

# The Practical Science of Bioremediation as an Oil Spill Response of Option 2006

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# Bioremediation of Oil Spills

Something good is happening, but what is it and can we make it better?

# PEPCO Spill Site Overview 4/15/00



# PEPCO Spill Site Close-up 4/15/00





## Flows within the Marsh





# Control Area





## Boardwalks in the Marsh



# ESTIMATED NUTRIENT REQUIREMENTS FOR SWANSON CREEK MARSH CLEANUP ZONE W-1 AREA A - MAY 31, 2000

**Area A - A 600' diameter circle within Work Area W-1**

Oiled Area of Marsh	6.49	acres	282,744	sq. ft.
Depth (1")	0.08	feet	23,562	cu. ft.
Mass of Soil @108 lbs./cu.ft.	2,543,565	lbs.	1,156,166	kgs. soil
Estimated Oil Remaining	5,000	gals.	15,922	kgs. oil
Estimated % Oil	1.38%		14,000	mg/kg (ppm)
Weight of Oil @ 7 lbs./gal.	35,000	lbs	15,909	kgs. oil
Mass of Carbon @75%	26,250	lbs C	11,932	kgs. C

**Application Rates**

Oil to be Treated	15,909	kgs. oil	11,932	kgs. C
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Total Nutrient Needed	C:N:P Ratio	N (kgs.)	P (kgs.)	N (lbs.)	P (lbs.)
	60:1:0.2	199	40	438	88

**Nutrient Application Rates**

Weights of fertilizer based on C:N:P of 60:1:0.2 in lbs. for 6.49 acres of contaminated marsh.

	%N	Total Applied		Per Application		
		Wt. (lbs.)	lbs./acre	Wt. (lbs.)	lbs./acre	lbs./1000 sq.ft.
<b>Diammonium Phosphate</b>	21.21%	<b>2,063</b>	<b>318</b>	<b>688</b>	<b>106</b>	<b>2</b>



# Applying Fertilizer



# Area B after 6 Weeks Fertilization





# Phases of Cleanup

Phase 1. Emergency - Primary Containment and Recovery

Phase 2. Removal - Secondary Recovery and Treatment

Phase 3. Long-term Removal - Tertiary Recovery,  
Treatment and Natural Attenuation

Phase 3 Focuses on very low criteria for TPH and PAH (10 mg/kg)  
Also on low ppm levels for specific PAH's through NOAA's  
“SQuiRTs”

# Sorbents





## Berming & Diking

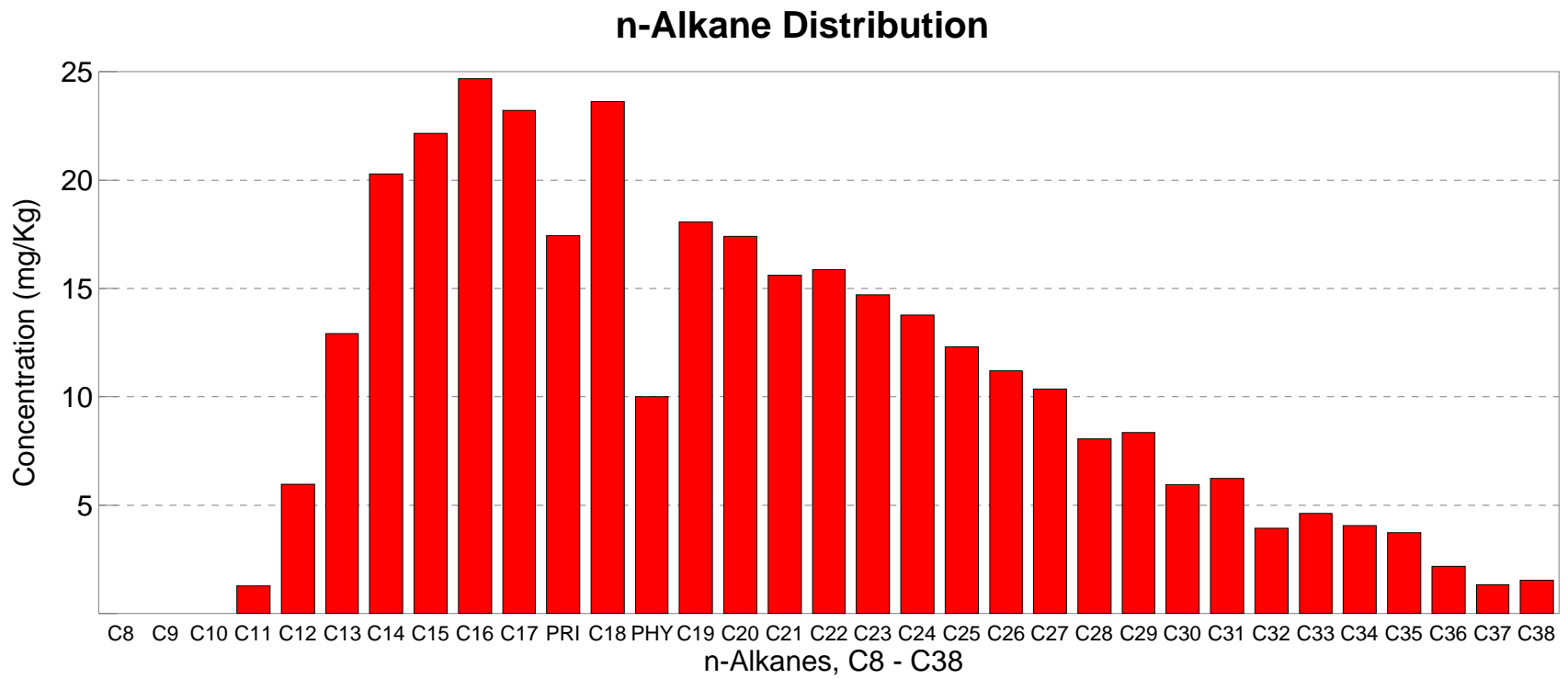


# Vacuuming





# W1BS05 Alkanes in Oil



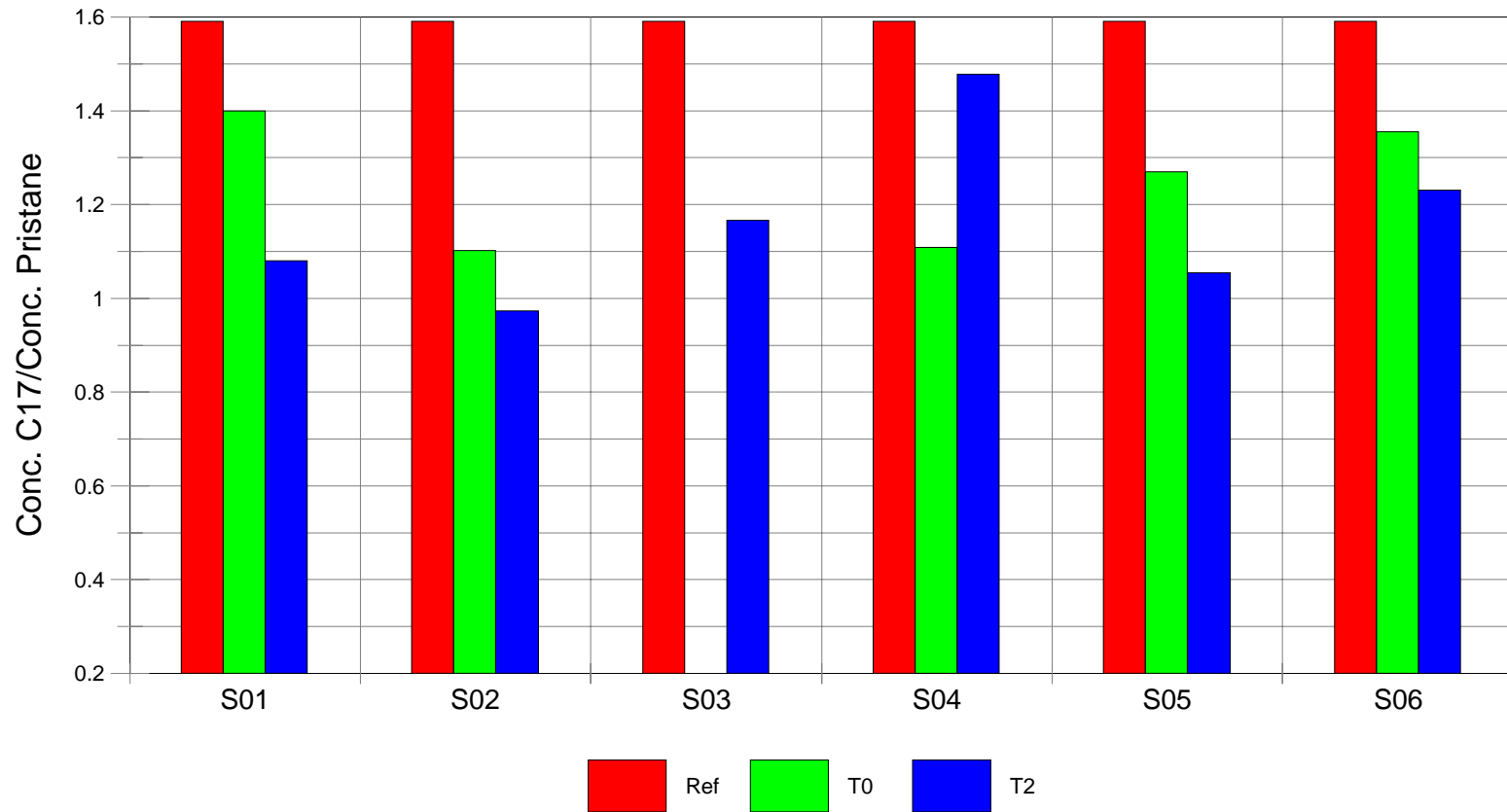
# Marsh Sampling Station





# Biodegradation in Mechanical Removal Area

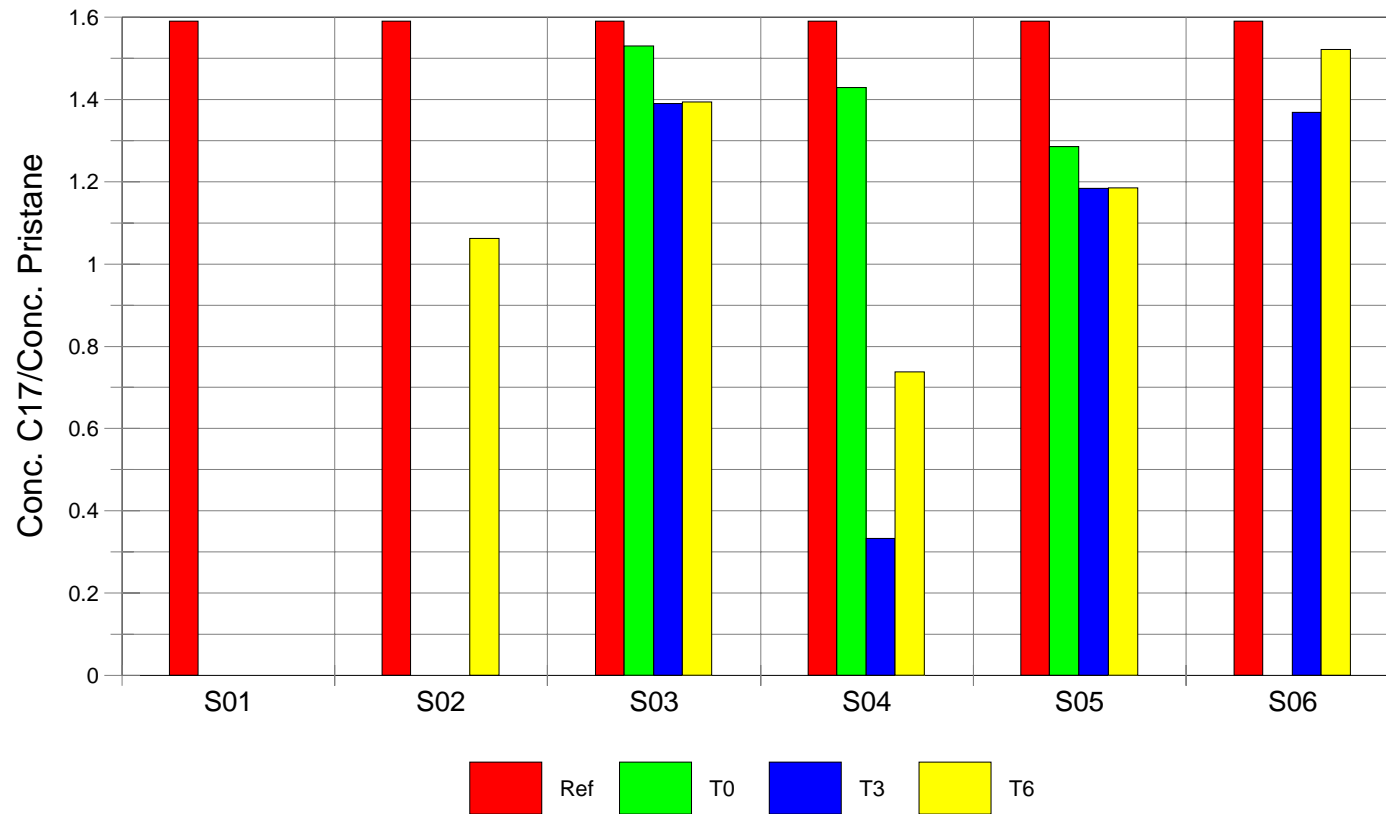
**C17/Pristane Ratio: Area A**  
Based on GC/MS Concentrations



