Site Characterization of Ethanol-Blended Fuel Releases

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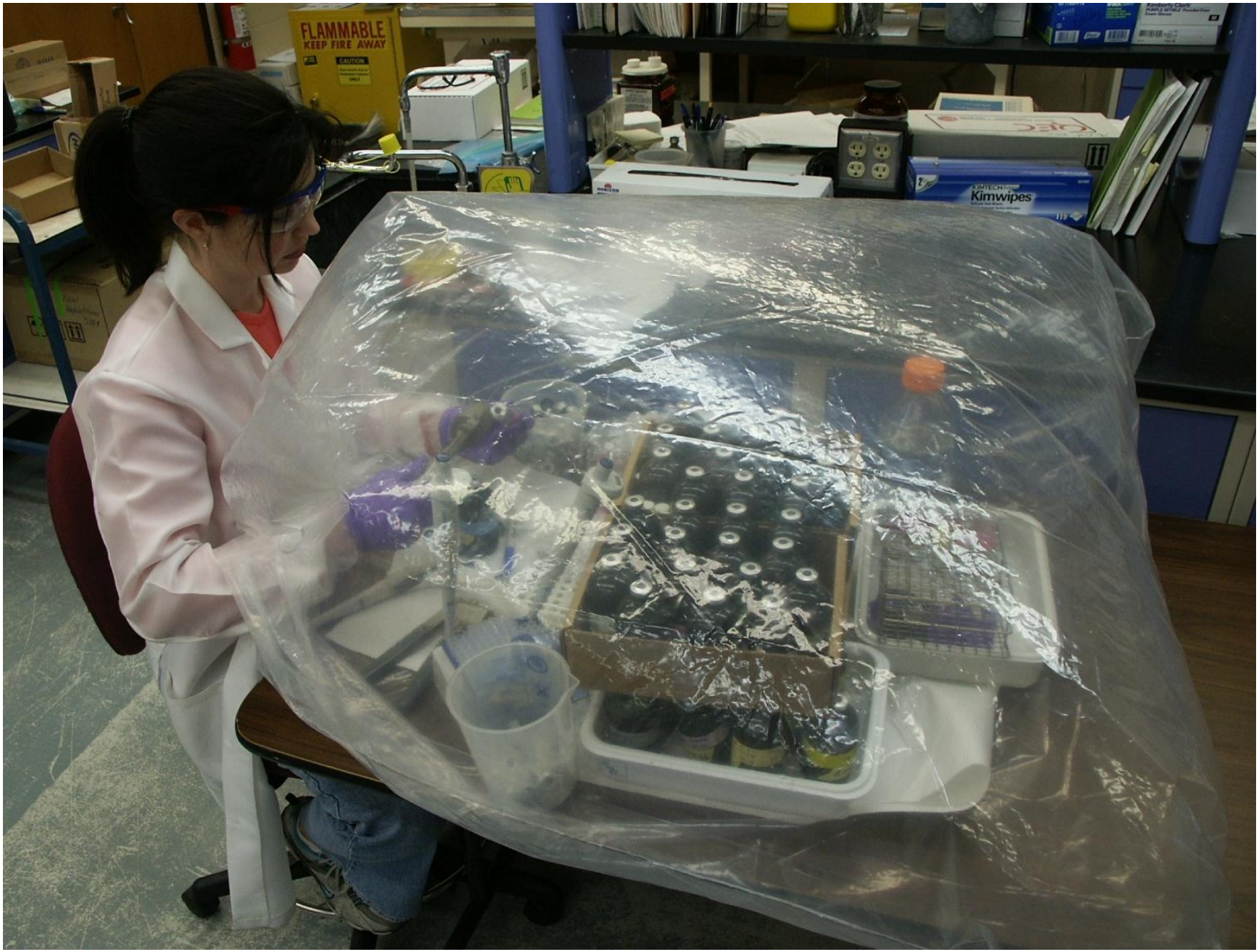
RESEARCH AND DEVELOPMENT

Building a scientific foundation for sound environmental decisions

What is the effect of ethanol on the persistence of benzene in ground water?

If ethanol is present, the concentration of its degradation products will be high enough to inhibit the biodegradation of benzene.


B-03C9-6
B-03C9-60
UNITED STATES OF AMERICA
LIBERTY
QUARTER DOLLAR


FLAMMABLE
KEEP FIRE AWAY
CAUTION
Kimwipes

Ethanol is fermented by acetic acid bacteria to acetic acid and molecular hydrogen

$$CH_3CH_2OH + H_2O \rightarrow CH_3COO^- + H^+ + 2\ H_2$$

Under anaerobic conditions, acetate is fermented to carbon dioxide and methane

$$CH_3COO^- + H^+ \rightarrow CO_2 + CH_4$$

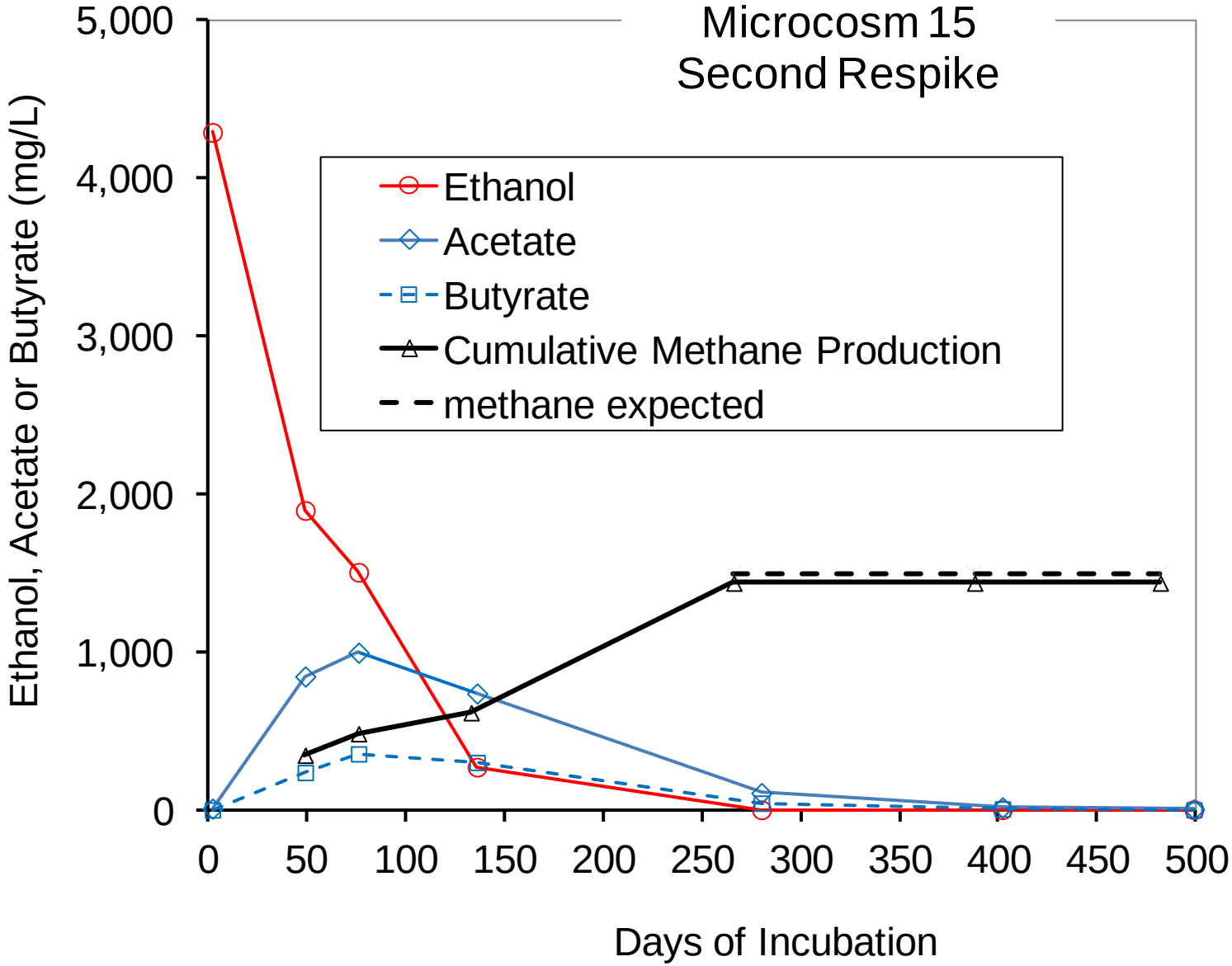
Hydrogen and bicarbonate can be fermented to acetate and water

