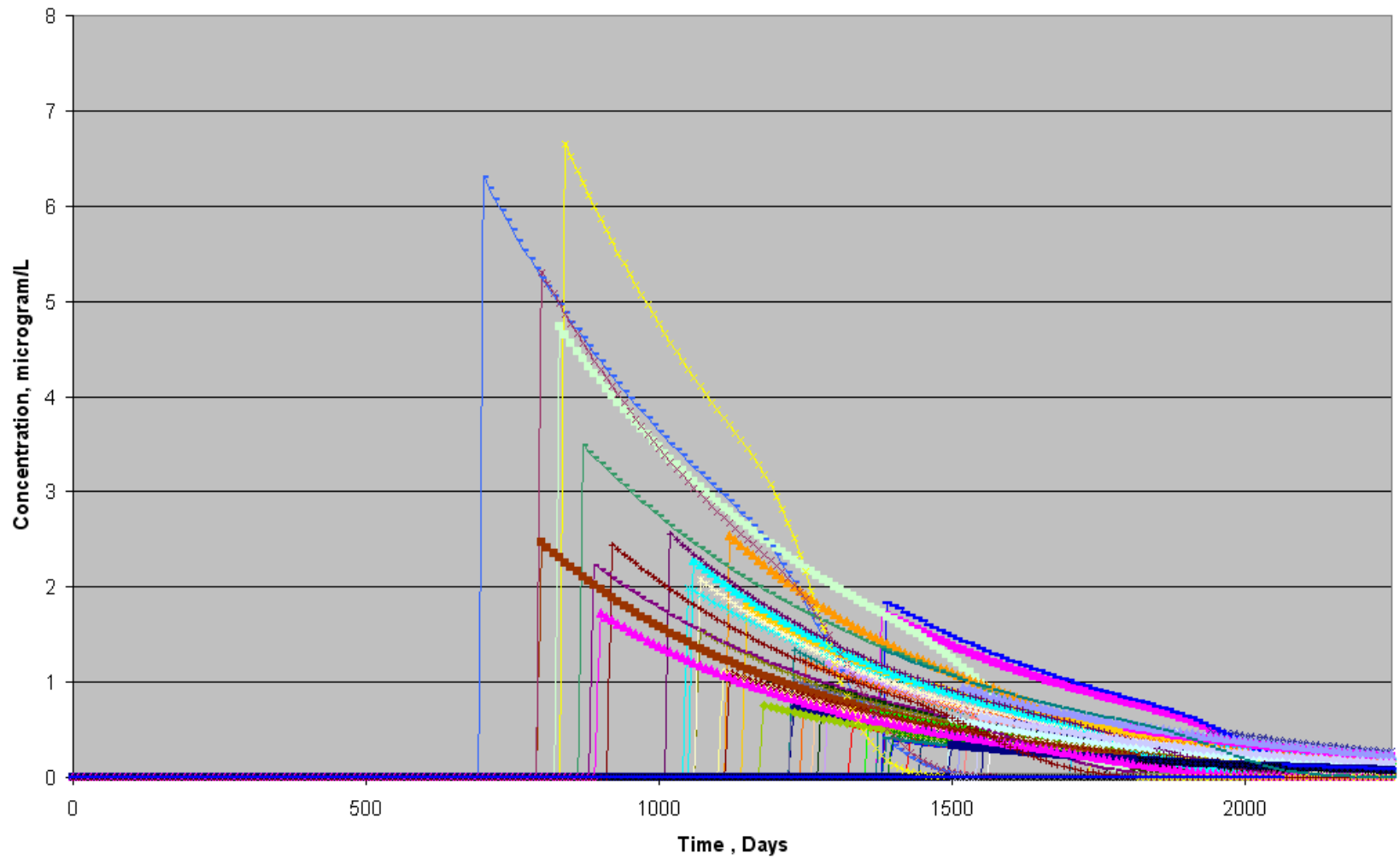
MTBE Concentration at Well



