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

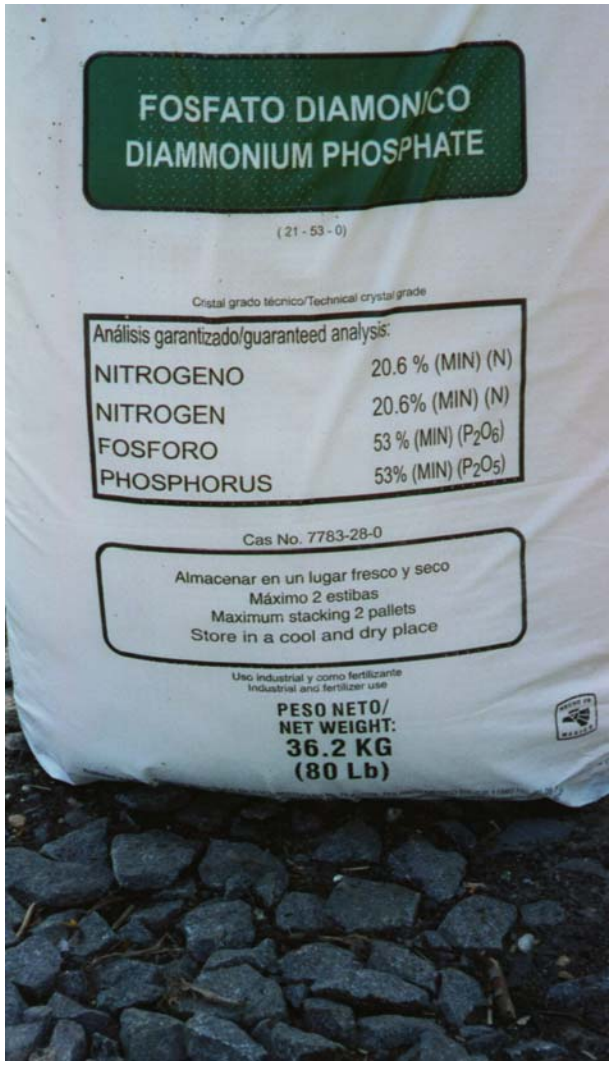
Total Nutrient Needed	C:N:P Ratio	N (kgs.)	P (kgs.)	N (lbs.)	P (lbs.)
	60:1:0.2	199	40	438	88

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.

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

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

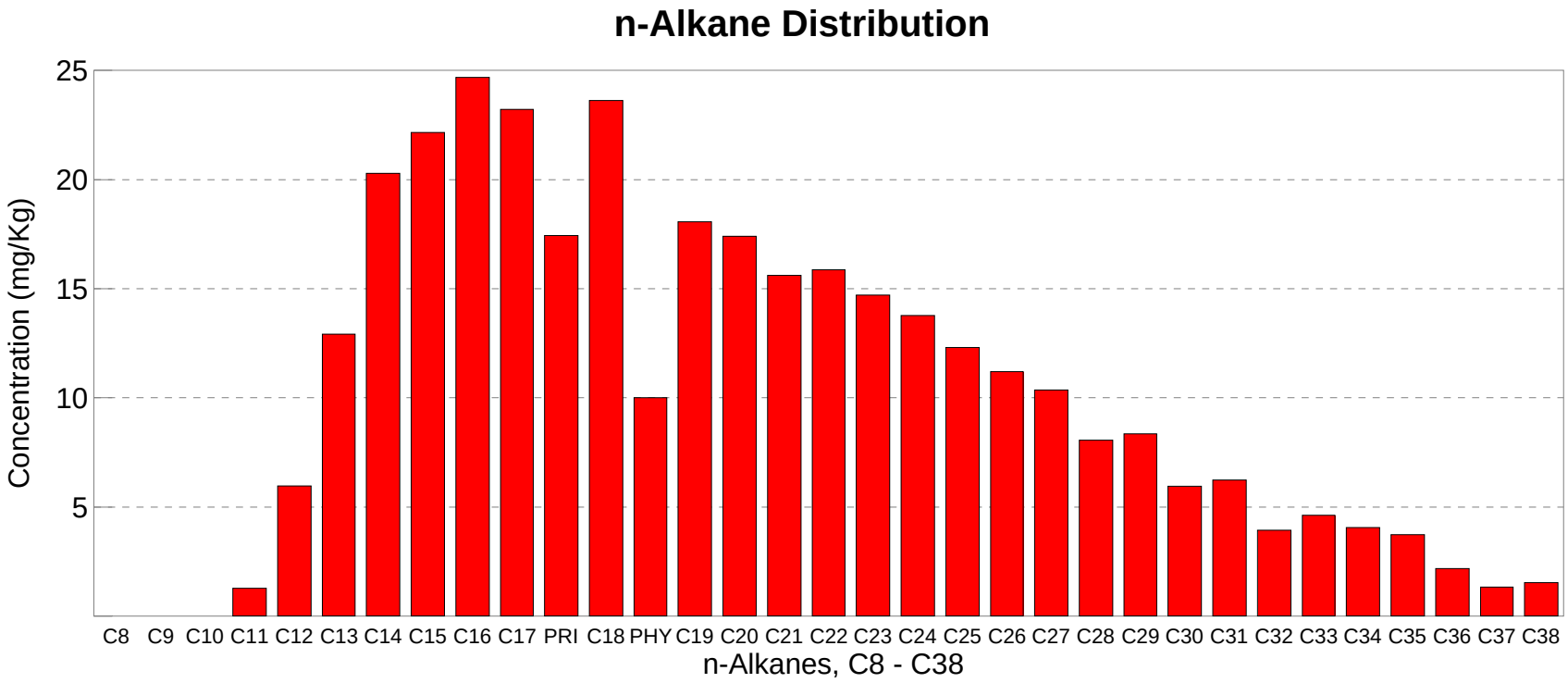
Phase 3 Focuses on very low criteria for TPH and PAH (10 mg/kg)
Also on low ppm levels for specific PAH's through NOAA's "SQuiRTs"

