Ethanol Impacts on BTEX Plumes

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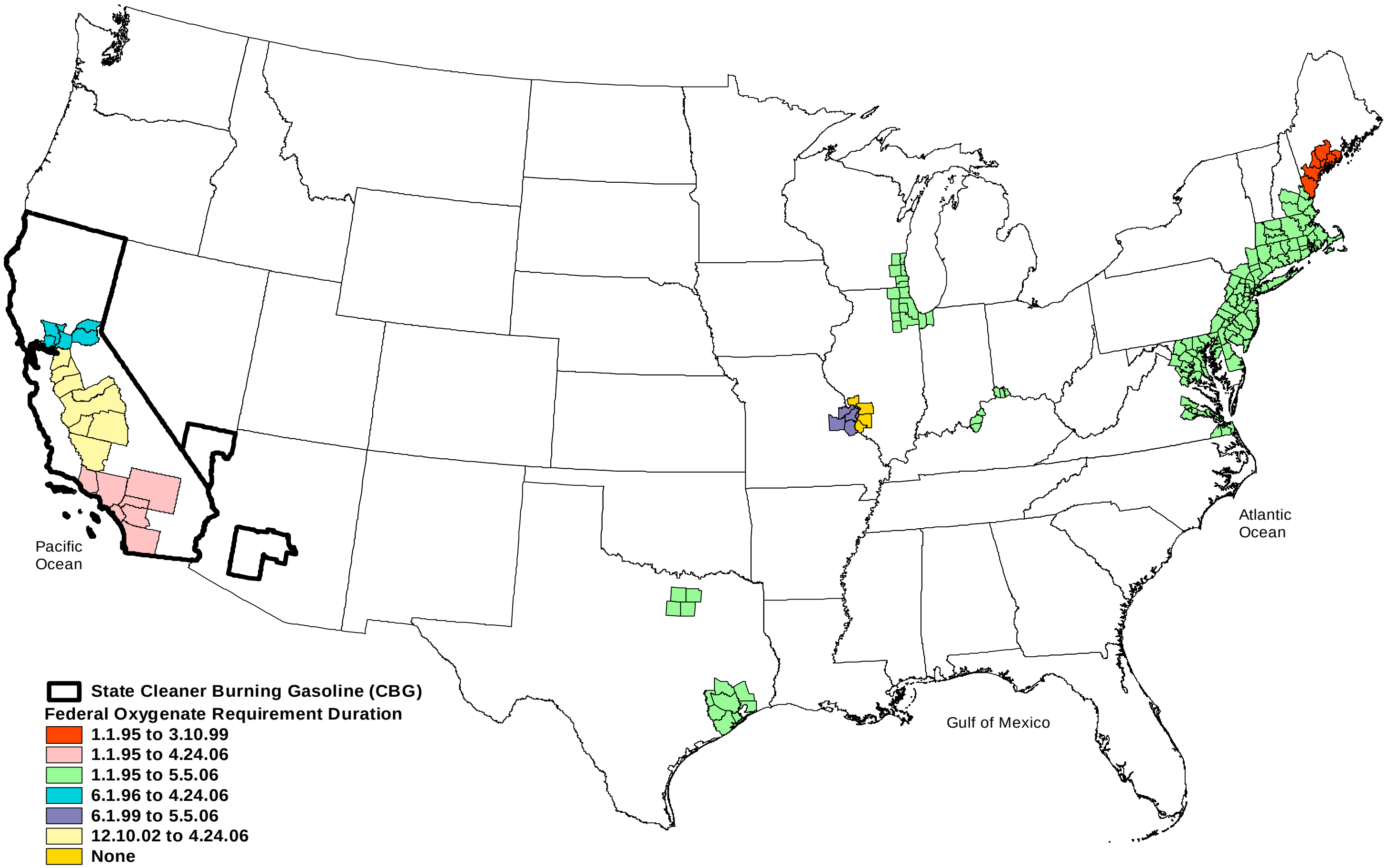
Outline

- Ethanol Impacts on BTEX plumes
- Footprint model from EPA
- Analysis of Transport in Regional Scale Aquifers

Clean Air Act Amendments of 1990

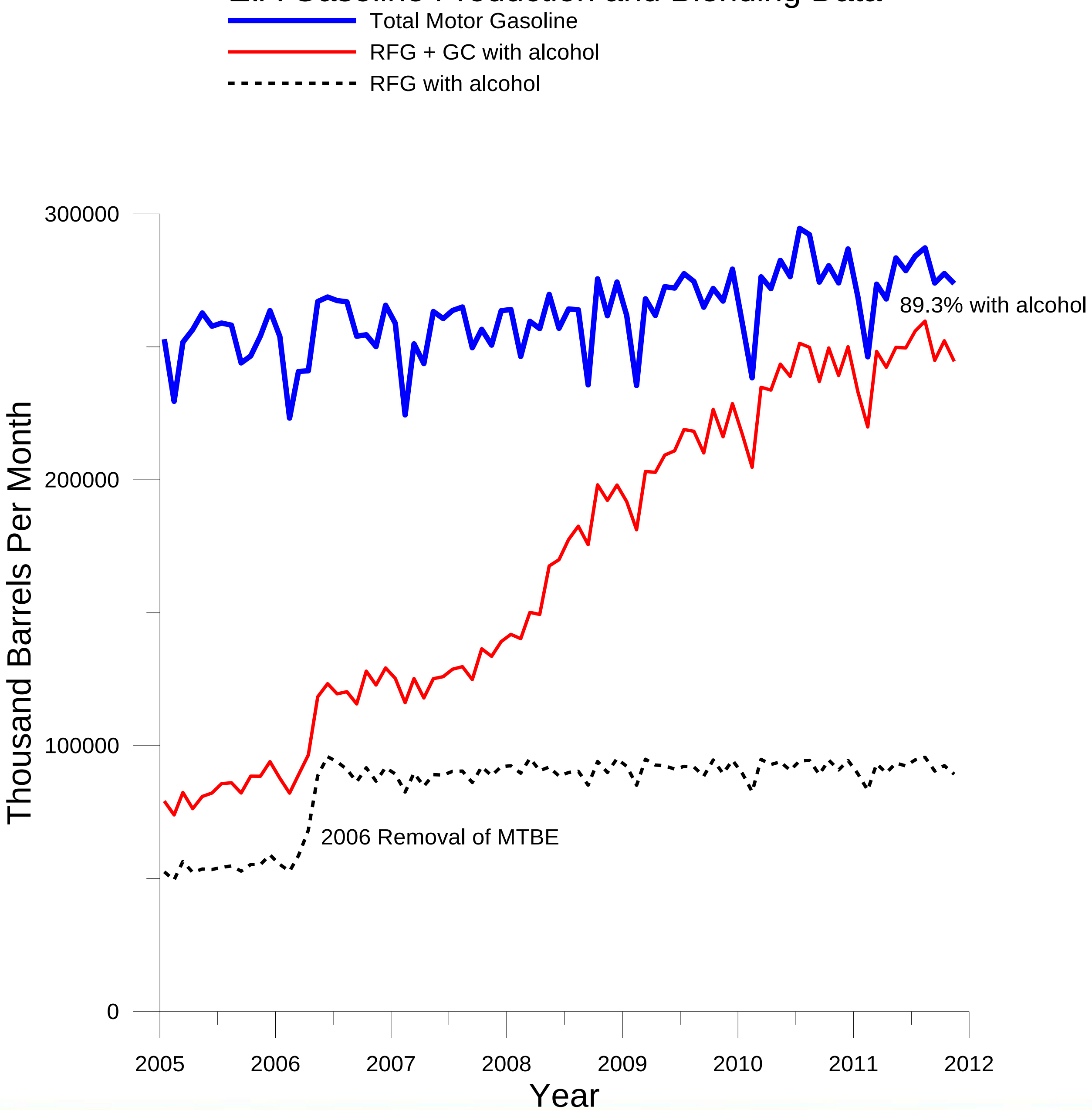
- Established framework for U.S. gasoline composition
  - Final lead phase out (1996)
  - Reformulated, conventional and oxygenated gasoline programs
    - Reformulated (RFG) – benzene < 1%; oxygenated additive until 2006
    - Conventional (CG) – benzene limited by anti-dumping provision – oxygenates boost octane
    - Oxygenated (OG) – control CO emissions in winter in selected cities
  - Mobile Sources Air Toxics Act (MSAT) 2007
    - Reduce benzene to 0.62% all U.S.
  - For more information:
    - Gasoline Composition Regulations Affecting L.U.S.T. Sites, 2010, EPA EPA/600/R-10/001

Reformulated and Conventional Gasoline



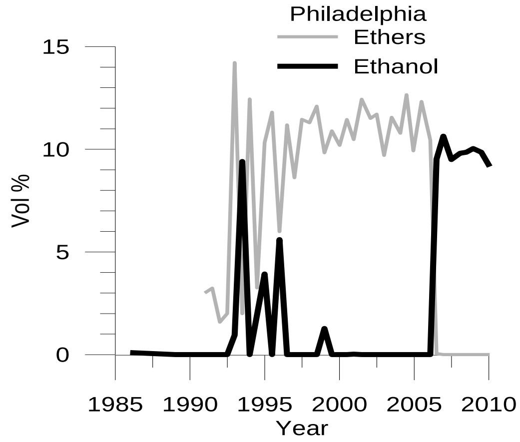
Whole county boundaries shown for partial counties: Grundy & Kendall in Illinois, Bullitt & Oldham in Kentucky. Not represented: above 4500' on White Face Mountain in Essex County, New York. All areas not indicated on the map use conventional gasoline.

