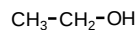


Anaerobic Biodegradation of Biofuels (Ethanol and Biodiesel) and Proposed Biofuels (n-Propanol, *iso*-Propanol, n-Butanol, and 2,5-Dimethylfuran) in Aquifer Sediments

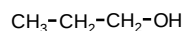
Cherri Adair and John T. Wilson
U.S. EPA/ORD/NRMRL
R.S. Kerr Center, Ada, Oklahoma

National Tanks Conference
March 30, 2009
Sacramento, CA

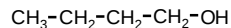
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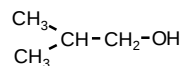
Ethanol



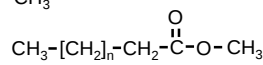
n-Propanol



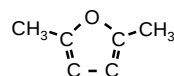
n-Butanol



iso-Butanol



Biodiesel
(simplified)



2,5-Dimethylfuran



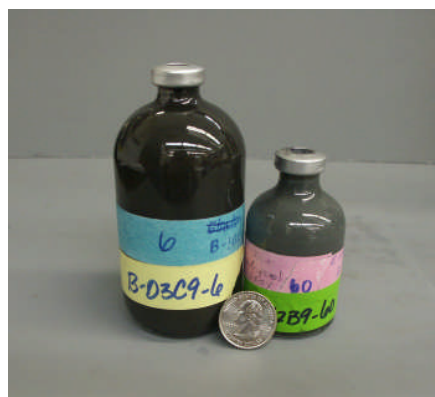
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Biofuel Questions

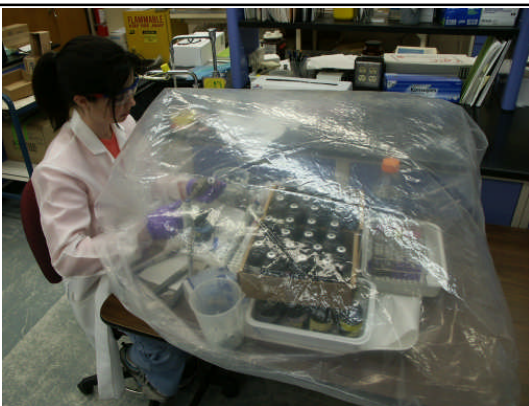
- Does the Biofuel Degrade?
- Does the Biofuel produce methane?



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Biofuel Treatments

- Ethanol
- n-Butanol
- *iso*-Butanol
- n-Propanol
- 2,5-Dimethylfuran
- Biodiesel Emulsion



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Westway Terminal #2 Saint Paul, MN



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Westway Ethanol Treatment Microcosms

Treatment	Ethanol (mg/L)		
	Day 0	Day 3-8	Day 29
Ethanol + BTEX	58.4	<0.94	<0.94
EtOH + BTEX + SO ₄	58.4	<0.94	<0.94
Autoclaved Control	36.5	51.2	25



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Westway n-Butanol Treatment Microcosms

Treatment	n-Butanol (mg/L)		
	Day 0	Day 3-8	Day 29
n-Butanol + BTEX	128	37.9	<0.37
n-Butanol + BTEX + SO ₄	128	14.7	<0.37
Autoclaved Control	117	133	41



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Westway iso-Butanol Treatment Microcosms

Treatment	iso-Butanol (mg/L)		
	Day 0	Day 3-8	Day 29
iso-Butanol + BTEX	123	71.6	<0.40
iso-Butanol + BTEX + SO ₄	123	59.9	<0.40
Autoclaved Control	100	147	63



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Westway n-Propanol Treatment Microcosms

Treatment	n-Propanol (mg/L)		
	Day 0	Day 3-8	Day 29
n-Propanol + BTEX	146	13.0	<1.17
n-Propanol + BTEX + SO ₄	146	<1.17	<1.17
Autoclaved Control	154	168	41



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Westway 2,5-Dimethylfuran Treatment Microcosms

Treatment	2,5-Dimethylfuran (mg/L)		
	Day 0	Day 3-8	Day 29
2,5-Dimethylfuran + BTEX	0.55	0.03	<0.01
2,5-Dimethylfuran + BTEX + SO ₄	0.55	0.03	<0.01
Autoclaved Control	0.26	0.05	0.02



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U.S. Coast Guard Support Center Fuel Farm Elizabeth City, NC



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Elizabeth City Ethanol Treatment Microcosms				
	Ethanol (mg/L)			
Treatment	Day 0	Day 9	Day 77	Day 110
Ethanol + BTEX	63.3	53.3	<0.94	<0.94
EtOH + BTEX + SO ₄	63.3	3.19	<0.94	<0.94
Autoclaved Control	73.3	64.4	66.2	64.5



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Elizabeth City n-Butanol Treatment Microcosms				
	n-Butanol (mg/L)			
Treatment	Day 0	Day 9	Day 77	Day 110
n-Butanol + BTEX	144	136	<0.37	<0.37
n-Butanol + BTEX + SO ₄	144	136	<0.37	<0.37
Autoclaved Control	132	125	111	123