# Biodegradation in Treated Area

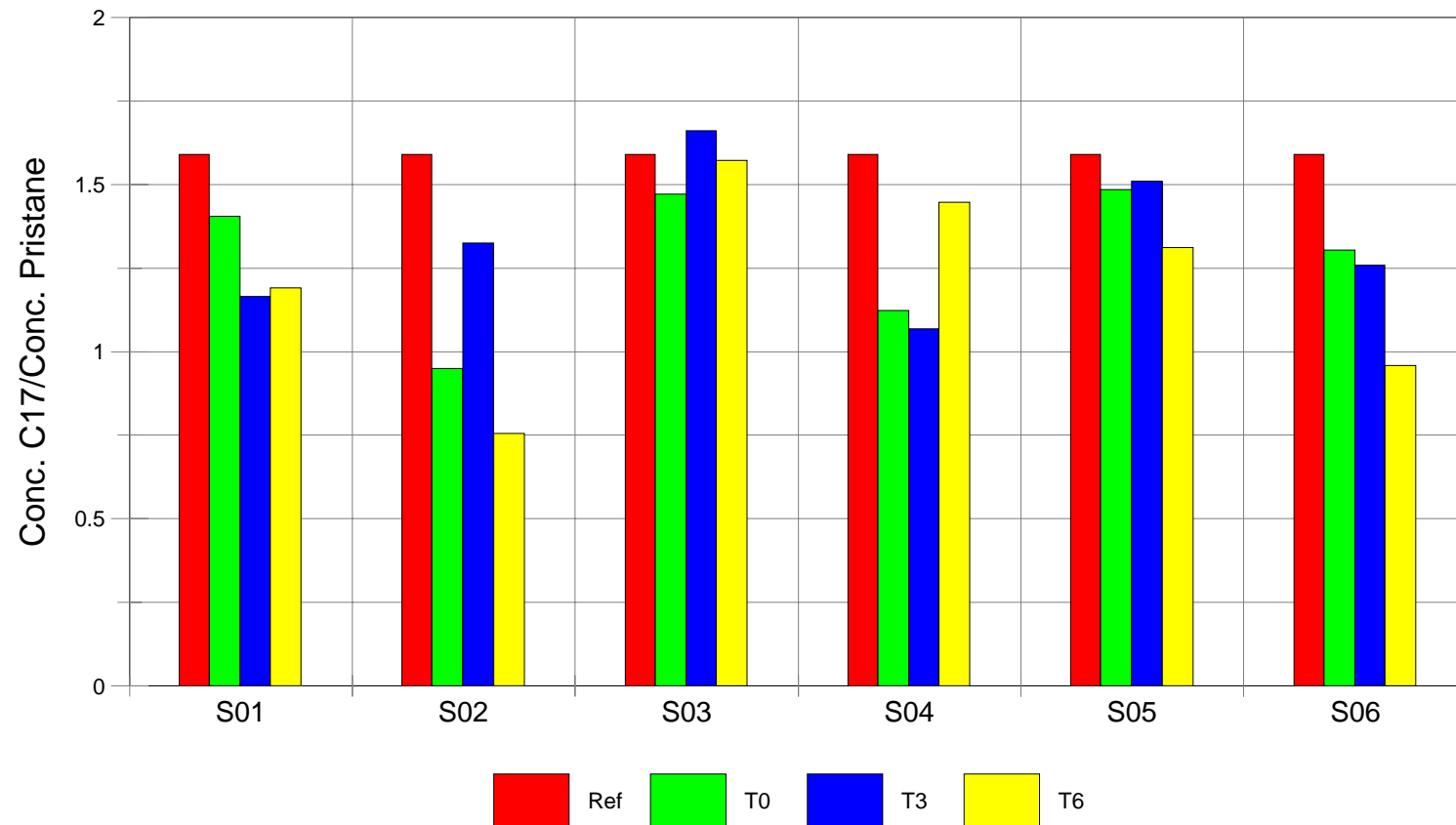
## C17/Pristane Ratio: Area B

Based on GC/MS Concentrations



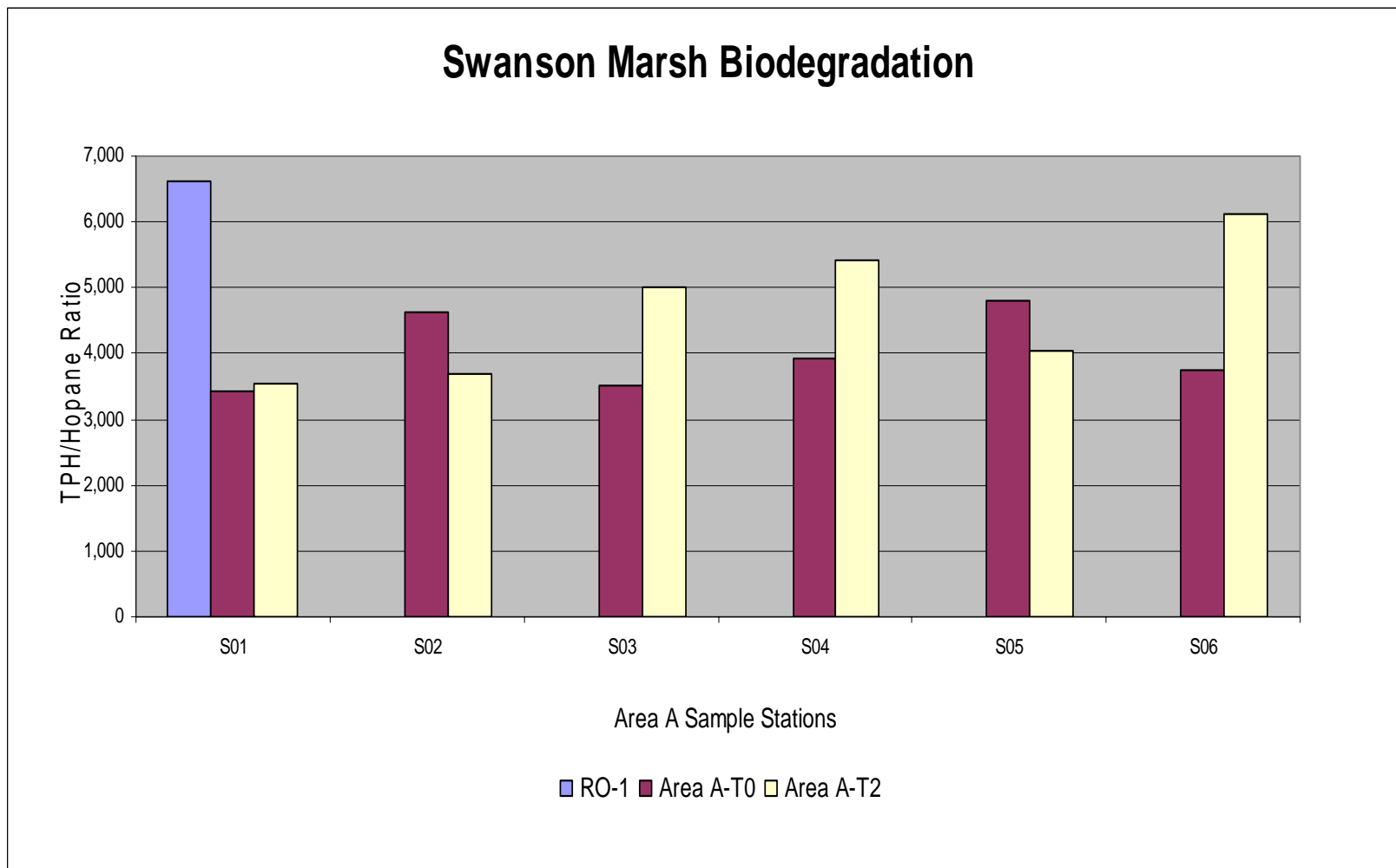
# Biodegradation in Non-Treated Area

## C17/Pristane Ratio: Area C Based on GC/MS Concentrations

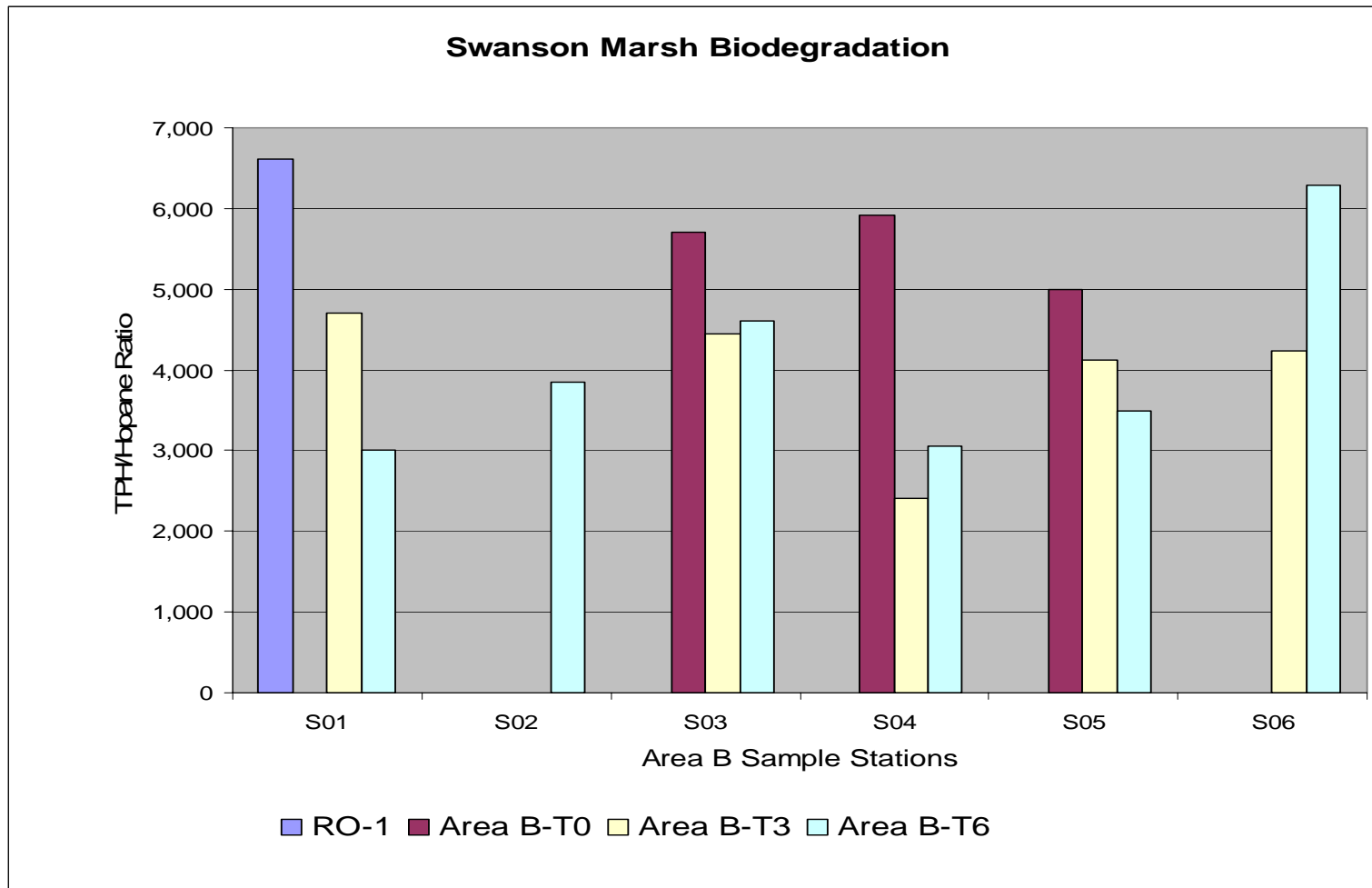




