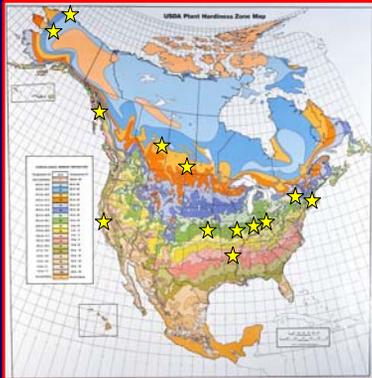


# **RTDF TPH Subgroup Phytoremediation Field Trials: Results and Preliminary Conclusions**



Peter Kulakow and Xiujuan Feng  
Kansas State University



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## **Acknowledgements**

- RTDF Cooperators under the leadership of
  - Steve Rock
  - Lucinda Jackson
  - Phil Sayre
- USEPA Technology Innovation Office
- Environment Canada
- Great/Plains Rocky Mountain HSRC
- Midwest HSRC
- Henry Camp - ICF Consulting

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## RTDF Partners

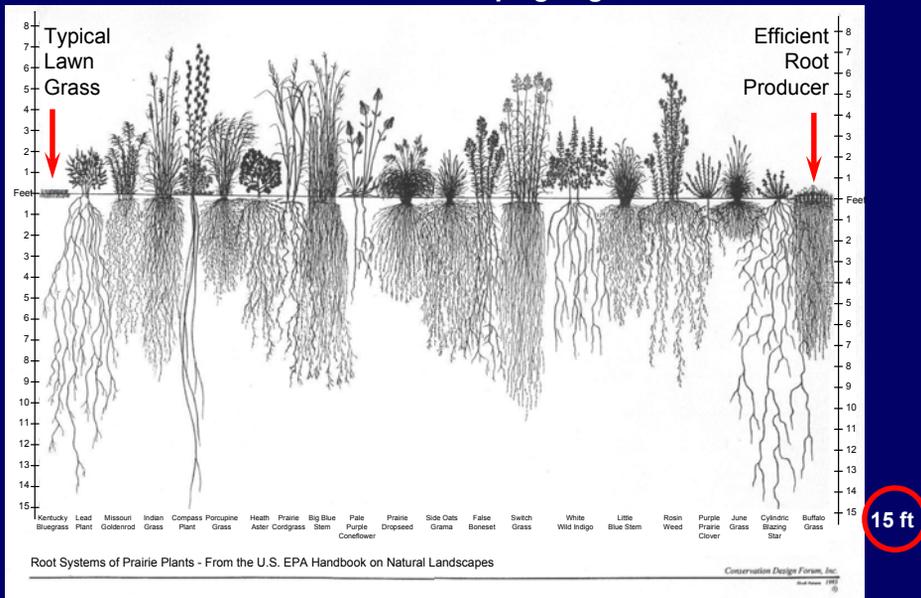
- US Environmental Protection Agency
- Environment Canada
- Major Oil Corporations
  - Petroleum Environmental Research Forum
- Public Utility Corporations
- US Department of Defense
- Universities
- Environmental Consultants

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## Deep-Rooted Species

4

ACCORDING TO: [www.epa.gov/greenacres/](http://www.epa.gov/greenacres/)



15 ft

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## Goal

- Assess the efficacy of vegetation to enhance degradation of aged petroleum hydrocarbons in soil
- Is there evidence that vegetation enhances progress toward practical environmental management objectives for petroleum sites within 3 years?

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## Rationale for Approach

- Hydrocarbon degradation
  - Changes are slow and subtle
- Monitoring is needed for a long period
- Contaminant distribution in soil is variable
- Standard protocol facilitates comparisons among locations
  - allowing for site specific adjustments