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Elizabeth City iso-Butanol Treatment Microcosms				
	iso-Butanol (mg/L)			
Treatment	Day 0	Day 9	Day 77	Day 110
iso-Butanol + BTEX	130	127	<0.40	<0.40
iso-Butanol + BTEX + SO ₄	130	128	<0.40	<0.40
Autoclaved Control	125	120	96.9	124



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Elizabeth City n-Propanol Treatment Microcosms				
	n-Propanol (mg/L)			
Treatment	Day 0	Day 9	Day 77	Day 110
n-Propanol + BTEX	143	112	<1.56	<1.17
n-Propanol + BTEX + SO ₄	143	103	<1.62	<1.17
Autoclaved Control	132	91.4	150	169



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Elizabeth City 2,5-Dimethylfuran Treatment Microcosms				
	2,5-Dimethylfuran (mg/L)			
Treatment	Day 0	Day 9	Day 77	Day 110
2,5-Dimethylfuran + BTEX	1.70	0.37	0.05	0.65
2,5-Dimethylfuran + BTEX + SO ₄	1.70	0.23	0.05	0.31
Autoclaved Control	1.87	1.26	0.09	0.96



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Biofuel Questions

✓ Does the Biofuel Degrade?

- Does the Biofuel produce methane?



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Westway Ethanol Treatment Microcosms			
Treatment	Methane (mg/L)		
	Day 0-7	Day 8-26	Day 27-53
Ethanol + BTEX	409	6265	4377
EtOH + BTEX + SO ₄	581	4464	4579
Autoclaved Control	0.00	0.54	30.3



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Westway BTEX Treatment Microcosms			
Treatment	Methane (mg/L)		
	Day 0-7	Day 8-26	Day 27-53
BTEX	550	5211	5365
BTEX + SO ₄	554	5567	4464
Autoclaved Control	0.00	0.54	30.3



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Elizabeth City Ethanol Treatment Microcosms			
Treatment	Methane (mg/L)		
	Day 0-6	Day 7-74	Day 75-105
Ethanol + BTEX	0.93	30.18	8.13
EtOH + BTEX + SO ₄	0.92	19.06	2.63
Autoclaved Control	0.08	0.11	0.02



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Elizabeth City n-Butanol Treatment Microcosms			
Treatment	Methane (mg/L)		
	Day 0-6	Day 7-74	Day 75-105
n-Butanol + BTEX	0.13	42.20	7.17
n-Butanol + BTEX + SO ₄	0.07	0.11	0.08
Autoclaved Control	0.08	0.11	0.02

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Elizabeth City iso-Butanol Treatment Microcosms			
Treatment	Methane (mg/L)		
	Day 0-6	Day 7-74	Day 75-105
iso-Butanol + BTEX	0.28	45.95	9.31
iso-Butanol + BTEX + SO ₄	0.09	1.64	0.29
Autoclaved Control	0.08	0.11	0.02

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Elizabeth City n-Propanol Treatment Microcosms			
Treatment	Methane (mg/L)		
	Day 0-6	Day 7-74	Day 75-105
n-Propanol + BTEX	0.17	16.81	8.55
n-Propanol + BTEX + SO ₄	0.23	0.41	0.09
Autoclaved Control	0.08	0.11	0.02

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Elizabeth City 2,5-Dimethylfuran Treatment Microcosms			
Treatment	Methane (mg/L)		
	Day 0-6	Day 7-74	Day 75-105
2,5-Dimethylfuran + BTEX	0.62	4.03	1.21
2,5-Dimethylfuran + BTEX + SO ₄	0.38	1.26	0.29
Autoclaved Control	0.08	0.11	0.02

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Elizabeth City BTEX Treatment Microcosms "Background Production"			
Treatment	Methane (mg/L)		
	Day 0-6	Day 7-74	Day 75-105
BTEX	0.51	3.23	1.03
BTEX + SO ₄	0.51	1.23	0.21
Autoclaved Control	0.08	0.11	0.02

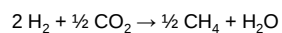
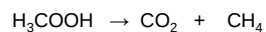
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Elizabeth City Biodiesel Treatment Microcosms			
Treatment	Methane (mg/L)		
	Day 0-6	Day 7-74	Day 75-105
Biodiesel + BTEX	0.44	24.12	30.81
Biodiesel + BTEX + SO ₄	0.04	17.83	16.32
Autoclaved Biodiesel + BTEX + SO ₄	0.05	0.15	0.07

Biodiesel makes methane as readily as the simple alcohols.