EIA Gasoline Production and Blending Data

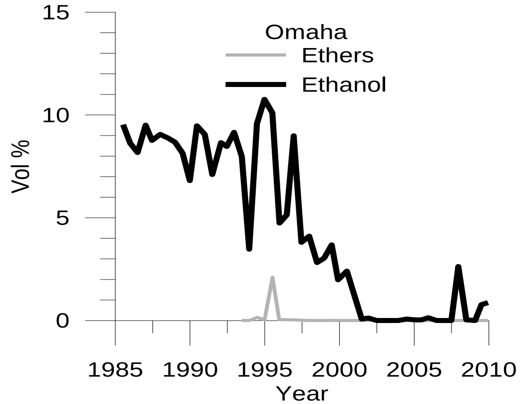


Some of the 10%

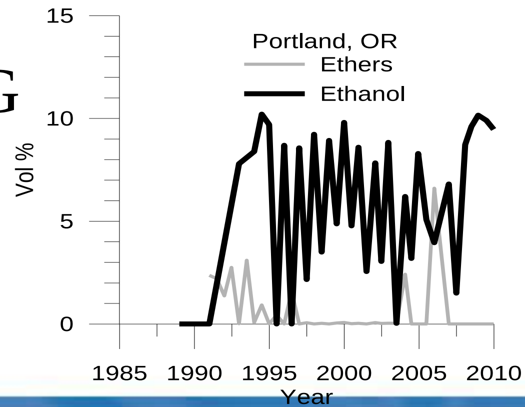
RFG



CG



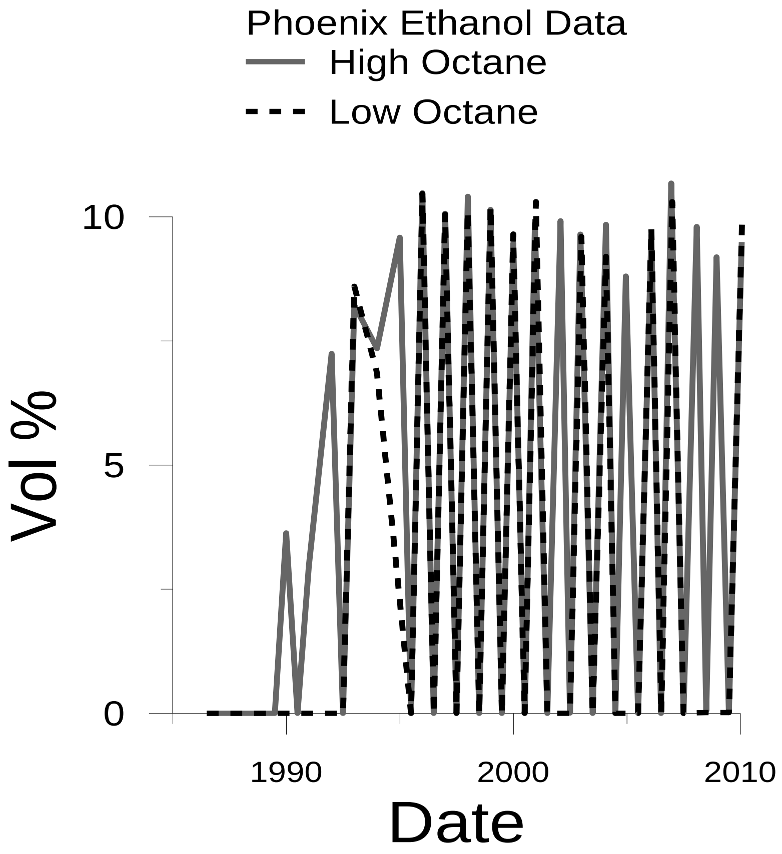
OG/CG

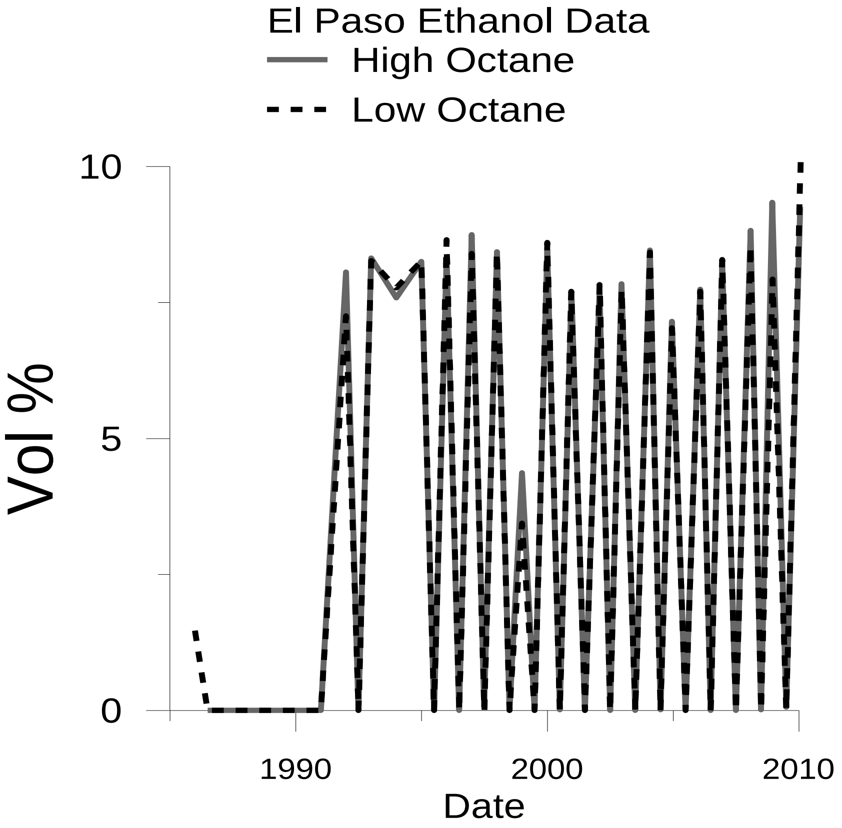


National Institute for Petroleum and Energy Research -API-TRW-Northrop Grumman Gasoline composition data from 1930s to 2010

See David Spidle's poster for these cases, Jim's poster for more cities and compounds