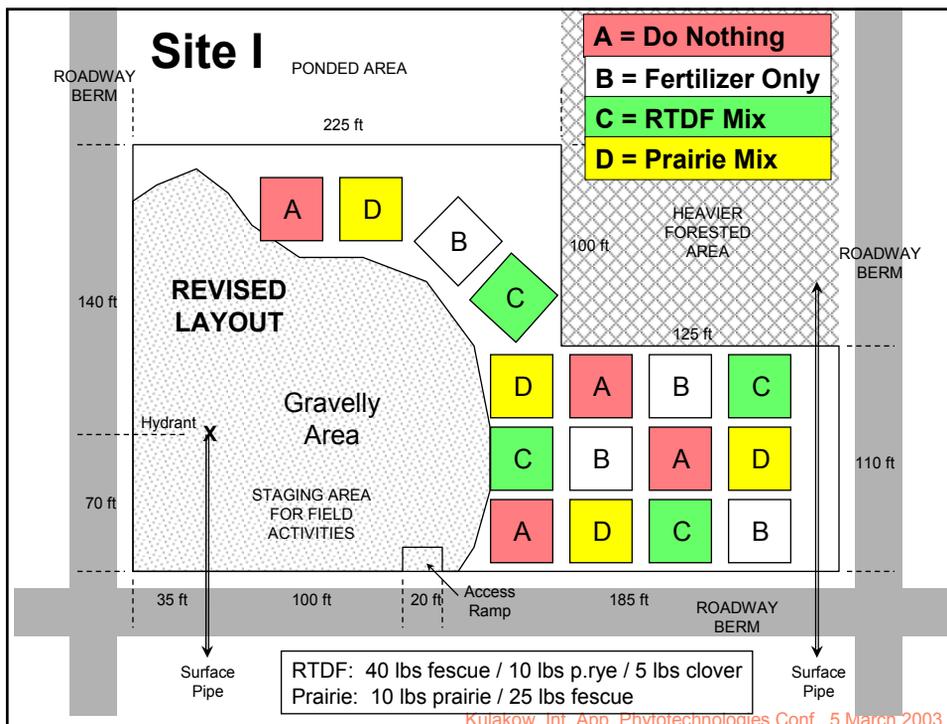
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# Standardized Protocol

- Experimental Design
  - Randomized complete block design with four replications
  - Treatments with site specific adjustments
    - Standardized grass/legume mixture
    - Local-optimized treatment
    - Unvegetated/unfertilized Control
  - Minimum plot size: 20 x 20 ft.

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## Sampling Plan

- Soil
  - Composite 8 soil cores/plot
  - Two depths: 0 – 15 cm and 15 – 45 cm
  - Sample Annually for 3 growing seasons
- Vegetation
  - Above ground biomass production
  - Plant species composition
  - Root growth
  - Hydrocarbon uptake at final sampling

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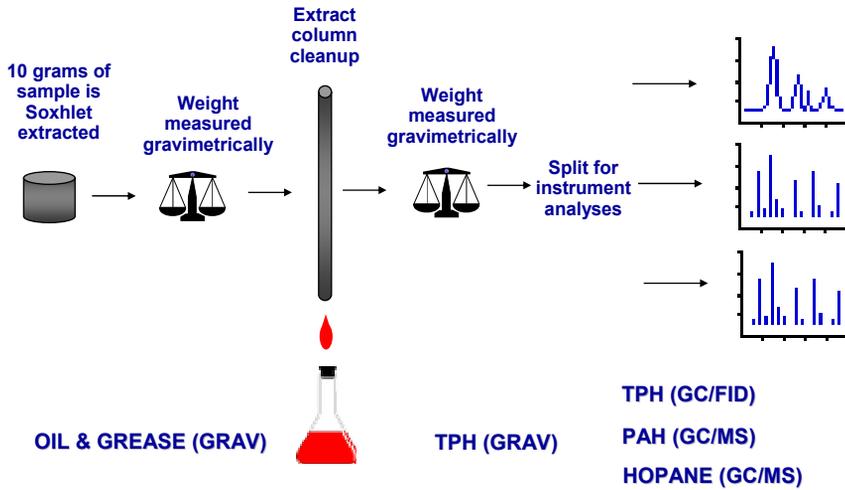