# Area A –TPH/Hopanes

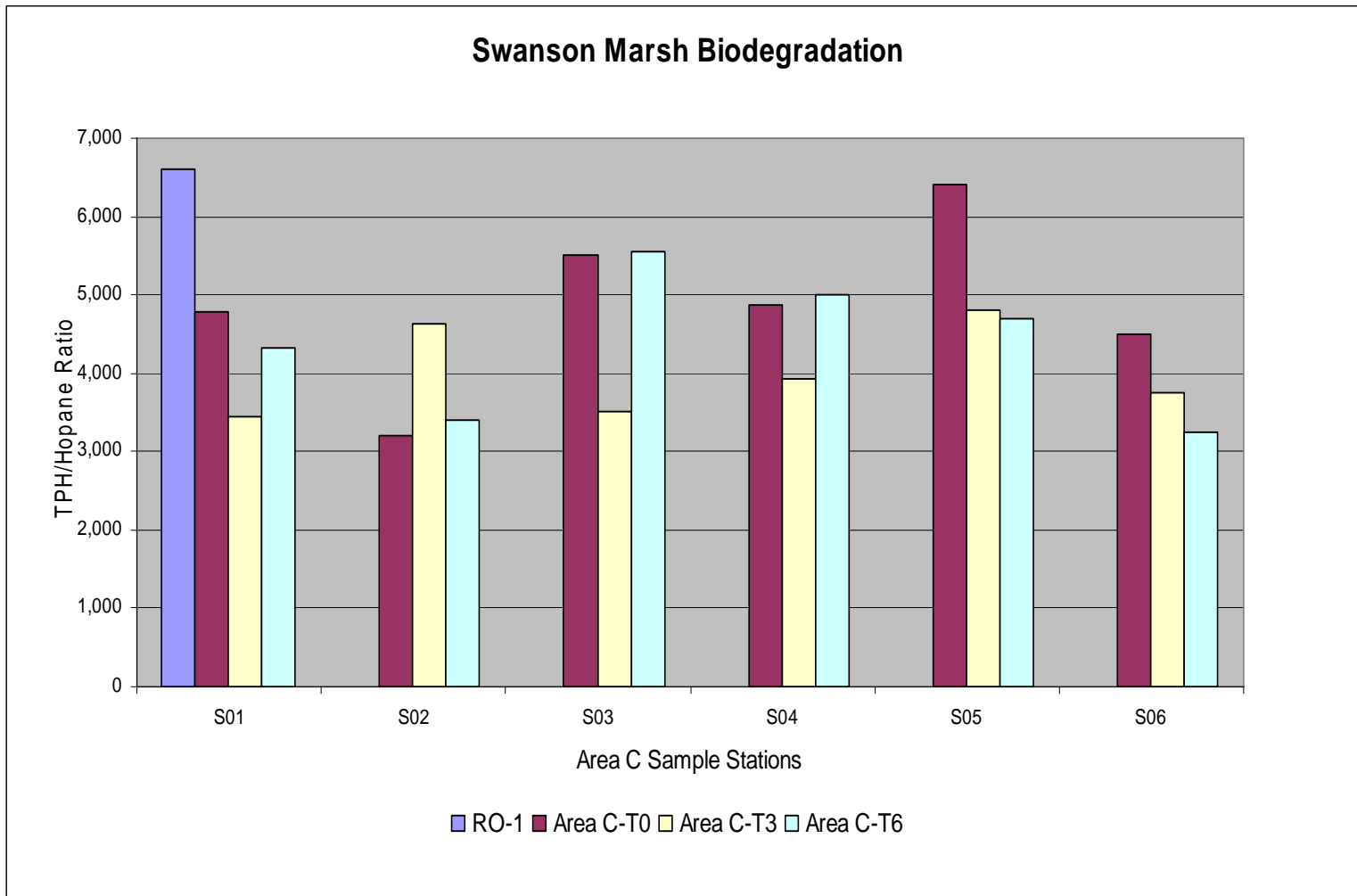


# Area B –TPH/Hopanes

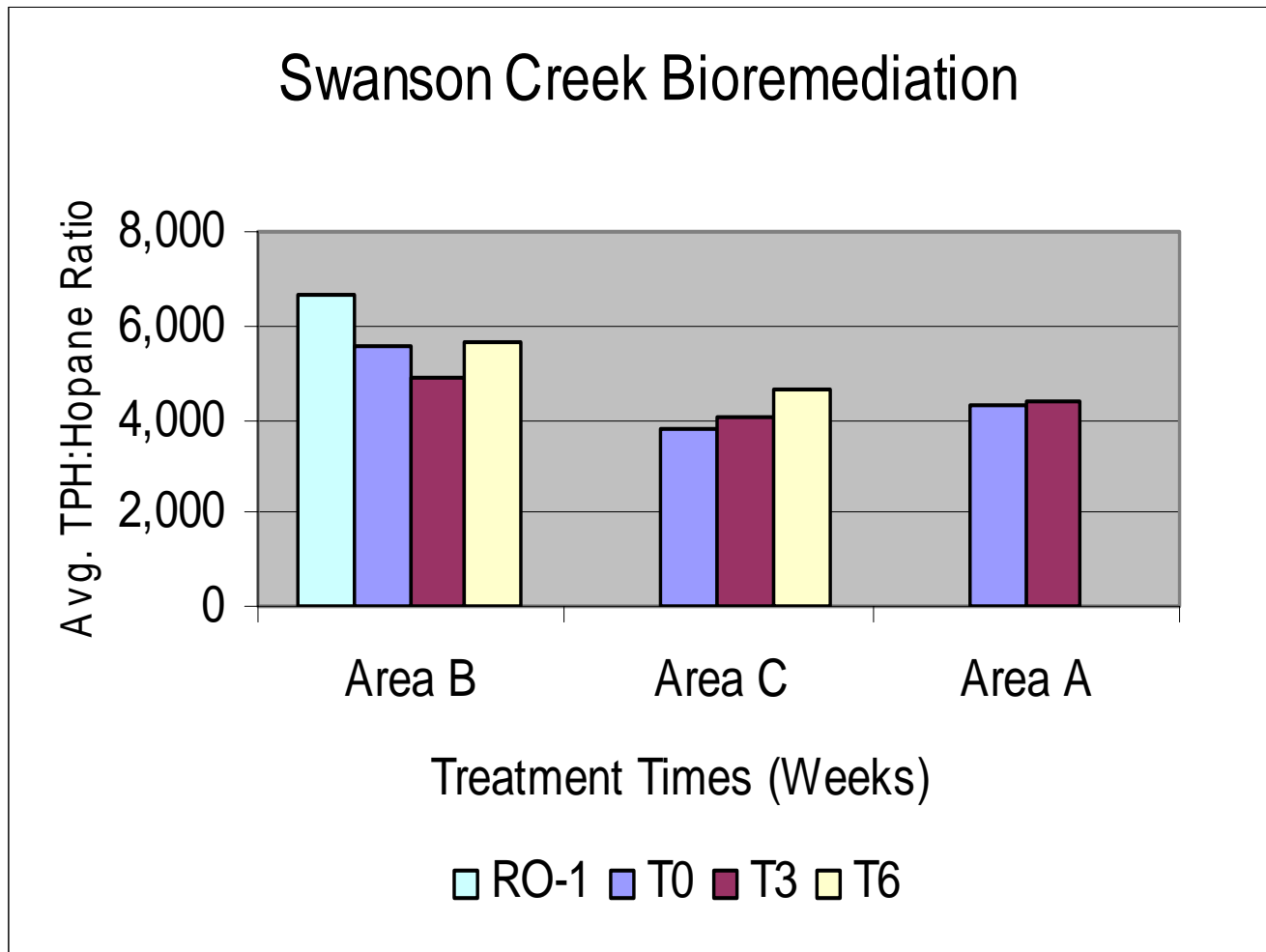




# Area C – TPH/Hopanes



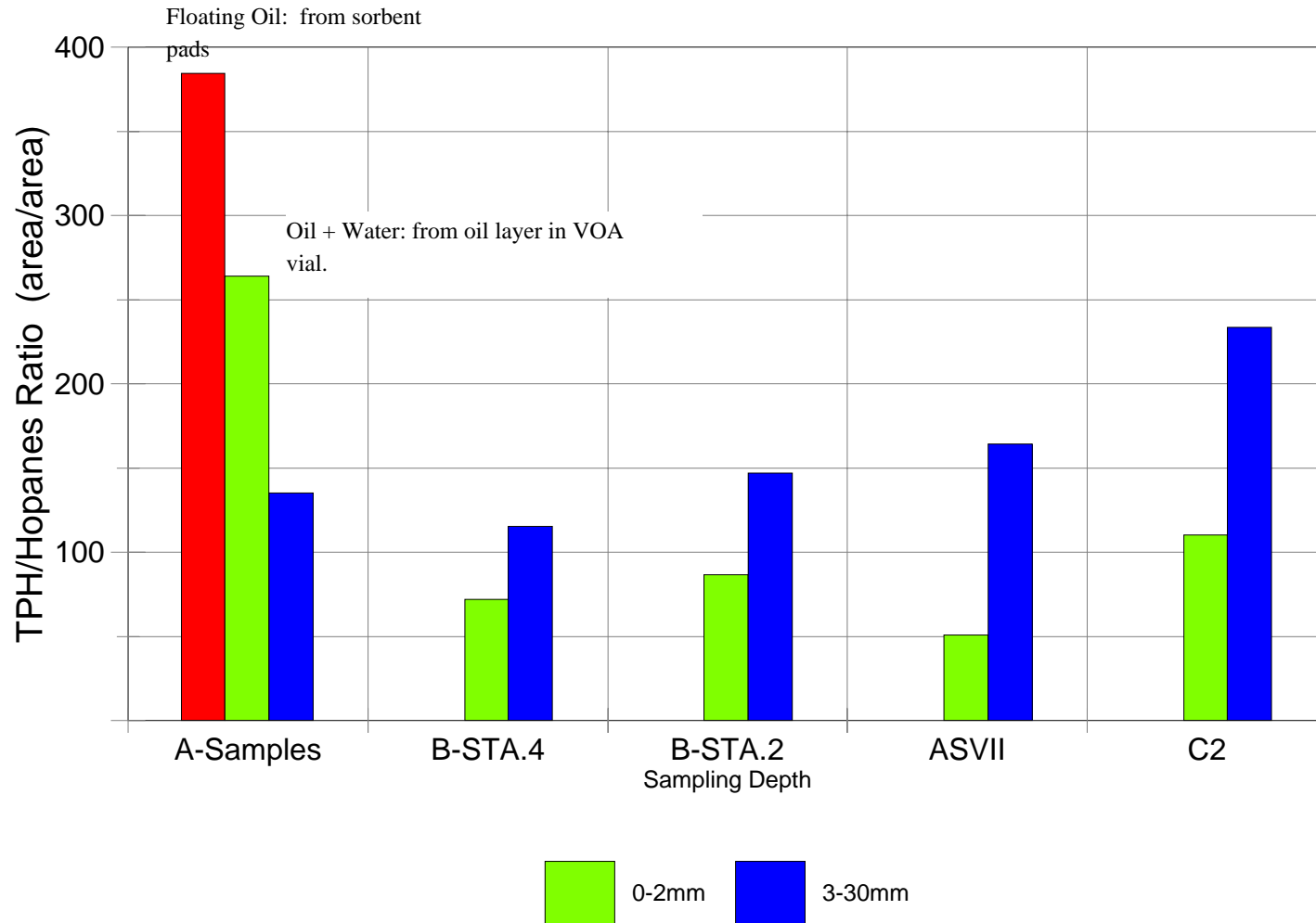
# Summary Areas A, B, C





# Depth Study – Oxygen Limitation

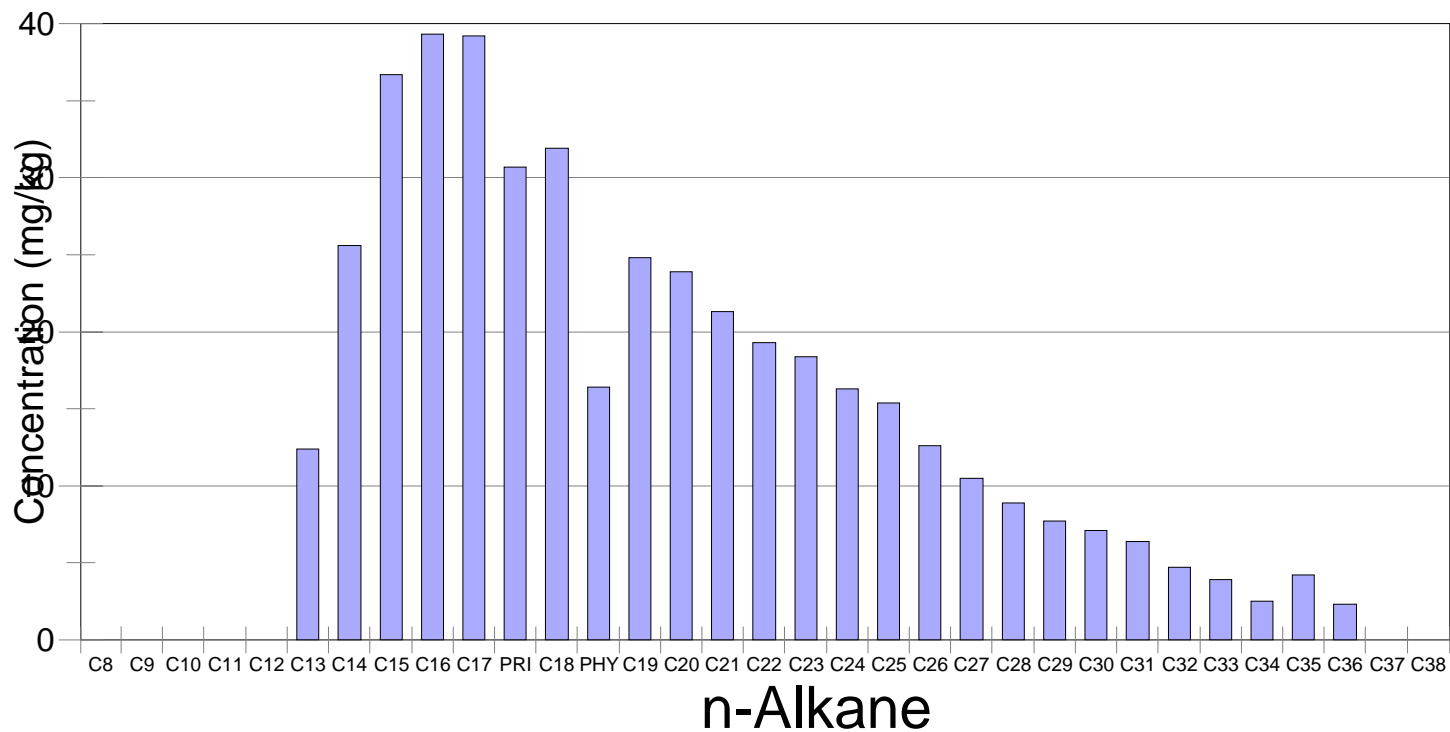
## Swanson Creek TPH/Hopanes Ratios Sediment Layer Study