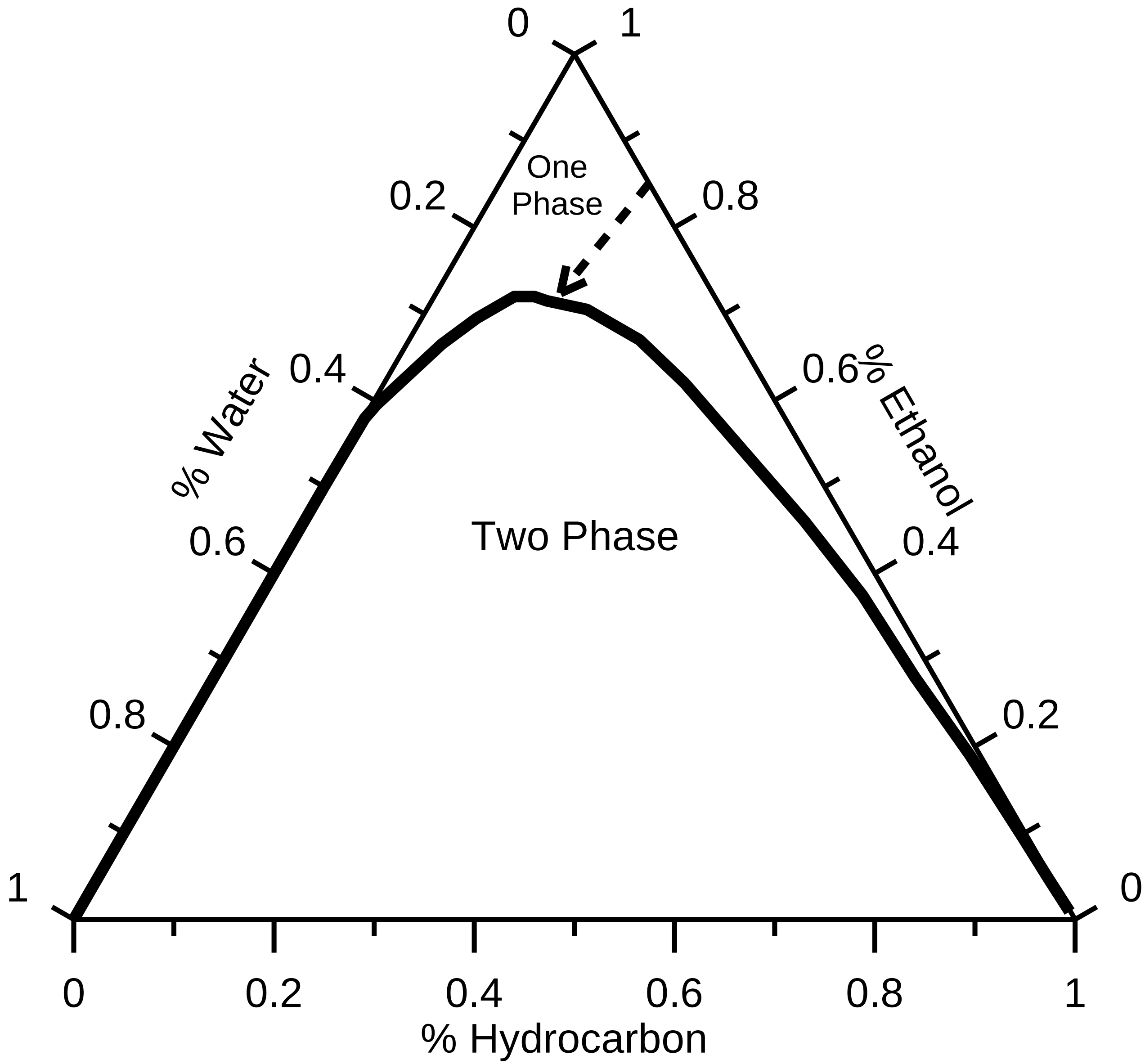
More of the 10%



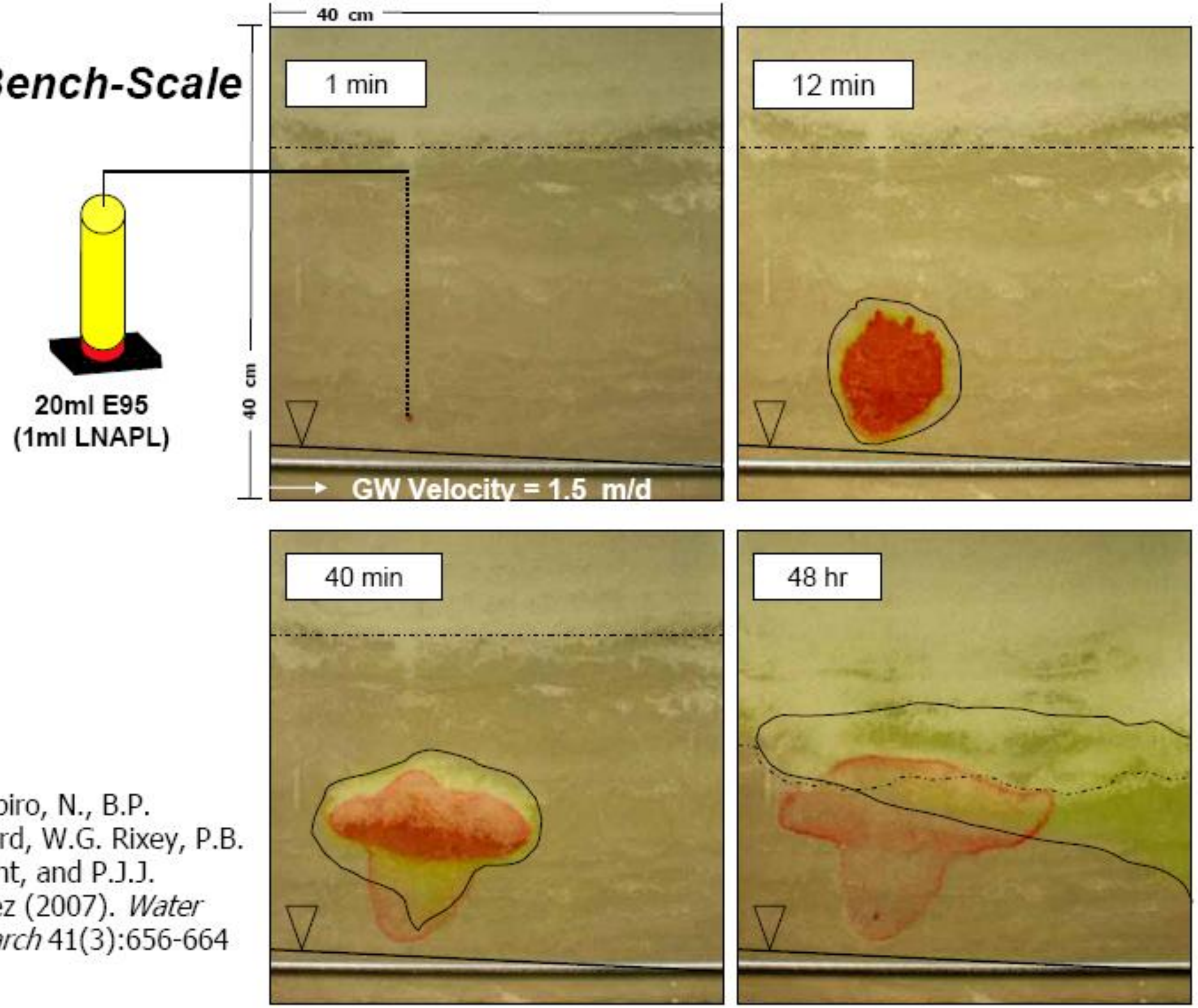


Ethanol Impacts on BTEX Transport

- What is the science telling us?
  - Water scavengers ethanol from fuel
  - Ethanol resides in the capillary fringe
  - Ethanol biodegrades preferentially over BTEX
    - BTEX plume elongated if in contact

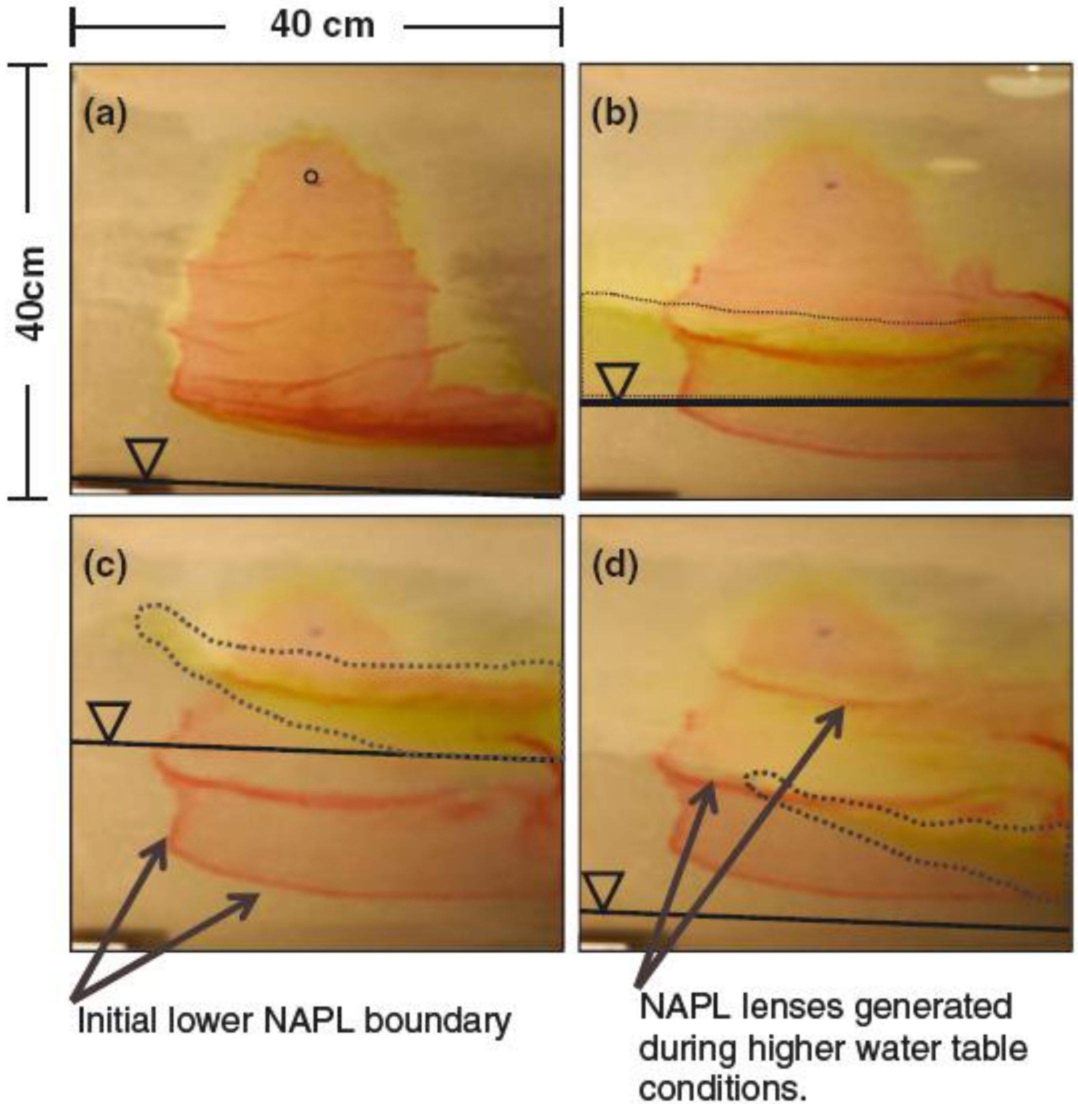

0
1
0.2
0.8
One Phase
0.4
0.6
% Water
% Ethanol
0.6
0.4
Two Phase
0.8
0.2
1
0
0
0.2
0.4
0.6
0.8
1
% Hydrocarbon

2D Bench-Scale



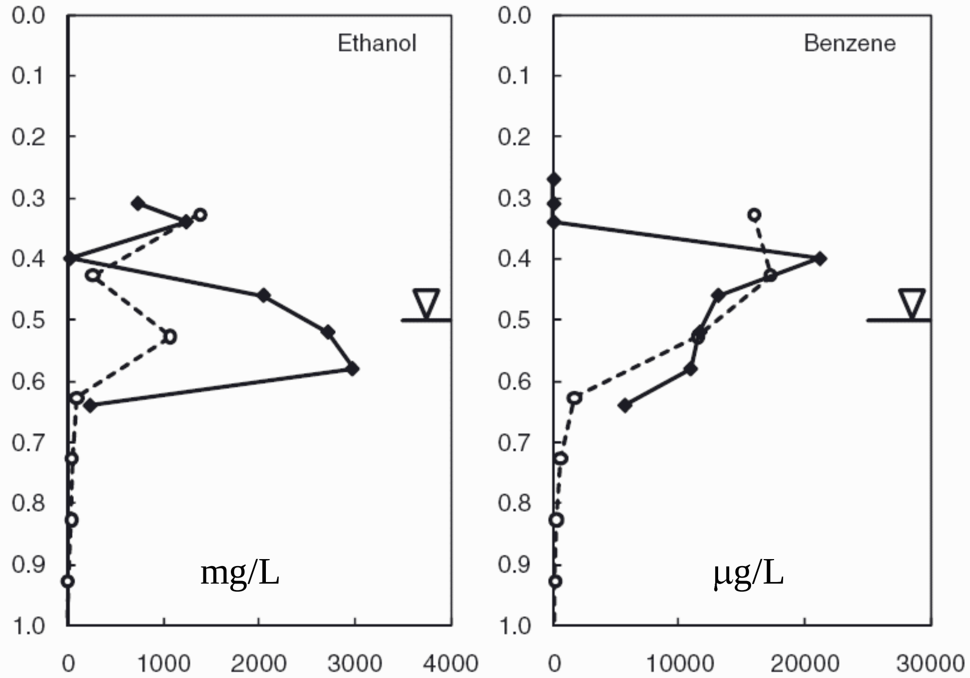
In Cápiro, N., B.P. Stafford, W.G. Rixey, P.B. Bedient, and P.J.J. Alvarez (2007). *Water Research* 41(3):656-664

Distribution of Fuel-Grade Ethanol near a Dynamic Water Table Brent P. Stafford and William G. Rixey, Ground Water Monitoring and Remediation, Summer 2011



Freitas and Barker, 2011, Monitoring Lateral Transport of Ethanol and Dissolved Gasoline Compounds in the Capillary Fringe, GWMR, Summer

1) Significant transport above water table in capillary fringe
2)No increase in benzene concentration when flushed with E97