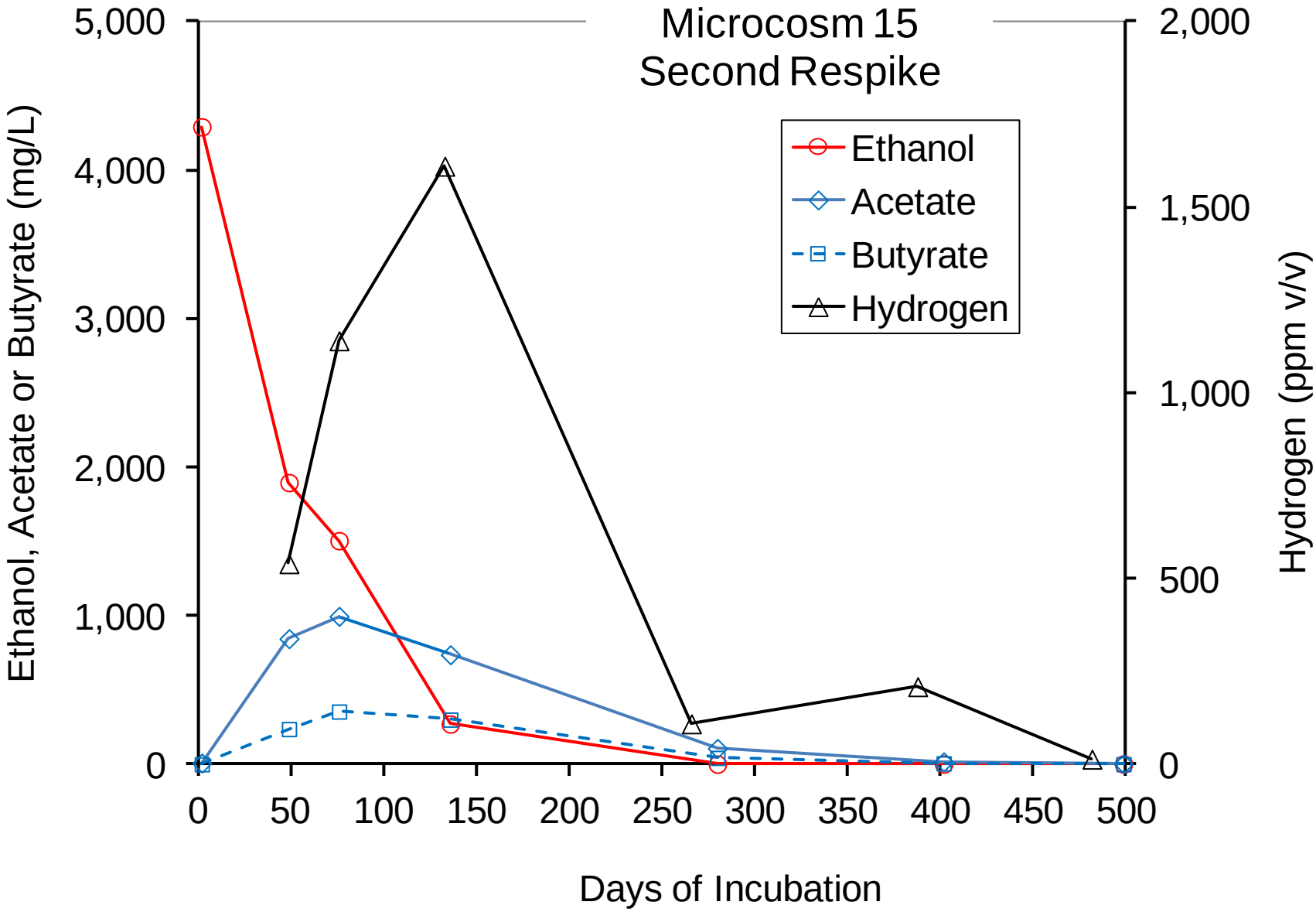
$$2\ HCO_3^- + 1\ H^+ + 4\ H_2 \rightarrow CH_3COO^- + 4\ H_2O$$

Acetate and hydrogen can be fermented to butyrate and water

$$2\ CH_3COO^- + H^+ + 2\ H_2 \rightarrow CH_3CH_2CH_2COO^- + H_2O$$

Both of these reactions are reversible depending on concentrations of reactants and products.


Microcosm 15
Second Respike
Ethanol
Acetate
Butyrate
Cumulative Methane Production
methane expected
Ethanol, Acetate or Butyrate (mg/L)
5,000
4,000
3,000
2,000
1,000
0
0
50
100
150
200
250
300
350
400
450
500
Days of Incubation


Microcosm 15
Second Respike
Ethanol
Acetate
Butyrate
Hydrogen
Ethanol, Acetate or Butyrate (mg/L)
Hydrogen (ppm v/v)
Days of Incubation
5,000
4,000
3,000
2,000
1,000
0
2,000
1,500
1,000
500
0
0
50
100
150
200
250
300
350
400
450
500

The energy available from a chemical reaction can be calculated by comparing the energy required to make the reactants and the energy required to make the products.

The change in energy between the reactants and products is the energy released (or consumed) in the reaction.

The Gibbs Free Energy (ΔG′) is a quantitative estimate of the energy that is available to microorganisms that carry out a particular reaction.

The values of ΔG′ depend on the energy content of reactants and products, and the concentrations of reactants and products. If the concentrations of reactants are low, and the concentrations of products is high, the value of ΔG′ is high.

$$C_6H_6 + 6\ H_2O \rightarrow\ 3\ CH_3COO^- + 3\ H^+ + 3\ H_2$$

$$\Delta G' = \Delta G^{o'} + RT * Ln\left[\frac{[CH_3COO^-]^3[H^+]^3[H_2]^3}{[C_6H_6]^3}\right]$$

If ΔG′ is positive, the reaction requires energy. Water does not run up hill, and bacteria can not gain energy to grow with a positive ΔG′.

If ΔG′ is more negative than -20 kJ/mole, generally bacteria can grow.

If ΔG′ is between 0 and -20 kJ/mole, bacteria may or may not be able to grow, depending on the stain of bacteria.

Both Ethanol and Benzene are fermented to acetic acid and molecular hydrogen

$$CH_3CH_2OH + H_2O \rightarrow CH_3COO^- + H^+ + 2\ H_2$$

$$C_6H_6 + 6\ H_2O \rightarrow 3\ CH_3COO^- + 3\ H^+ + 3\ H_2$$

If Ethanol is available in the water, the fermentation of Ethanol can produce so much hydrogen and acetate that the fermentation of Benzene is not possible.

In the following slides:

Green means Benzene fermentation is possible.

Yellow means Benzene fermentation is probably not possible,

Red means Benzene fermentation is not possible.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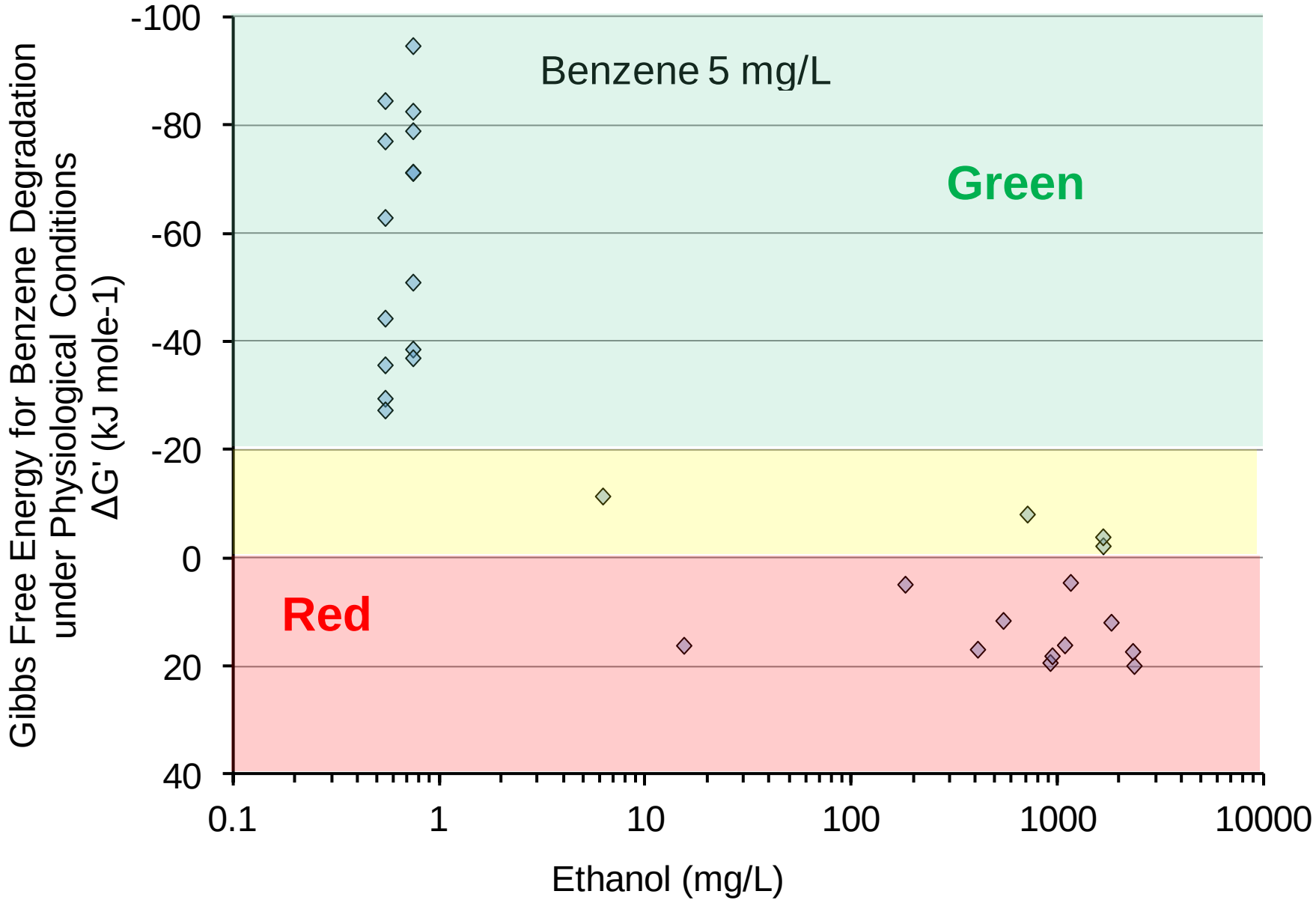
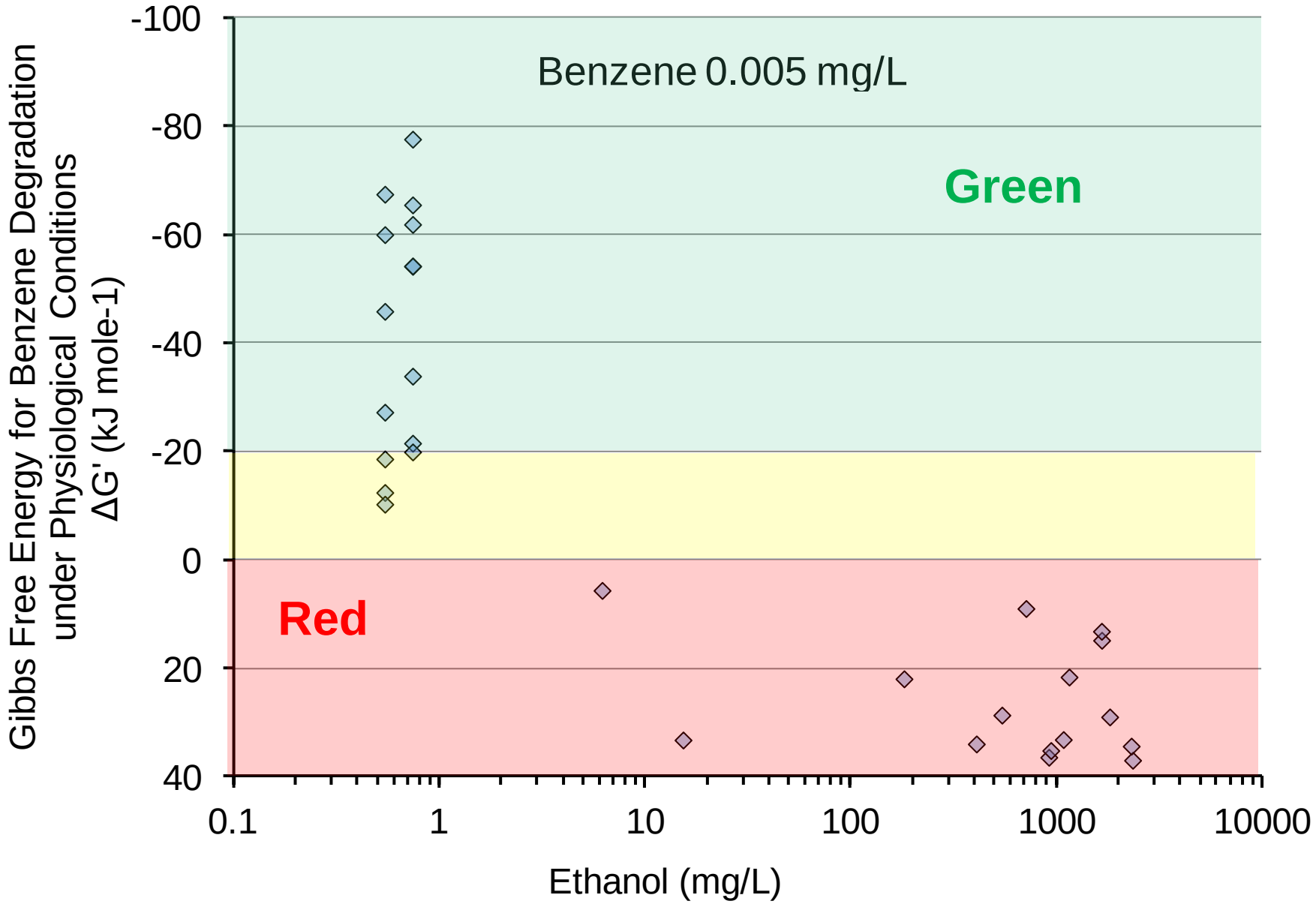