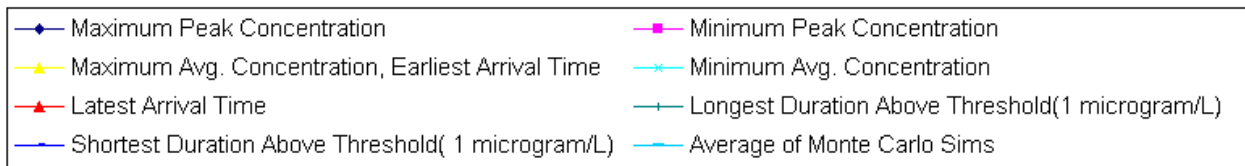
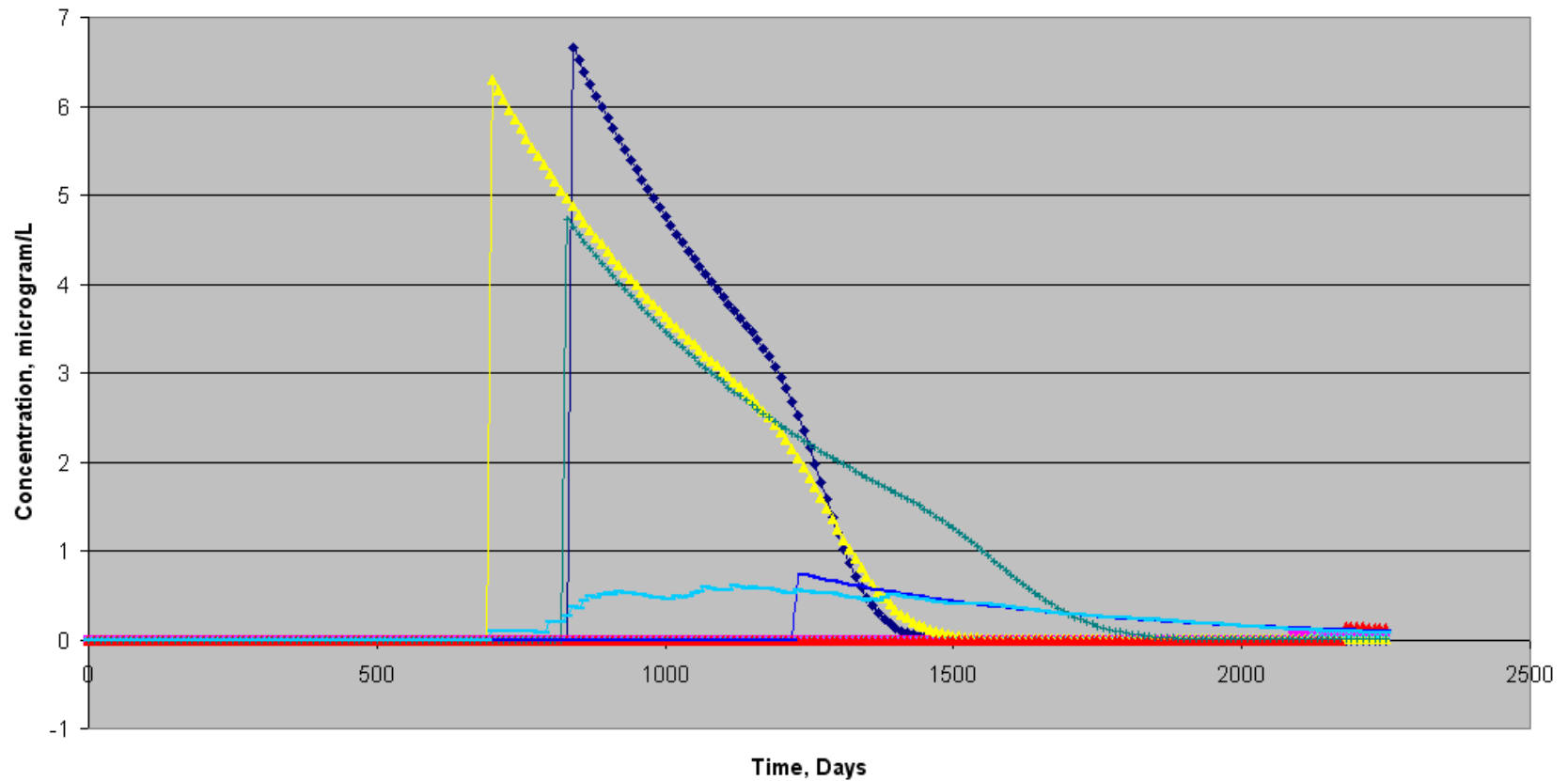
Extreme Values