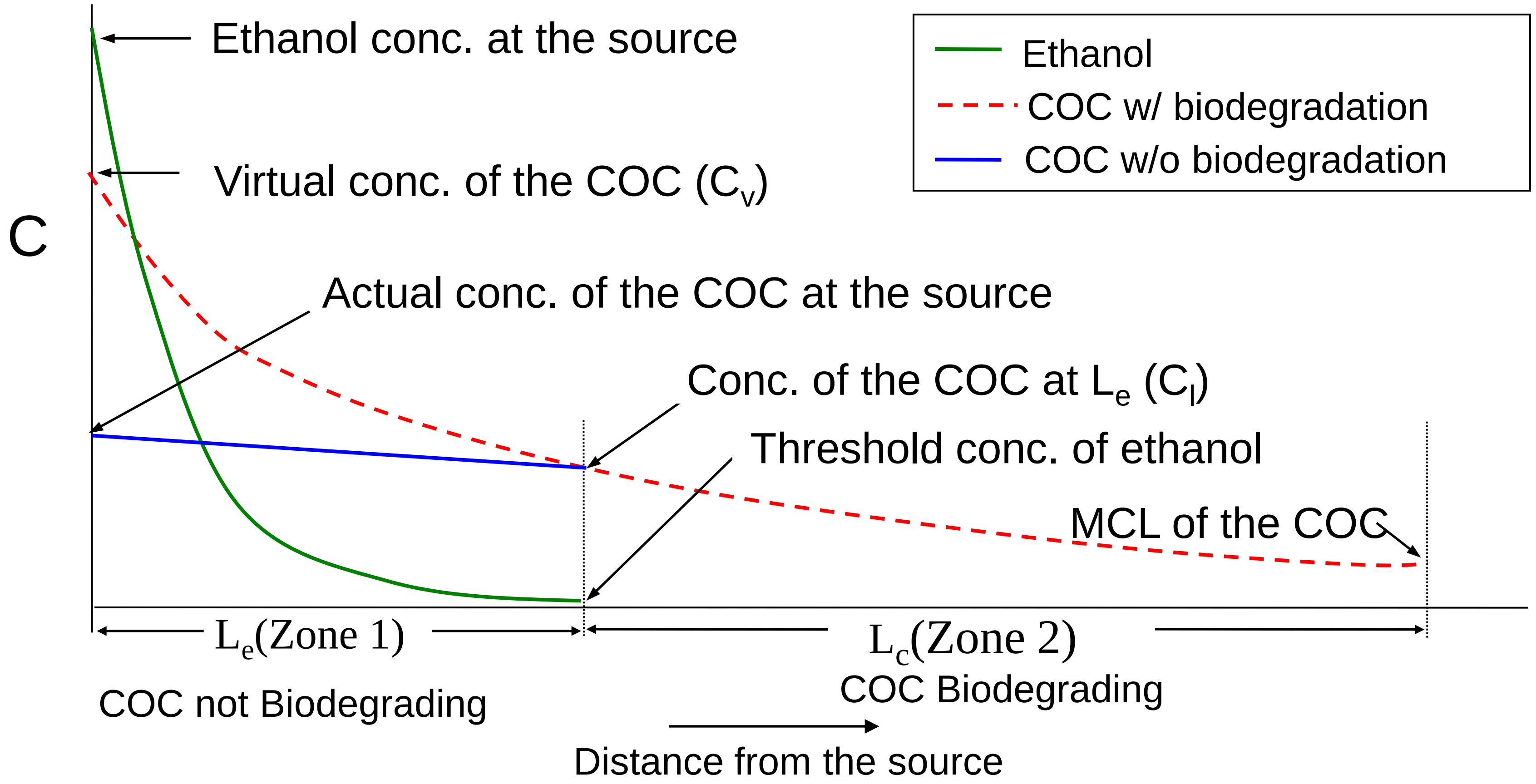


Soil data from April 24, 2010 (611 days after E10 release and 234 days after E95 release); groundwater data from multilevel well RA-W07, April 27, 2010 (Figure 2).

EPA's FOOTPRINT Code

- What is the extent of a benzene plume when ethanol is present?
  - BTEX presumed not to degrade until after ethanol degrades

Conceptual Model



COC = Chemical Of Concern (e.g., Benzene)

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Free Public Domain Ground Water and Vadose Zone Models

The Center for Subsurface Modeling Support (CSMoS) distributes various public domain ground water and vadose zone models developed by EPA's Ground Water and Ecosystem Restoration Division. There are three ways to get models and manuals:

- Click the links in the table below to view model specifications, descriptions, minimum system requirements, and files available for downloading.
- Send blank CDs or ZIP disks to CSMoS. CSMoS will copy the requested models or manuals to disks and return them to you.
- Contact Rob Earle, 580-436-8656, for other arrangements

Important Information

Potential Limitations of Four Domenico-Based Fate and Transport Models

- BIOCHLOR
- BIOSCREEN
- FOOTPRINT
- REMChlor

CSMoS provides free technical assistance for many of the models listed in the table below.

Click on the "Mailing List" tab above to join the CSMoS e-mail list. Receive information about new releases of public domain ground water models, version updates, bugs, fixes, and other important items.

Want more? Click or the "Search Database" tab above to search our database of commercially available ground water modeling software.

CSMoS Models

Model	Version	Release Date	Platform	Additional Information
2DFATMIC	1.0	August 1997	DOS	2-D subsurface flow/transport
3DFATMIC	1.0	August 1997	DOS	3-D subsurface flow/transport
BIOCHLOR	2.2	June 2002	Windows 95/98/NT, Excel	1-D Domenico screening model
BIOPLUME II	1.1	October 1989	DOS	2-D USGS MOC transport
BIOPLUME III	1.0	September 1997	Windows 95/98	2-D USGS MOC transport with Windows GUI
BIOSCREEN	1.4	July 1997	Windows 95/98/NT, Excel	3-D Domenico transport
CHEMFLO	1.3	August 1990	DOS	1-D vadose zone numerical transport
CHEMFLO-2000		April 2003	Windows 95/98/NT/2000/XP, Linux, Solaris, Mac OS X	Updated CHEMFLO
CZAEM	1.1	August 1996	DOS	Analytic element capture zone model
FOOTPRINT	1.0	June 2008	Windows 98/XP	2-D transport of BTEX and ethanol

FOOTPRINT1Manual.pdf   Show all downloads...

http://www.epa.gov/ada/csmos

EPA/600/R-08/058
June 2008

FOOTPRINT

(A Screening Model for Estimating the Area of a Plume Produced from Gasoline Containing Ethanol)

Version 1.0

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[2]U.S. EPA, Office of Research and Development, National Risk Management Research Laboratory

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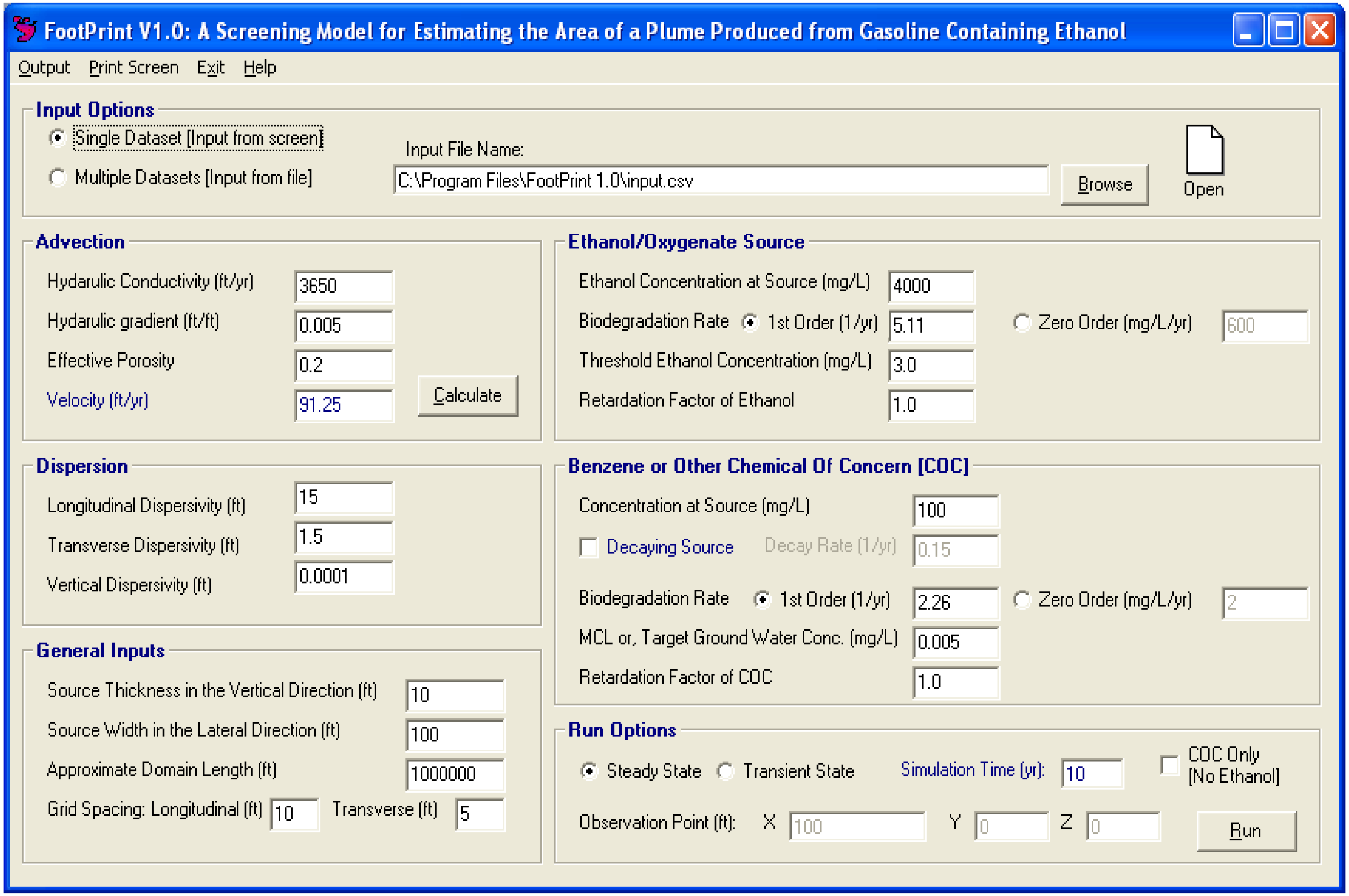
Ground Water and Ecosystem Restoration Division
Ada, OK
U.S. Environmental Protection Agency

Assumptions

- 2 biodegradation zones for BTEX:
  - 1st (adjacent to the source) allows no decay for BTEX; here, ethanol only decays to a threshold concentration (3 mg/L)
  - 2nd (away from the source) allows decay of BTEX at a given rate; here, ethanol is below the threshold concentration (3 mg/L)
- Zero or 1st order decay for both ethanol and BTEX
- Constant or decaying (1st order) source for BTEX
- Homogeneous aquifer
- Unidirectional groundwater flow
- Linear sorption for both ethanol and BTEX
- Complete vertical distribution