Benzene 5 mg/L
Green
Red
Gibbs Free Energy for Benzene Degradation under Physiological Conditions ΔG' (kJ mole-1)
-100
-80
-60
-40
-20
0
20
40
0.1
1
10
100
1000
10000
Ethanol (mg/L)


Benzene 0.005 mg/L
Green
Red
Gibbs Free Energy for Benzene Degradation under Physiological Conditions ΔG' (kJ mole-1)
-100
-80
-60
-40
-20
0
20
40
0.1
1
10
100
1000
10000
Ethanol (mg/L)

In the microcosm study, when there was more than 3 mg/L of Ethanol in the water, the fermentation of Benzene was not possible.

How much Ethanol should we expect in ground water from a gasohol spill?

It should be directly related to the amount of gasoline that was spilled, and the Ethanol content of the gasoline.

Fuel-grade Ethanol Transport and Impacts to Groundwater in a Pilot-Scale Aquifer Tank. Capiro, N. B. Stafford, W.G. Rixey, P.B. Bedient, P.J.J. Alvarez. *Water Research* 41(2007) 656-664.

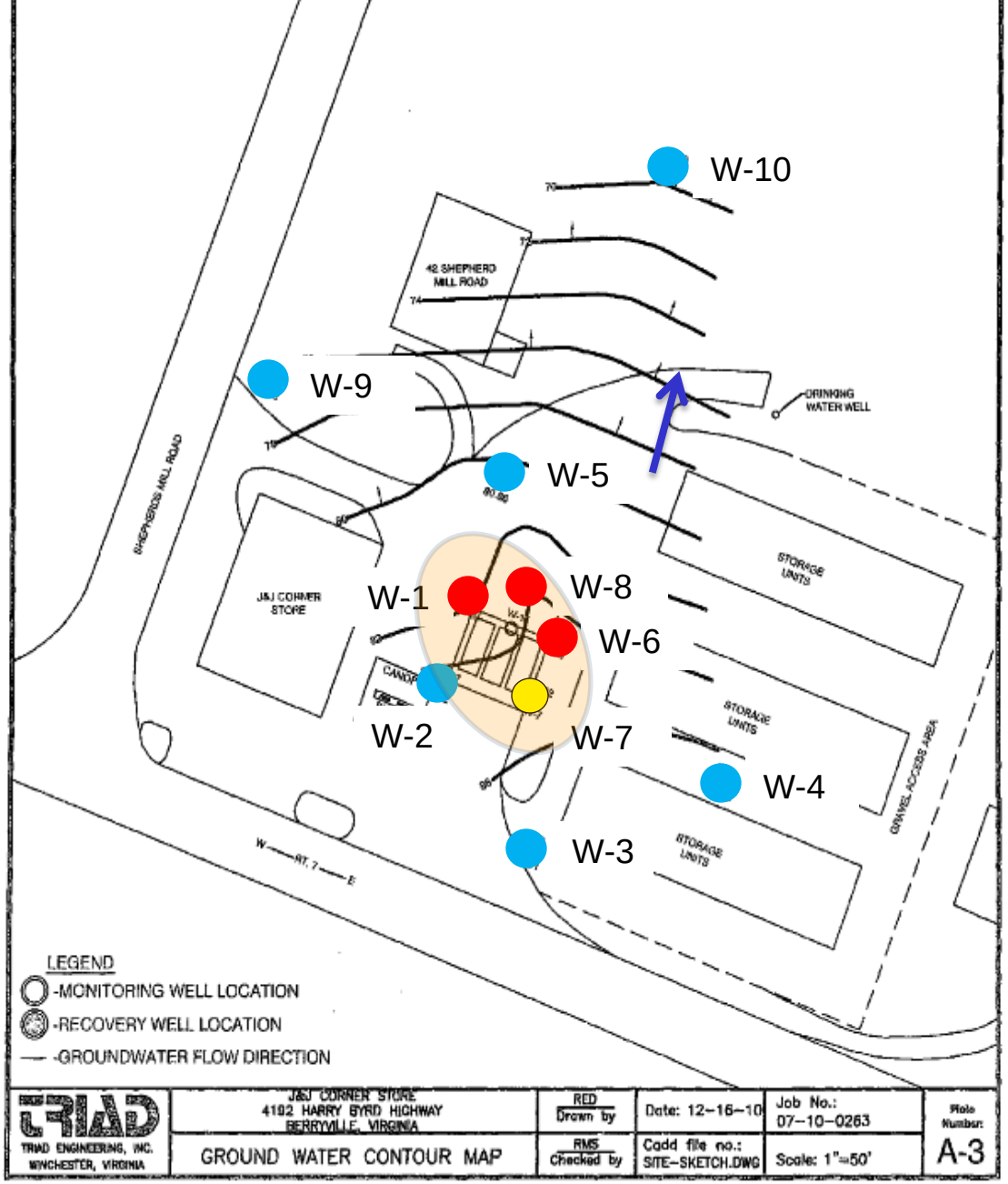
They released 76 liters of 95% ethanol, 5% synthetic gasoline to a large sand tank (8,150 liters).

The maximum concentration of ethanol measured in miniature monitoring wells was **10,000 mg/L** or about 1.2% on a volume basis.

Assume gasoline is measured at a residual saturation of **4,000 mg/kg TPH.**

Assume the gasoline is 15% ethanol (mass basis).

The “expected” ethanol content would be approximately 5,000 mg/liter.


W-10
W-9
W-5
W-1
W-8
W-6
W-2
W-7
W-4
W-3
42 SHEPHERD MILL ROAD
DRINKING WATER WELL
J&J CORNER STORE
STORAGE UNITS
GRAVEL ACCESS AREA
SHEPHERDS MILL ROAD
LEGEND
-MONITORING WELL LOCATION
-RECOVERY WELL LOCATION
-GROUNDWATER FLOW DIRECTION
TRIAD ENGINEERING, INC.
WINCHESTER, VIRGINIA
J&J CORNER STORE
4192 HARRY BYRD HIGHWAY
BERRYVILLE, VIRGINIA
GROUND WATER CONTOUR MAP
RED
Drawn by
RMS
Checked by
Date: 12-16-10
Cadd file no.: SITE-SKETCH.DWG
Job No.: 07-10-0263
Scale: 1"=50'
Plate Number:
A-3