## Site A – May 2001 Hydrocarbon Uptake Sampling

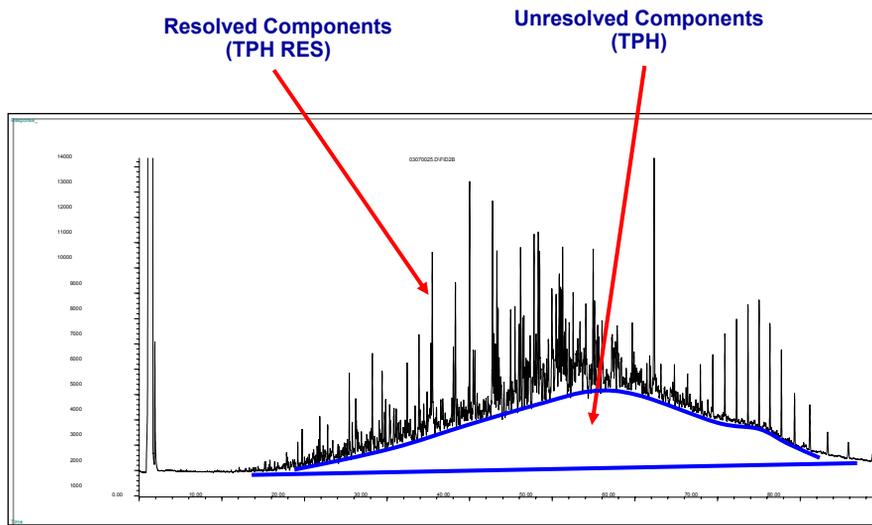


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# Sample Preparation and Analysis Flow