FOOTPRINT Input



FOOTPRINT Output

Output: Numeric Output from a Single Run

Area of the plume = 174400 (or, 1.74E+05) sft = 4.00 acre

Length of the no biodegradation zone (Le) = 198.00 ft

Length of the plume from the source (Le + Lc) = 697.00 ft

Concentration of the COC at Le (Cl) = 9.60E+01 mg/L

Virtual concentration of the COC at the source (Cv) = 4.50E+03 mg/L

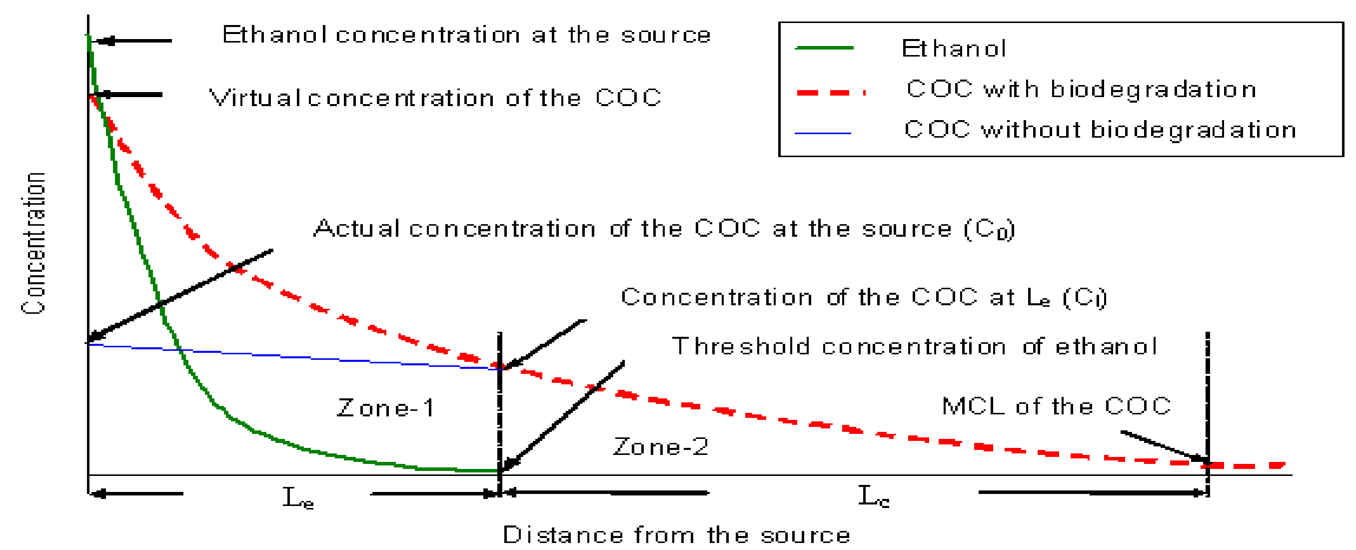
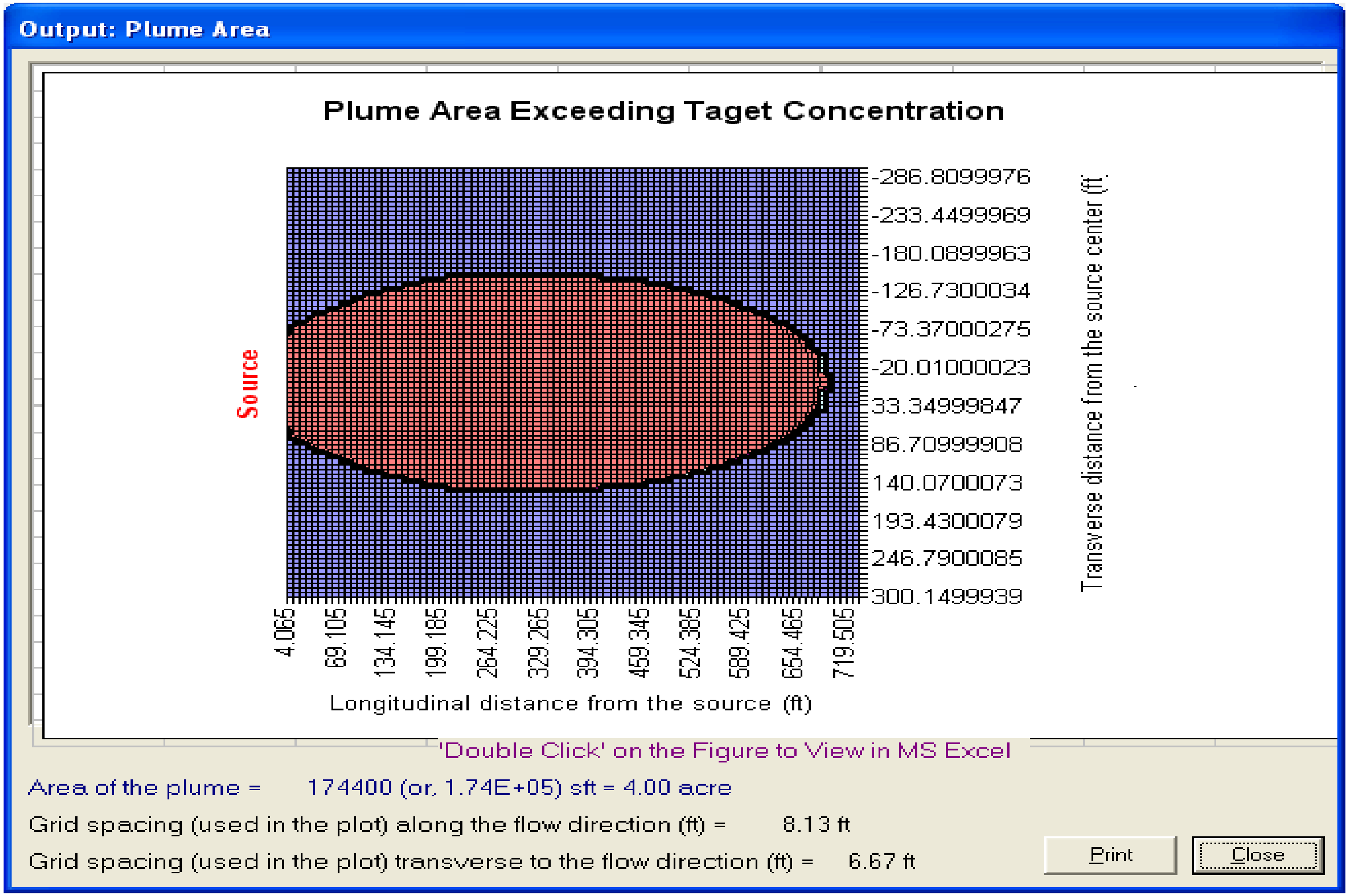


Figure 1. Conceptual model for transport of ethanol-blended gasoline constituents.

Print | Close

FOOTPRINT Output



Improvements, anyone?

- FOOTPRINT uses observed ethanol concentration, not composition of fuel as a starting point
- FOOTPRINT is limited by assumptions of analytical transport solutions:
  - Homogeneous aquifer
  - Steady-state, one-dimensional ground water flow
  - Only one direction of flow
  - No accounting for vertical flows or their lack
- Newest information on ethanol impacts:
  - Ethanol residing in capillary fringe
  - Ethanol Scavenging in the vadose zone—ethanol actually colocated with petroleum hydrocarbons?

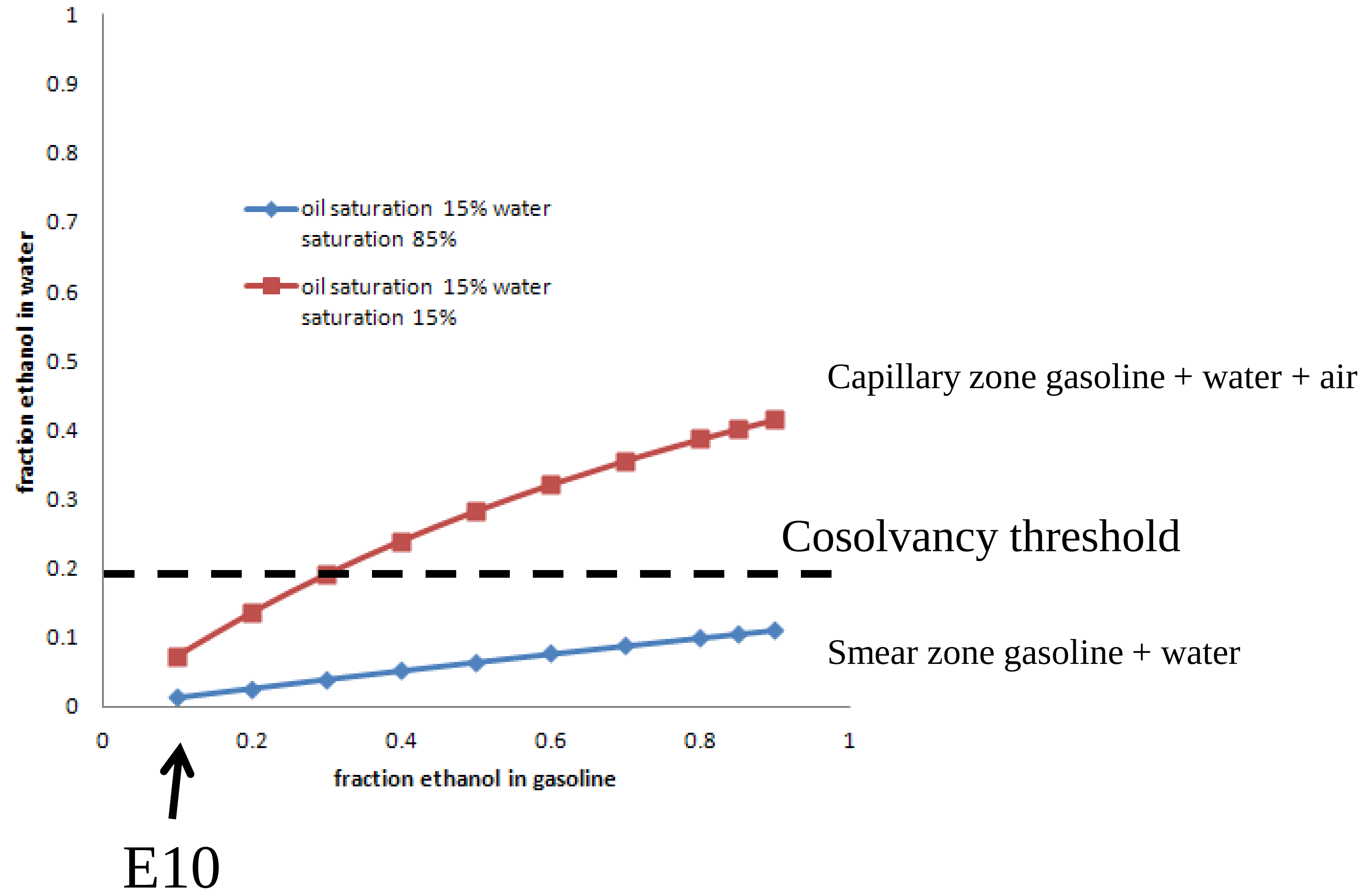
To overcome limits

- Starting point = gasoline
- Numerical model = heterogeneity, multidirectional flow, transients
- Capillary fringe effects from how the pieces are put together.