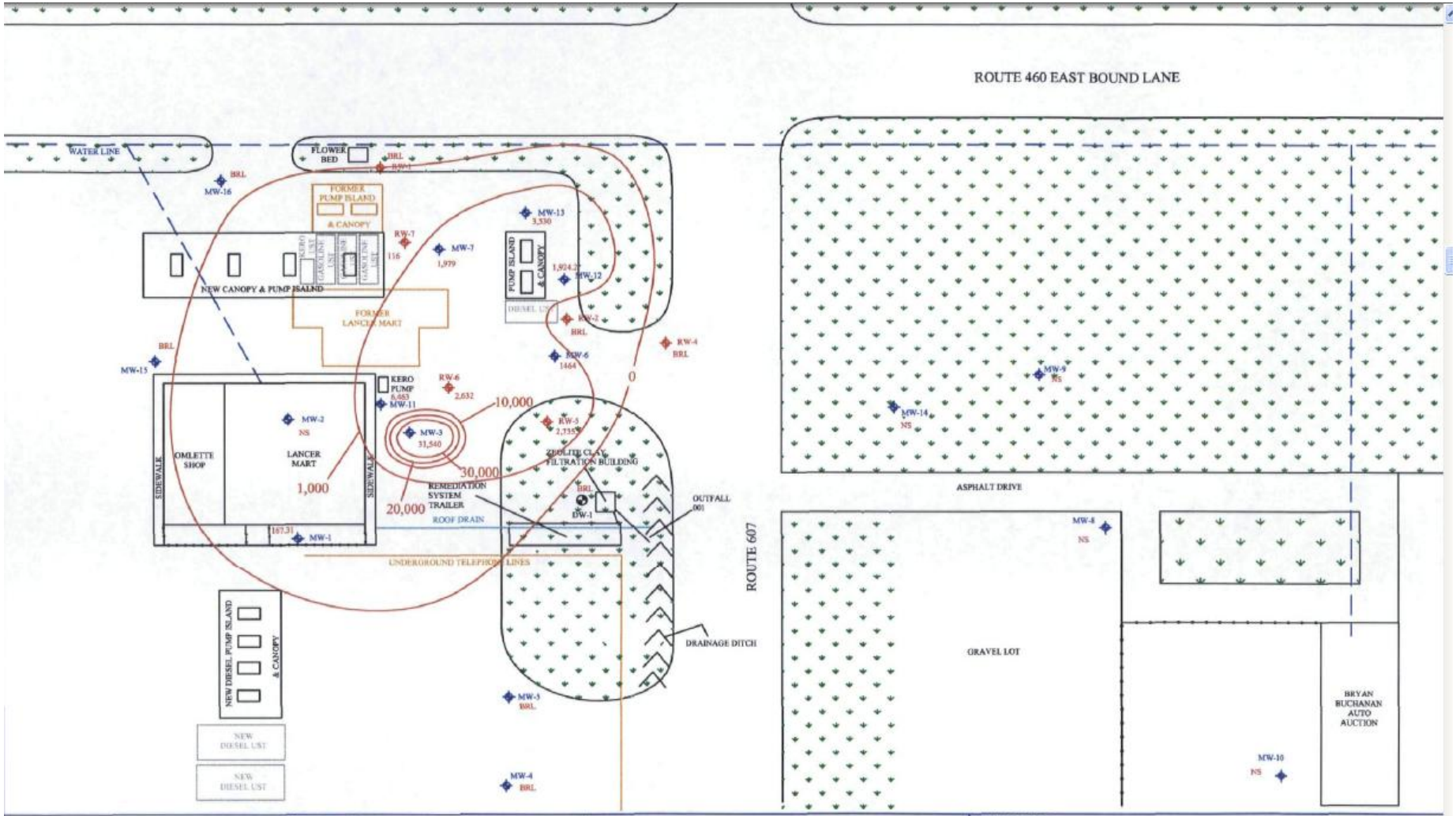
	12/10/2010	4/25/2011	9/13/2011
	Day since new release reported		
	59	195	336
	Ethanol (mg/L)		
W-8	205,000	596	393
W-6	24,800	1,112	79
W-1	9,270	426	2,930
W-7	7,740	0.563	<0.1
W-9	3.73	<0.1	<0.1
W-10	1.67	<0.1	<0.1
W-5	<0.1	<0.1	<0.1
W-2	<0.1	0.428	36

Well	Date	Ethanol	Benzene	Hydrogen	Acetate	ΔG′ Benzene
		mg/L	mg/L	ppm	mg/L	kJ/ mole
W-8	4/2011	569	1.4	85,000	189	14
W-6	4/2011	1112	7.8	171,000	194	11
W-1	4/2011	462	1.1	141,000	441	17
W-7	4/2011	0.56	2.3	157,000	19.5	-4.1

High concentrations of ethanol were sustained in ground water.

This may be related to the fact that ground water was largely confined to fractured rock.

There was no “soil” to provide capillary attraction and hold the ethanol in the capillary fringe above the ground water.



LEGEND

- MONITOR WELL LOCATION
- RECOVERY WELL LOCATION

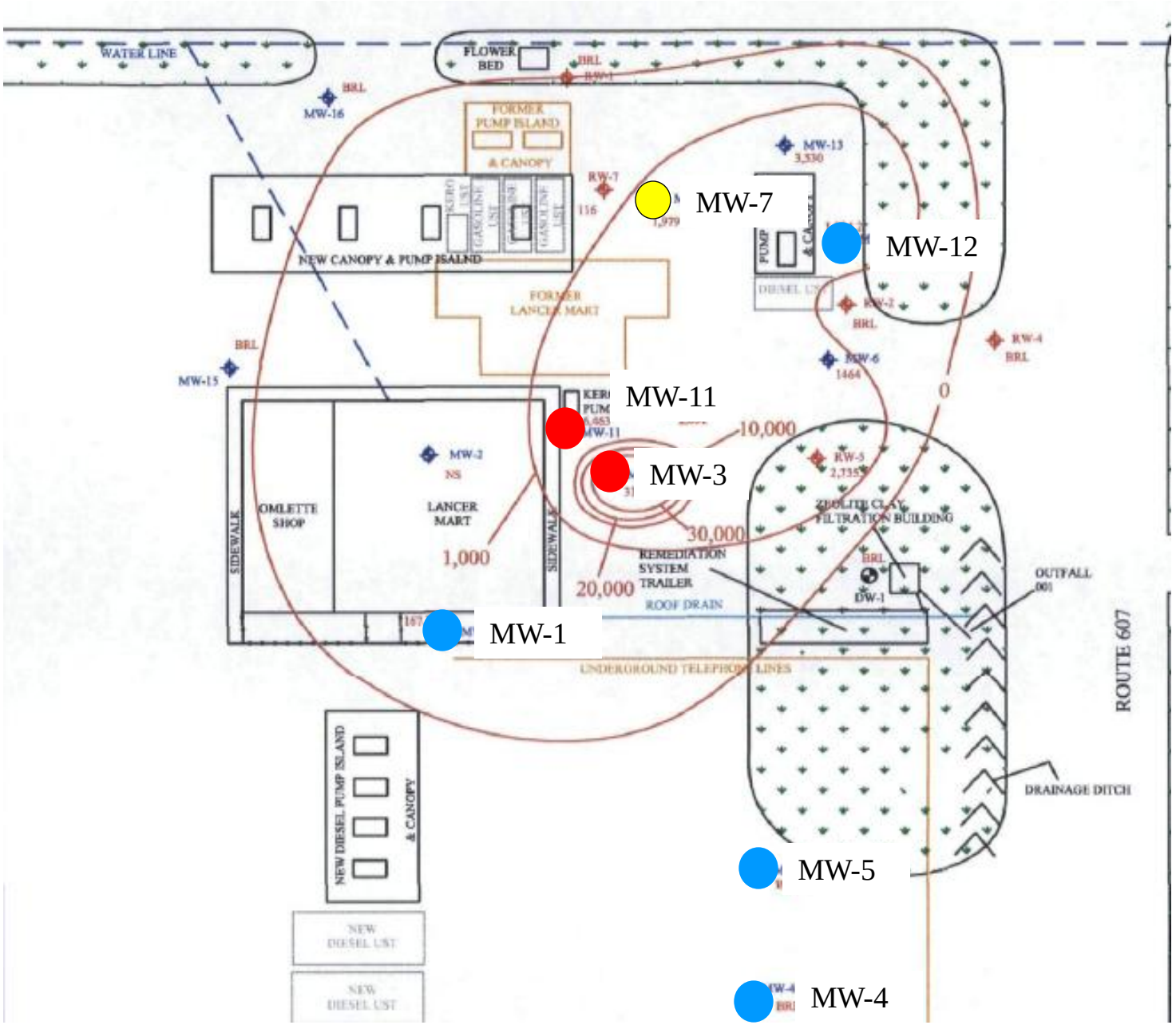
APPROXIMATE SCALE
0 100 Ft

2.0 DISSOLVED PHASE BTEX ISOCONCENTRATION LINES (ug/L)

N

VEI
VISTA ENVIRONMENTAL, INC.

FIGURE NAME: DISSOLVED PHASE TOTAL BTEX PLUM
SITE NAME: WESTERN ENERGY
CLIENT: WESTERN ENERGY
DATE: 6/10
JOB NUMBER: 01-018
FIGURE NUMBER:


WATER LINE
FLOWER BED
MW-16
FORMER PUMP ISLAND & CANOPY
NEW CANOPY & PUMP ISLAND
MW-13
3,330
RW-7
116
1,979
MW-7
MW-12
FORMER LANCER MART
RW-2
RW-4
RW-6
1464
MW-15
MW-11
10,000
MW-3
MW-2
NS
OMLETTE SHOP
LANCER MART
SIDEWALK
1,000
30,000
20,000
REMEDIATION SYSTEM TRAILER
ROOF DRAIN
RW-5
2,735
ZEOLITE CLAY FILTRATION BUILDING
RW-1
OUTFALL 001
MW-1
UNDERGROUND TELEPHONE LINES
ROUTE 607
NEW DIESEL PUMP ISLAND & CANOPY
NEW DIESEL UST
NEW DIESEL UST
DRAINAGE DITCH
MW-5
MW-4

	Ethanol	Benzene	Acetate	pH	Hydrogen	Methane	DIC
	mg/L	mg/L	mg/L		ppm in gas above water	mg/L	mg/L
MW-3	6130	8.50	269.0	4.9	64634	8.13	772
MW-11	930	2.00	310.0	5.2	4947	11.3	361
MW-7	19.2	0.33	28.4	6.1	476	2.39	40.0
MW-4	0.8	0.0011	<0.1	6.6	342	0.331	6.59
MW-5	0.2	0.00069	<0.1	5.1	<32	0.0328	2.10
MW-12	<0.1	0.34	<0.1	6.3	182	14.6	15.2
MW-1	<0.1	0.09	<0.1	6.5	527	15.3	315