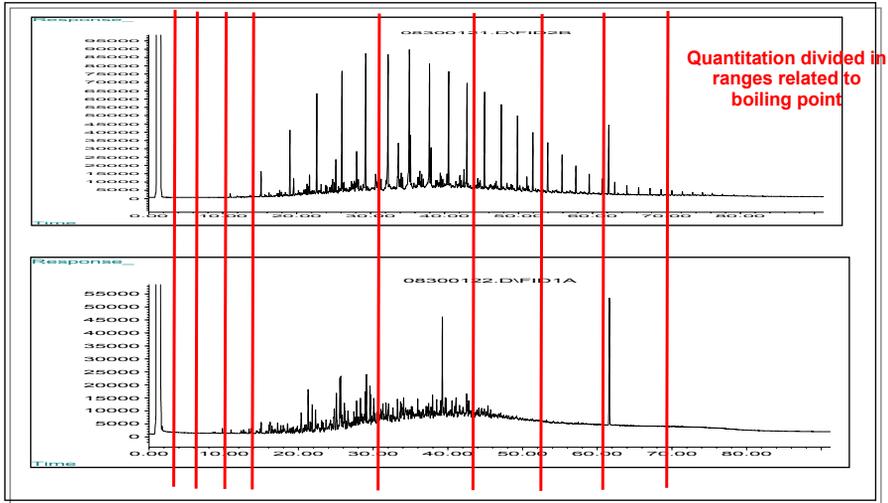


# Example GC/FID Chromatogram Output

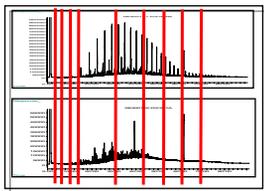




# Example TPHCWG Chromatogram Output

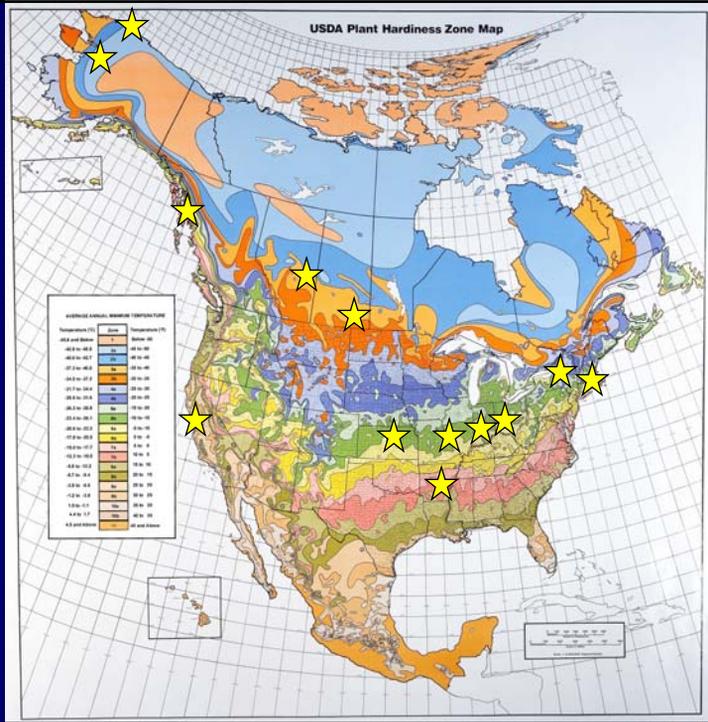


## TPHCWG Data



TPH-CWGM	
Total Resolved	210
Total PHC	2000
<b>Aliphatic Total Resolved</b>	
Aliphatic TPH	1500
Aliphatic TPH>nC6-nC8	ND
Aliphatic TPH>nC8-nC10	1.3 J
Aliphatic TPH>nC10-nC12	10 J
Aliphatic TPH>nC12-nC16	120
Aliphatic TPH>nC16-nC21	210
Aliphatic TPH>nC21-nC25	240
Aliphatic TPH>nC25-nC30	500
Aliphatic TPH>nC30-nC35	280
Aliphatic TPH>nC35+	140
<b>Aromatic Total Resolved</b>	
Aromatic TPH	480
Aromatic TPH>nC6-nC7 (B)	ND
Aromatic TPH>nC7-nC8 (T)	ND
Aromatic TPH>nC8-nC10	ND
Aromatic TPH>nC10-nC12	0.15 J
Aromatic TPH>nC12-nC16	26
Aromatic TPH>nC16-nC21	90
Aromatic TPH>nC21-nC25	74
Aromatic TPH>nC25-nC30	120
Aromatic TPH>nC30-nC35	98
Aromatic TPH>nC35+	70

# Thirteen RTDF Field Site Locations



April 1999



**Site A – Refinery Site**

**Three Complete Growing Seasons**

June 2000



May 2001



# Site B - Closed Refinery

RTDF Mix



Unvegetated



Poplar/Willow

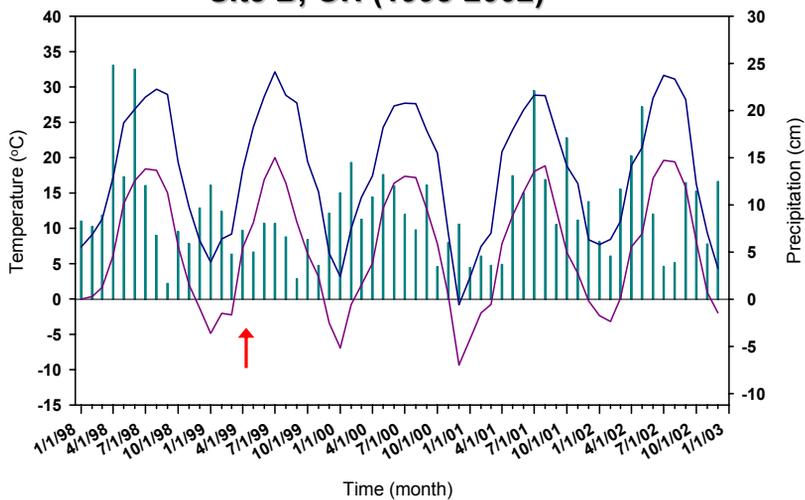


Hackberry



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## Site B, OH (1998-2002)