Ethanol Modeling

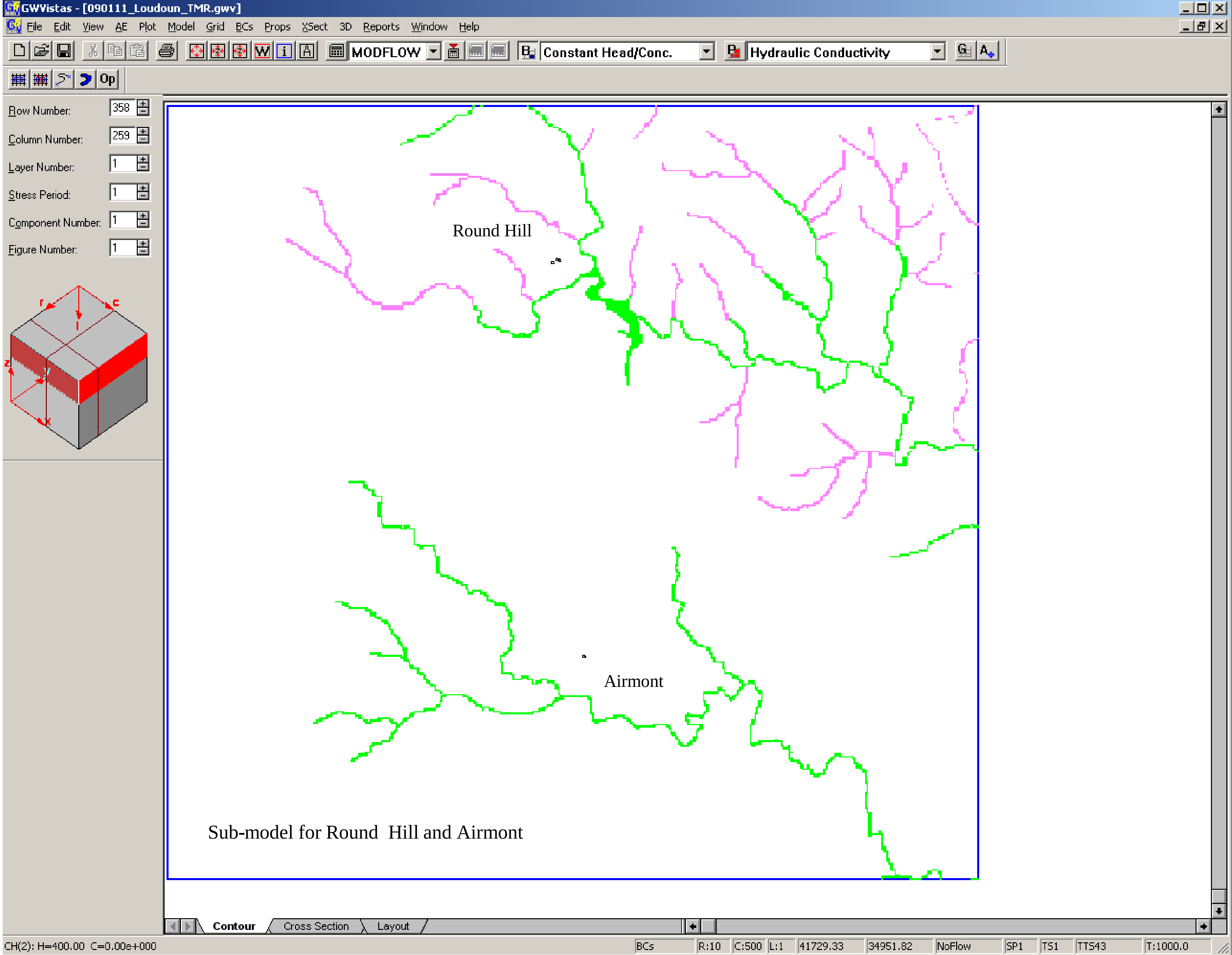
- Preliminary work
- Leaching of gasoline perched in capillary fringe
- Ethanol concentration determined from extend of gasoline, vadose zone water saturation

Potential for Cosolvancy



Numerical ground water flow model

- County-scale ground water flow model
  - Modflow 3.5 million grid blocks
  - What modifications are needed for shallow spills?
    - Refined vertical gridding near the water table
  - Demonstrate that transport model reproduces known plumes.

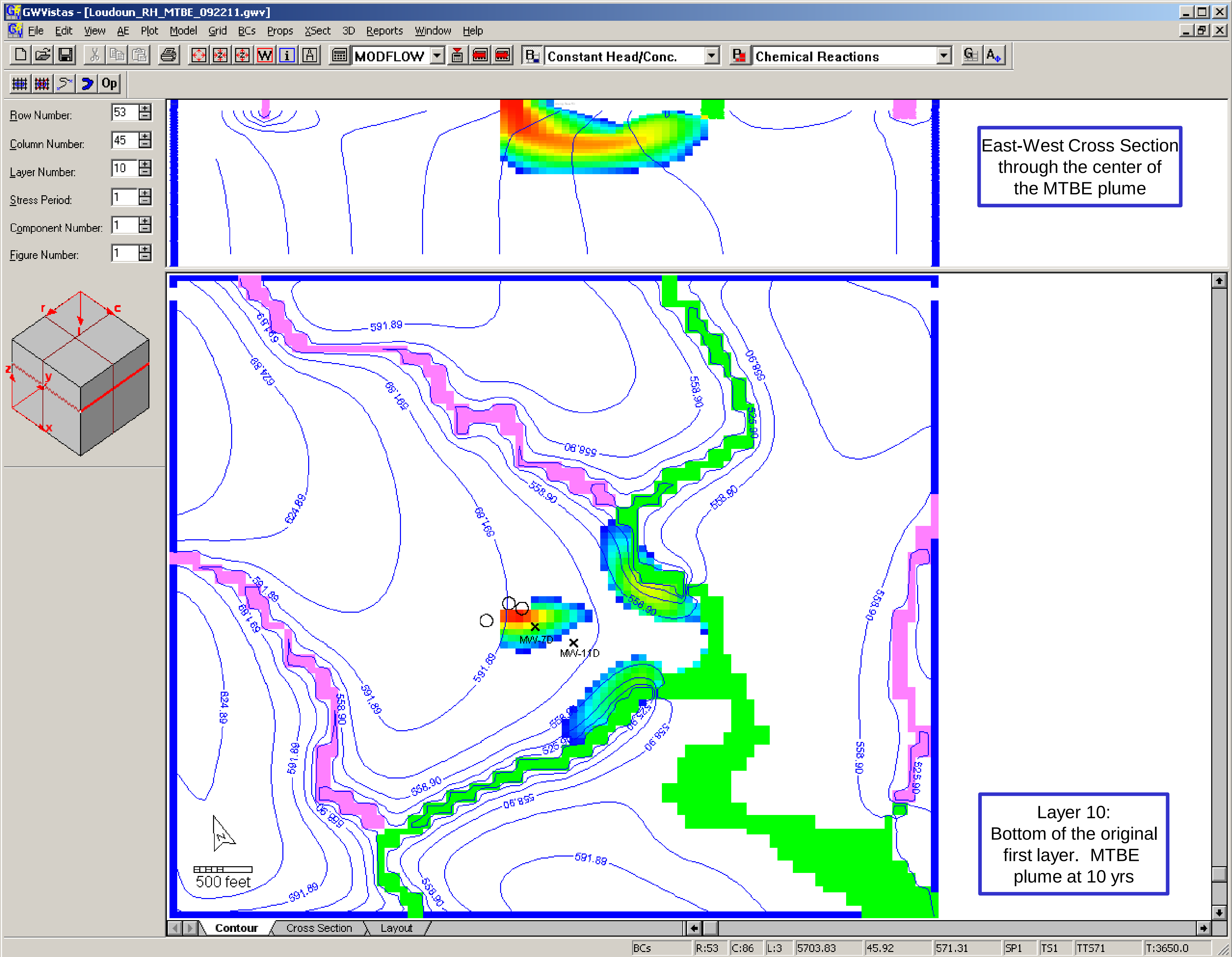

GWVistas - [090111_Loudoun_TMR.gwv]
File Edit View AE Plot Model Grid BCs Props XSect 3D Reports Window Help
MODFLOW
Constant Head/Conc.
Hydraulic Conductivity
Op
Row Number: 358
Column Number: 259
Layer Number: 1
Stress Period: 1
Component Number: 1
Figure Number: 1
Round Hill
Airmont
Sub-model for Round Hill and Airmont
Contour
Cross Section
Layout
CH(2): H=400.00 C=0.00e+000
BCs
R:10
C:500
L:1
41729.33
34951.82
NoFlow
SP1
TS1
TTS43
T:1000.0

Calibration simulation of MTBE plume at Harper's BP in Round Hill

- Hydraulic Conductivity: $K_x = K_y = 0.6$ ft/day, $K_z = 0.1$ ft/day
- Recharge: N = 1.826e-3 ft/day over Round Hill
  [MTBE] = 8,000 ug/L in six cells held constant for 10 years

- Dispersivity/Diffusion: 0 throughout the model
- Transport: No reactions / No decay

- Flow Model: MODFLOW (88/96), PCG2 Solver
- Transport Model: MT3DMS, Finite Difference Solver