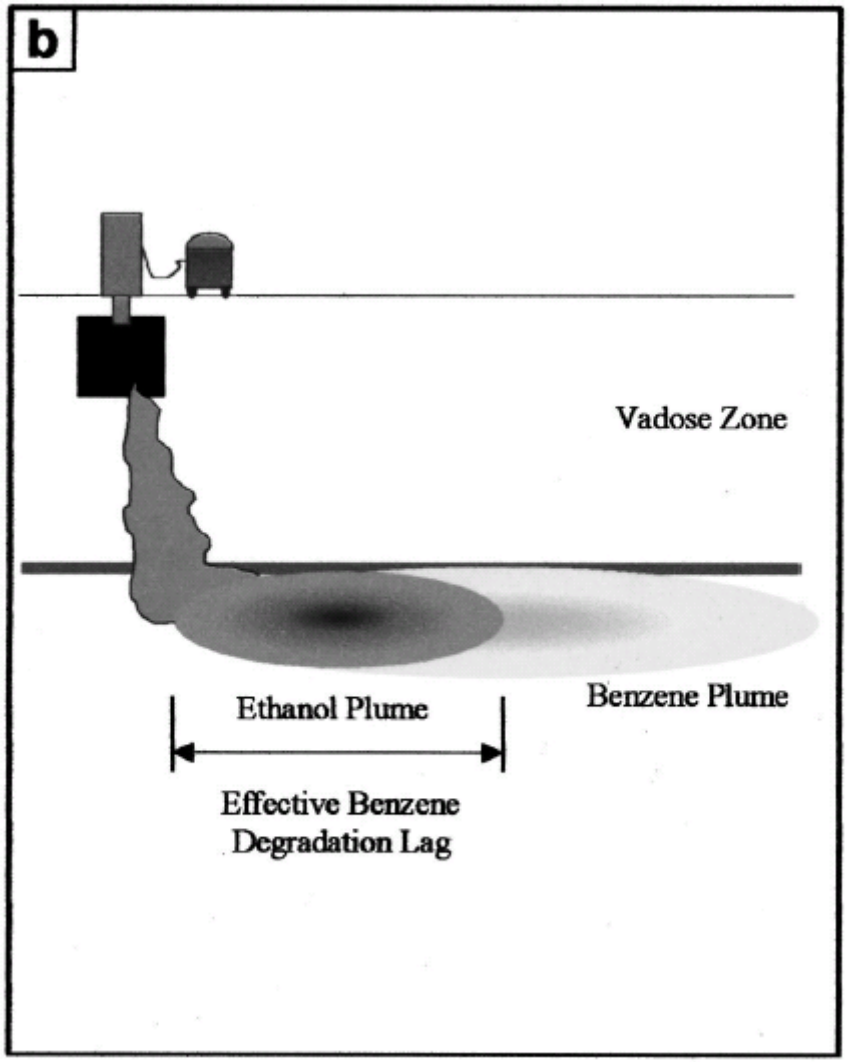
Values in red are below the analytical detection limit.

	Ethanol	Benzene	Acetate	pH	Hydrogen	ΔG′ Benzene
	mg/L	mg/L	mg/L		ppm	kJ/mole
MW-3	6130	8.50	269.0	4.9	64634	59
MW-11	930	2.00	310.0	5.2	4947	40
MW-7	19.2	0.33	28.4	6.1	476	-6
MW-4	0.8	0.0011	<0.1	6.6	342	-45
MW-5	0.2	0.00069	<0.1	5.1	<32	-42
MW-12	<0.1	0.34	<0.1	6.3	182	-58
MW-1	<0.1	0.09	<0.1	6.5	527	-52

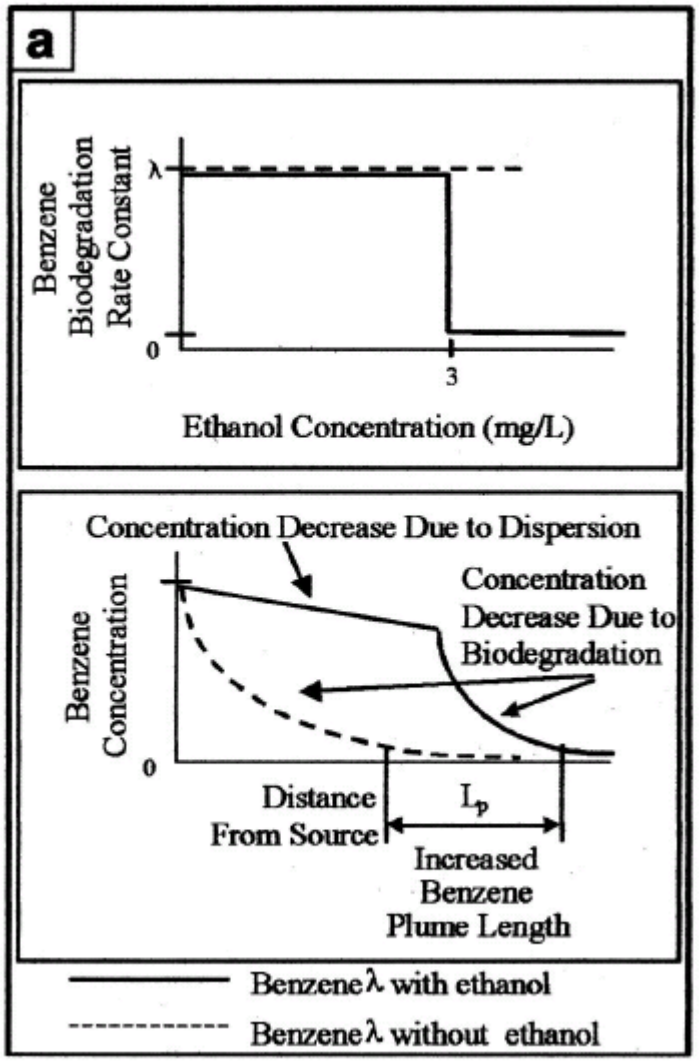
If ethanol is present, the concentration of its degradation products will be high enough to inhibit the biodegradation of benzene.

What can be expected to happen when the presence of ethanol degradation products inhibits biodegradation of benzene?

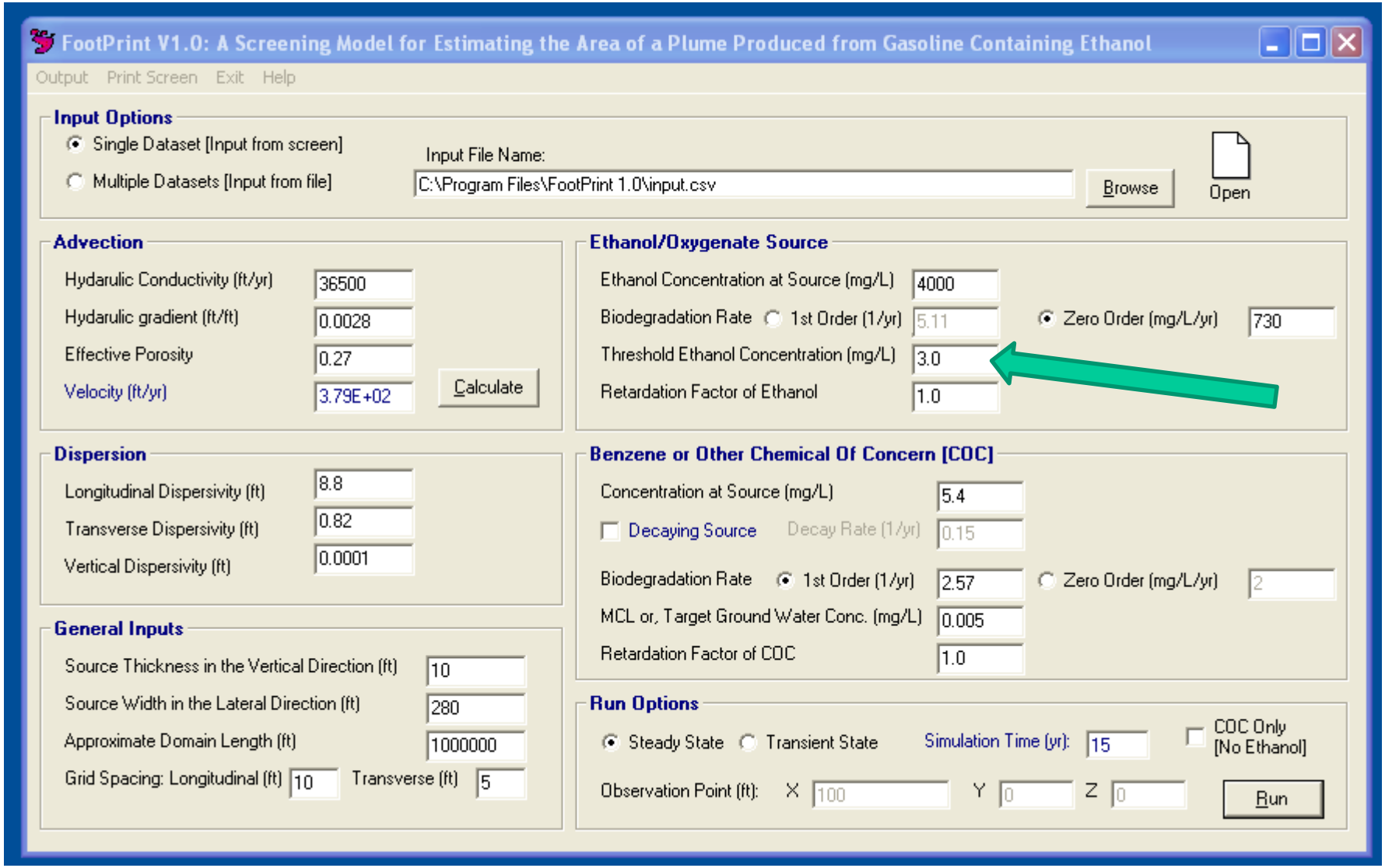
Conceptual Model of a co-mingled ethanol/benzene plume.