# Free Oil Chromatogram

## PEPCO Bioremediation

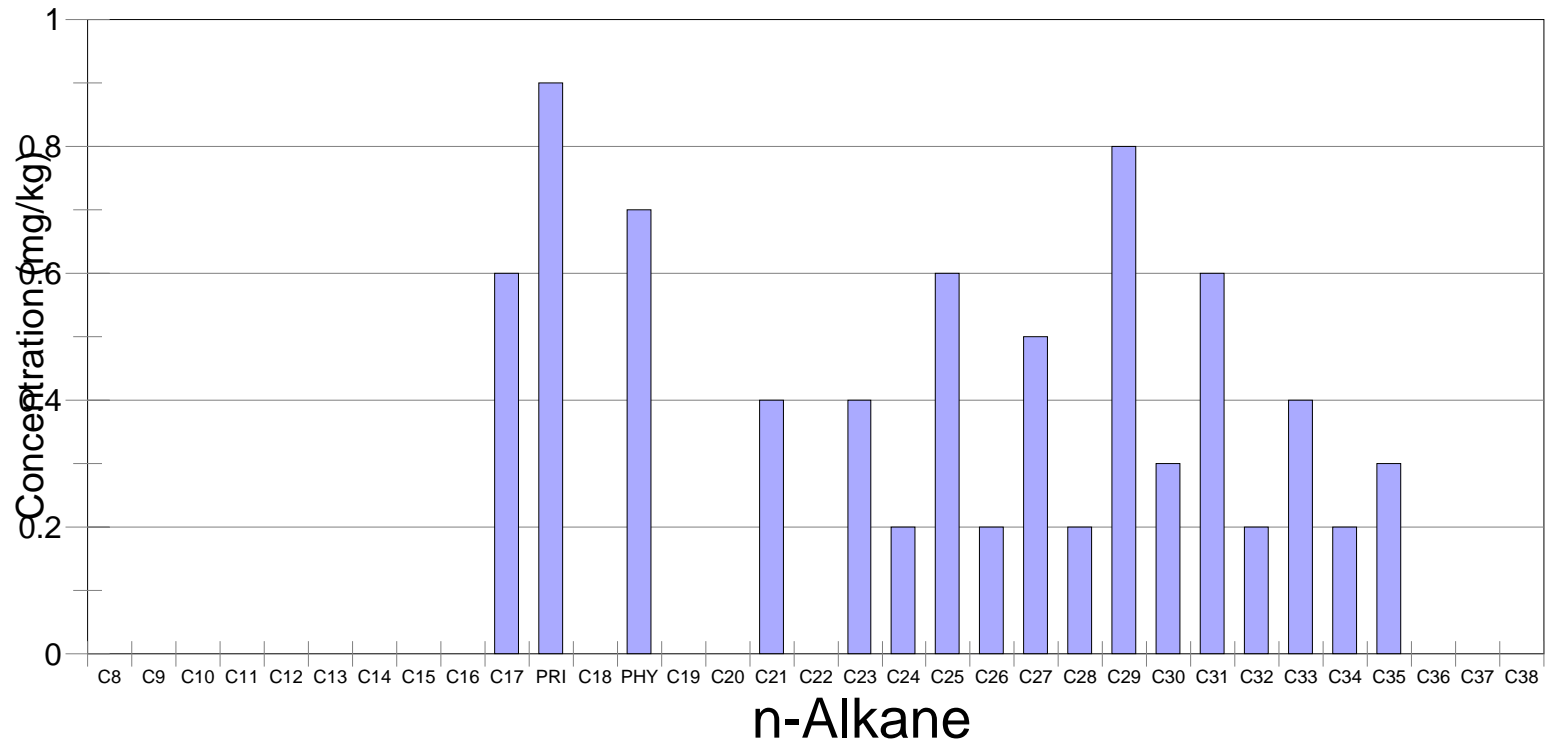
Free Surface Oil, 9/24/00



# Weathering in Treated Area

## PEPCO Bioremediation

Area B 0-3 mm, 9/24/00

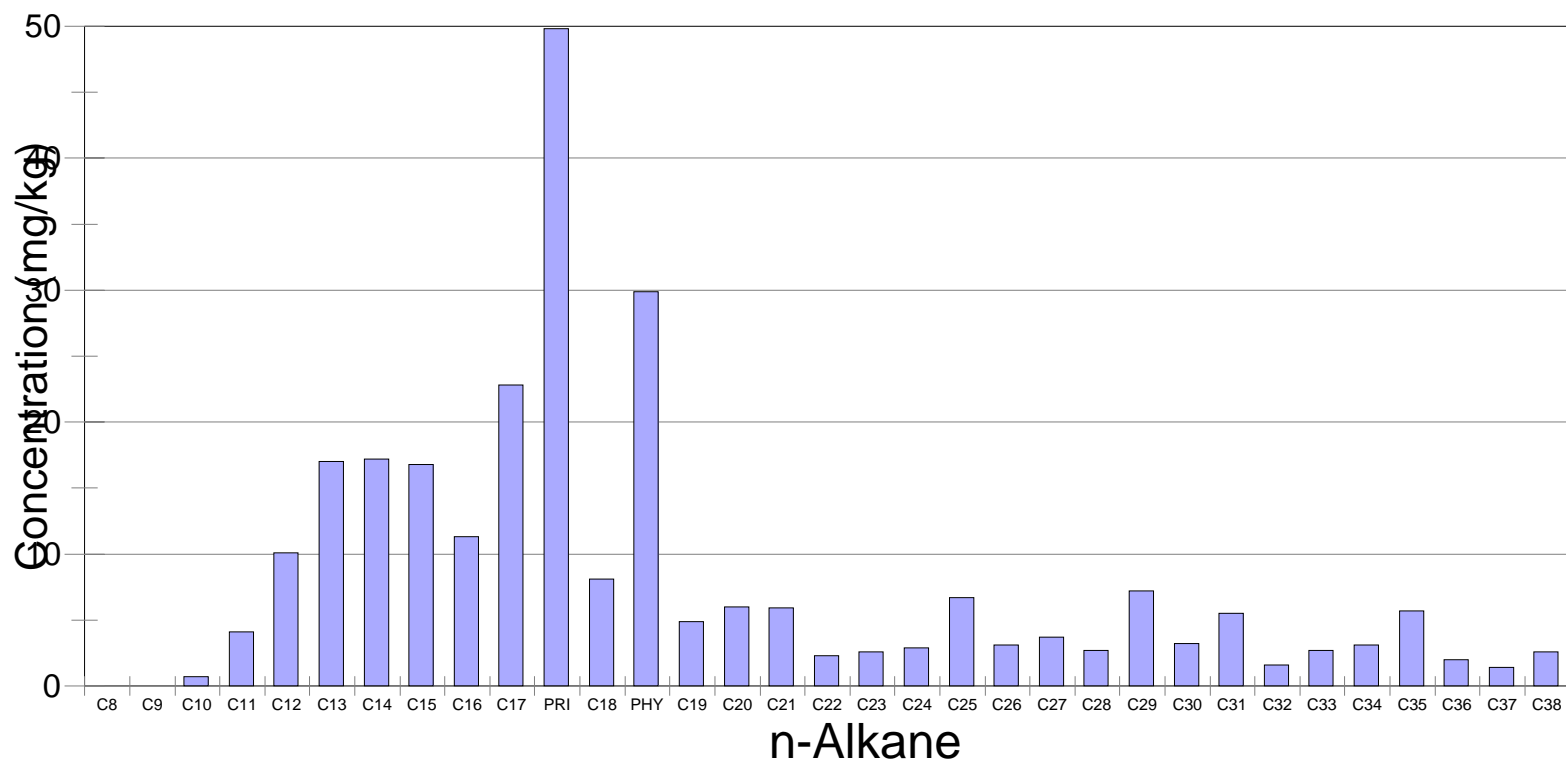




# Weathering in Untreated Area

## PEPCO Bioremediation

Area C, 0-3mm, 9/24/00



## Oil in the Sands





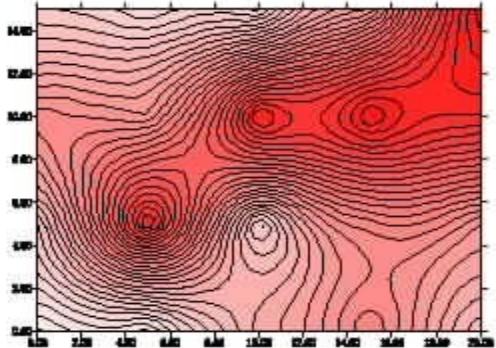
# Allegheny Forest Sites - McCracken Farm Loading the Biopod



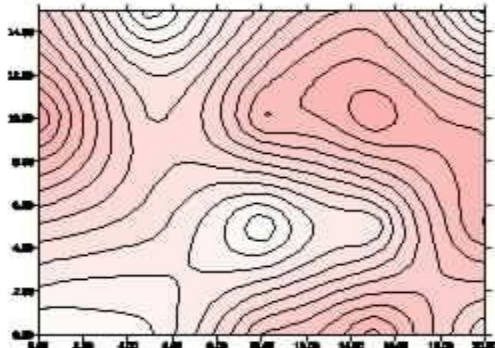


# Effect of Soil Mixing

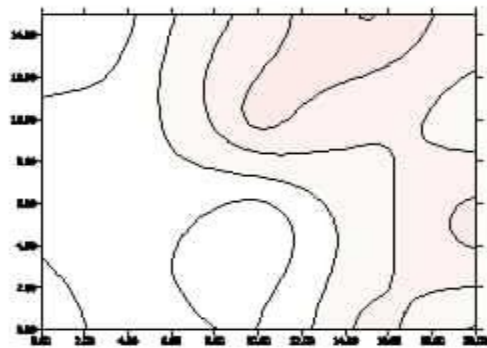
## TPH at McCracken #2



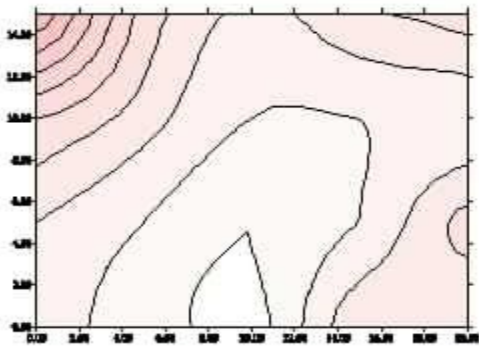
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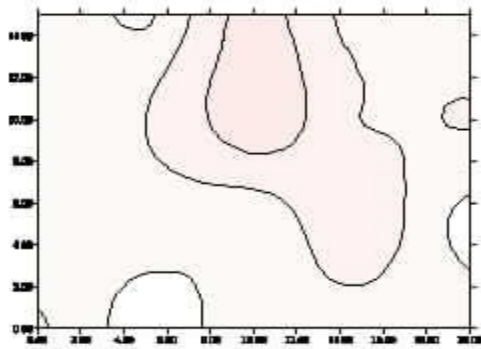
8-8-01



9-14-01



10-26-01



11-30-01

## Conclusion

- Biodegradation of Oiled Soil is an Effective Removal Technology if the Soil can be Worked.
- Biostimulation is Effective only at Surface Because of Oxygen Limitations.
- Gross Measurements of Oil Loss Have Limited Usefulness in Measuring Biodegradation
- Sophisticated Analytical Techniques are Needed
- Sampling is Key to Interpreting the Process.

## Conclusion (Cont.)

- Statistics are Necessary, but Should be Used With Caution.
- Natural Attenuation of Oiled Soil will Probably be a Very Long Process.
- Plant Root Growth may Accelerate Biodegradation, but More Work is Needed and the Jury is Still Out.