Sorbents

Berming & Diking

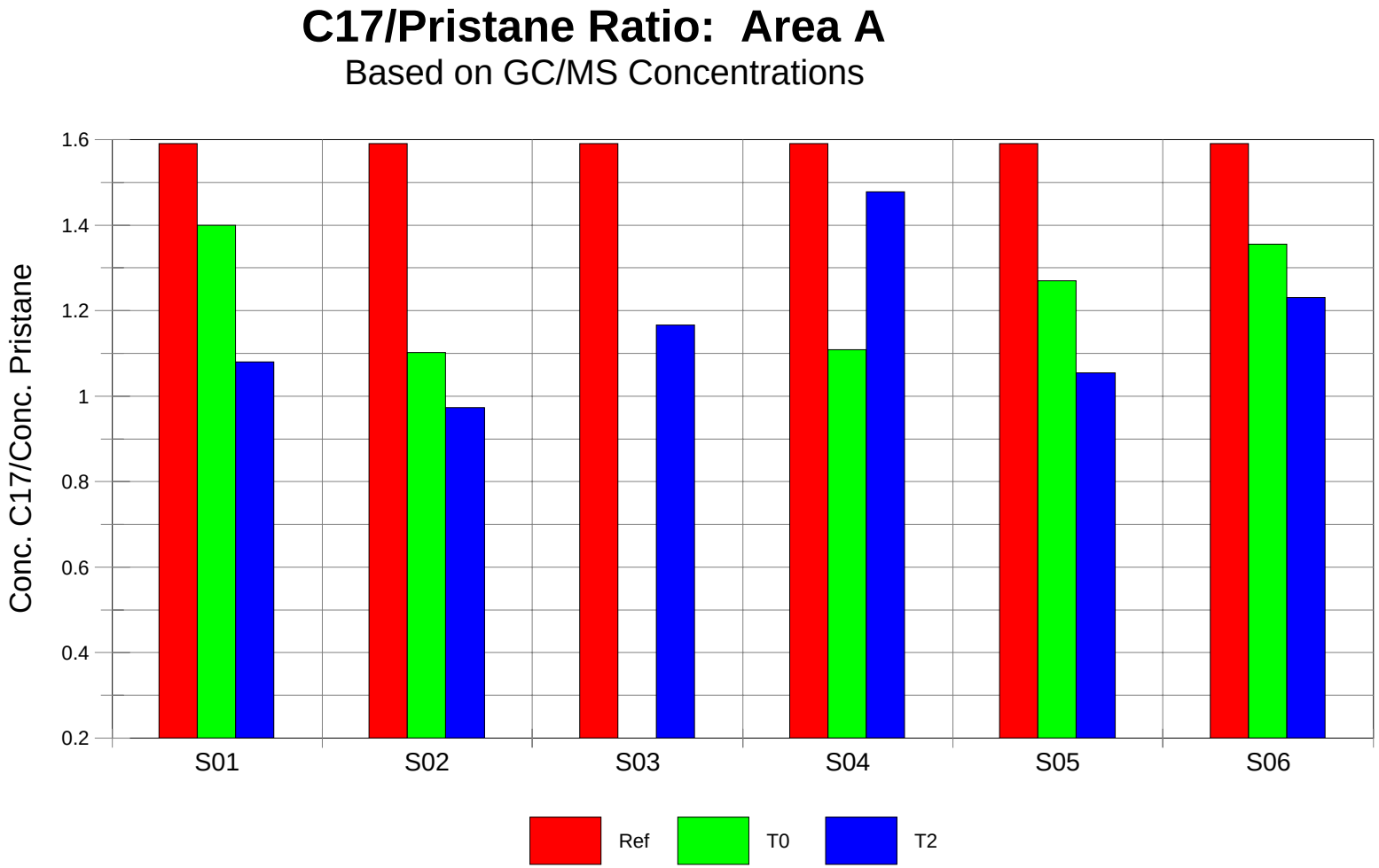
Vacuuming

W1BS05 Alkanes in Oil

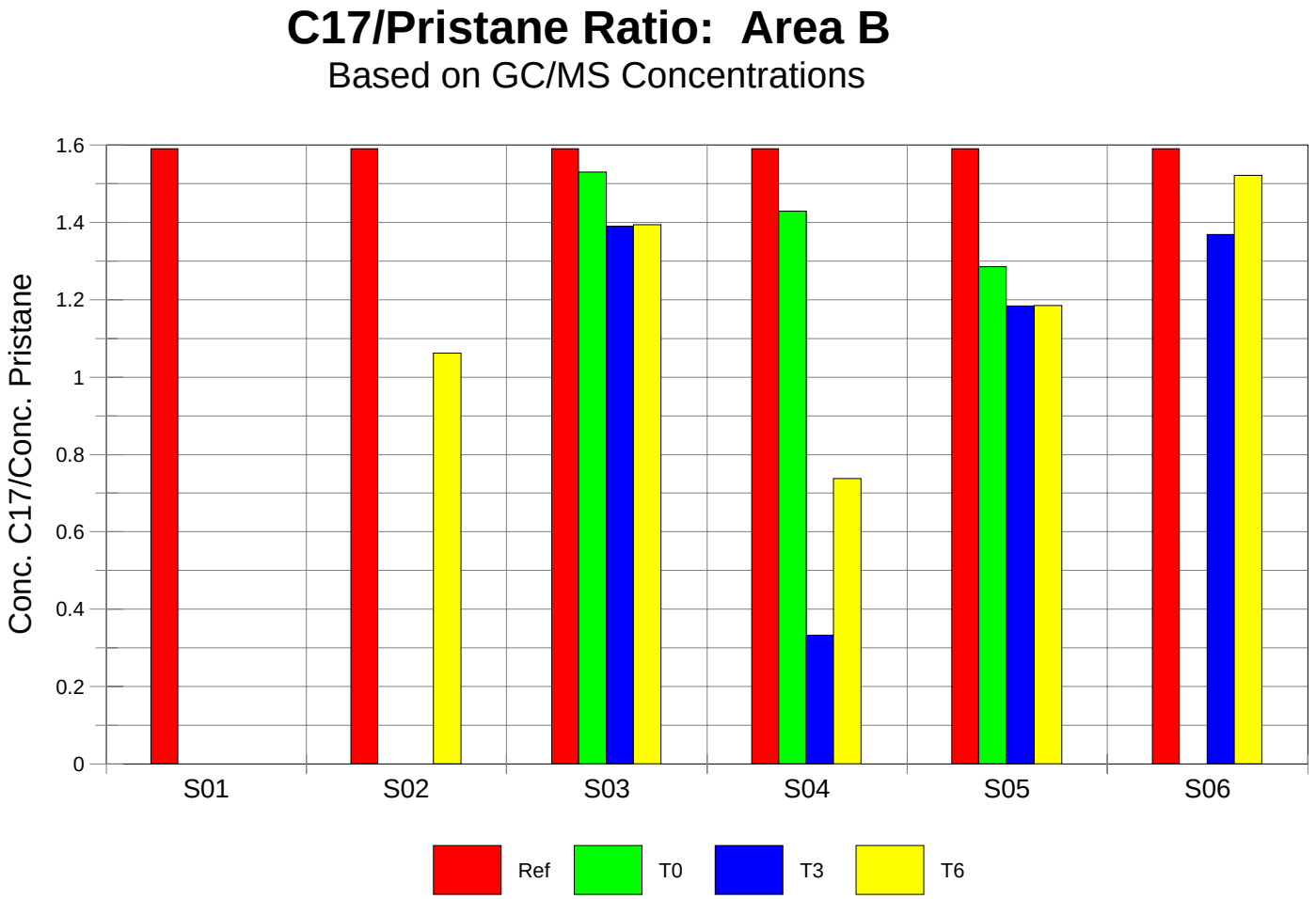


Marsh Sampling Station

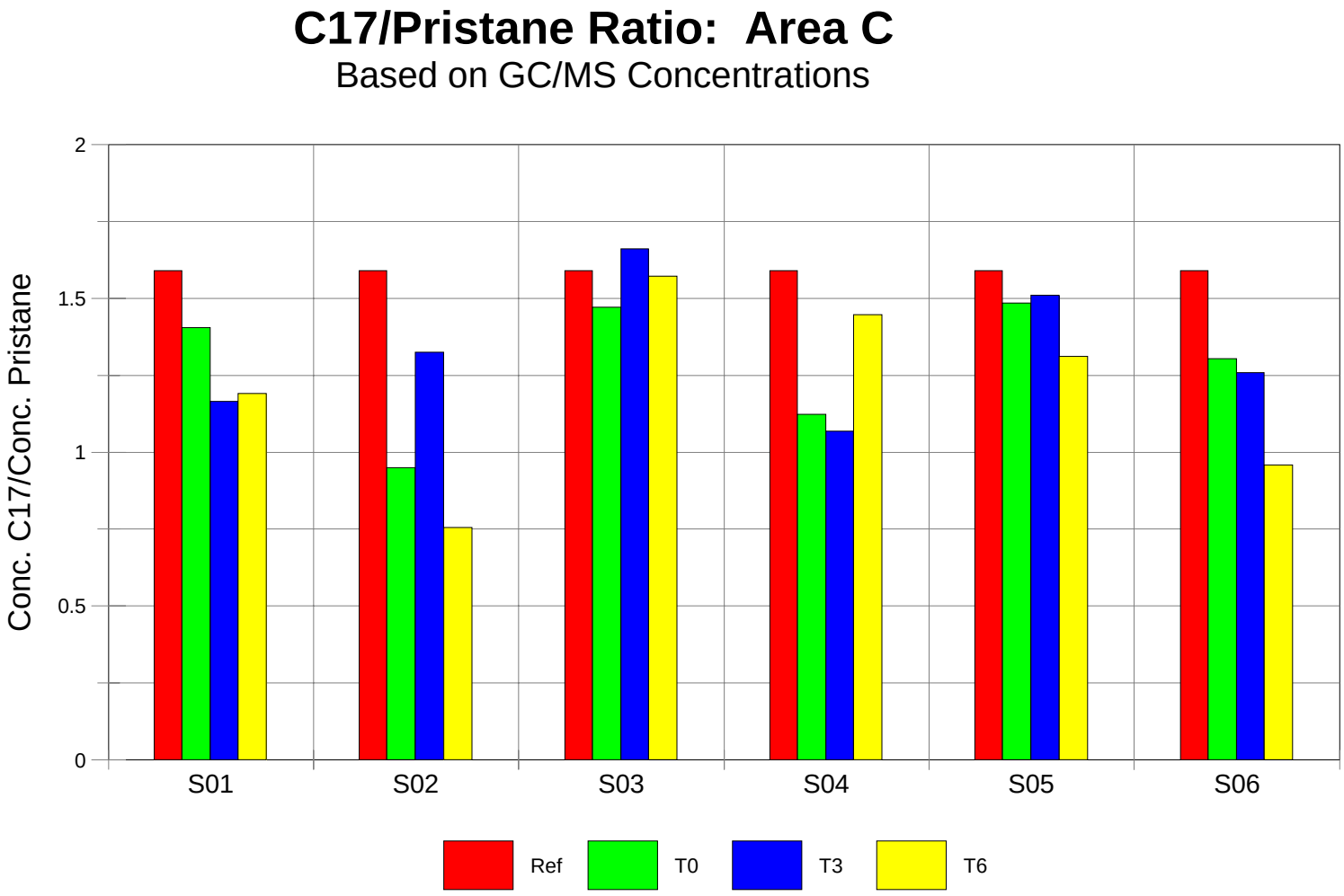
Biodegradation in Mechanical Removal Area