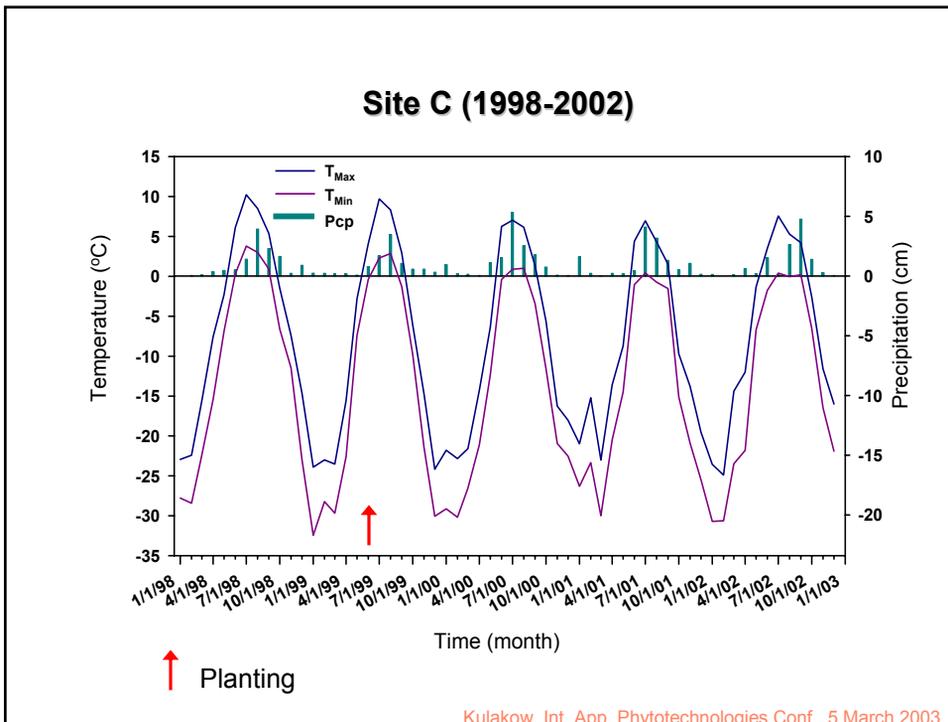
↑ Planting

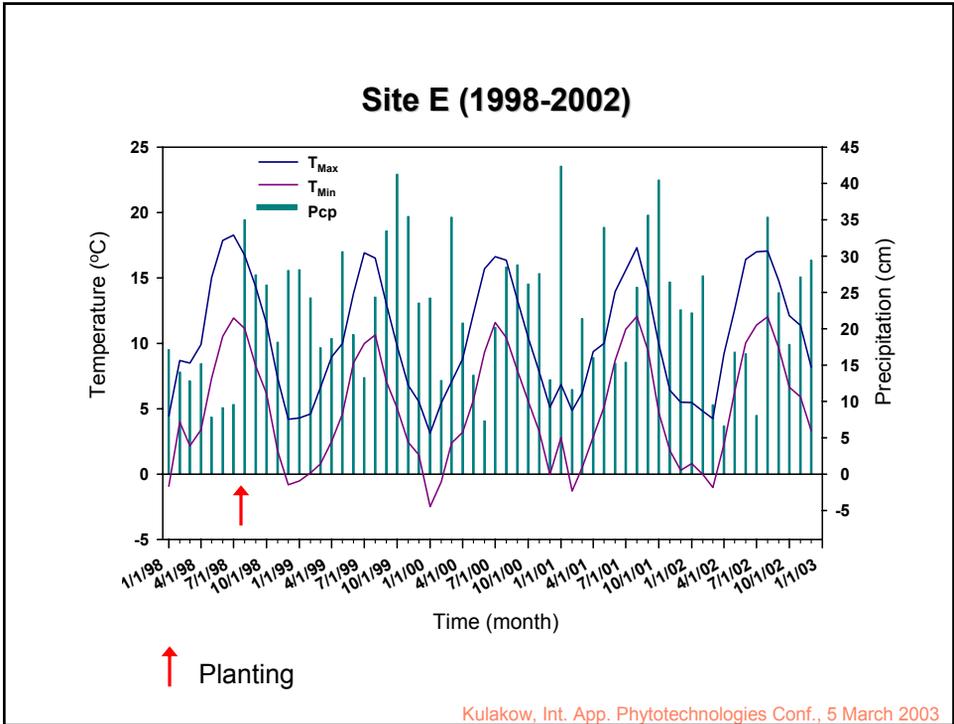
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# Three Alaskan Sites – Cold Regions



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## Site F – Manufactured Gas Plant