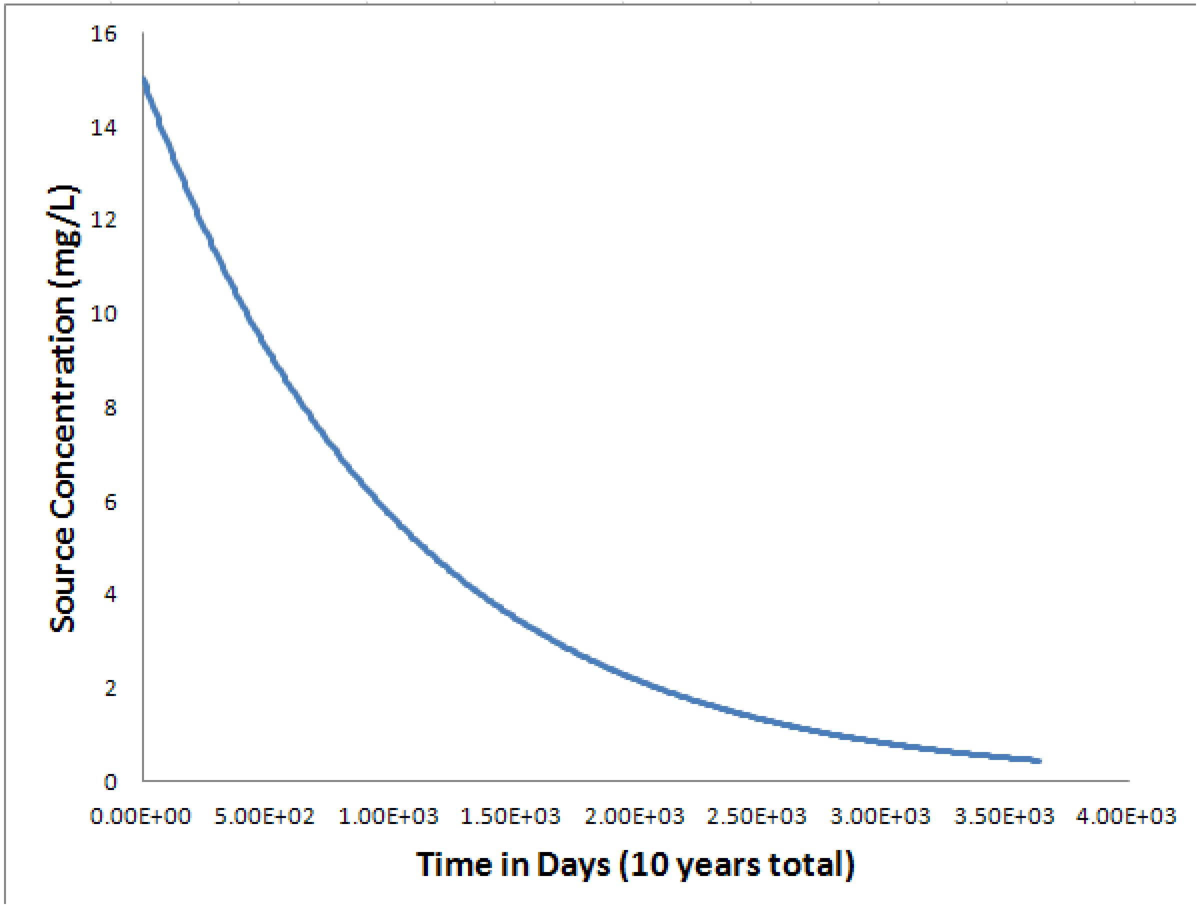

GWVistas - [Loudoun_RH_MTBE_092211.gwv]
File Edit View AE Plot Model Grid BCs Props XSect 3D Reports Window Help
MODFLOW
Constant Head/Conc.
Chemical Reactions
Op
Row Number: 53
Column Number: 45
Layer Number: 10
Stress Period: 1
Component Number: 1
Figure Number: 1
East-West Cross Section through the center of the MTBE plume
591.89
624.89
558.90
525.90
MW-7D
MW-11D
500 feet
Layer 10: Bottom of the original first layer. MTBE plume at 10 yrs
Contour
Cross Section
Layout
BCs
R:53
C:86
L:3
5703.83
45.92
571.31
SP1
TS1
TTS71
T:3650.0

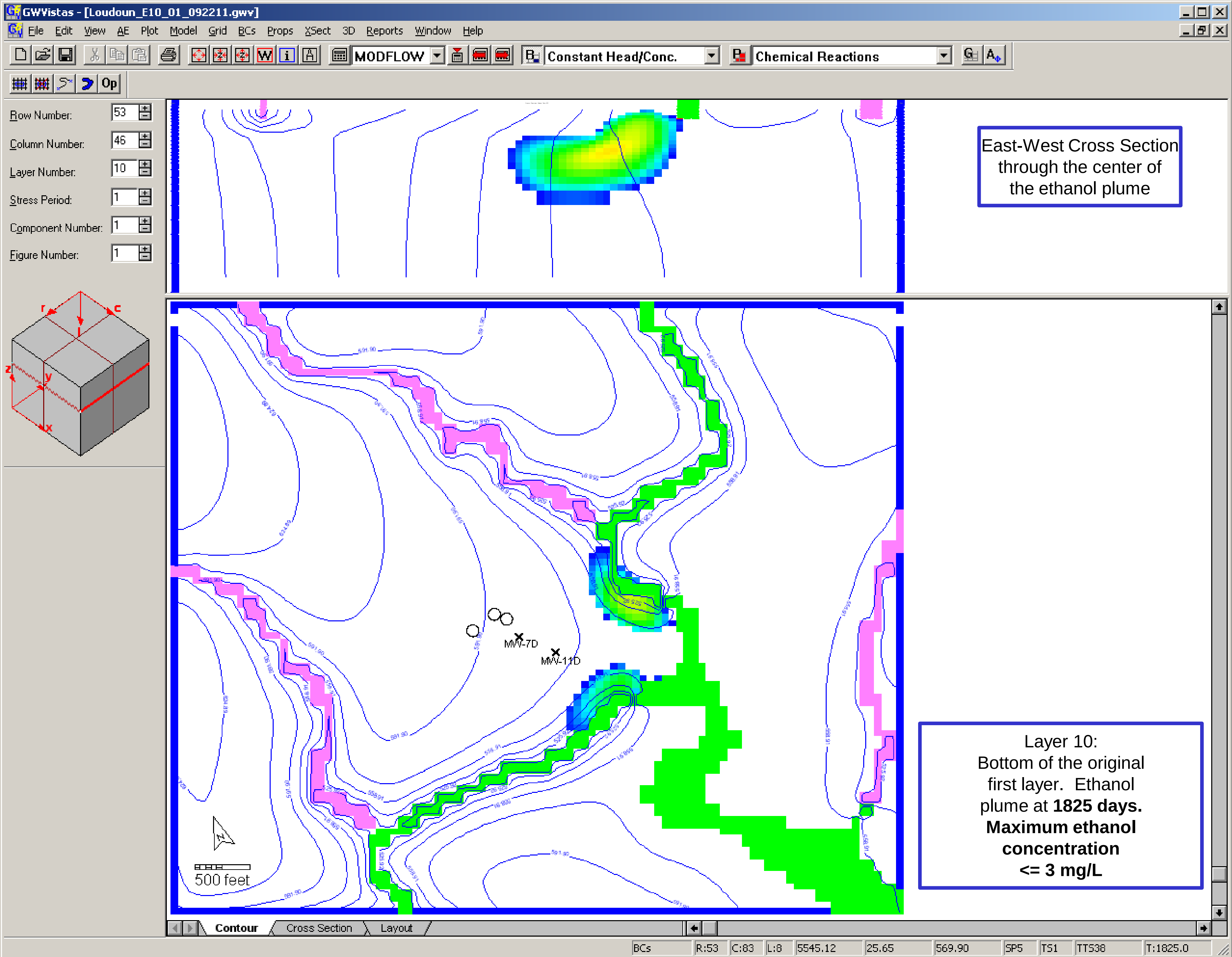
Ethanol gasoline simulation (preliminary results)

- 1) Simulate ethanol transport with 1.5 year half life (Corseuil et al, 2011, BTEX Plume Dynamics.., ES&T 45, 3422-3429)
    - Determine when ethanol concentration goes below 3 mg/L
- 2) Simulate benzene transport with no degradation ethanol above 3 mg/L
- 3) Simulate benzene transport with 2.0 year half life ethanol below 3 mg/L

- 250 gallon gasoline release
  - Occupies 15% of pore space
  - Layer 1 ft thick
  - Covers 6 67ft x 57ft grid blocks
- Ethanol simulation concentration 78,900 mg/L
  - Initially present
- Benzene at 0.62% of gasoline (MSAT concentration)
  - Boundary condition supplied by compartment model

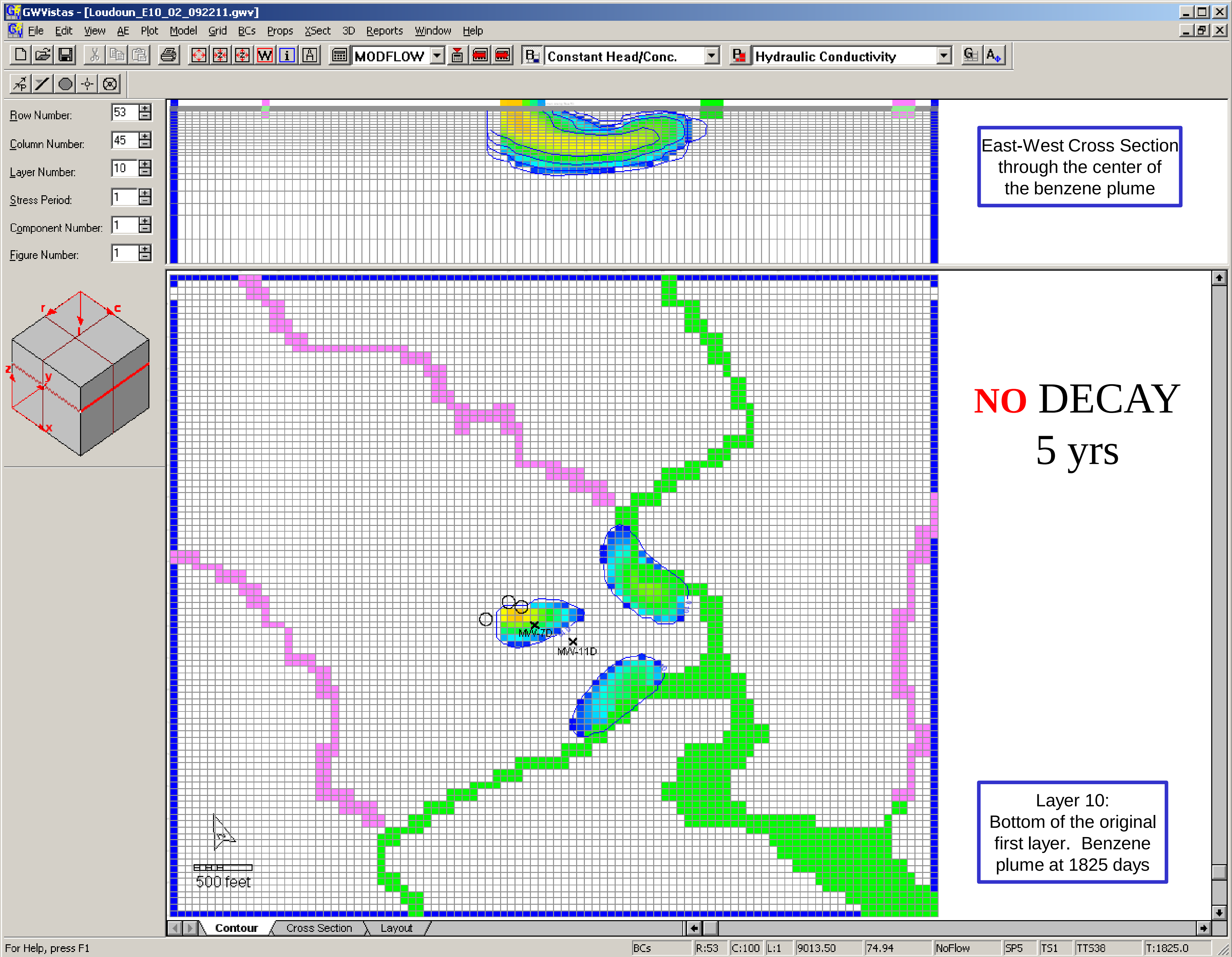
Source benzene concentration from leaching model