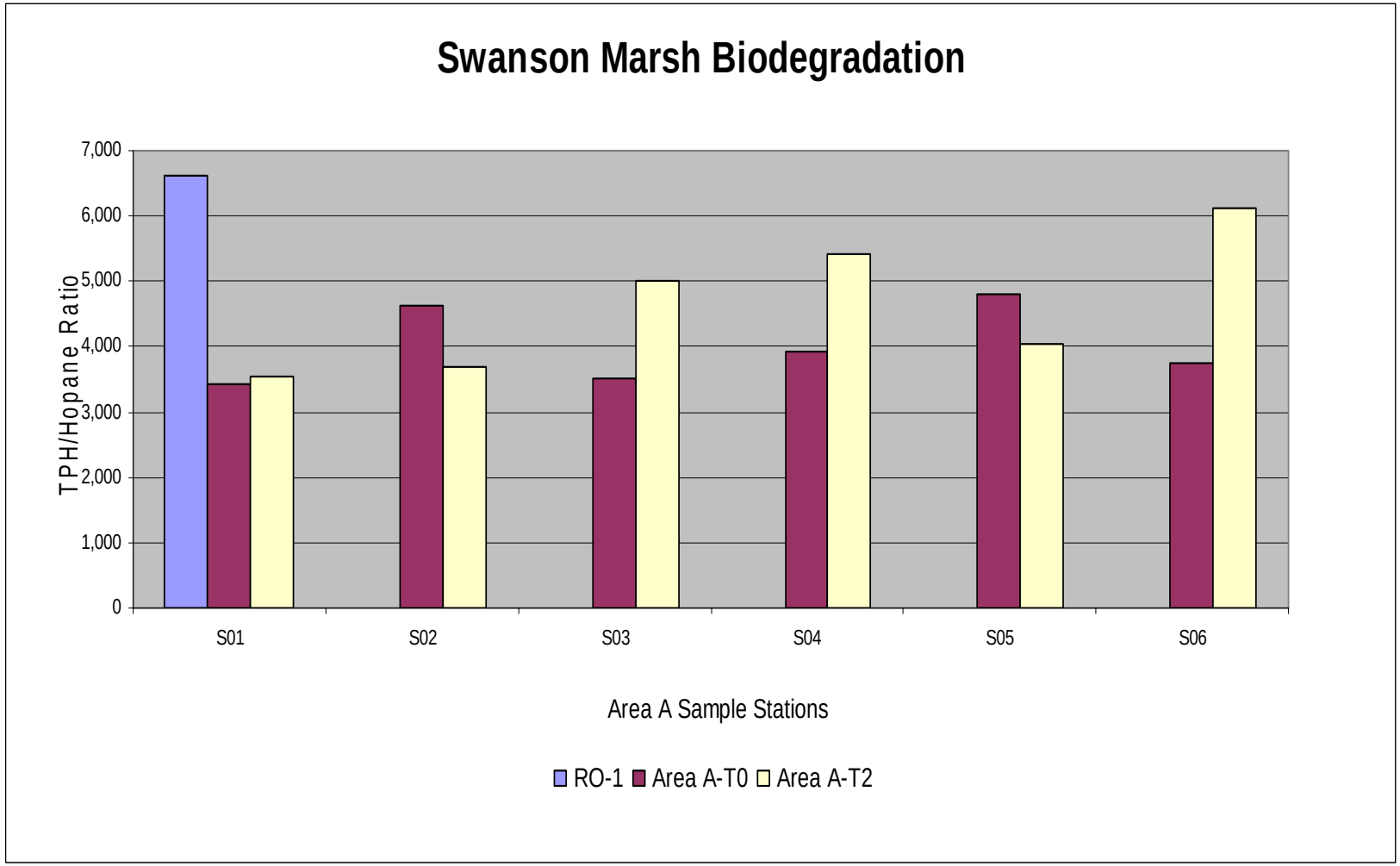
Biodegradation in Treated Area



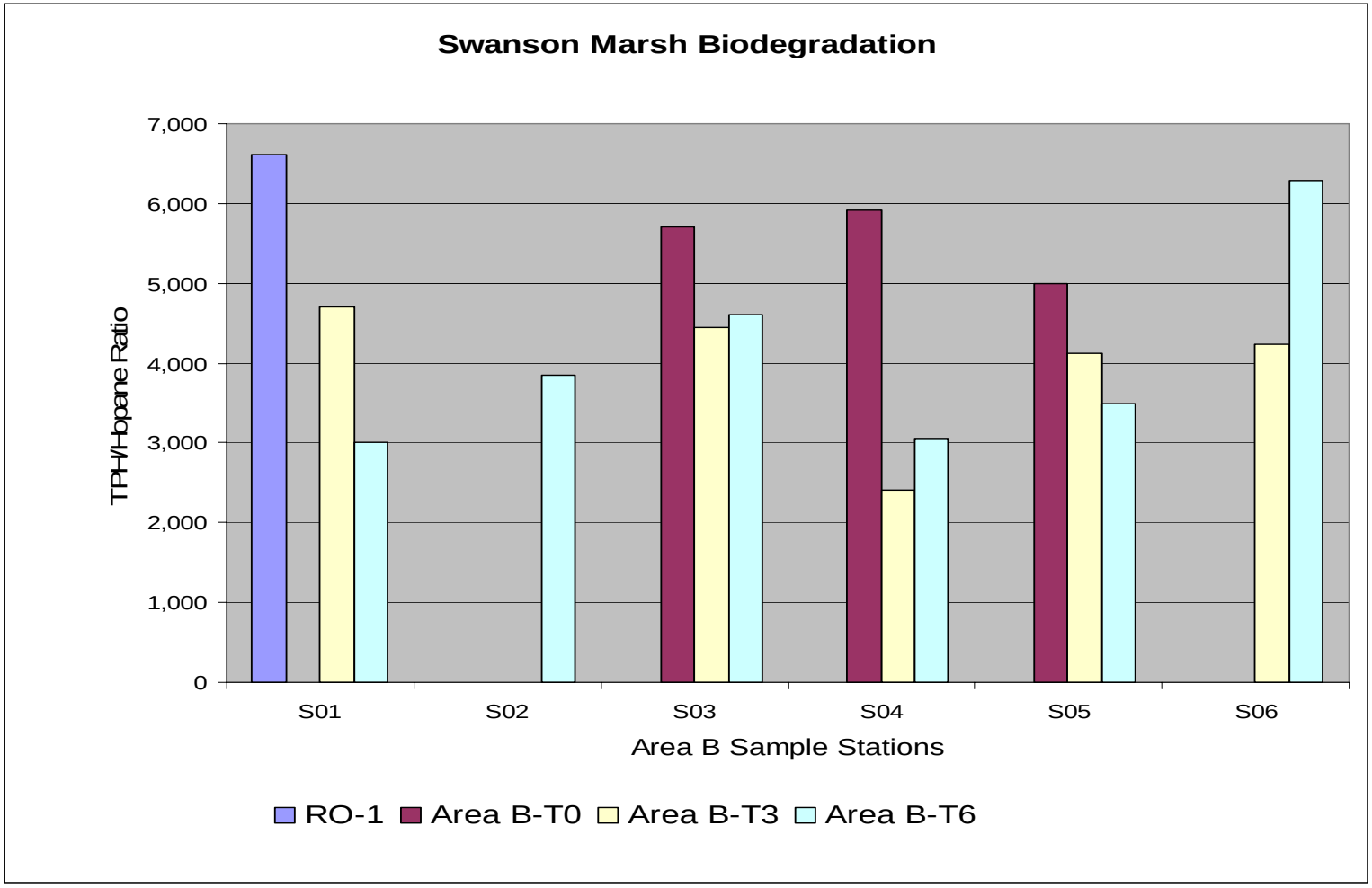
Biodegradation in Non-Treated Area



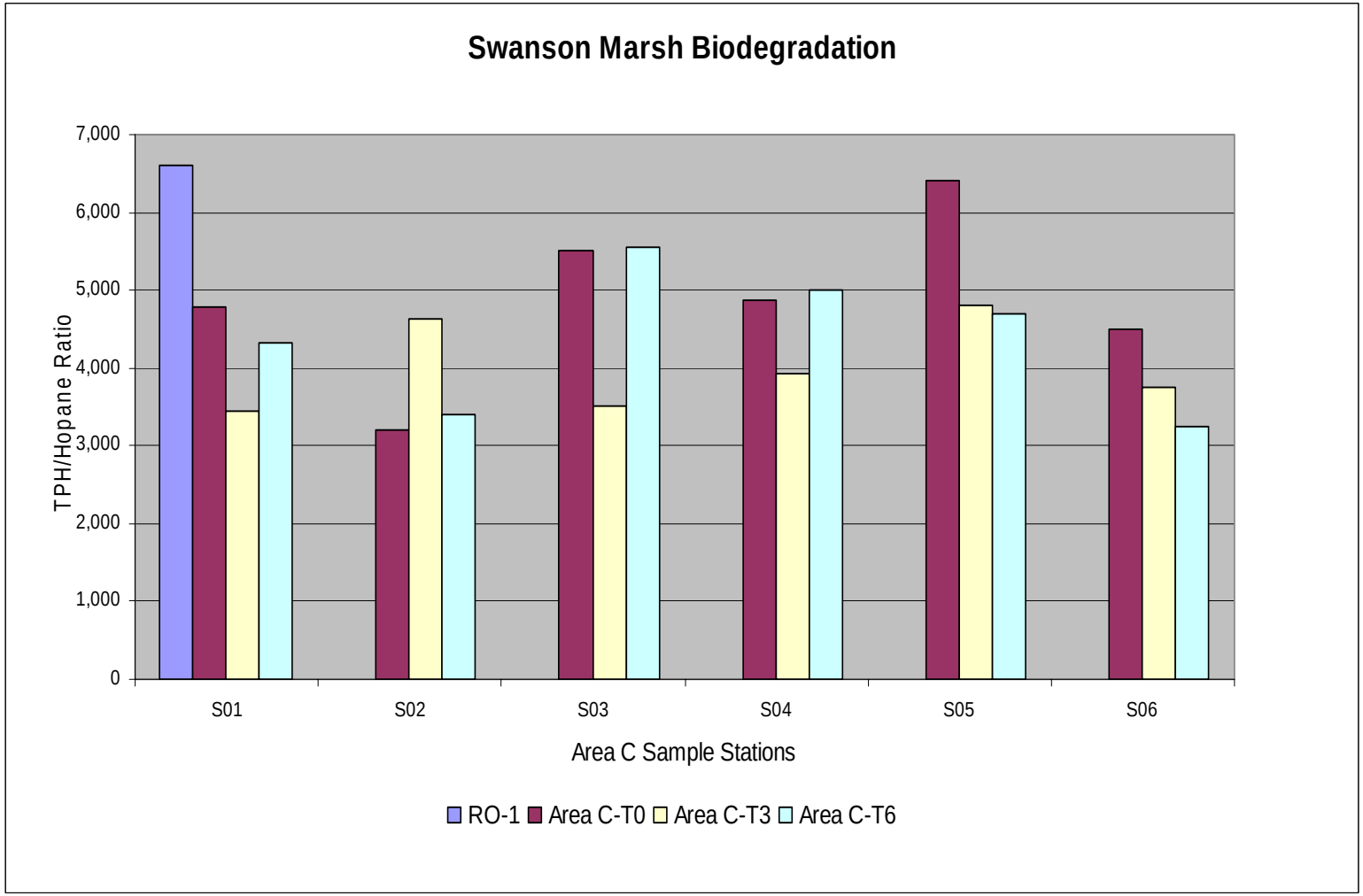
Area A –TPH/Hopanes



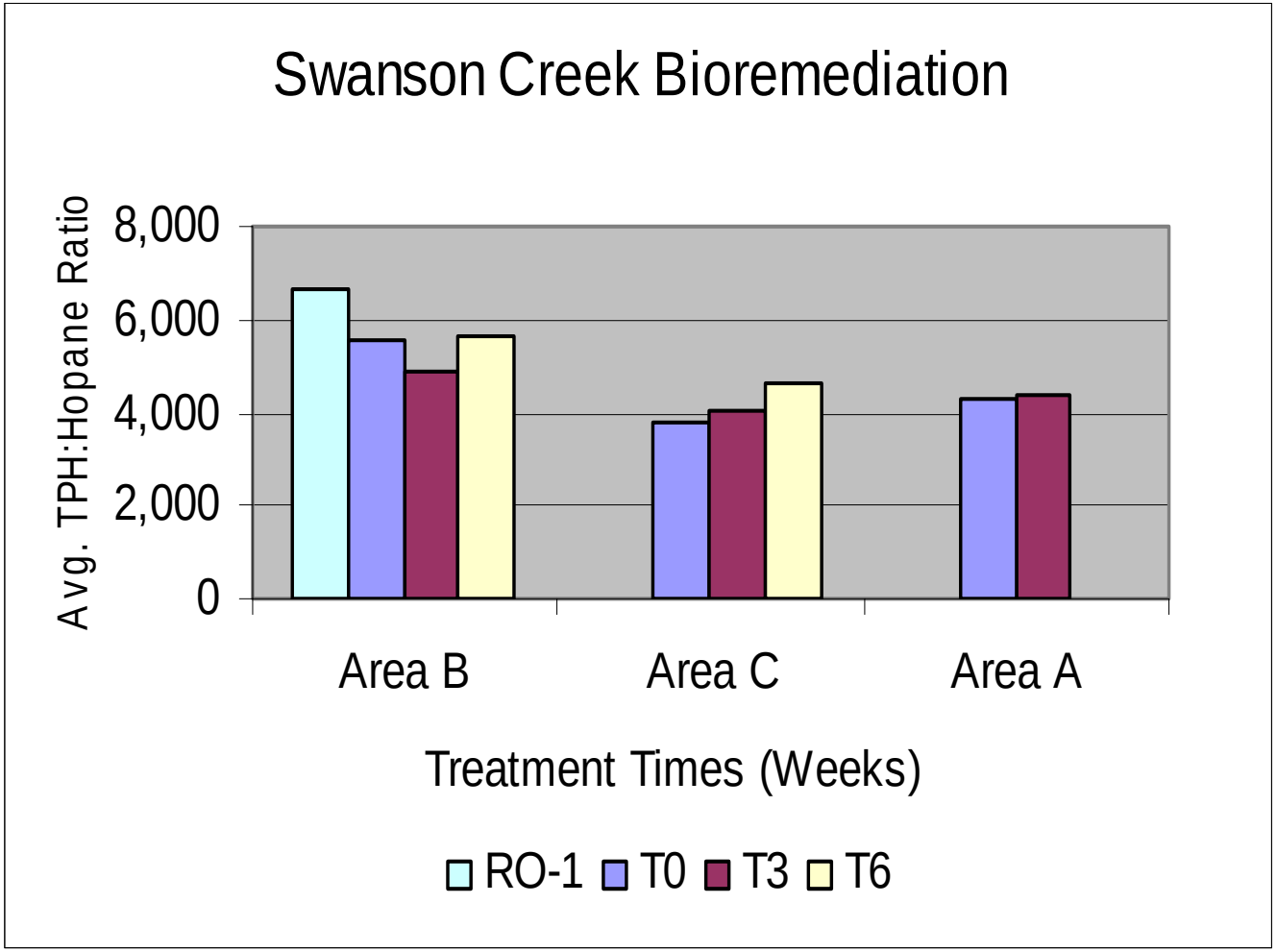
Area B –TPH/Hopanes



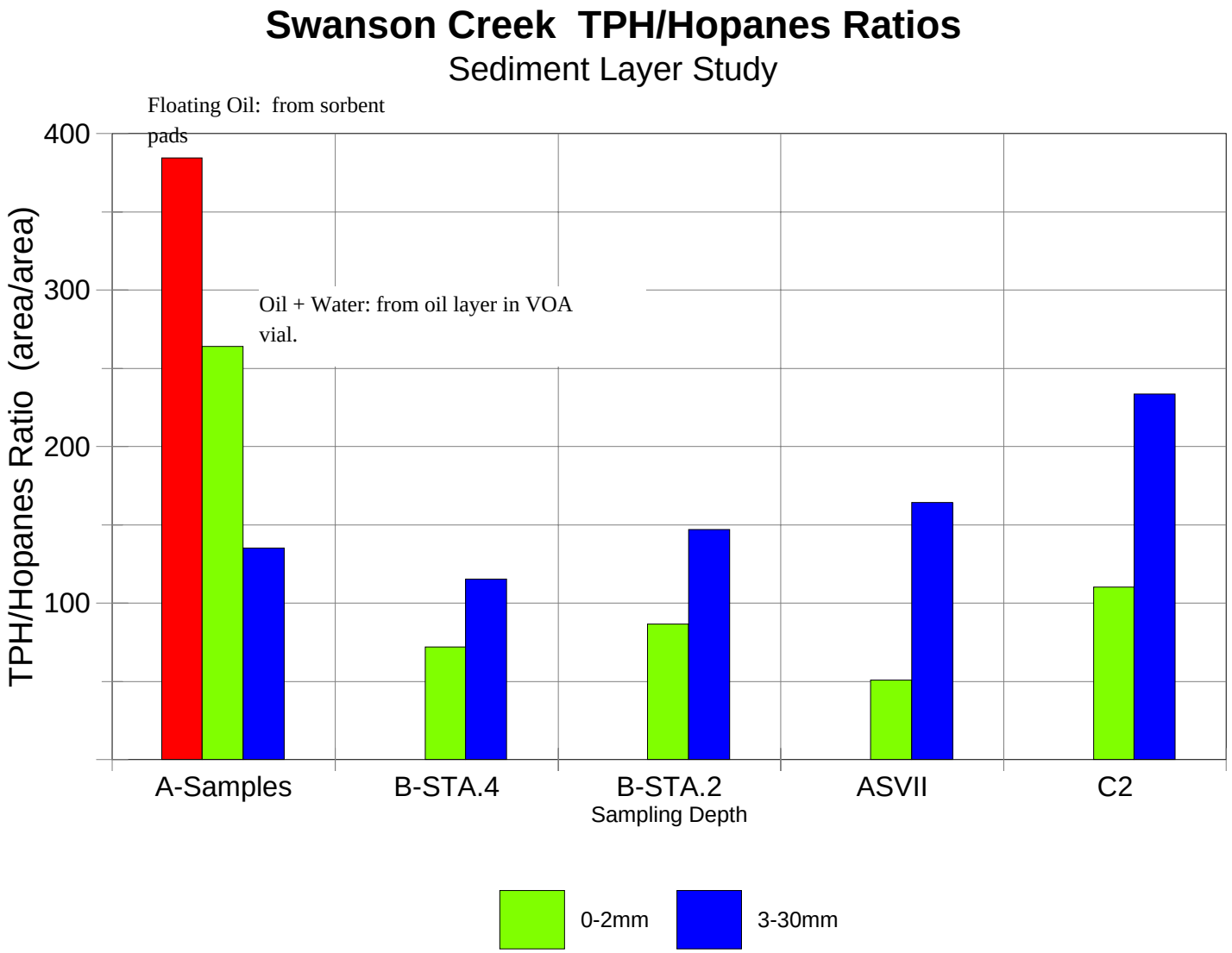
Area C – TPH/Hopanes



Summary Areas A, B, C



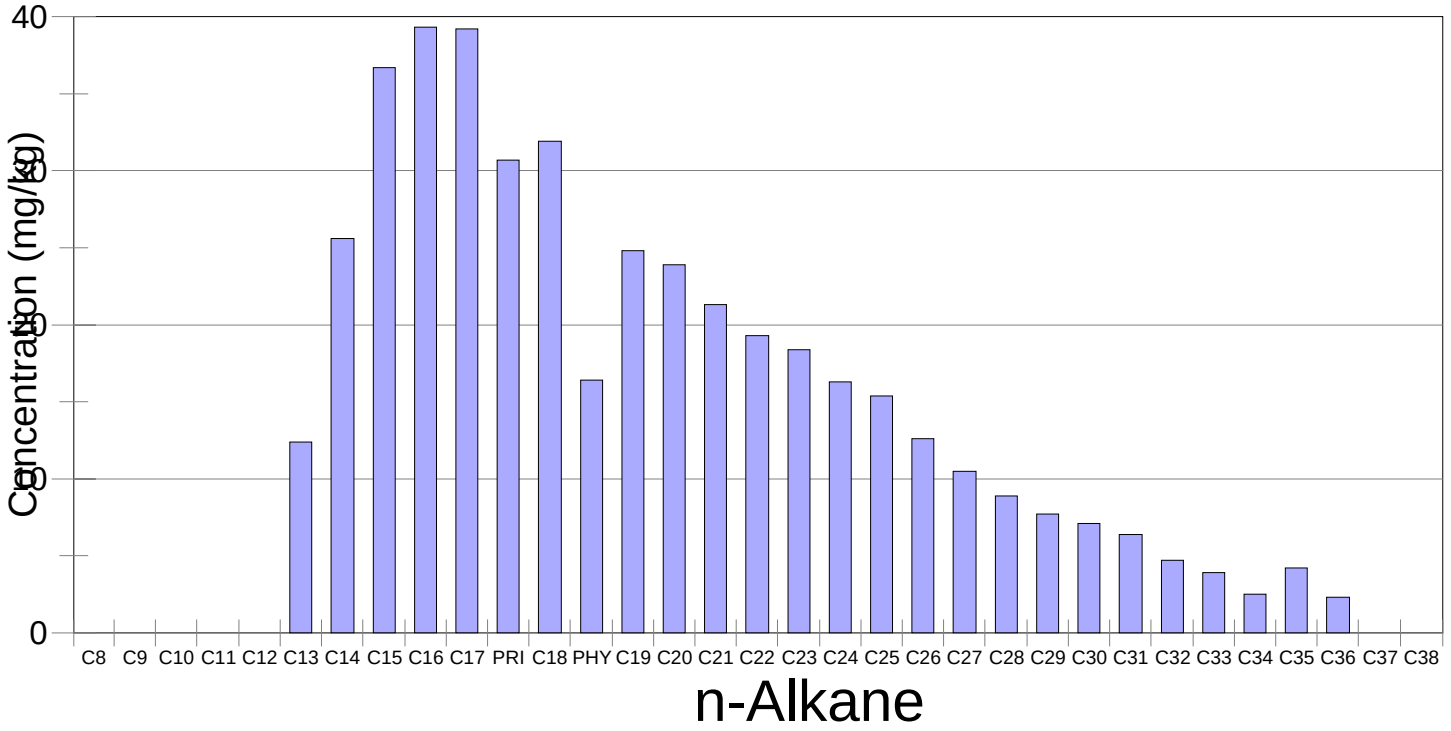
Depth Study – Oxygen Limitation



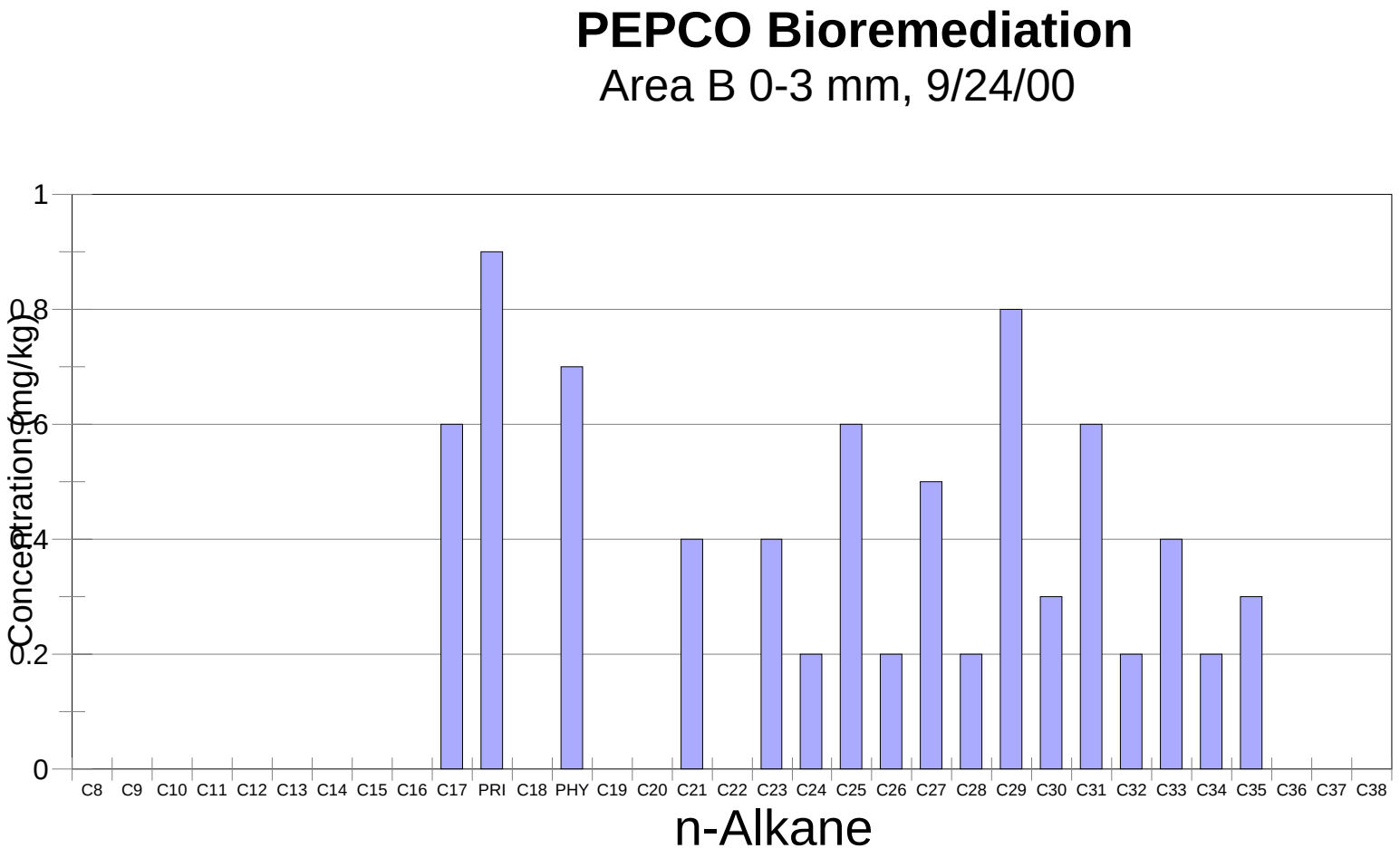
Free Oil Chromatogram

PEPCO Bioremediation

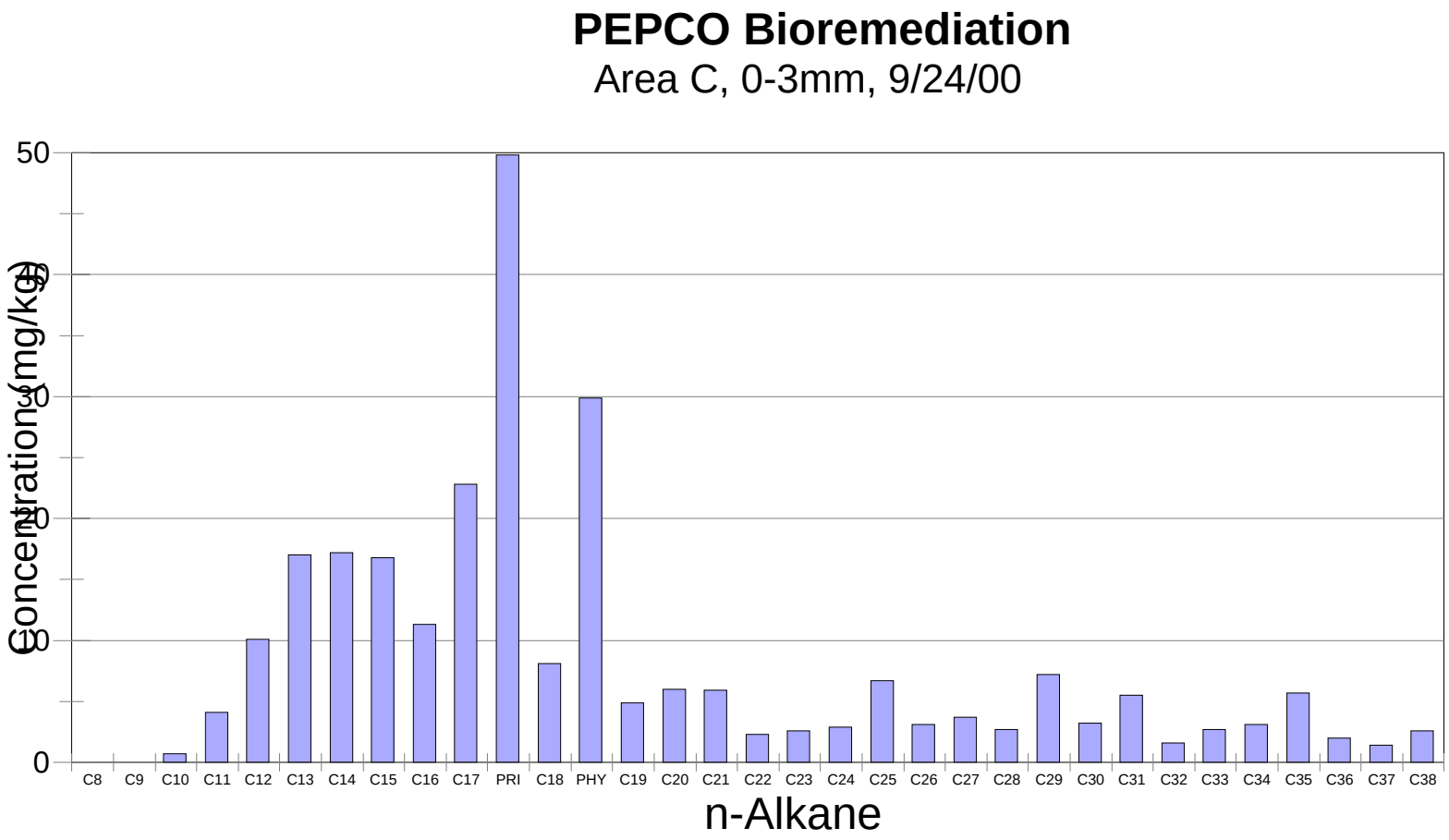
Free Surface Oil, 9/24/00



Weathering in Treated Area



Weathering in Untreated Area

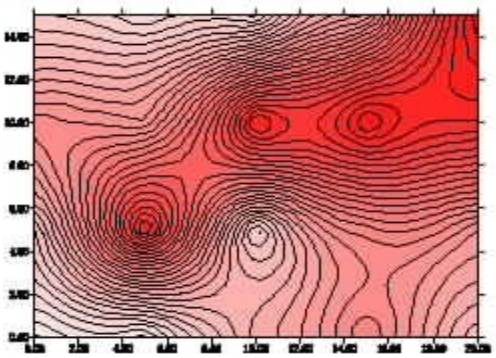


Oil in the Sands

Allegheny Forest Sites - McCracken Farm
Loading the Biopod

Effect of Soil Mixing

TPH at McCracken #2



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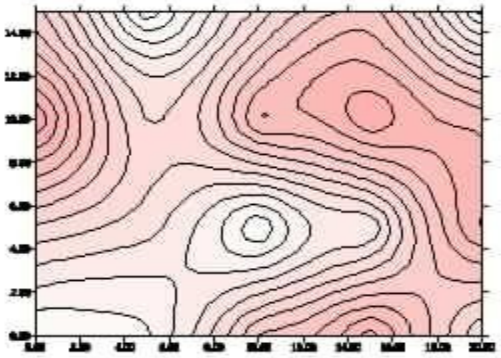

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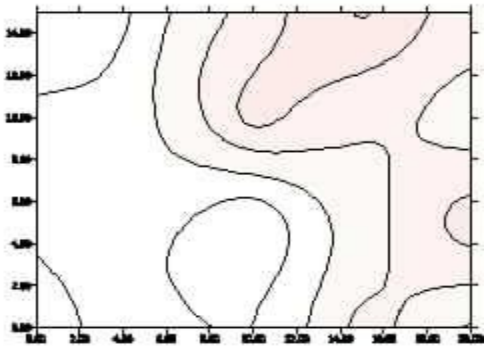