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# FIELD-SCALE STUDIES ON REMOVAL OF CREOSOTE FROM CONTAMINATED SOIL

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# Superfund Site

## Walker Springs Wood Treating Site





# Abandoned Equipment at Walker Springs Site



**Coal Tar Creosote Composition (EPA/625/7-90/011)**

	EPA/ORD Paper	
	Percent of PAH	Percent Total Creosote
<b>Group 1 PAHs</b>		<b>28.9 %</b>
Naphthalene	17.0 %	11.05 %
2-Methylnaphthalene	6.5 %	4.23 %
1-Methylnaphthalene	3.5 %	2.28 %
Biphenyl	1.9 %	1.24 %
2,3-Dimethylnaphthalene		
2,6-Dimethylnaphthalene		
<b>Group 2 PAHs</b>		<b>36.2 %</b>
Acenaphthylene	0.5 %	0.33 %
Acenaphthene	7.8 %	5.07 %
Fluorene***	6.0 %	3.9 %
Phenanthrene	19.4 %	12.61 %
Anthracene	2.5 %	1.63 %
2-Methylanthracene		
<b>Group 3 PAHs</b>		<b>24.4 %</b>
Fluoranthene**	11.8 %	7.67 %
Pyrene**	8.4 %	5.46 %
Benz(a)anthracene** (Chrysene)**	4.2 %	2.73 %
Benzo(b)fluoranthene		
Benzo(a)pyrene*		
<b>Heterocycles</b>		<b>10.3 %</b>
Dibenzofuran	5.2 %	3.38 %
Carbazole	5.1 %	3.32 %
Anthraquinone		
<b>Phenolics</b>		<b>&lt;1.0 %</b>

NOTES:

14

14

\*Not Biodegradable: Material Unchanged by Bacterial Action.

\*\*Biodegradation Indicator: Good Group 3 PAH-Degrading Soil; Bioaugmentation is Unnecessary.

\*\*\*Biotransformed Only: Material Changed, But Not Mineralized to Carbon Dioxide and Water.

**TABLE 1. Target Creosote Components Evaluated in Bioremediation Studies**

<b>Analyte Group</b>	<b>Creosote Compound</b>
Group 1 PAHs	Naphthalene, 1-Methylnaphthalene, 2-Methylnaphthalene, 2,6-Dimethylnaphthalene, Biphenyl
Group 2 PAHs	Acenaphthalene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, 2-Methylanthracene
Group 3 PAHs	Fluoranthene, Pyrene, Chrysene, Benzo(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Indeno(1,2,3-c,d)pyrene
Phenolics	o-Cresol, m-Cresol, p-Cresol, Pentachlorophenol (PCP)
Heterocycles	Dibenzofuran, Carbazole



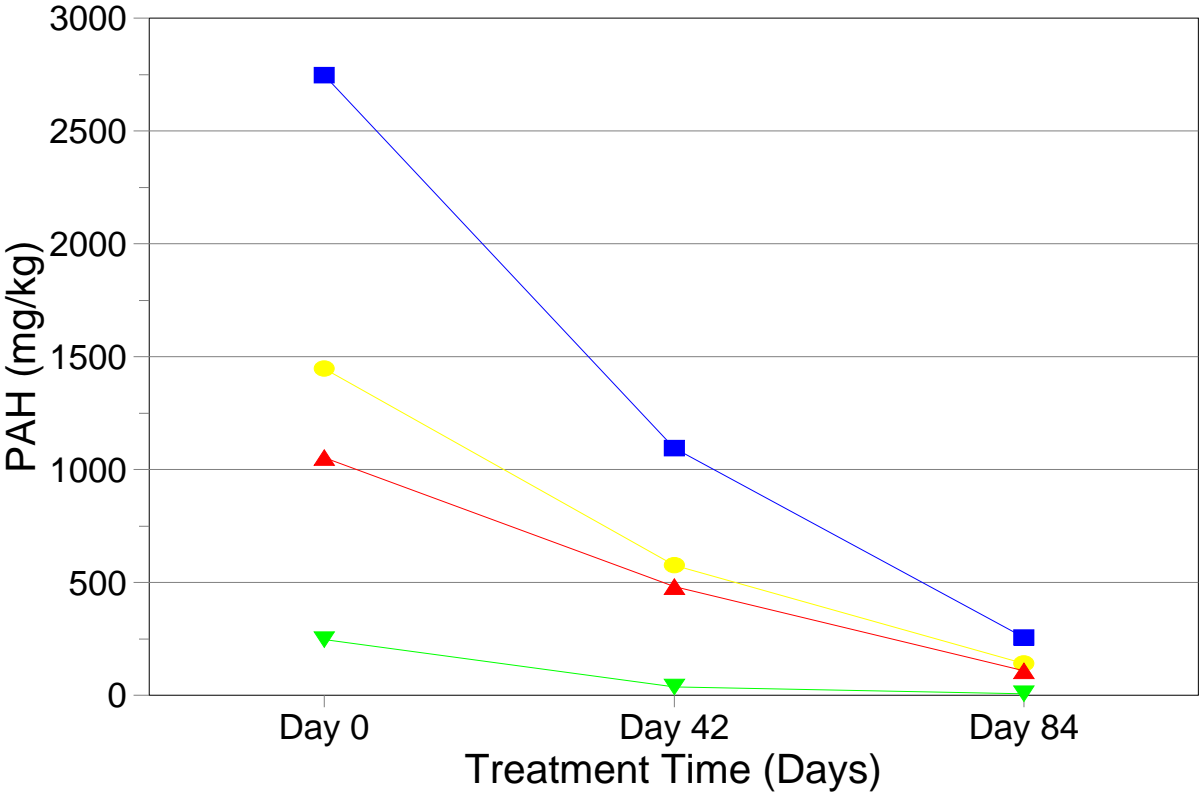
# Old Wood Chip Pile





# PAH Degradation in Bench-Scale Solid Phase Amended with Limestone, Sawdust and Nutrients

## Bench-Scale #4

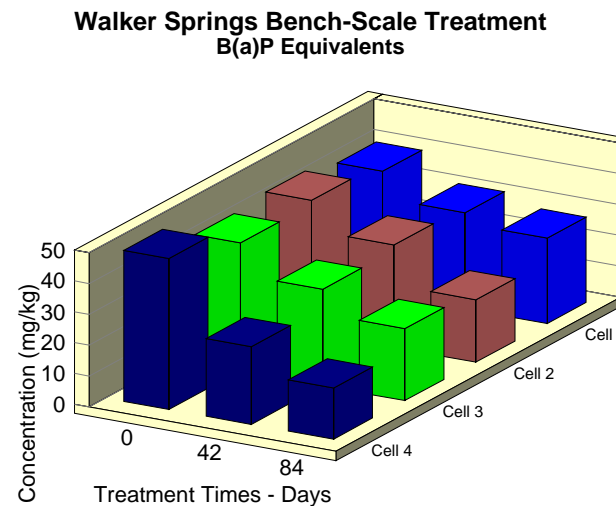
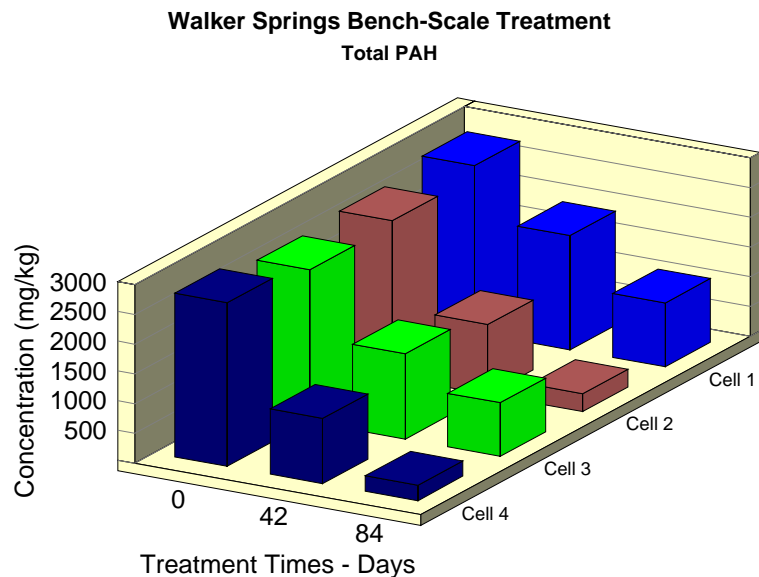


■ Total PAH    ▼ Group 1 PAH    ● Group 2 PAH    ▲ Group 3 PAH

# B(a)P Toxic Equivalency Factors

PAH	TEF
acenaphthylene	N
acenaphthene	6.5E-06
fluorene	9.5E-06
phenanthrene	N
anthracene	1.3E-06
pyrene	1.3E-05
chrysene*	0.001
benzo(a)pyrene*	1
benz(a)anthracene*	0.1
benzo(b)fluoranthene*	0.1
benzo(k)fluoranthene*	0.01
indeno(c,d-1,2,3)pyrene*	0.1
1,2-dibenz(a,h)anthracene*	1
*Carcinogen	

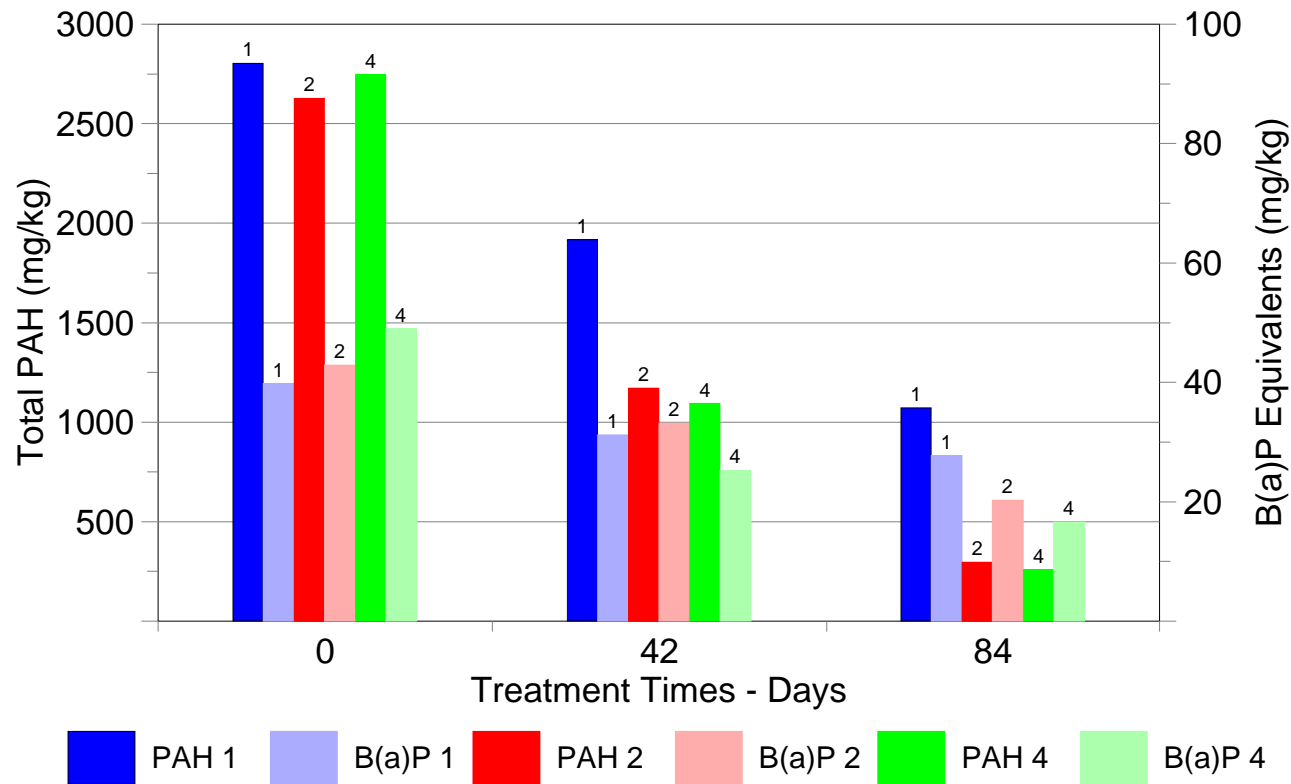
# Bench-Scale Results Showing Effect of Recipe



- Recipe 1: Limestone
- Recipe 2: LS & Nutrient
- Recipe 3: LS & Sawdust
- Recipe 4: LS & Nut.& SD