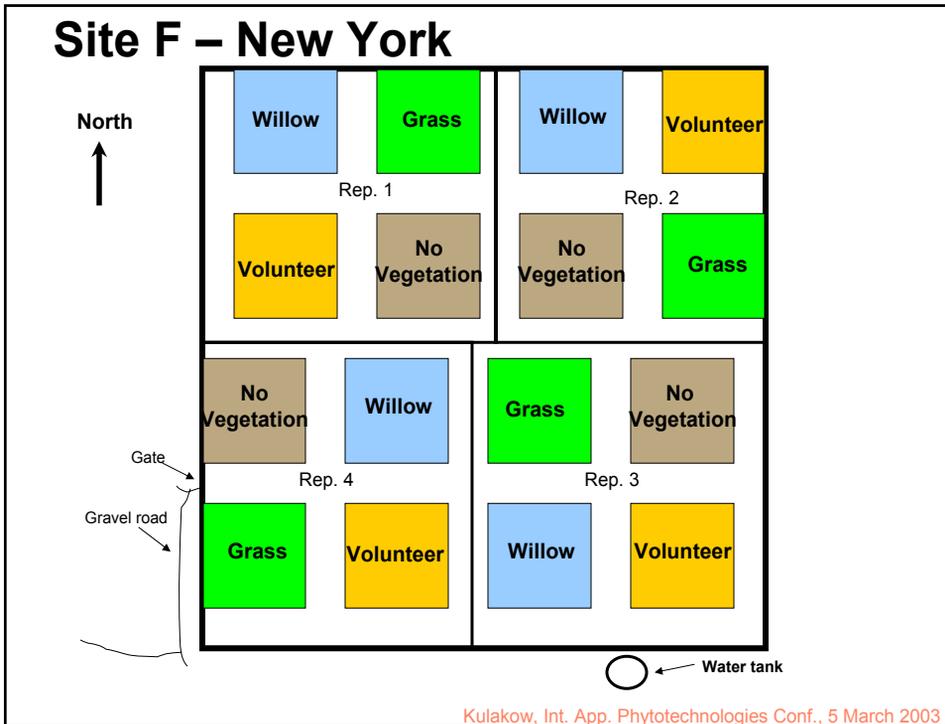
**Willow/Poplar Mix**

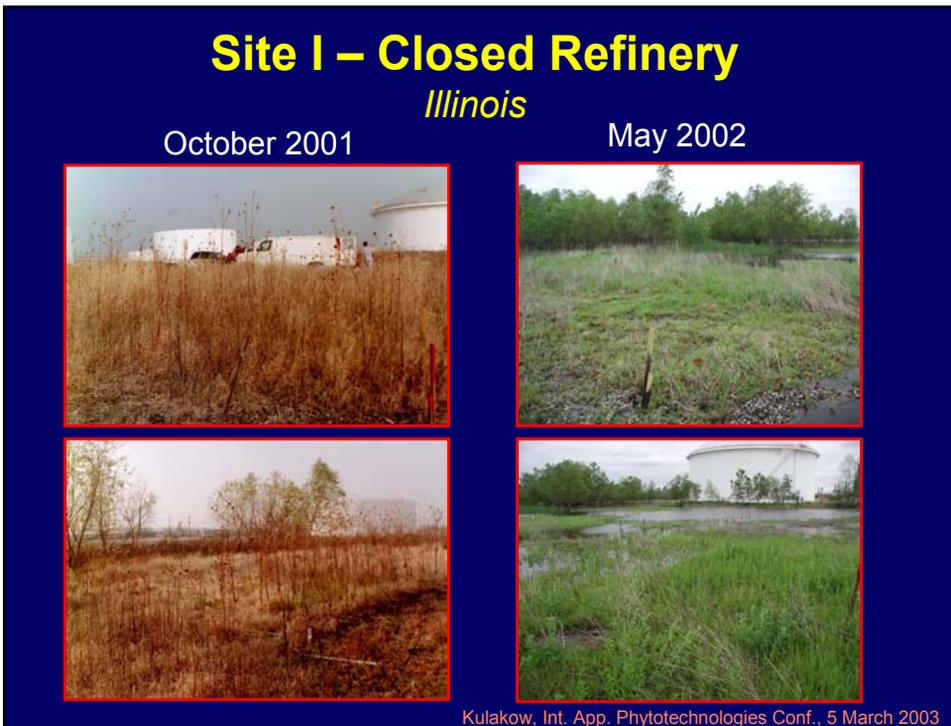
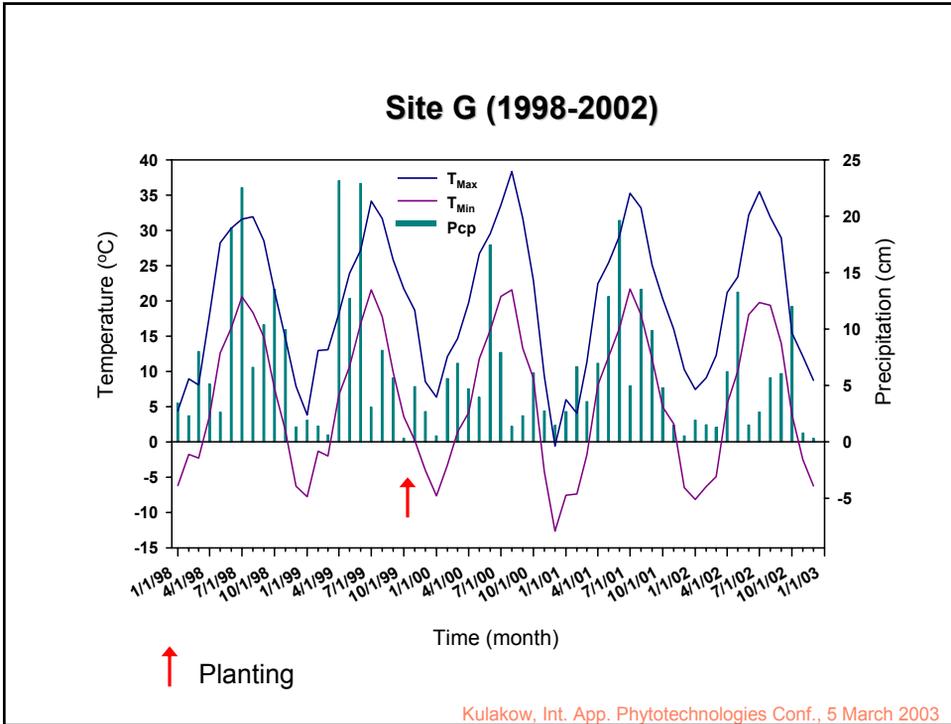


**RTDF Mix**



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# Site H – Closed Distribution Facility

*Rhode Island*

October 2002



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# Site J – Production Site

*Arkansas*



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## Site K – Manufactured Gas Plant, *Indiana*



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## Site L – SK, Canada – Buried Flare Pit



Planted June 2002



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# Results

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## Status of Field Sites – 36 Data Sets

	Planting Date	Sampling Events				
		Time 0	Year 1	Year 2	Year 3	Year 4
Site A, CA	Dec-98					
Site B, OH	Apr-99				Nov-02	
Site C, AK	Jun-99					
Site D, AK	Aug-98	Aug-98				
Site E, AK	Aug-98					
Site F, NY	Jun-99					Oct-02
Site G, KS	Oct-99				Oct-02	
Site H, RI	May-01	May-01		Oct-02	Nov-03	
Site I, MO	Nov-00			Oct-02	Nov-03	
Site J, AR	Oct-99			Oct-01	May-02	
Site K, IN	May-99					
Site L, SK Canada	Jun-02	Jun-02	Oct-02		Oct-04	
Site M, AL Canada	May-03	May-03			Oct-05	