Benzene Concentration at Well



Benzene Extreme Values



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

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

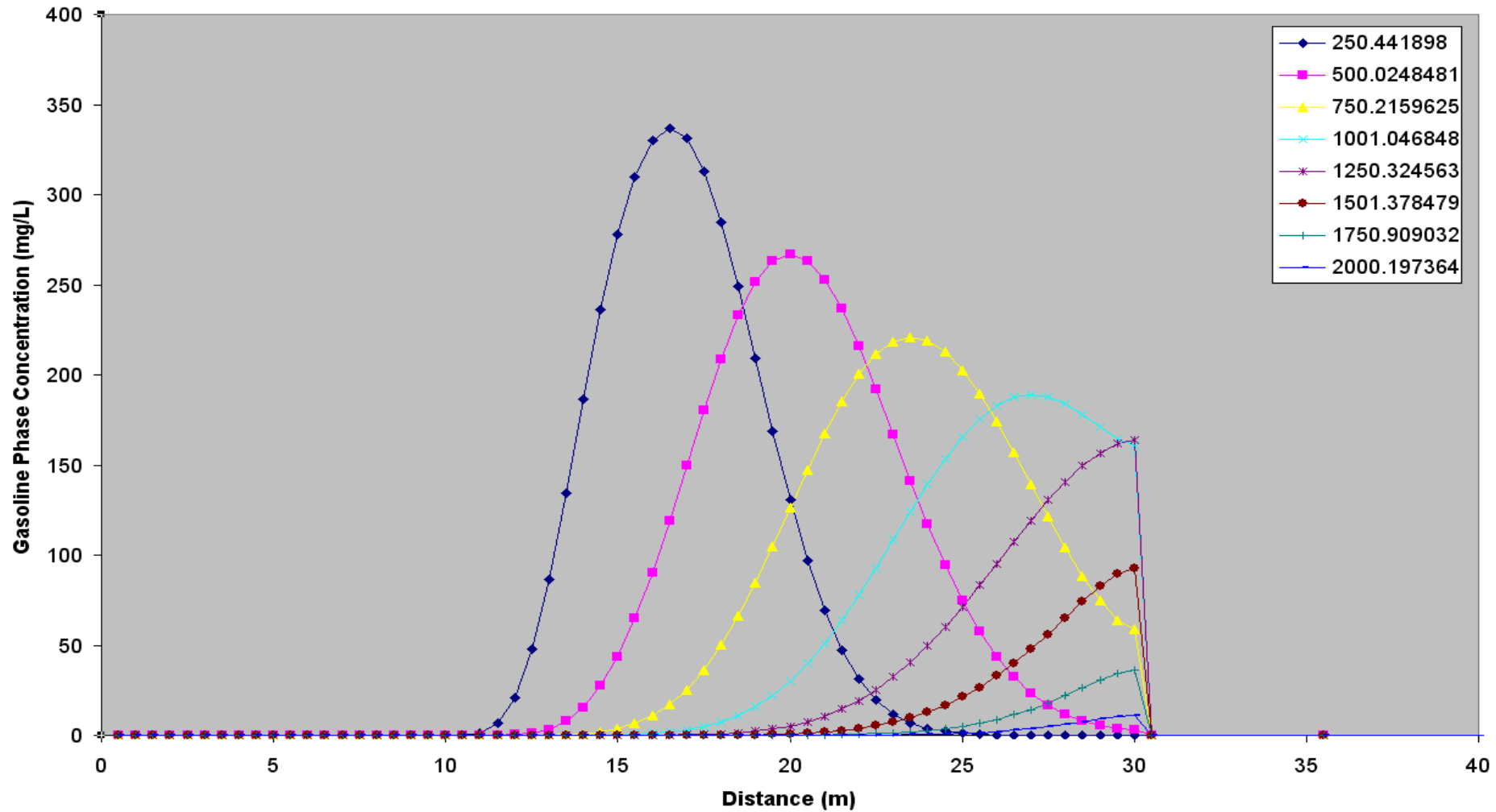
$$B = \left(S_{w-aq} + S_o K_o + \frac{\rho_b}{\eta} K_{oc} f_{oc} \right)$$