# Effect of Recipe on PAH Removal

## Walker Springs Bench-Scale Treatment





# Walker Springs Pilot Units





# Tilling Pilot Units

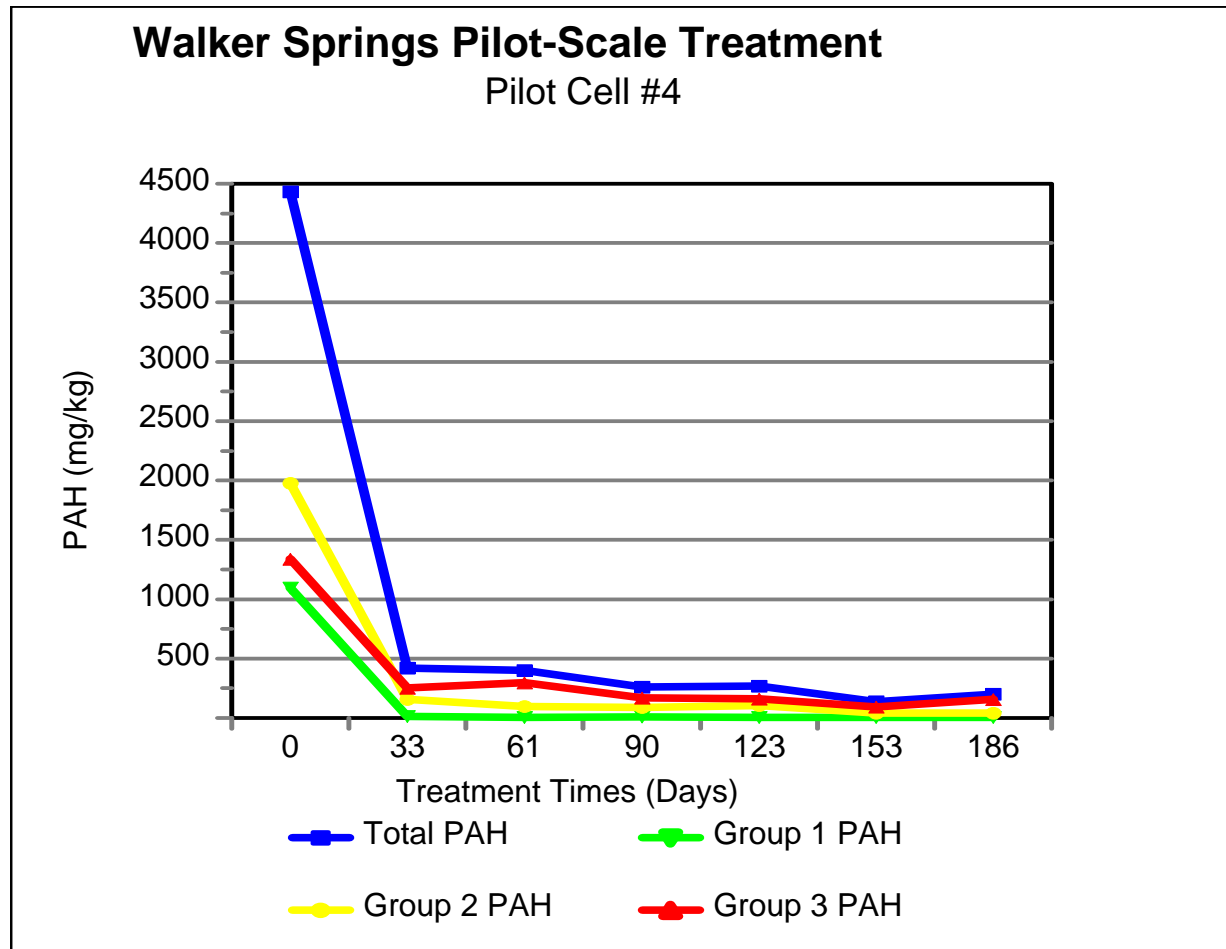


# Sampling Locations in Pilot Units





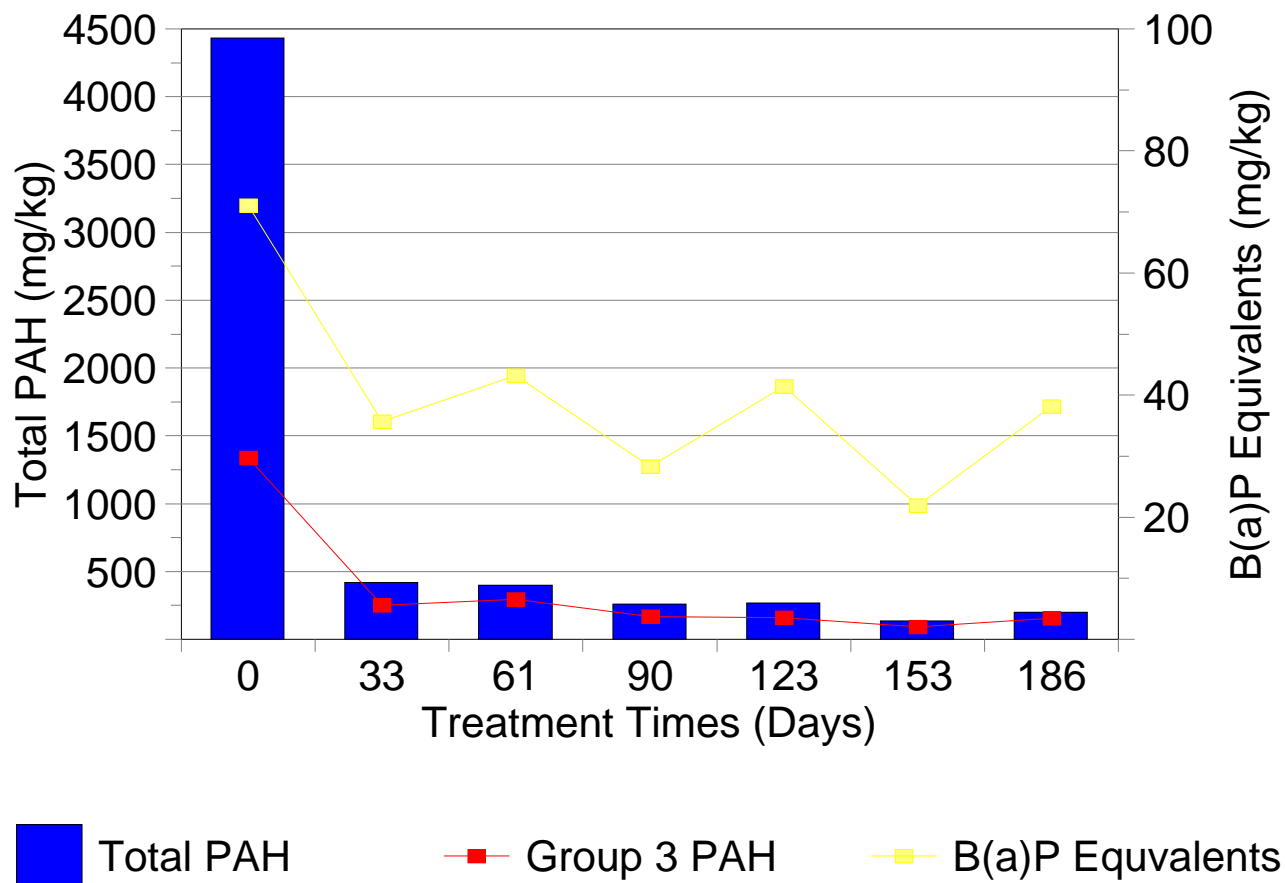
# PAH Degradation in Field-Scale Solid Phase Studies Using Recipe 4





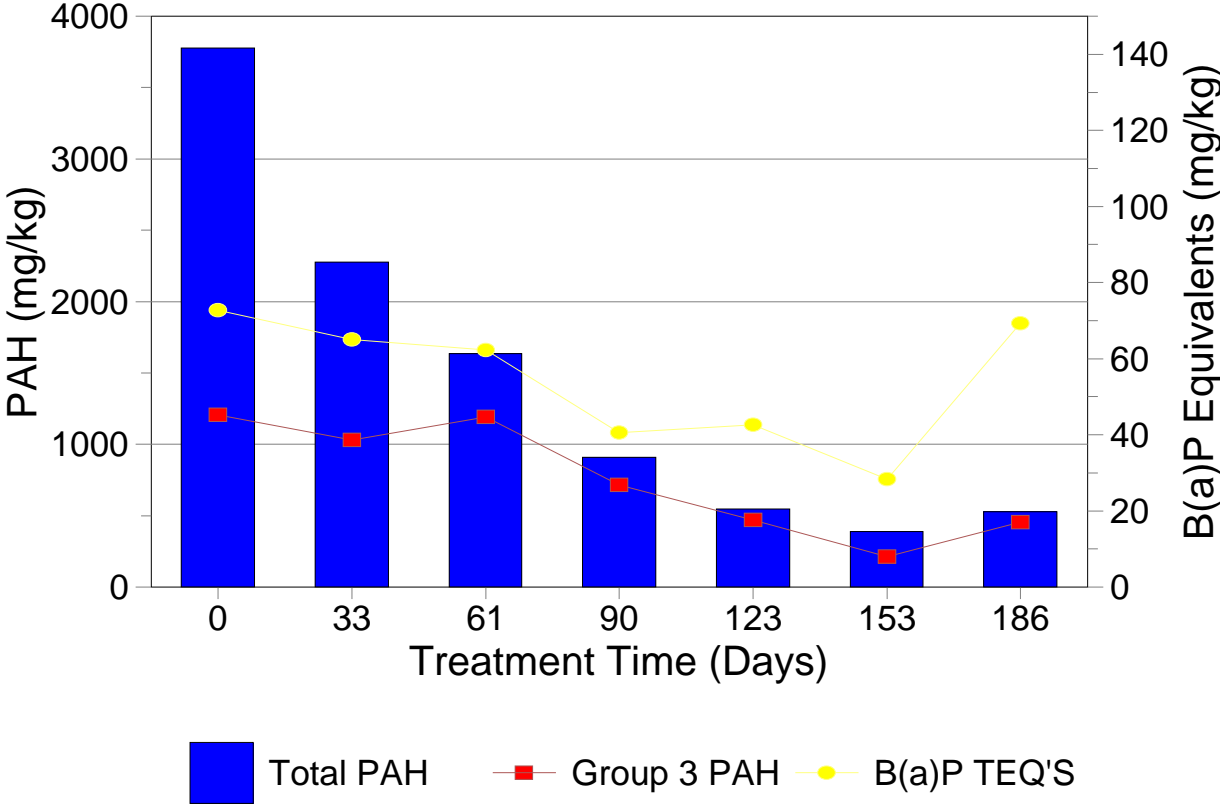
# PAH Degradation in Field-Scale Pilot Unit Using Recipe 4 – Added Limestone, Sawdust, Nutrients

## Walker Springs Pilot-Scale Treatment Pilot Cell #4



# PAH Degradation in Field-Scale Pilot Unit Using Recipe 3 –No Added Nutrients

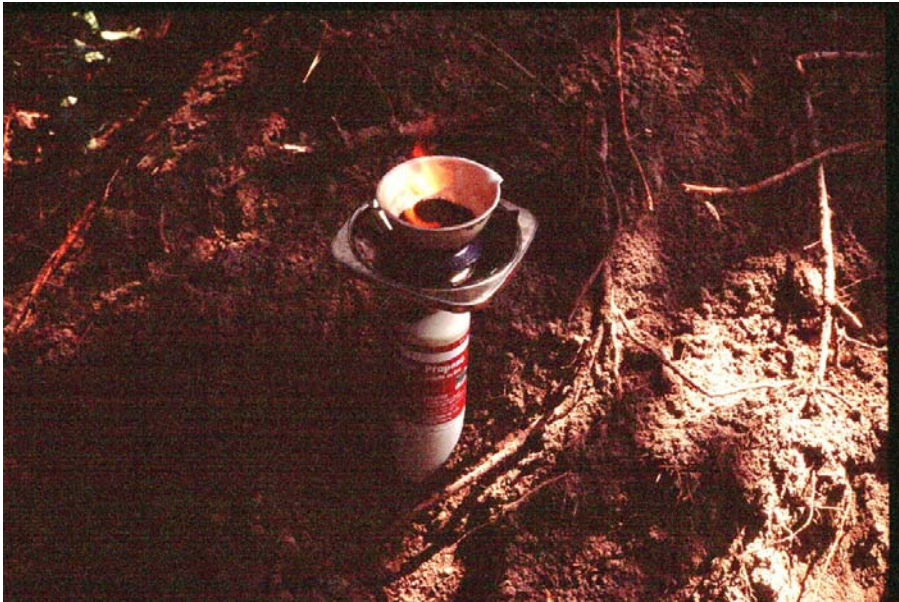
## Walker Springs Wood Treating Site Pilot-Scale Treatment Unit #3