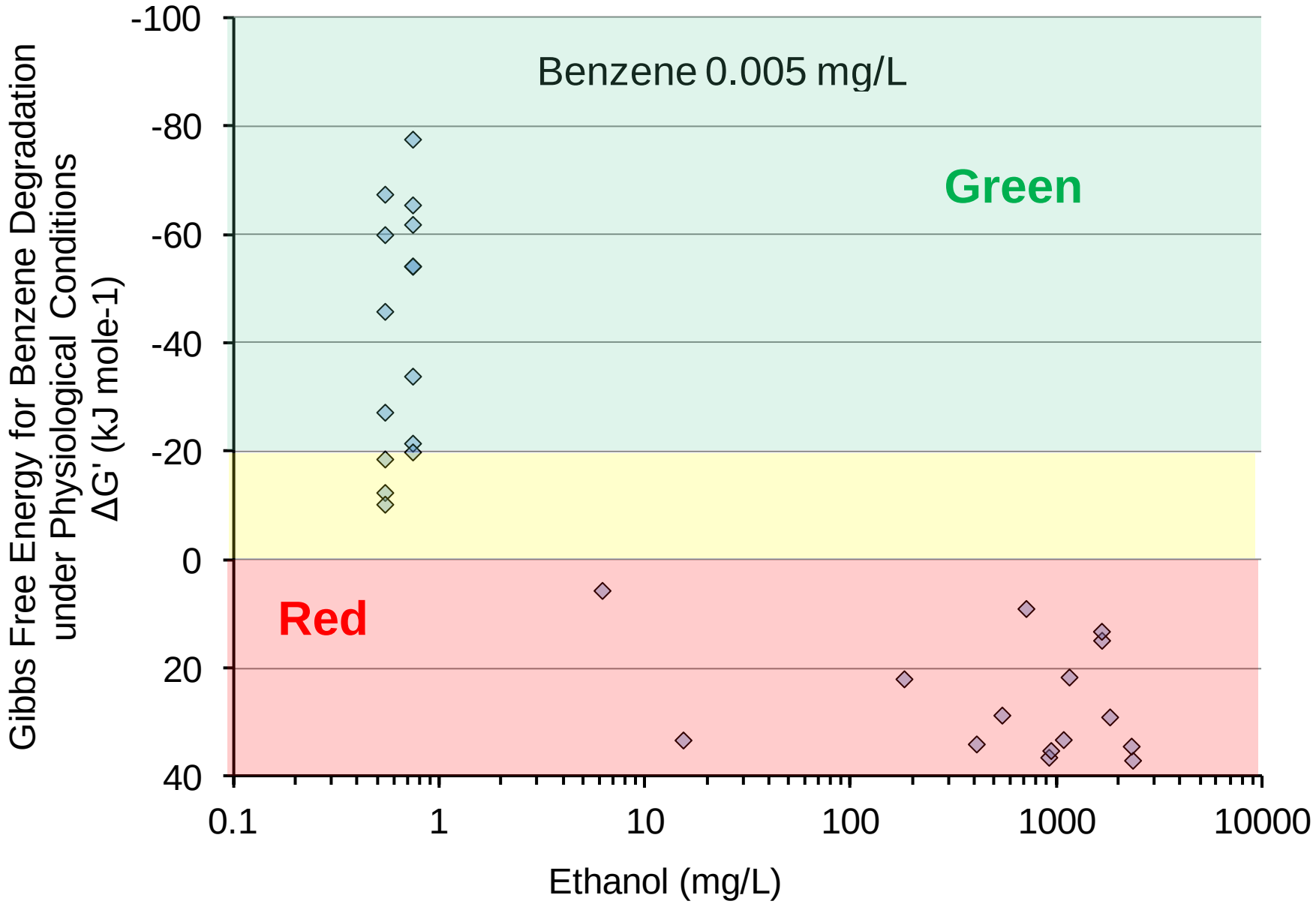


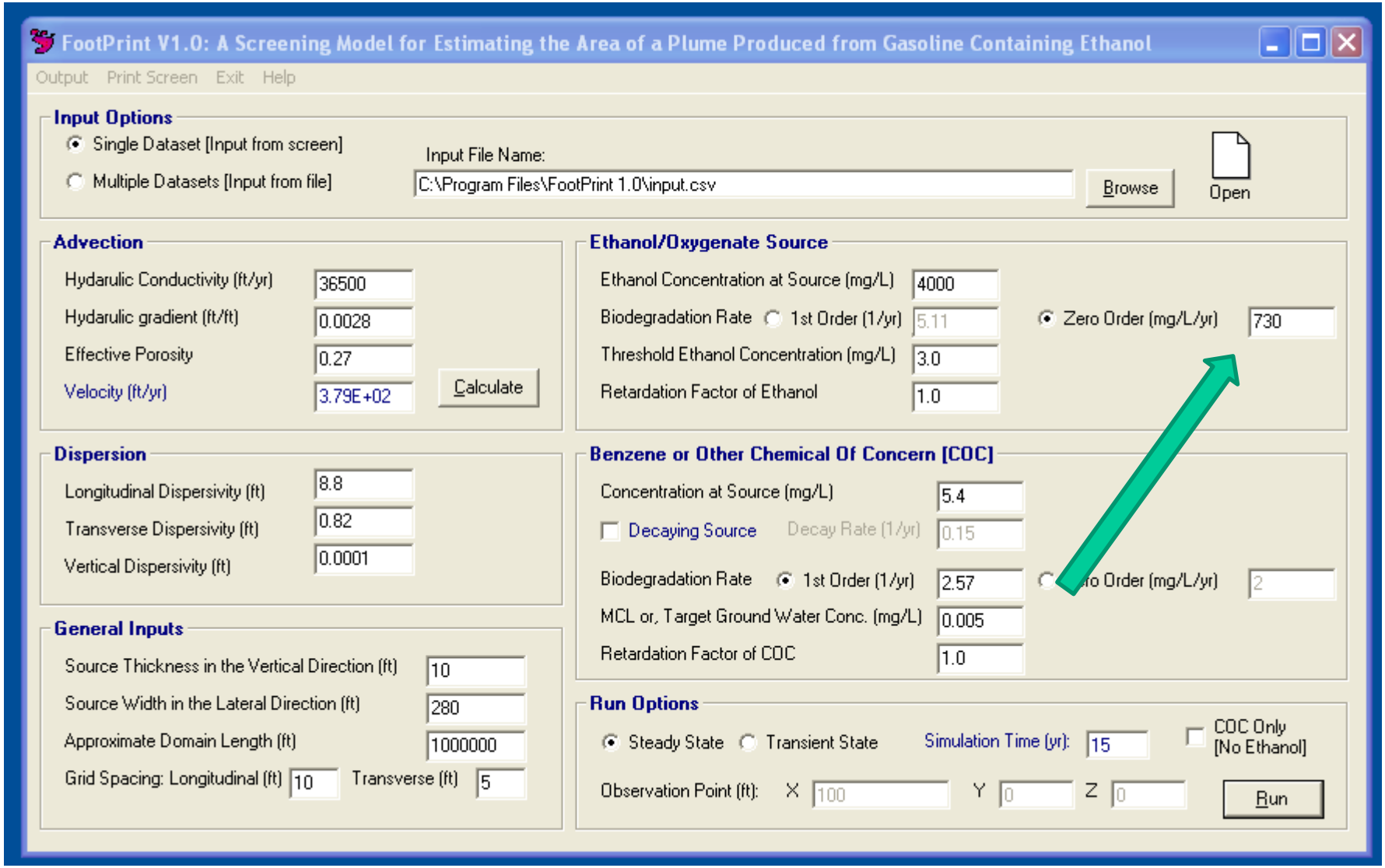
Impact of Ethanol on Benzene Plume, Lengths: Microbial and Modeling Studies. Deeb, R. A., J. O. Sharp, A. Stocking, S. McDonald, K. A. West, M. Laugier, P. J. J. Alvarez, M. C. Kavanaugh, and L. Alvarez-Cohen, 2002, Journal of Environmental Engineering, ASCE, 128(9): 868-875.