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

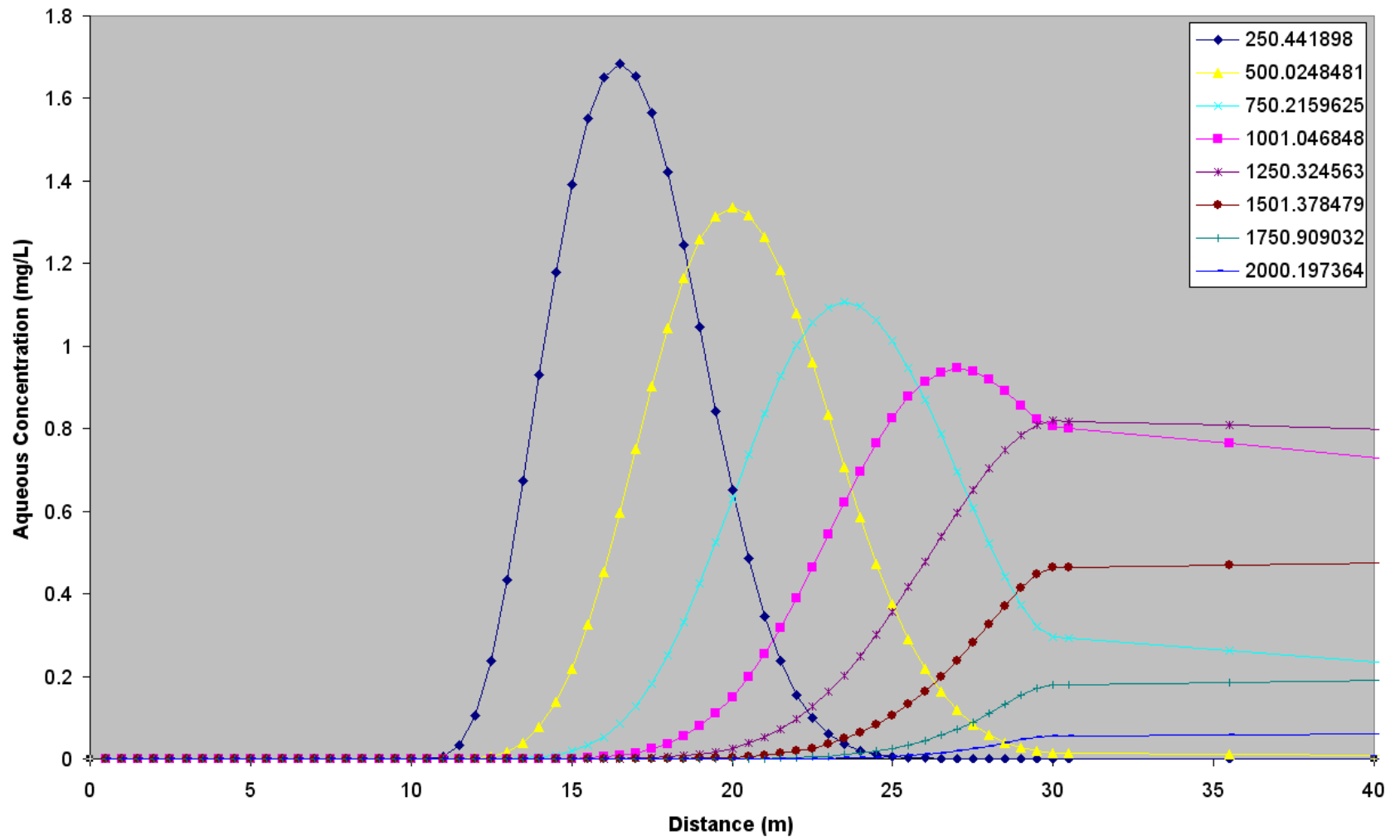
Example

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

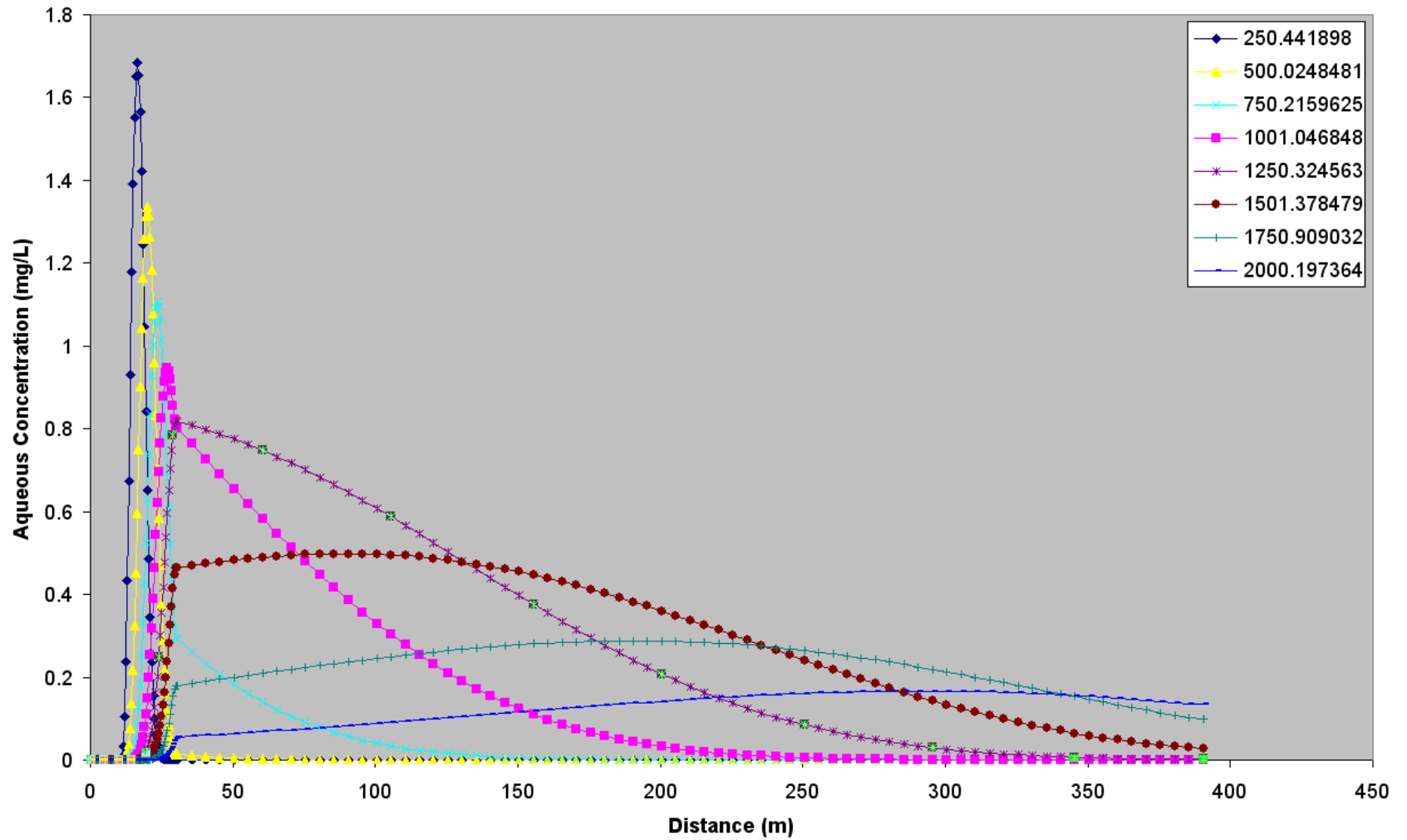
EDB in Gasoline



EDB



EDB



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