# Preparation and Management of Soil Treatment



# Field Testing for Moisture Content



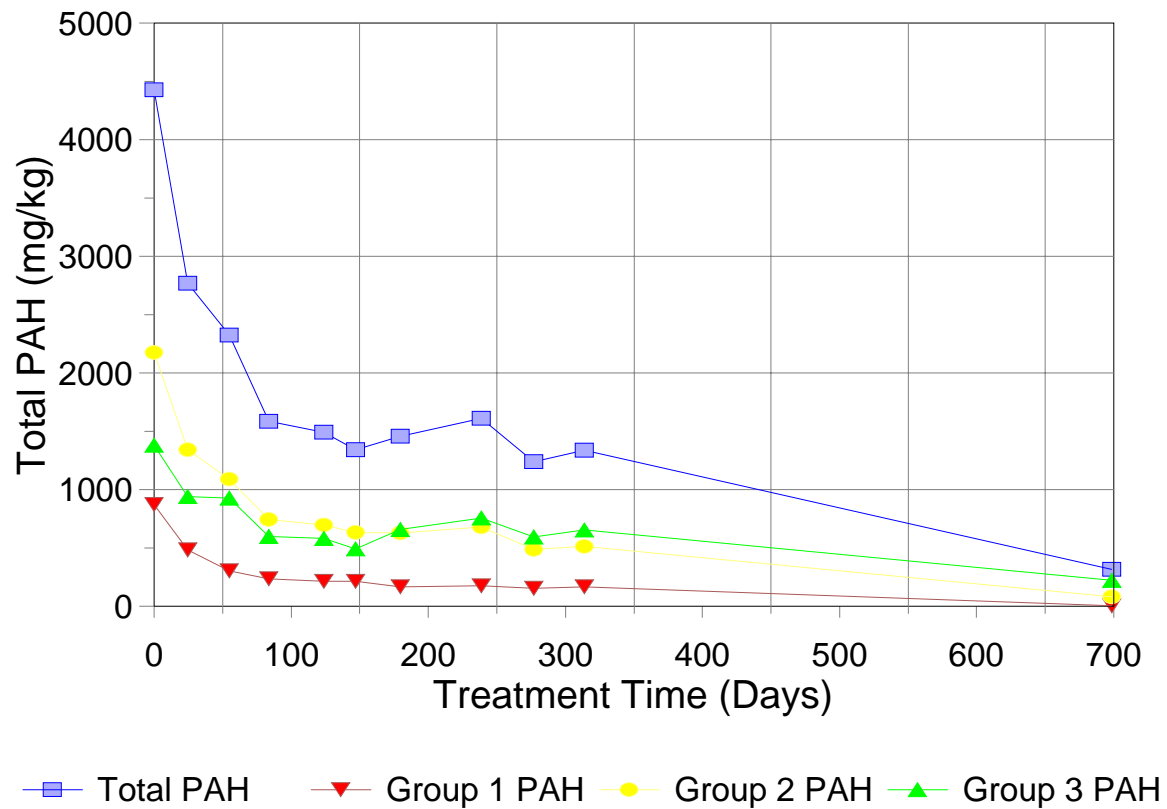


# Covering to Control Moisture

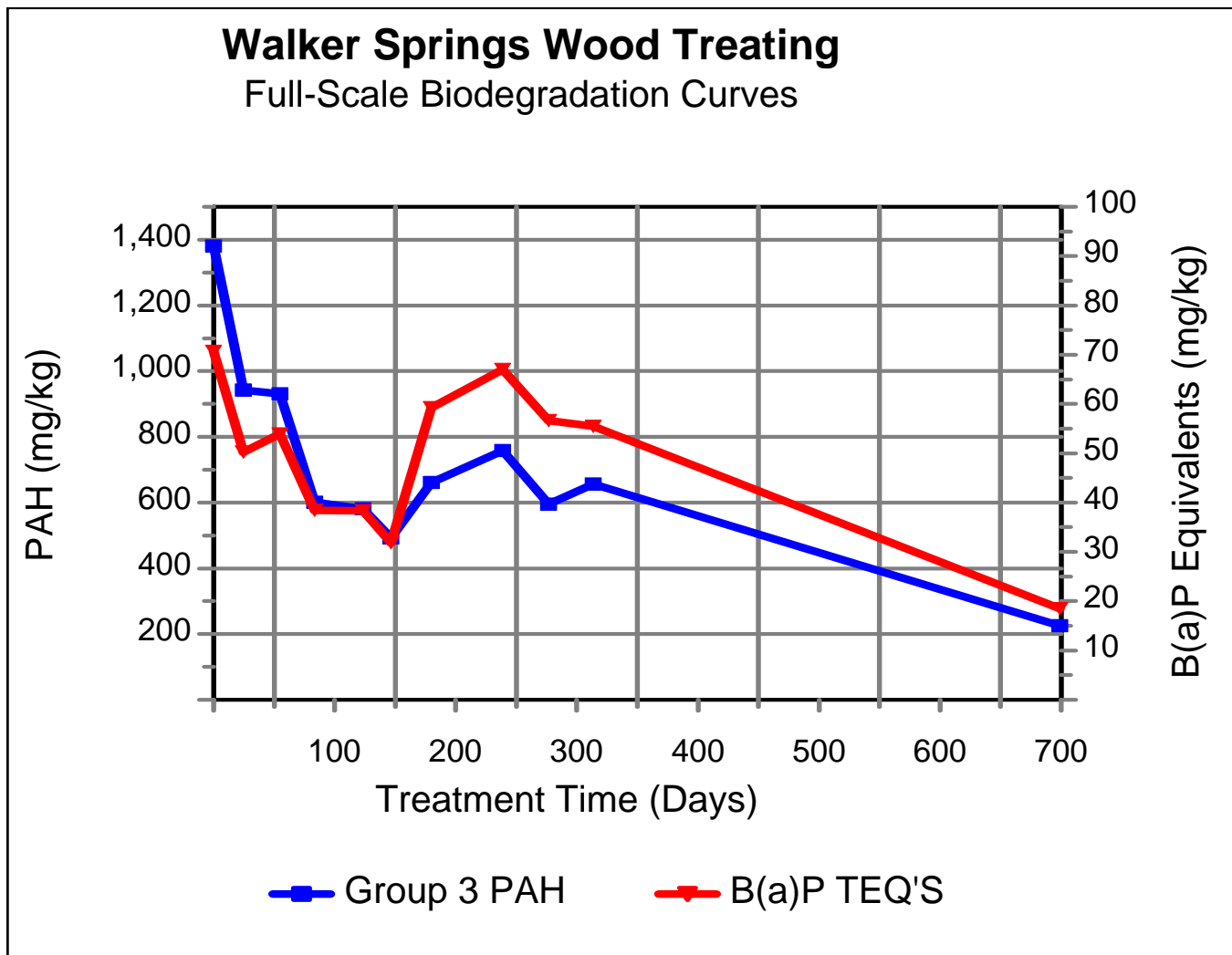


# PAH Degradation in Full-Scale Treatment

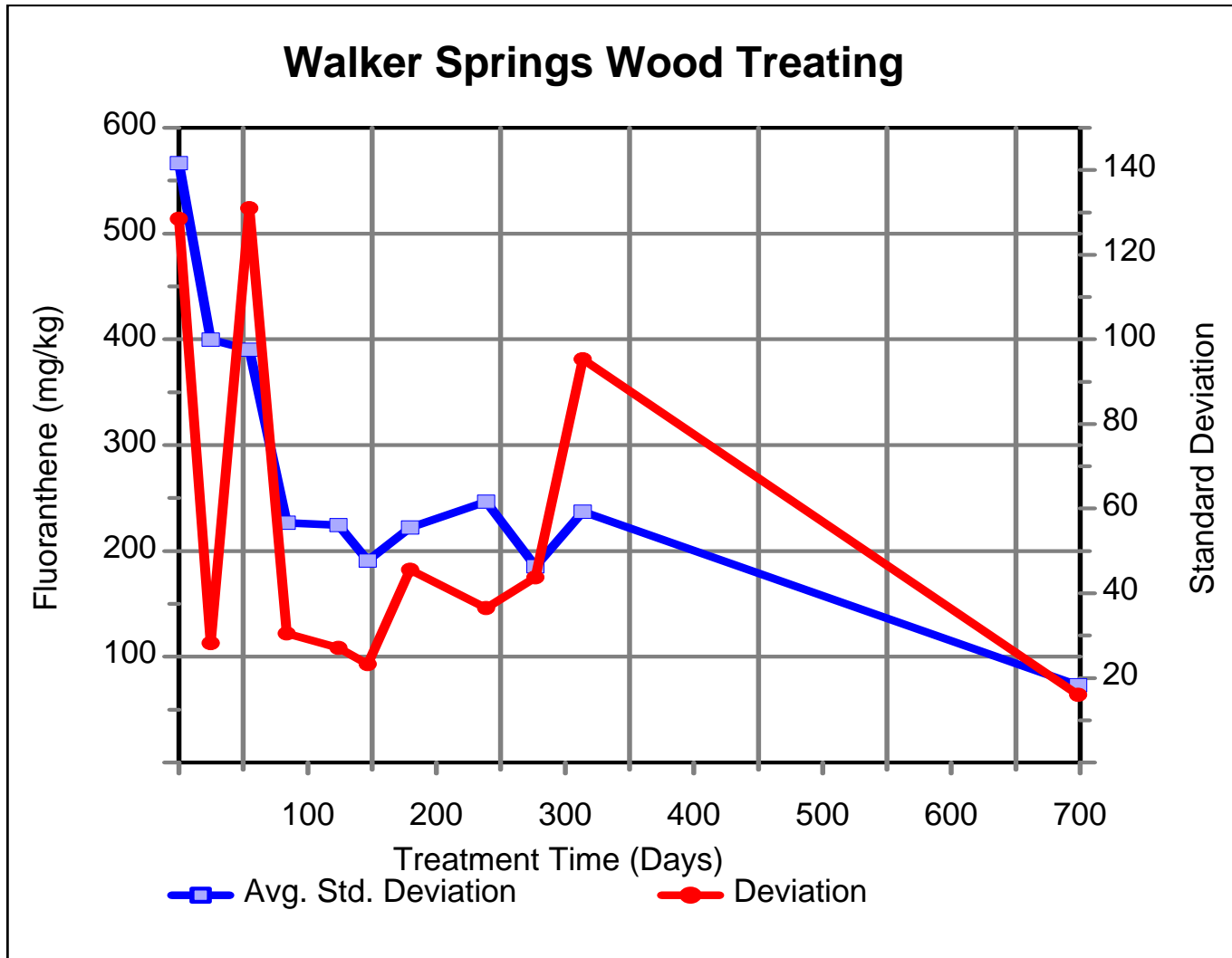
**Walker Springs Wood Treating**  
Full-Scale Biodegradation Results