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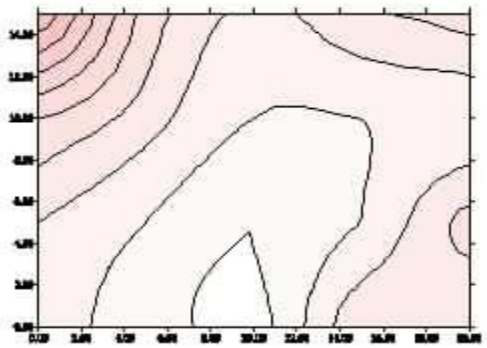
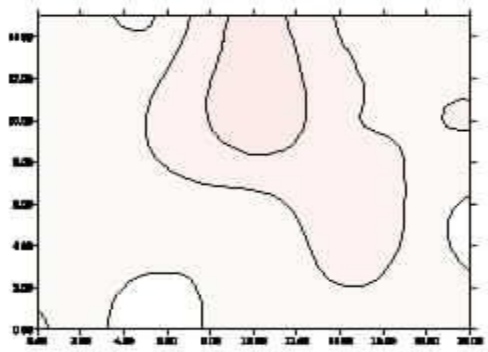


10-26-01



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 Limitiations.
- 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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UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL RESPONSE
EPA
TEAM

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
Group 1 PAHs		28.9 %
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		
Group 2 PAHs		**36.2 %**
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		
Group 3 PAHs		**24.4 %**
Fluoranthene**	11.8 %	7.67 %
Pyrene**	8.4 %	5.46 %
Benz(a)anthracene** (Chrysene)**	4.2 %	2.73 %
Benzo(b)fluoranthene		
Benzo(a)pyrene*		
Heterocycles		**10.3 %**
Dibenzofuran	5.2 %	3.38 %
Carbazole	5.1 %	3.32 %
Anthraquinone		
Phenolics		**<1.0 %**
NOTES:	14	14

*Not Biodegradable: Material Unchanged by Bacterial Action.