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

RESEARCH &
DEVELOPMENT

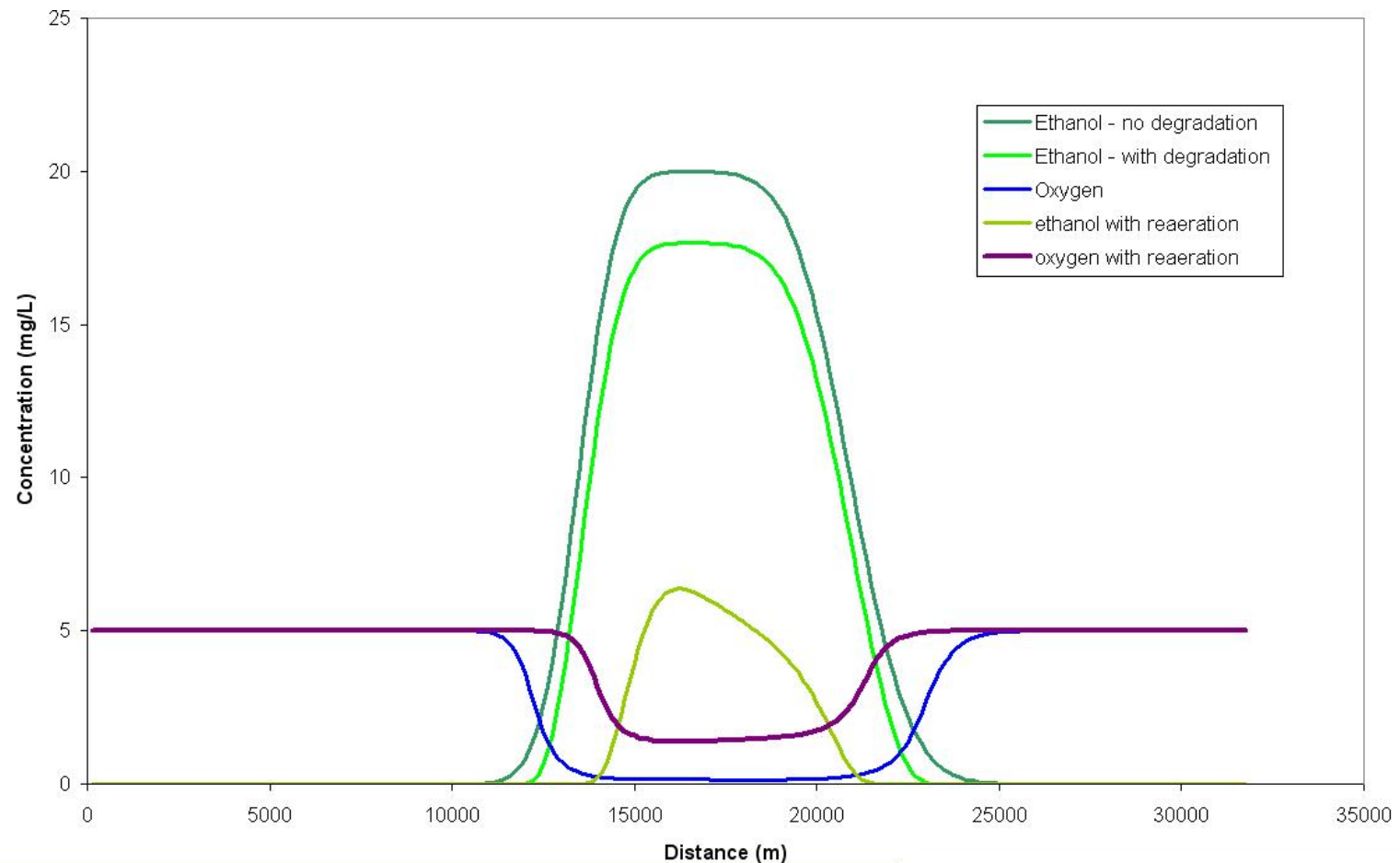
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Reactive Transport for Ethanol/BTEX and oxygen

- Ethanol degrades aerobically in the presence of oxygen
- Approximately 2 g of O₂ 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



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

National Exposure Research Laboratory

- Acknowledgements
 - 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.
- weaver.jim@epa.gov, 706-355-8329