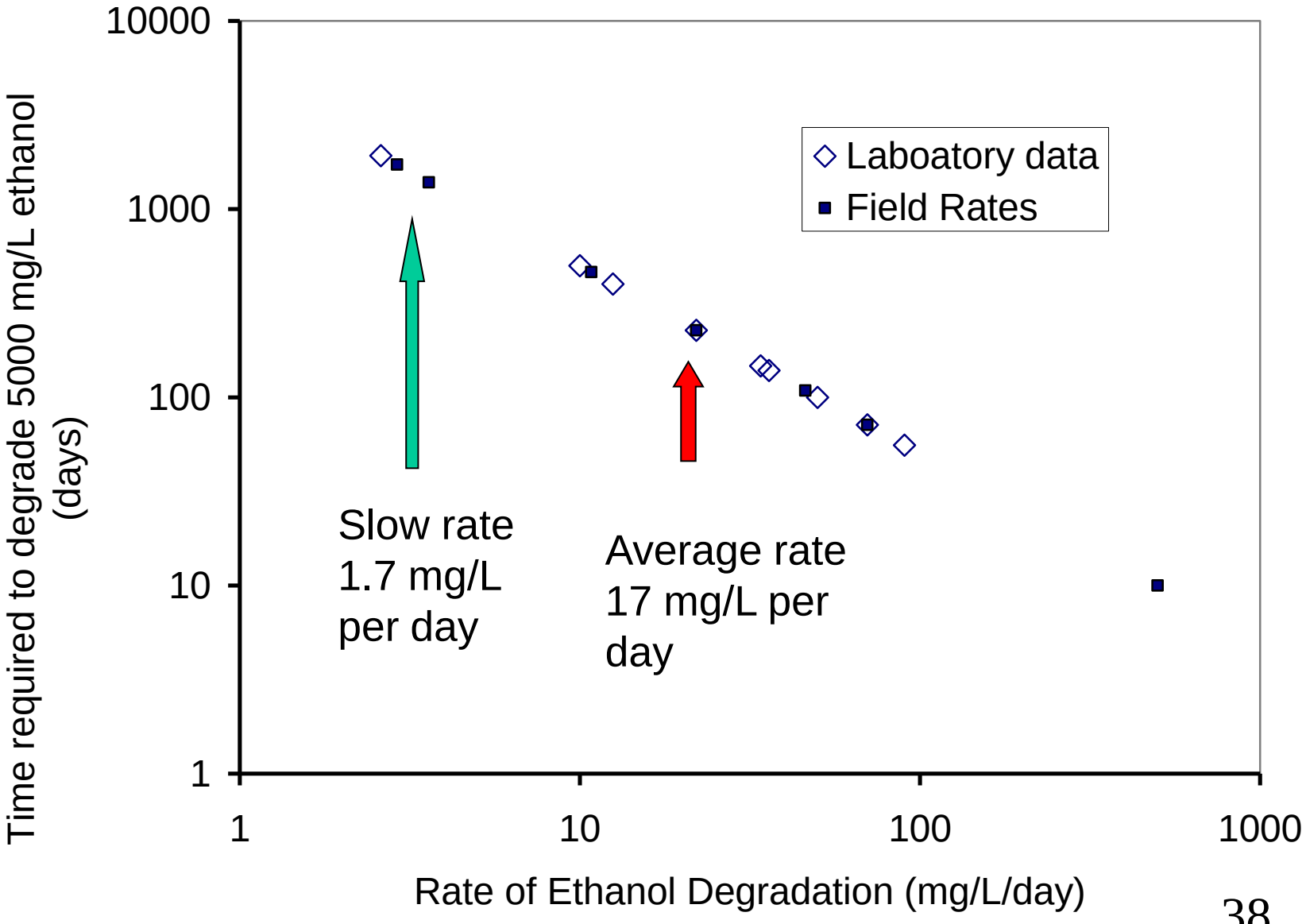

a
Benzene Biodegradation Rate Constant
λ
0
3
Ethanol Concentration (mg/L)
Concentration Decrease Due to Dispersion
Concentration Decrease Due to Biodegradation
Benzene Concentration
0
Distance From Source
L_p
Increased Benzene Plume Length
Benzene λ with ethanol
Benzene λ without ethanol

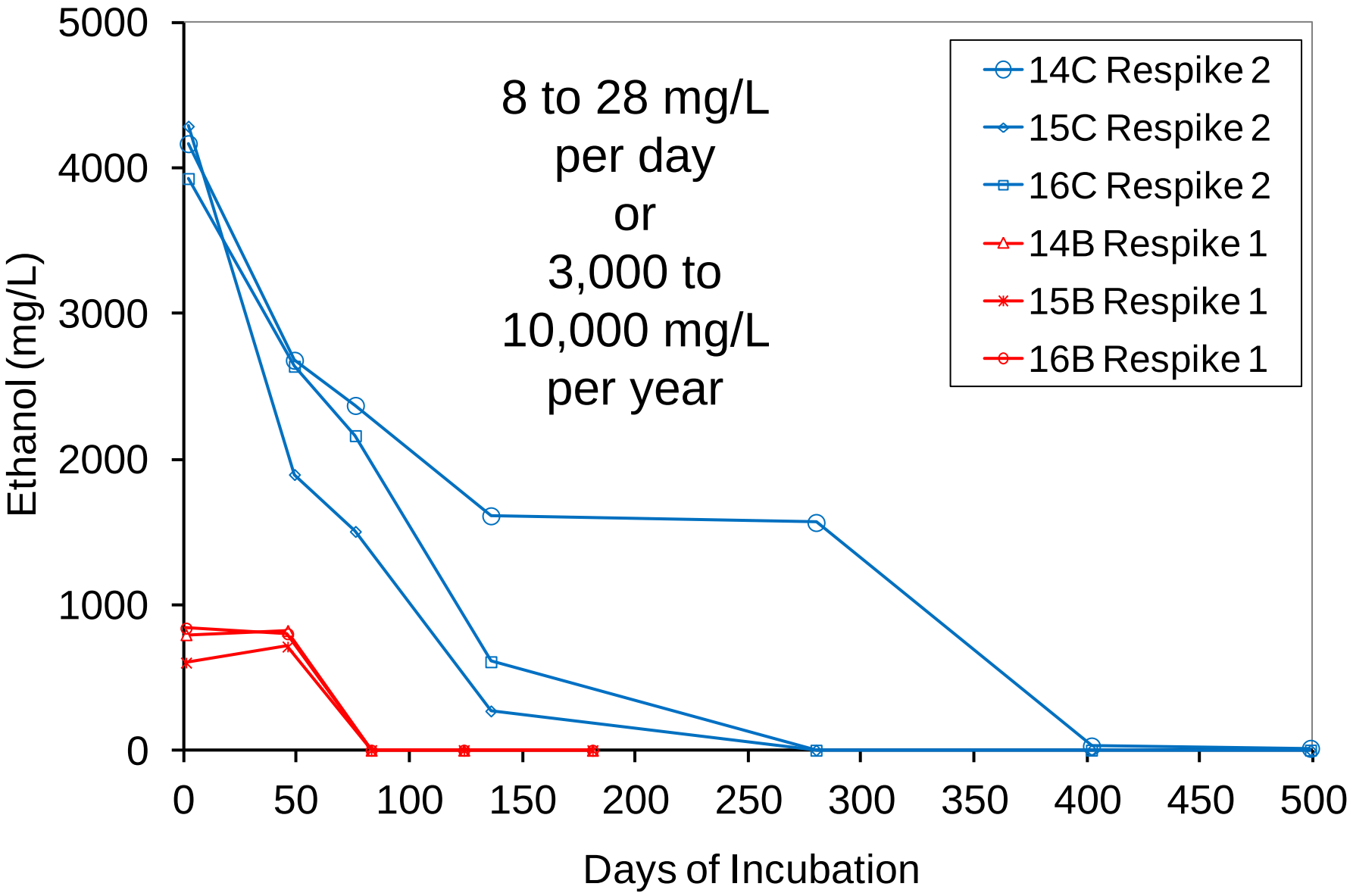
U.S. EPA has developed a simple screening model to describe the interactions of ethanol and benzene. It uses the concept of a virtual concentration to extract an analytical solution based on Domenico (1987).