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

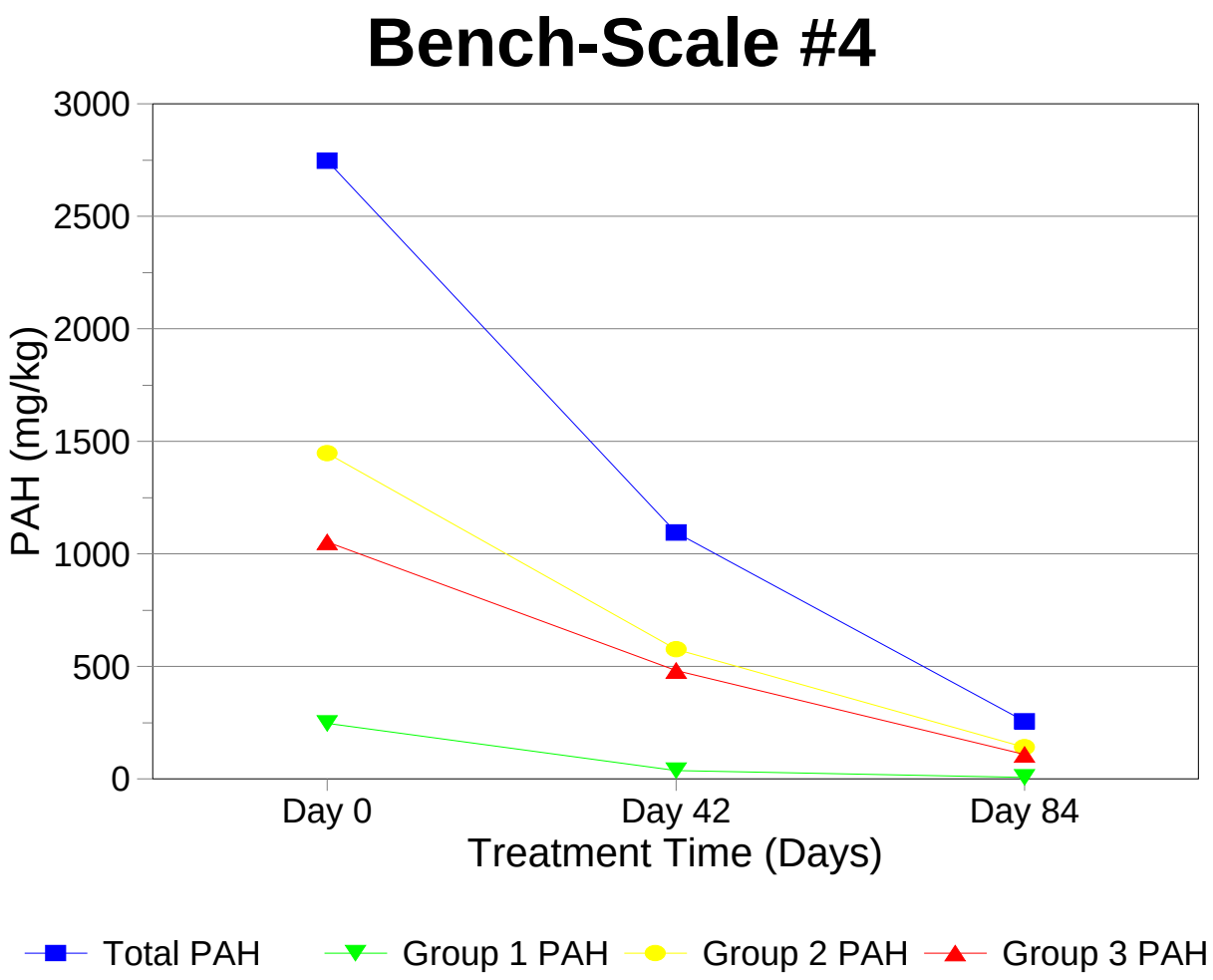
***Biotransformed Only: Material Changed, But Not Mineralized to Carbon Dioxide and Water.

TABLE 1. Target Creosote Components Evaluated in Bioremediation Studies

Analyte Group	Creosote Compound
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

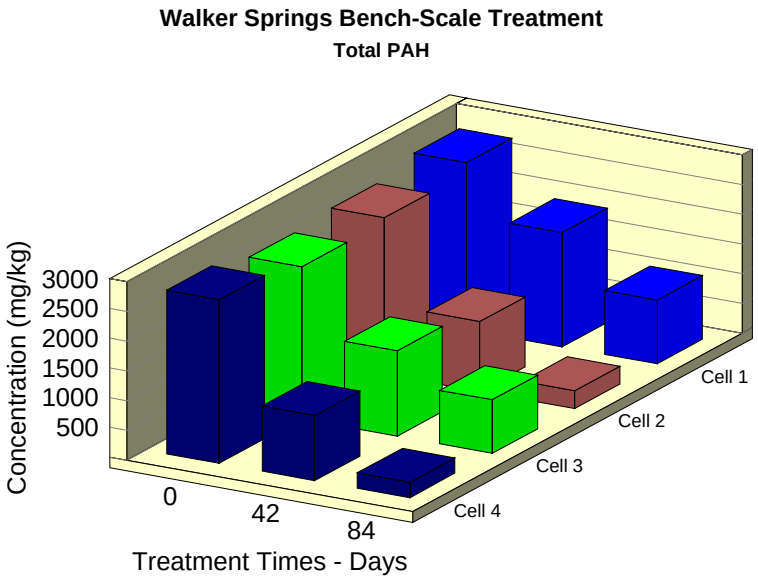


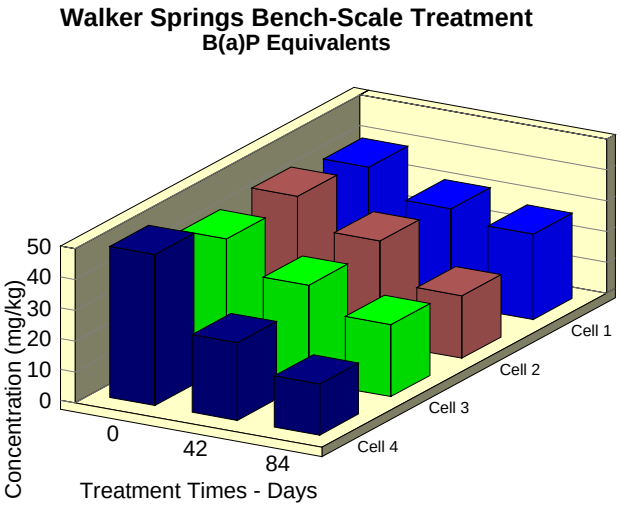
B(a)P Toxic Equivalency Factors

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

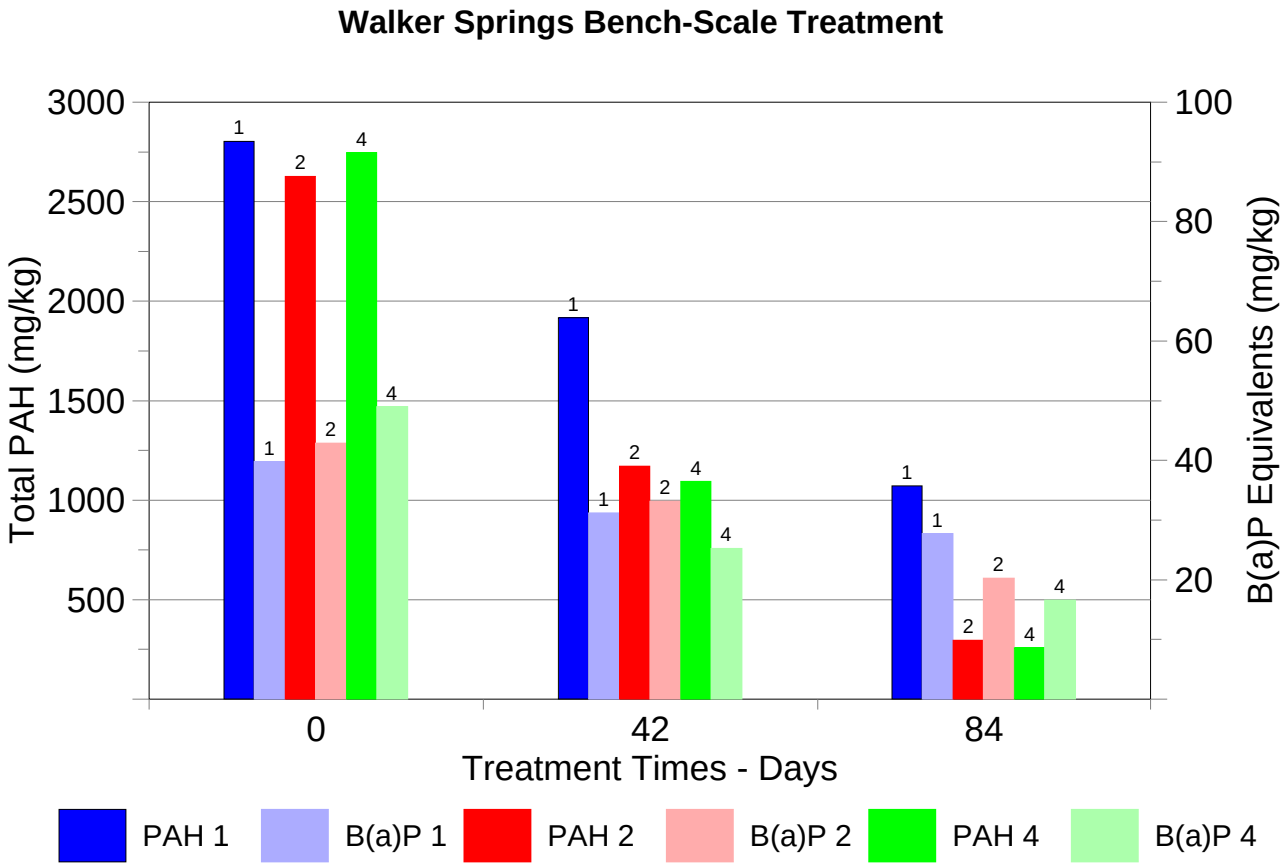
Bench-Scale Results Showing Effect of Recipe