GWVistas - [Loudoun_E10_01_092211.gwv]
File Edit View AE Plot Model Grid BCs Props XSect 3D Reports Window Help
MODFLOW
Constant Head/Conc.
Chemical Reactions
Row Number: 53
Column Number: 46
Layer Number: 10
Stress Period: 1
Component Number: 1
Figure Number: 1
East-West Cross Section through the center of the ethanol plume
MW-7D
MW-11D
500 feet
Layer 10:
Bottom of the original first layer. Ethanol plume at **1825 days.**
Maximum ethanol concentration <= 3 mg/L
Contour
Cross Section
Layout
BCs R:53 C:83 L:8 5545.12 25.65 569.90 SP5 TS1 TTS38 T:1825.0

E10 simulation #2: Benzene with NO DECAY for 1825 days

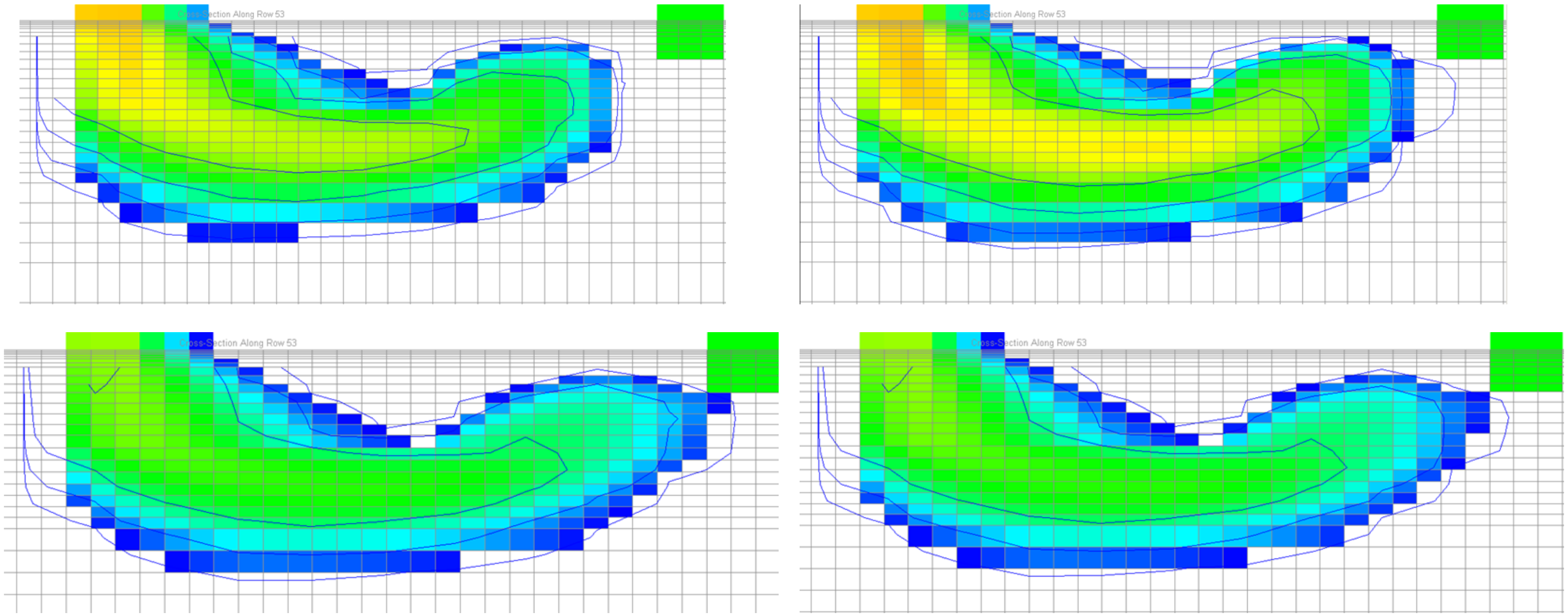
•Hydraulic Conductivity:	$K_x = K_y = 0.6$ ft/day, $K_z = 0.1$ ft/day
•Recharge:	N = 1.826e-3 ft/day over Round Hill [benzene] in six cells varies over first 5 years per leaching model
•Dispersivity/Diffusion:	0 throughout the model
•Transport:	Benzene retardation, no decay
•Flow Model:	MODFLOW (88/96), PCG2 Solver
•Transport Model:	MT3DMS, Finite Difference Solver


GWVistas - [Loudoun_E10_02_092211.gwv]
File Edit View AE Plot Model Grid BCs Props XSect 3D Reports Window Help
MODFLOW
Constant Head/Conc.
Hydraulic Conductivity
Row Number: 53
Column Number: 45
Layer Number: 10
Stress Period: 1
Component Number: 1
Figure Number: 1
East-West Cross Section through the center of the benzene plume
NO DECAY
5 yrs
MW-7D
MW-11D
500 feet
Layer 10: Bottom of the original first layer. Benzene plume at 1825 days
Contour
Cross Section
Layout
For Help, press F1
BCs
R:53
C:100
L:1
9013.50
74.94
NoFlow
SP5
TS1
TTS38
T:1825.0

250 gallon spill: benzene results at 5 and 10 years

5 years

10 years



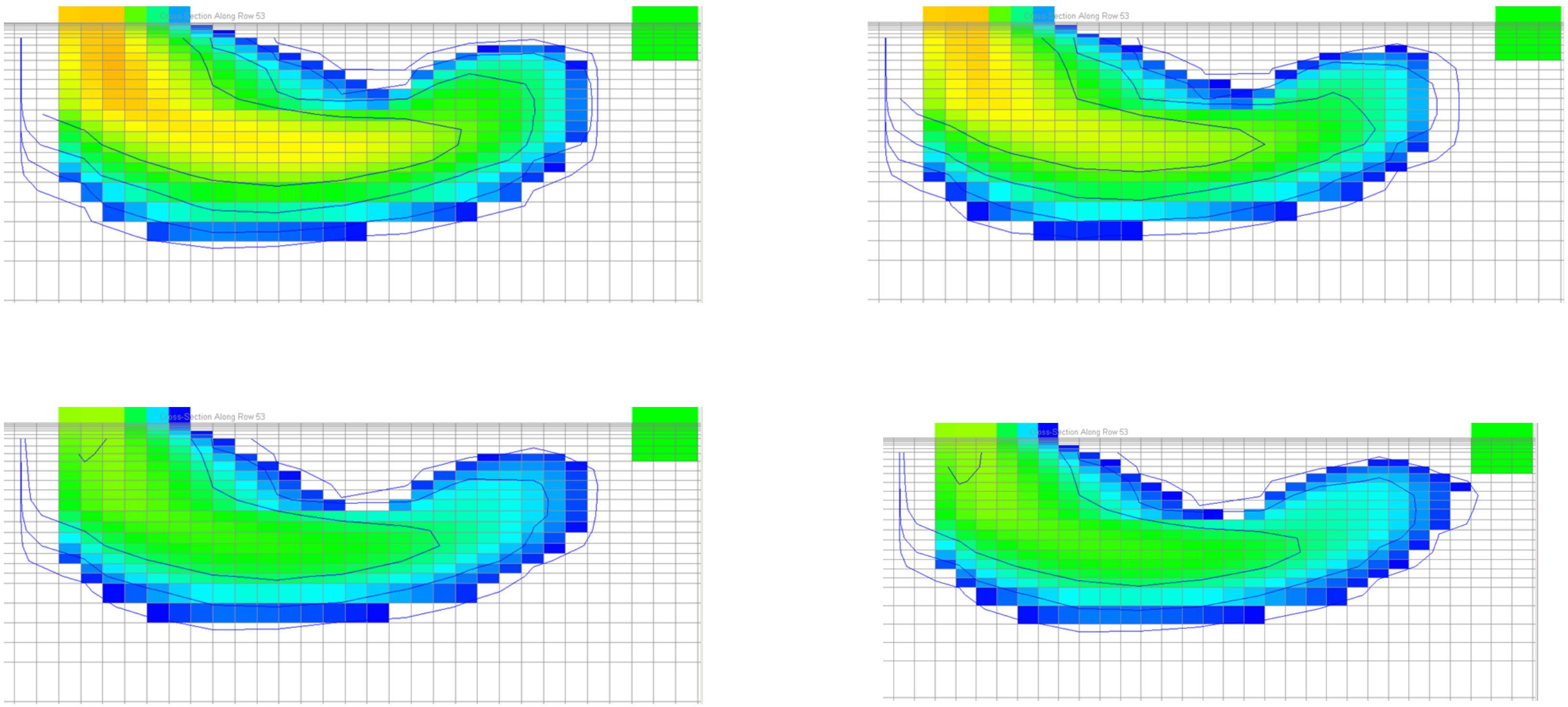
No ethanol

E10

125 Gallon spill: benzene results at 5 and 10 years

5 yr

10 yr



No Ethanol

E10

- Small differences between E00 and E10 plumes observed for this site
  - E00 benzene plumes slightly shorter than E10 plumes
  - (Smaller amount of ethanol than E95/E85)
- Ethanol degradation
  - 1825 days for 250 gallons,
  - 1700 days for 125 gallons
- Plume extent driven by:
  - Ground water velocity
  - Degradation
  - (Weakly) Source mass

Score Card

- Gasoline Source
- **Numerical Model**
- **Capillary Fringe**
- **Beginning development of a self-contained "practical" model for these problems**