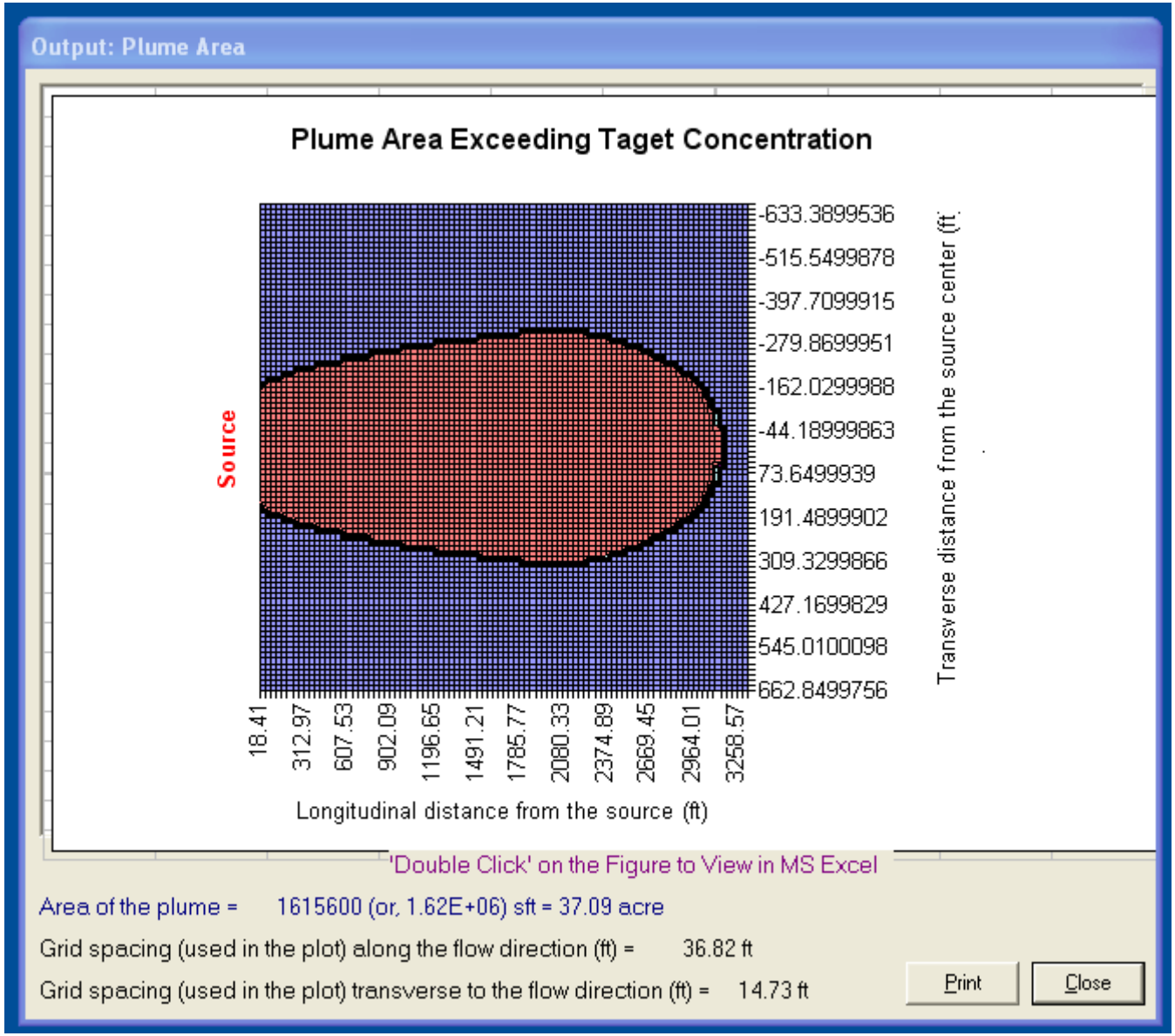

FootPrint V1.0: A Screening Model for Estimating the Area of a Plume Produced from Gasoline Containing Ethanol
Output
Print Screen
Exit
Help
Input Options
Single Dataset [Input from screen]
Multiple Datasets [Input from file]
Input File Name:
C:\Program Files\FootPrint 1.0\input.csv
Browse
Open
Advection
Hydarulic Conductivity (ft/yr) 36500
Hydarulic gradient (ft/ft) 0.0028
Effective Porosity 0.27
Velocity (ft/yr) 3.79E+02
Calculate
Ethanol/Oxygenate Source
Ethanol Concentration at Source (mg/L) 4000
Biodegradation Rate 1st Order (1/yr) 5.11
Zero Order (mg/L/yr) 730
Threshold Ethanol Concentration (mg/L) 3.0
Retardation Factor of Ethanol 1.0
Dispersion
Longitudinal Dispersivity (ft) 8.8
Transverse Dispersivity (ft) 0.82
Vertical Dispersivity (ft) 0.0001
Benzene or Other Chemical Of Concern [COC]
Concentration at Source (mg/L) 5.4
Decaying Source
Decay Rate (1/yr) 0.15
Biodegradation Rate 1st Order (1/yr) 2.57
Zero Order (mg/L/yr) 2
MCL or, Target Ground Water Conc. (mg/L) 0.005
Retardation Factor of COC 1.0
General Inputs
Source Thickness in the Vertical Direction (ft) 10
Source Width in the Lateral Direction (ft) 280
Approximate Domain Length (ft) 1000000
Grid Spacing: Longitudinal (ft) 10
Transverse (ft) 5
Run Options
Steady State
Transient State
Simulation Time (yr): 15
COC Only [No Ethanol]
Observation Point (ft): X 100 Y 0 Z 0
Run

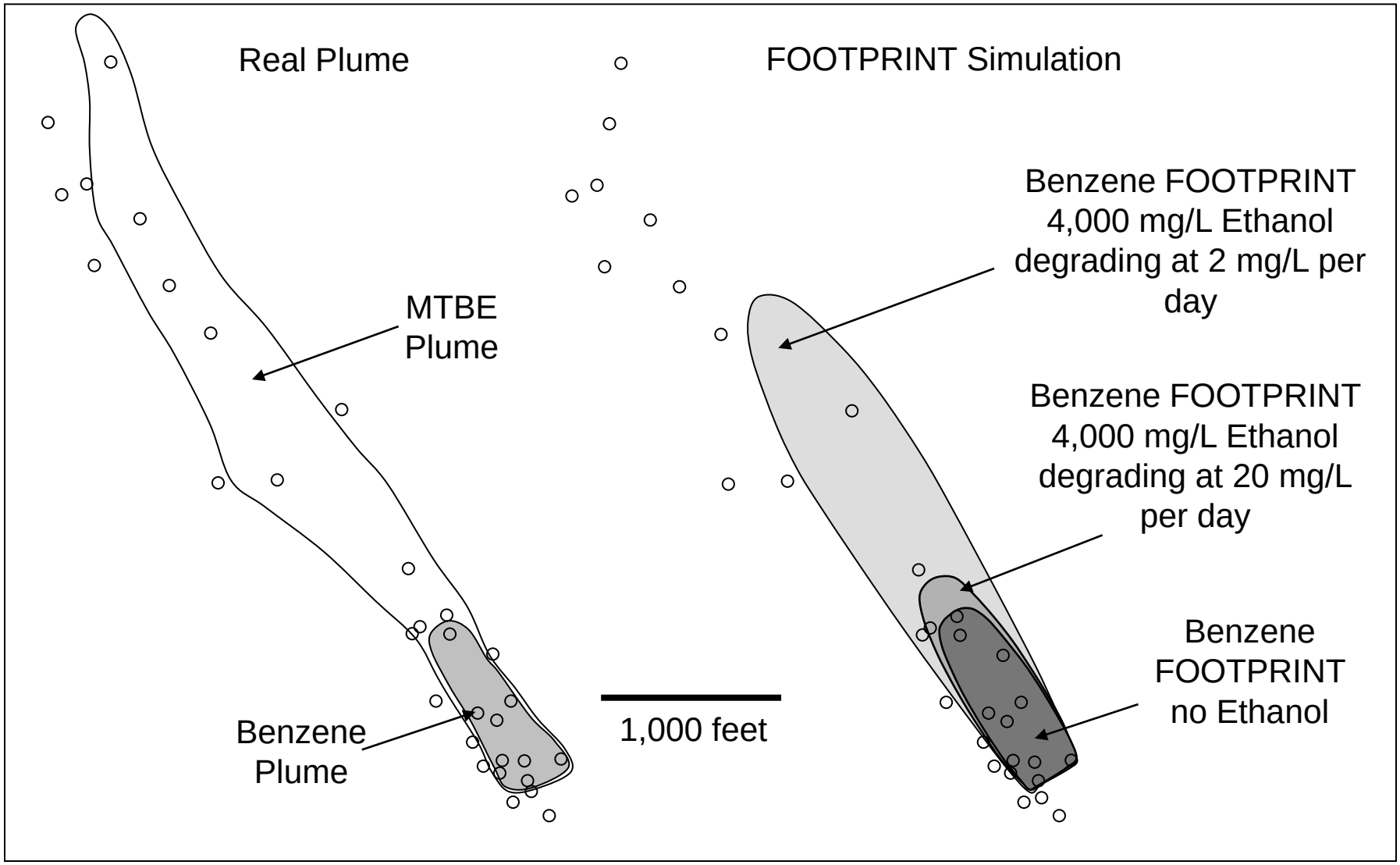

Benzene 0.005 mg/L
Green
Red
Gibbs Free Energy for Benzene Degradation under Physiological Conditions ΔG' (kJ mole-1)
-100
-80
-60
-40
-20
0
20
40
0.1
1
10
100
1000
10000
Ethanol (mg/L)


FootPrint V1.0: A Screening Model for Estimating the Area of a Plume Produced from Gasoline Containing Ethanol
Output
Print Screen
Exit
Help
Input Options
Single Dataset [Input from screen]
Multiple Datasets [Input from file]
Input File Name:
C:\Program Files\FootPrint 1.0\input.csv
Browse
Open
Advection
Hydarulic Conductivity (ft/yr) 36500
Hydarulic gradient (ft/ft) 0.0028
Effective Porosity 0.27
Velocity (ft/yr) 3.79E+02
Calculate
Ethanol/Oxygenate Source
Ethanol Concentration at Source (mg/L) 4000
Biodegradation Rate 1st Order (1/yr) 5.11
Zero Order (mg/L/yr) 730
Threshold Ethanol Concentration (mg/L) 3.0
Retardation Factor of Ethanol 1.0
Dispersion
Longitudinal Dispersivity (ft) 8.8
Transverse Dispersivity (ft) 0.82
Vertical Dispersivity (ft) 0.0001
Benzene or Other Chemical Of Concern [COC]
Concentration at Source (mg/L) 5.4
Decaying Source
Decay Rate (1/yr) 0.15
Biodegradation Rate 1st Order (1/yr) 2.57
Zero Order (mg/L/yr) 2
MCL or, Target Ground Water Conc. (mg/L) 0.005
Retardation Factor of COC 1.0
General Inputs
Source Thickness in the Vertical Direction (ft) 10
Source Width in the Lateral Direction (ft) 280
Approximate Domain Length (ft) 1000000
Grid Spacing: Longitudinal (ft) 10
Transverse (ft) 5
Run Options
Steady State
Transient State
Simulation Time (yr): 15
COC Only [No Ethanol]
Observation Point (ft): X 100 Y 0 Z 0
Run


10000
1000
100
10
1
1
10
100
1000
Time required to degrade 5000 mg/L ethanol (days)
Rate of Ethanol Degradation (mg/L/day)
Laboatory data
Field Rates
Slow rate 1.7 mg/L per day
Average rate 17 mg/L per day


5000
4000
3000
2000
1000
0
Ethanol (mg/L)
0
50
100
150
200
250
300
350
400
450
500
Days of Incubation
8 to 28 mg/L
per day
or
3,000 to
10,000 mg/L
per year
14C Respike 2
15C Respike 2
16C Respike 2
14B Respike 1
15B Respike 1
16B Respike 1


Output: Plume Area
Plume Area Exceeding Taget Concentration
Source
-633.3899536
-515.5499878
-397.7099915
-279.8699951
-162.0299988
-44.18999863
73.6499939
191.4899902
309.3299866
427.1699829
545.0100098
662.8499756
Transverse distance from the source center (ft)
18.41
312.97
607.53
902.09
1196.65
1491.21
1785.77
2080.33
2374.89
2669.45
2964.01
3258.57
Longitudinal distance from the source (ft)
'Double Click' on the Figure to View in MS Excel
Area of the plume = 1615600 (or, 1.62E+06) sft = 37.09 acre
Grid spacing (used in the plot) along the flow direction (ft) = 36.82 ft
Grid spacing (used in the plot) transverse to the flow direction (ft) = 14.73 ft
Print
Close


Real Plume
FOOTPRINT Simulation
MTBE Plume
Benzene Plume
1,000 feet
Benzene FOOTPRINT 4,000 mg/L Ethanol degrading at 2 mg/L per day
Benzene FOOTPRINT 4,000 mg/L Ethanol degrading at 20 mg/L per day
Benzene FOOTPRINT no Ethanol