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Ethanol Fermentation to Methane



46 mg/L ethanol produces 24 mg/L methane



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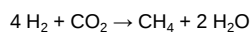
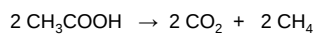
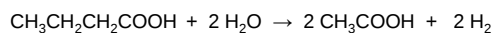
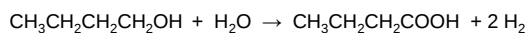
Elizabeth City Ethanol Treatment Microcosms

	Ethanol (mg/L)		Methane (mg/L)	
			Total Expected	Total Measured
Treatment	Day 0	Day 110	Day 105	
Ethanol + BTEX	63.3	<0.94	21.7	39.2
EtOH + BTEX + SO ₄	63.3	<0.94	21.7	22.6
Autoclaved Control	73.3	64.5	3.05	0.2



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Butanol Fermentation to Methane



74 mg/L butanol produces 48 mg/L methane



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Elizabeth City n-Butanol Treatment Microcosms

	n-Butanol (mg/L)		Methane (mg/L)	
			Total Expected	Total Measured
Treatment	Day 0	Day 110	Day 105	
n-Butanol + BTEX	144	<0.37	93.1	49.5
n-Butanol + BTEX + SO ₄	144	<0.37	93.1	0.3
Autoclaved Control	132	123	5.29	0.2



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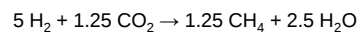
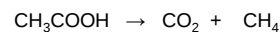
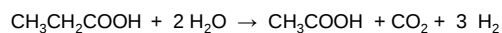
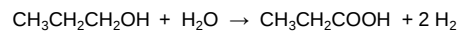
Elizabeth City iso-Butanol Treatment Microcosms

	iso-Butanol (mg/L)		Methane (mg/L)	
			Total Expected	Total Measured
Treatment	Day 0	Day 110	Day 105	
iso-Butanol + BTEX	130	<0.40	84.3	55.5
iso-Butanol + BTEX + SO ₄	130	<0.40	84.3	2.0
Autoclaved Control	125	124	0.73	0.2



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Propanol Fermentation to Methane



60 mg/L propanol produces 36 mg/L methane



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Elizabeth City n-Propanol Treatment Microcosms				
	n-Propanol (mg/L)		Methane (mg/L)	
	Day 0	Day 110	Total Expected	Total Measured
Treatment			Day 105	
n-Propanol + BTEX	143	<1.17	84.9	25.5
n-Propanol + BTEX + SO4	143	<1.17	84.9	0.7
Autoclaved Control	132	169	-22.5	0.2

Elizabeth City 2,5-Dimethylfuran Treatment Microcosms				
	2,5-Dimethylfuran (mg/L)		Methane (mg/L)	
	Day 0	Day 110	Total Expected	Total Measured
Treatment			Day 105	
2,5-Dimethylfuran + BTEX	1.70	0.65	0.36	5.9
2,5-Dimethylfuran + BTEX + SO4	1.70	0.31	0.48	1.9
Autoclaved Control	1.87	0.96	0.32	0.2

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.

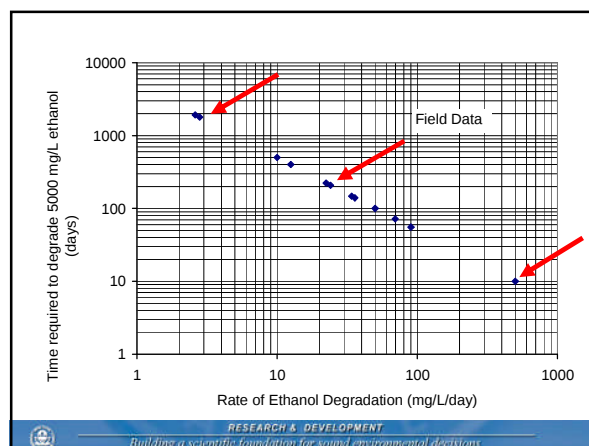
They released 76 liters of 95% ethanol, 5% synthetic gasoline to a large sand tank (8,150 liters).

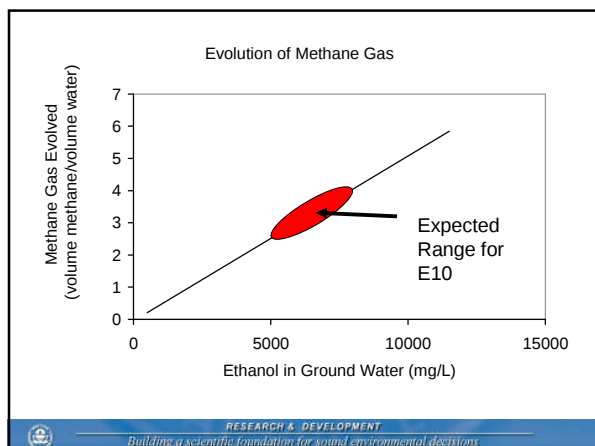
The maximum concentration of ethanol measured in miniature monitoring wells was **10,000 mg/L** or about 1.2% on a volume basis. This is a high concentration of ethanol, but not enough to cause co-solvency effects.

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.





Thanks to:

- Ken Jewell, U.S.EPA/ORD/NRMRL
- Mark Toso, Minnesota Pollution Control Agency

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