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

Effect of Recipe on PAH Removal

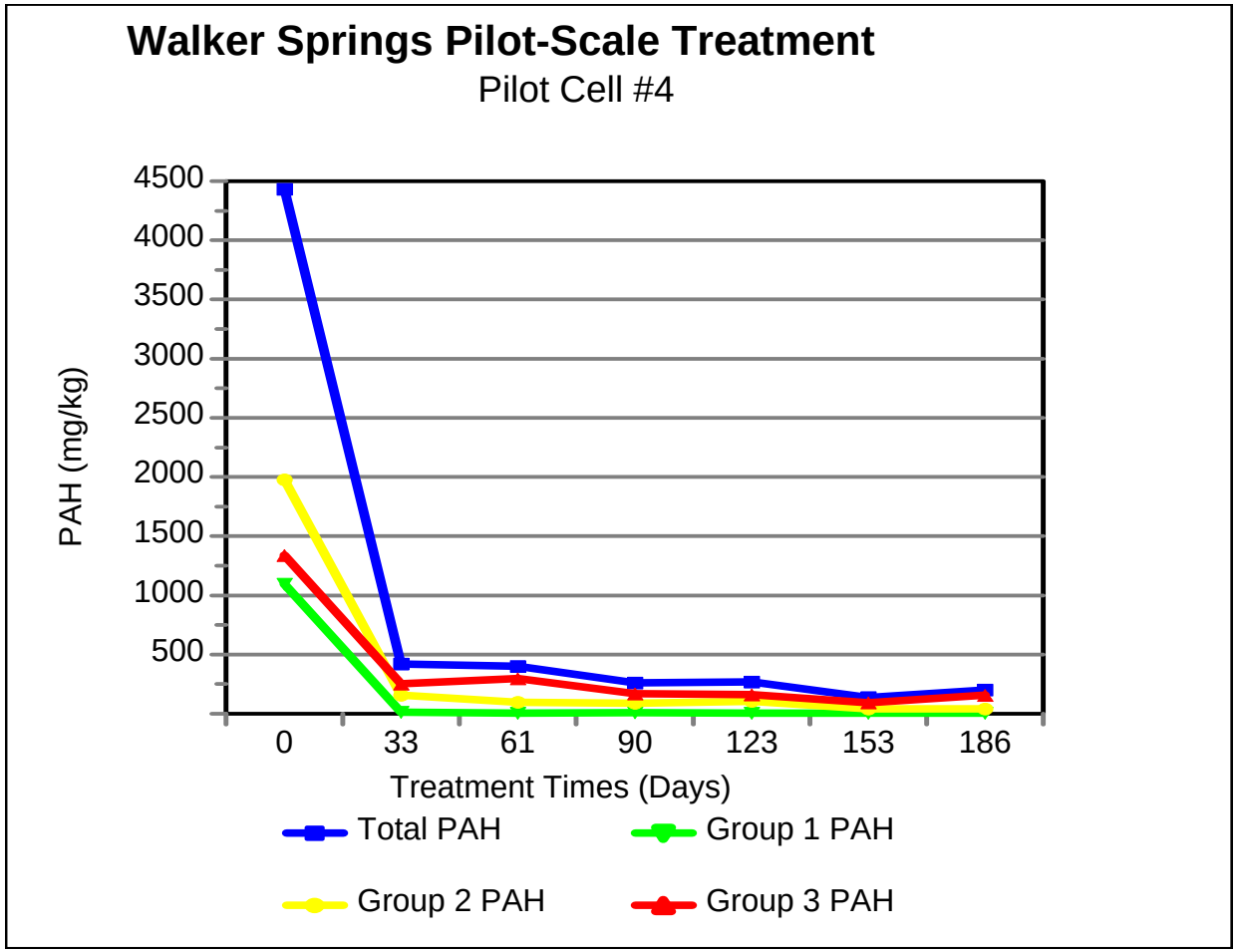


Walker Springs Pilot Units

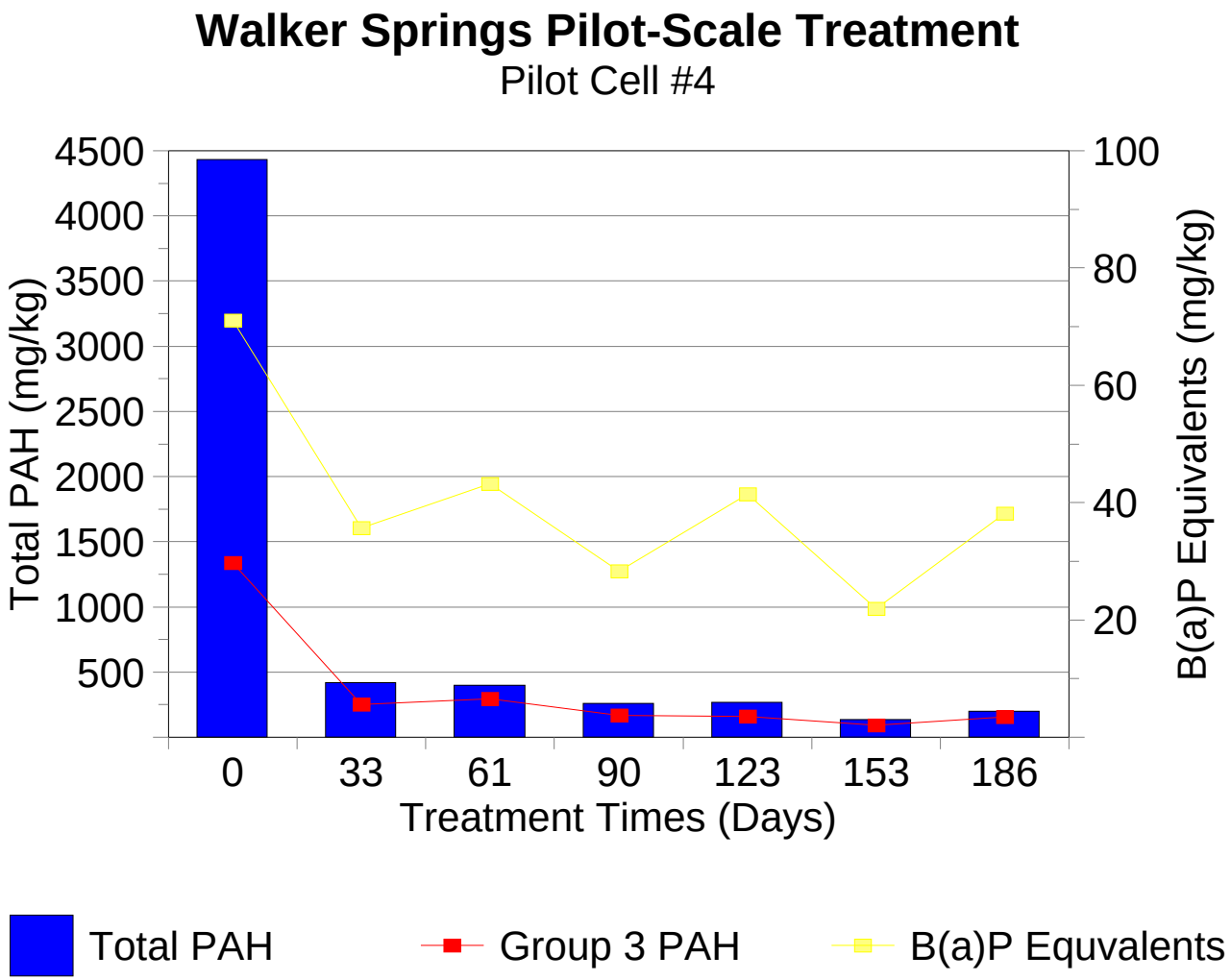
Tilling Pilot Units

Sampling Locations in Pilot Units

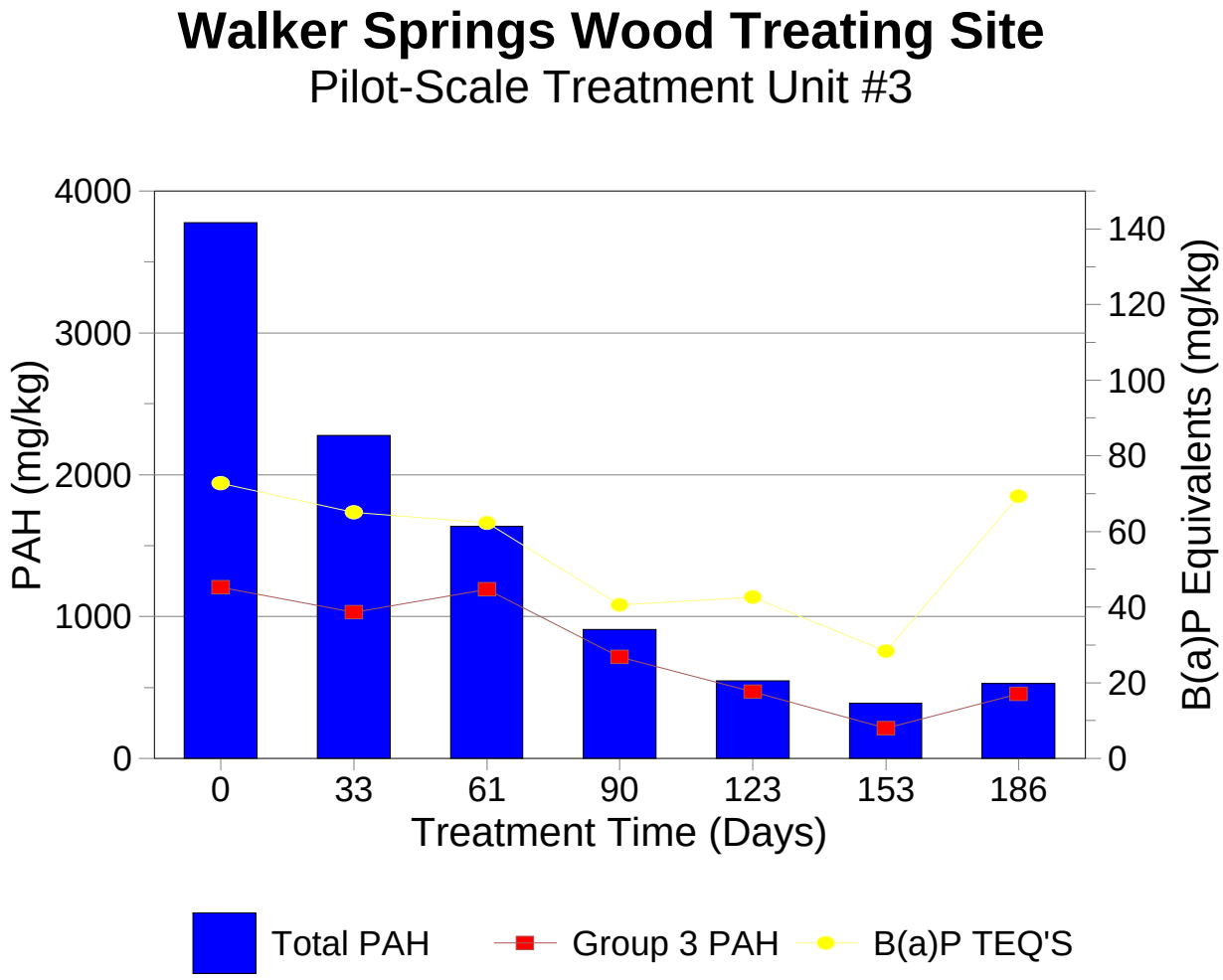
PAH Degradation in Field-Scale Solid Phase Studies Using Recipe 4