# Group 3 and B(a)P Equivalents Degradation in Full-Scale Treatment

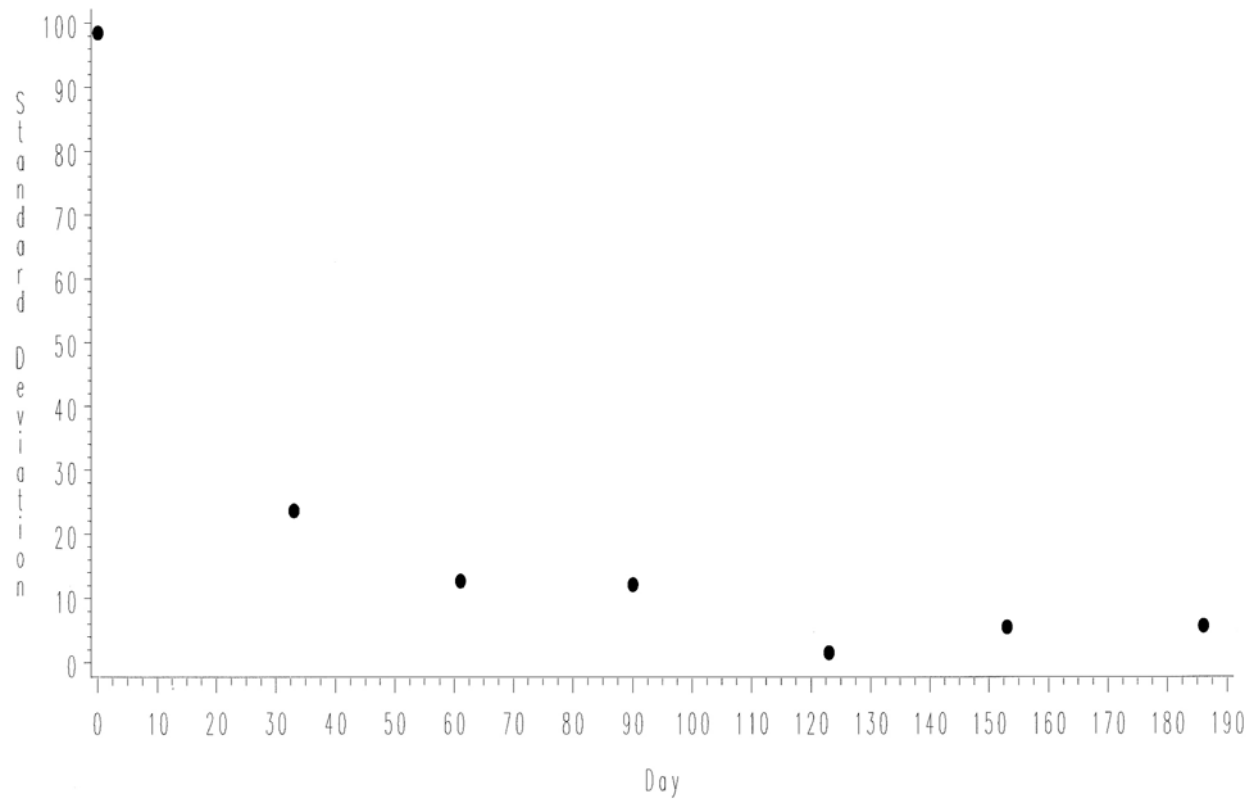


# Change in Data Variation With Time for Fluoranthene in Full-Scale Treatment



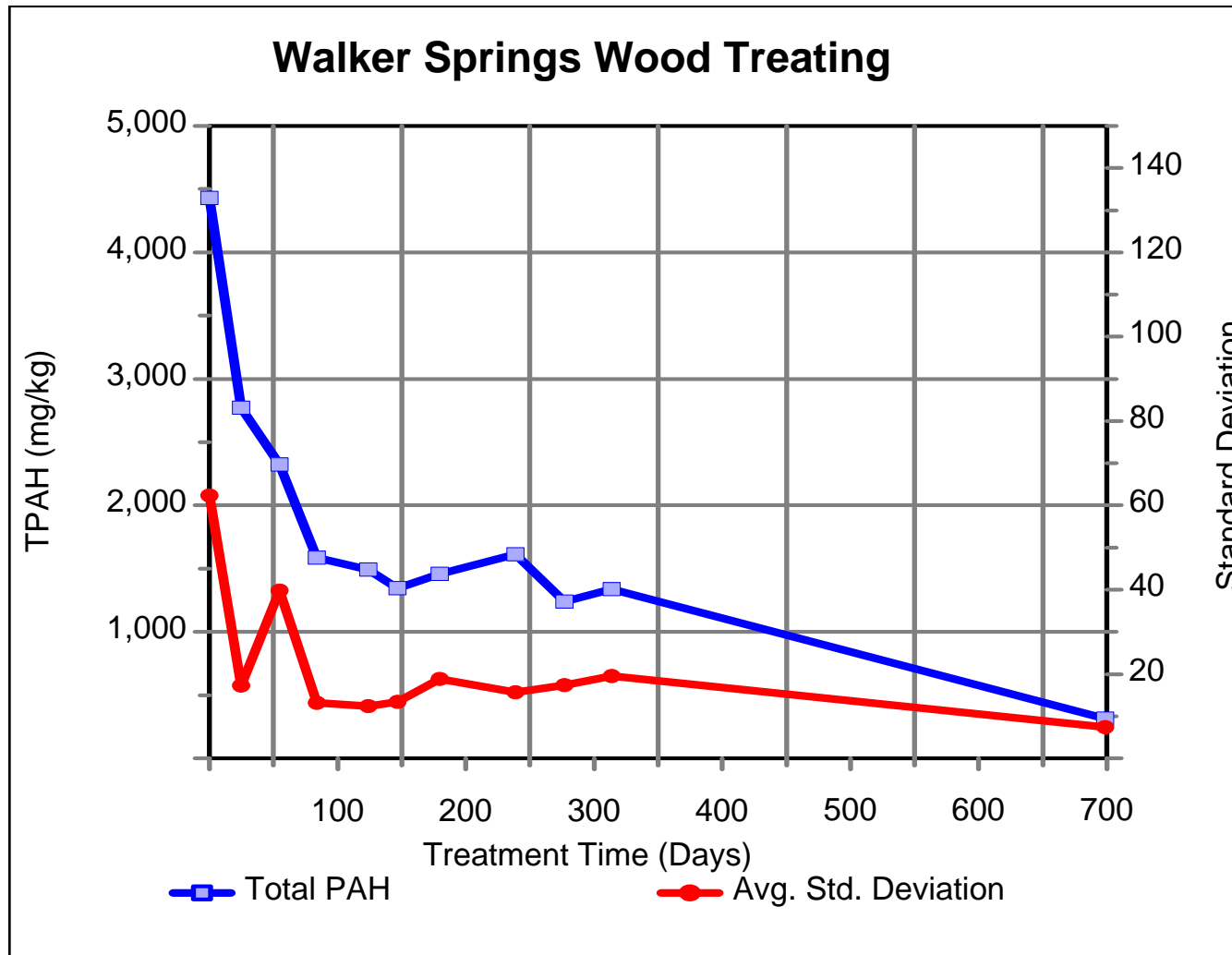
# Plot of Standard Deviation vs. Day

Walker Springs Pilot Study - Unit #4  
COMPOUND=fluoranthene

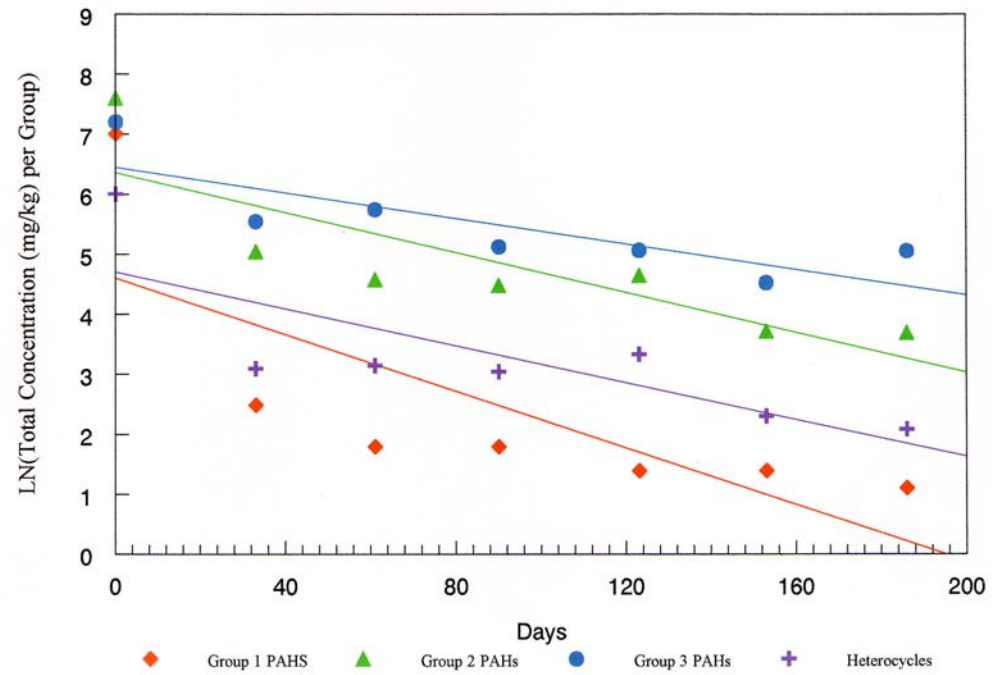




# Change in Data Variation With Time for TPAH in Full-Scale Treatment

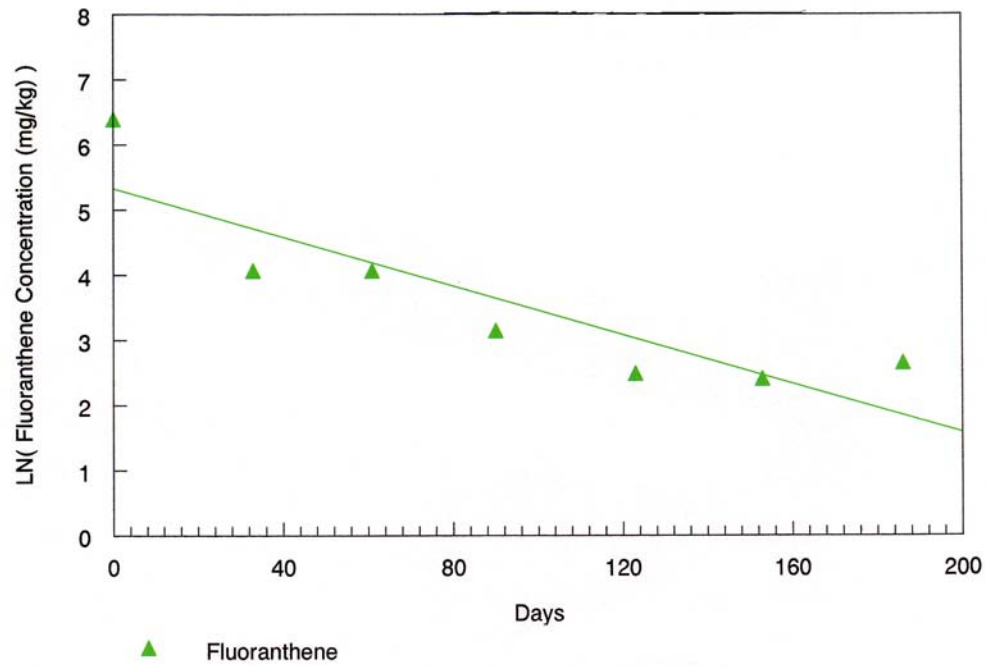


### Regression of Total Concentration Per Group vs. Time Walker Springs Pilot Study - Unit #4

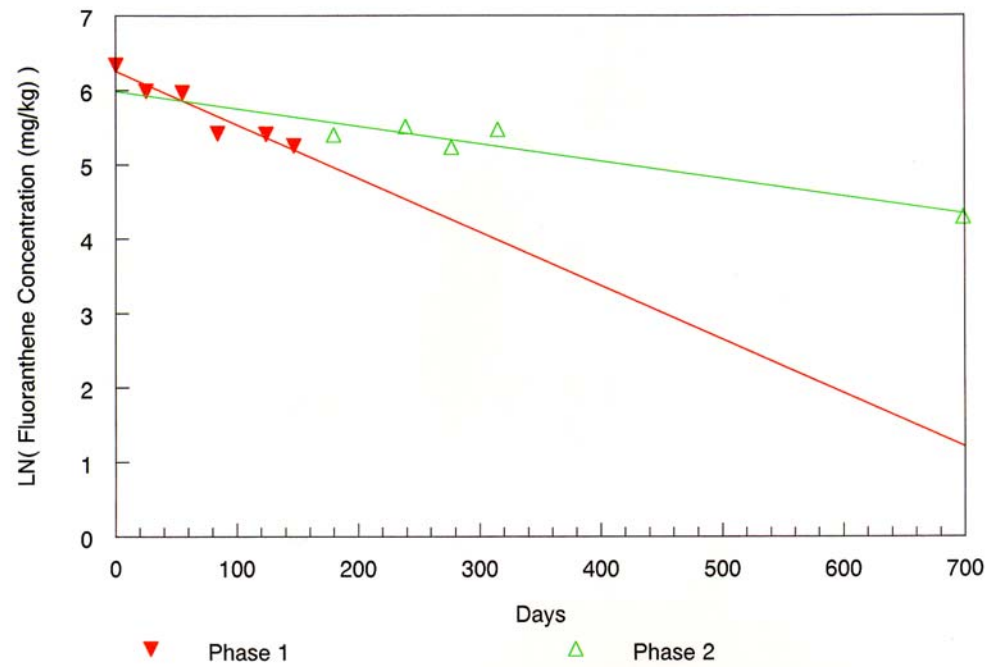


# Regression of Fluoranthene vs. Time

## Walker Springs Pilot Study - Unit #4



## Regression of Fluoranthene vs. Time Walker Springs Field Unit





**Walker Springs Field Treatment Unit Bioremediation  
Calculation of Half-Life Based on Semi-Logarithmic Regression Studies**

<b>Compound</b>	<b>Days 0 to 147</b>		<b>Days 180 to 699</b>	
	<b>Half-life (days)</b>	<b>R-Squared</b>	<b>Half-life (days)</b>	<b>R-Squared</b>
Group 1 PAHs	78	0.8251	102	0.9583
Group 2 PAHs	88	0.9004	165	0.9720
Group 3 PAHs	107	0.9162	301	0.9352
Heterocycles	82	0.8115	169	0.9640
Phenanthrene	80	0.9388	133	0.9769
<b>Fluoranthene</b>	<b>96</b>	<b>0.9096</b>	<b>295</b>	<b>0.9062</b>
Pyrene	99	0.8892	330	0.9329
Chrysene	114	0.9120	257	0.9372
Benz(a)anthracene	110	0.9564	267	0.8768
	<b>Days 0 to 699</b>			
<b>Fluoranthene</b>	<b>289</b>	<b>0.7929</b>		

# Conclusions

- Walker Springs Cleaned Up
- PAH Degraded or Immobilized in a Reasonable Timeframe
- Addition of Bulking Agent and Nutrients Effective
- Bioaugmentation with Active Soil is Effective
- Destruction of Carcinogenic PAH Can Be Done But Special Care May Be Necessary
- Sampling May Be a Problem in Interpreting Results

# Cleanup Criteria for PAH in Soil

Carcinogenic Equivalents: 8.8 mg/kg (Commercial or Industrial)

Individual PAH:

PAH Soil Cleanup Criteria	Maryland Delisting Level (TC) (mg/L)	Delisting Level x1%Koc (mg/Kg)	ATSDR 11/14/94 Ind. Goal (mg/Kg)	R III 8/7/96 Ind. Goal (mg/Kg)
NON-CARCINOGEN (Group)				
Naphthalene (1)	60			82000
Acenaphthylene (2)				
Acenaphthene (2)	100	3890		120000
Fluorene (2)				82000
Phenanthrene (2)	0.1	4		
Anthracene(2)	600	23340		610000
Fluoranthene (3)*	60	2334		82000
Pyrene (3)*	60	2334		61000
CARCINOGEN (Group)				
Benz(a)anthracene (3)*	0.0002	0.01	2.85	7.8
Chrysene (3)*	0.06	2.33	4.90	780
Benzo(b)fluoranthene (3)	0.006	0.23	5.35	7.8
Benzo(k)fluoranthene (3)	0.2	7.78	2.62	78
Benzo(a)pyrene (3)	0.01	0.39	2.35	0.78
Benzo(g,h,i)perylene (3)				
Indeno(1,2,3-cd)pyrene (3)	0.006	0.23	1.60	7.8
Dibenz(a,h)anthracene (3)	0.0001	0.00	1.80	0.78