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

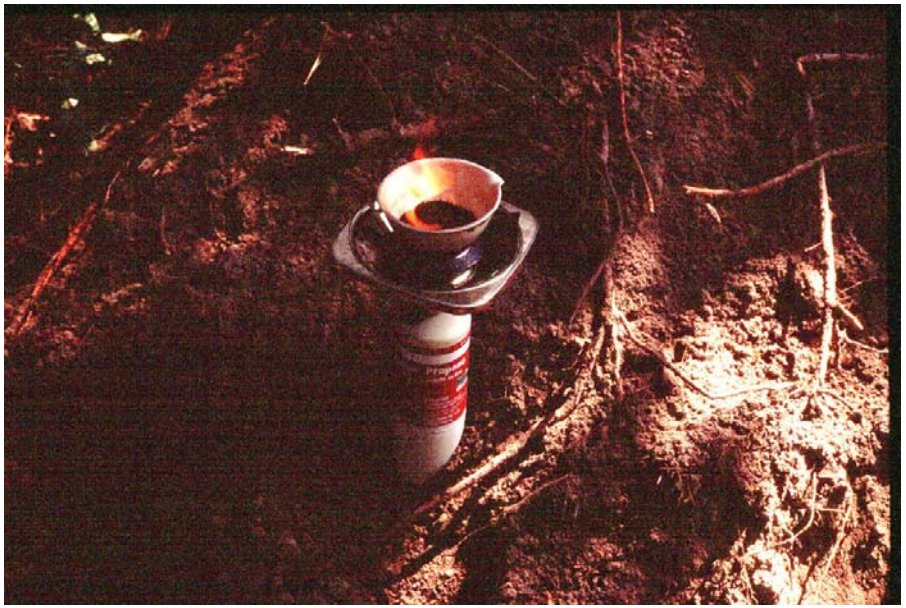


PAH Degradation in Field-Scale Pilot Unit Using Recipe 3 –No Added Nutrients



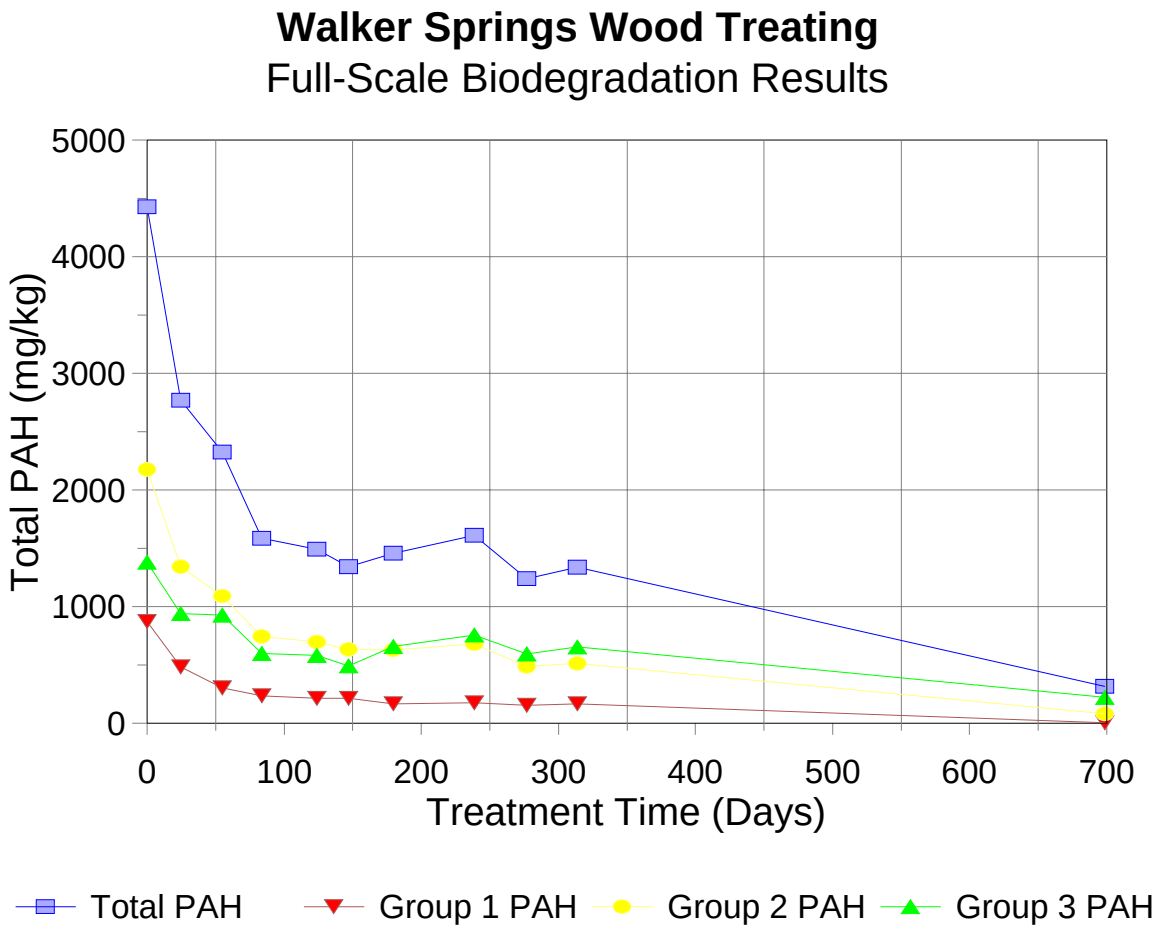
Preparation and Management of Soil Treatment

Field Testing for Moisture Content

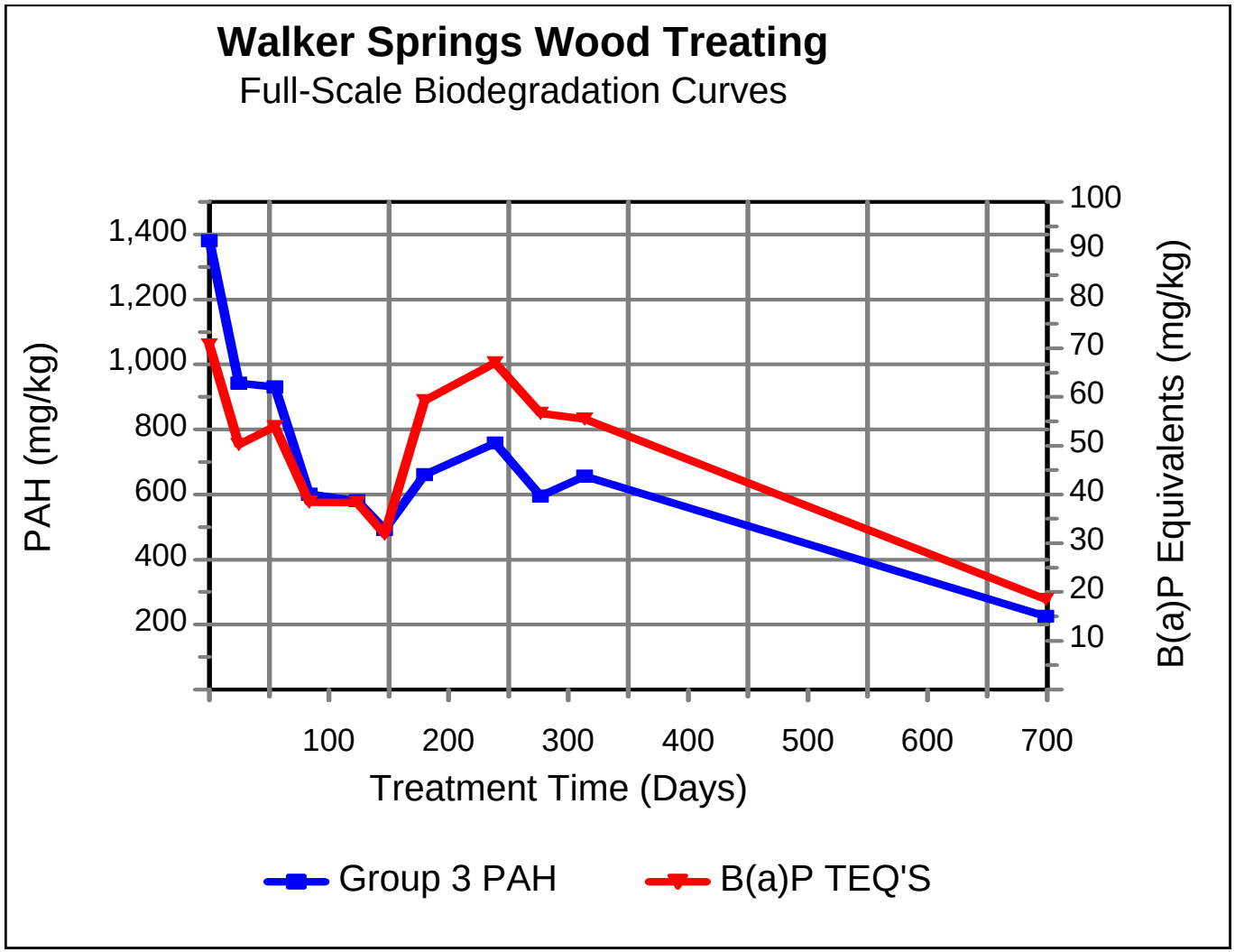


Covering to Control Moisture

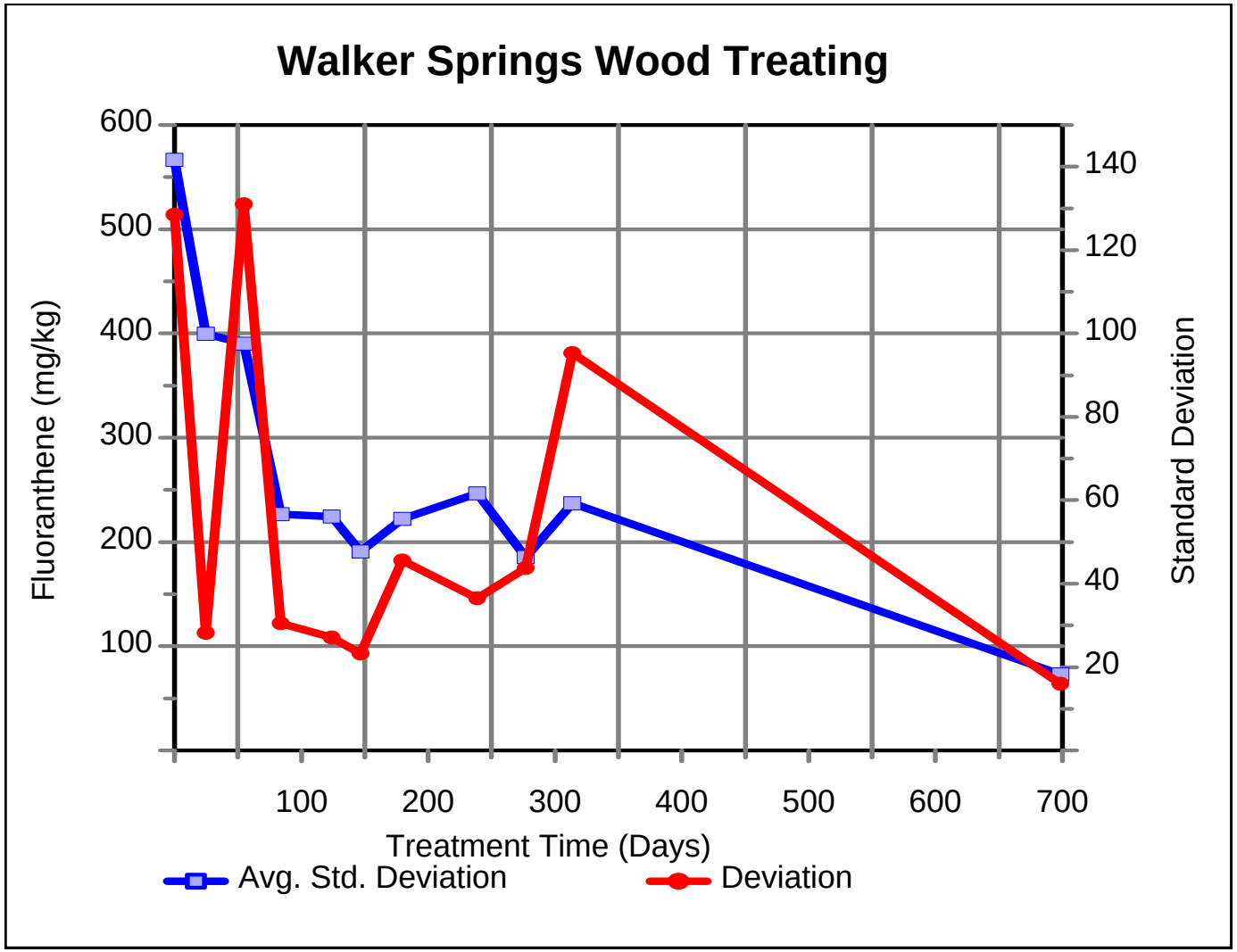
PAH Degradation in Full-Scale Treatment



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

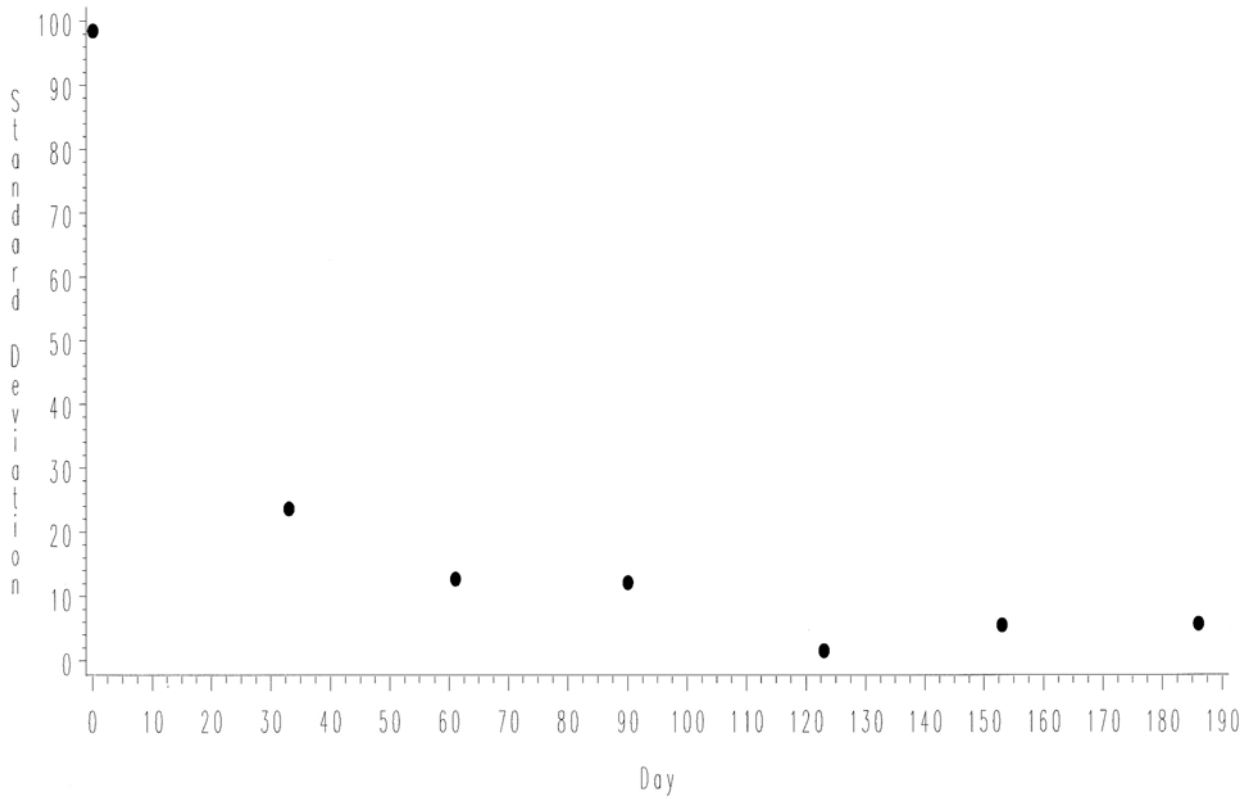


Change in Data Variation With Time for Fluoranthene in Full-Scale Treatment

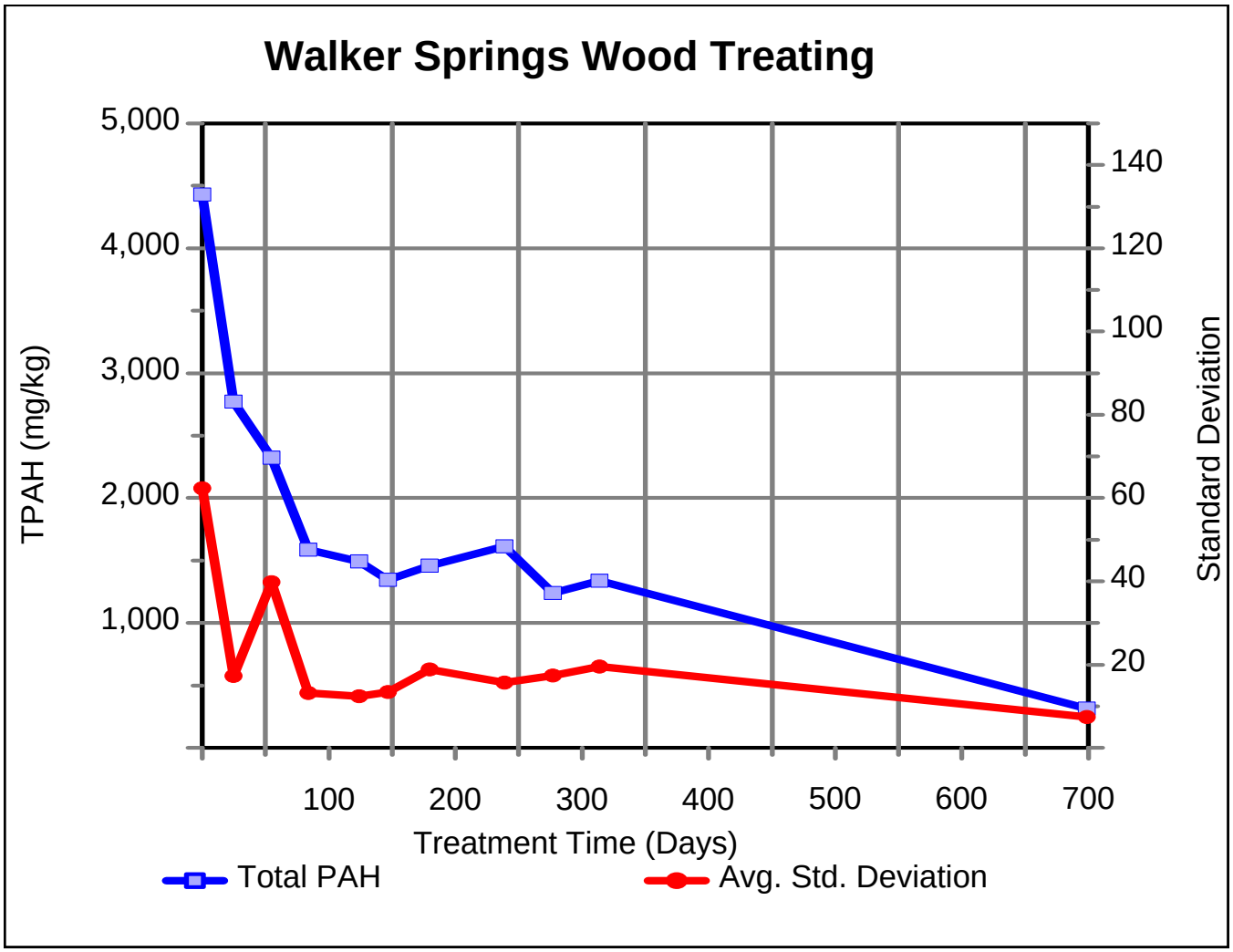


Plot of Standard Deviation vs. Day

Walker Springs Pilot Study - Unit #4
COMPOUND=fluoranthene

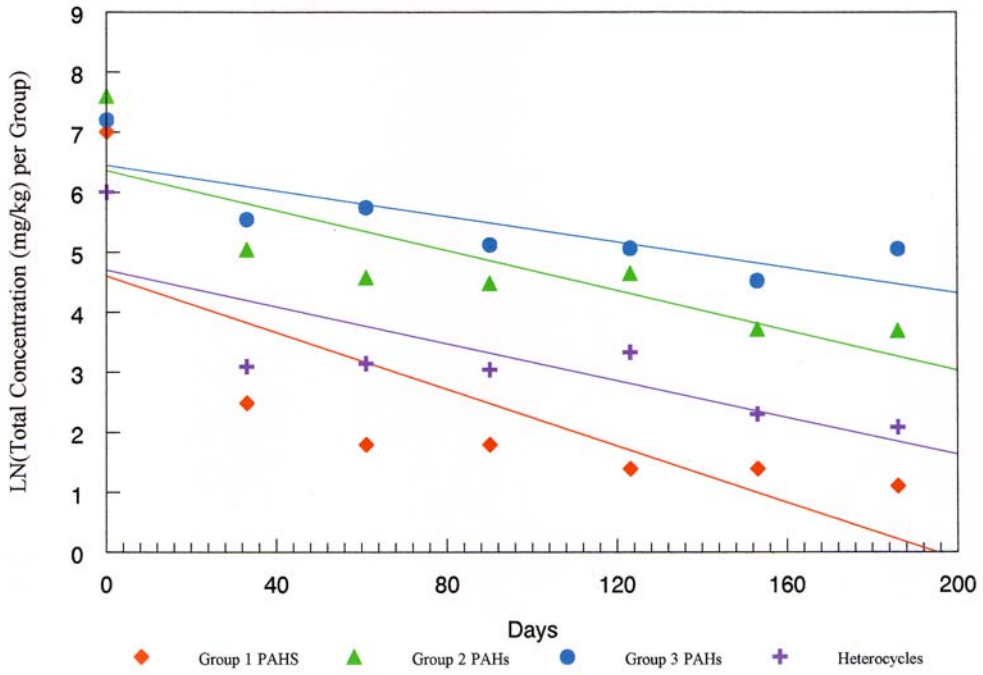


Change in Data Variation With Time for TPAH in Full-Scale Treatment



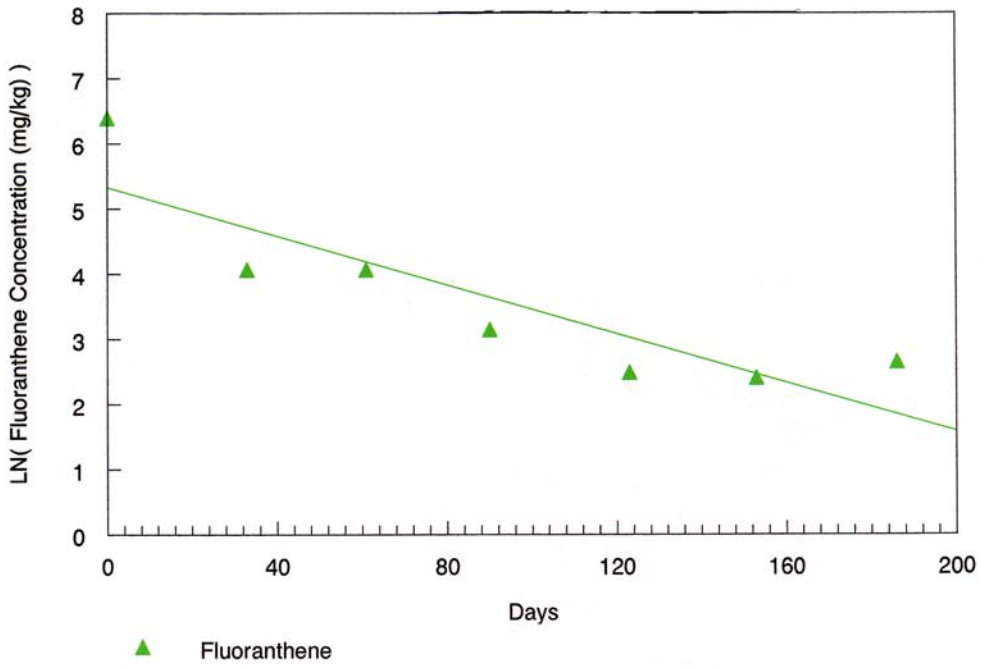
Regression of Total Concentration Per Group vs. Time

Walker Springs Pilot Study - Unit #4



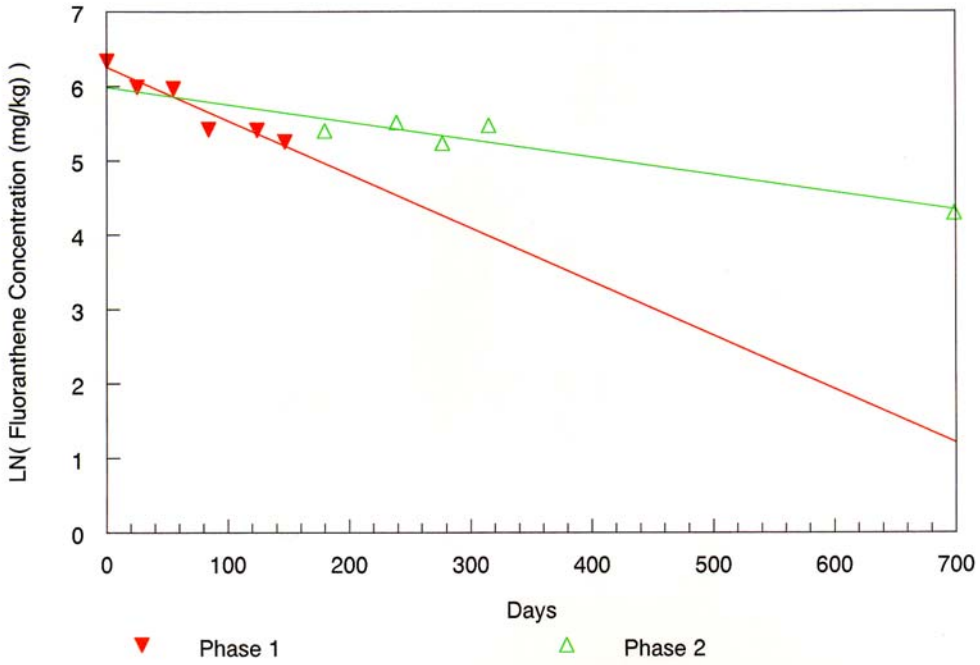
Regression of Fluoranthene vs. Time

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

Compound	Days 0 to 147		Days 180 to 699	
	Half-life (days)	R-Squared	Half-life (days)	R-Squared
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
Fluoranthene	**96**	**0.9096**	**295**	**0.9062**
Pyrene	99	0.8892	330	0.9329
Chrysene	114	0.9120	257	0.9372
Benz(a)anthracene	110	0.9564	267	0.8768

	Days 0 to 699	
Fluoranthene	**289**	**0.7929**

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 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)	Delisting Level x1%Koc	ATSDR 11/14/94 Ind. Goal	R III 8/7/96 Ind. Goal
NON-CARCINOGEN (Group)	(mg/L)	(mg/Kg)	(mg/Kg)	(mg/Kg)
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