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## Dealing with the Data

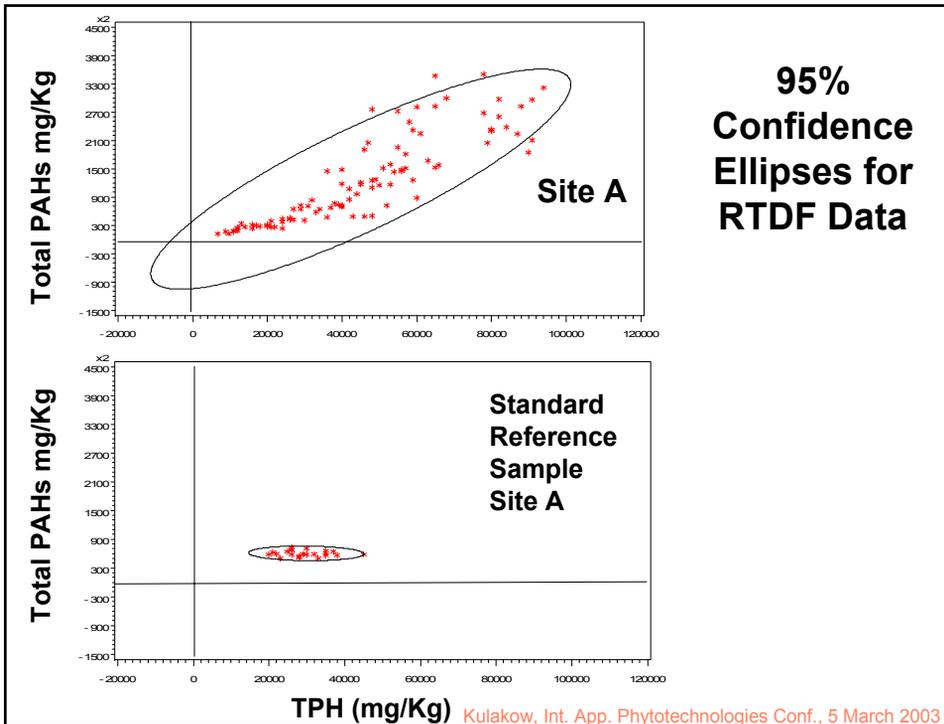
- Nondetect data
  - Used a nonzero substitution
- Numerous derived variables such as Total PAHs
  - >100 variables analyzed
- Analyzed
  - Original data
  - Hopane normalized data

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## Statistical Analysis

- Randomized Complete Block Design
- Soil depth usually analyzed separately
- Time is a repeated measure
  - Derived variables approach
  - Each time interval analyzed separately
- Considered assumptions of analysis of variance
  - Homogeneity of variances most important
- Treatment differences tested by analysis of variance and lsd tests.

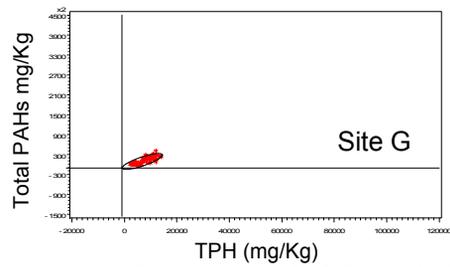
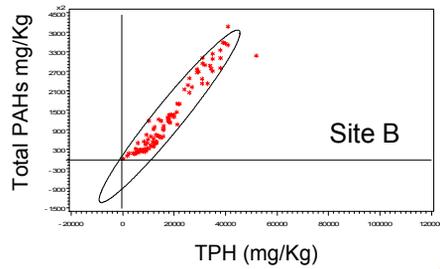
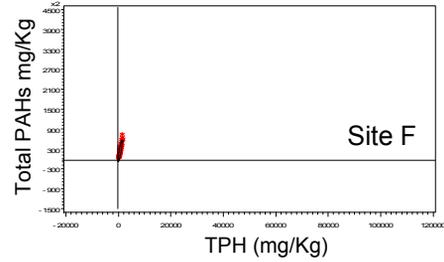
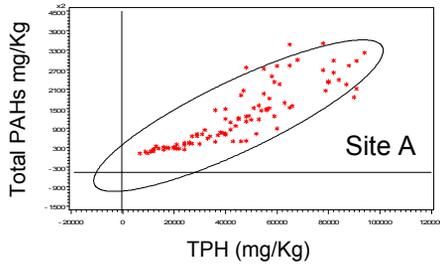
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## High Variability in TPH and PAH Concentrations

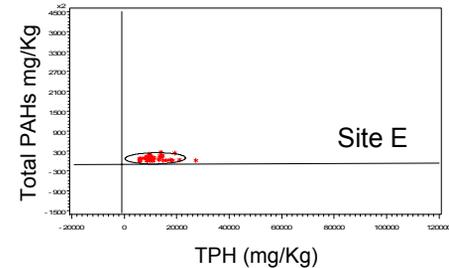
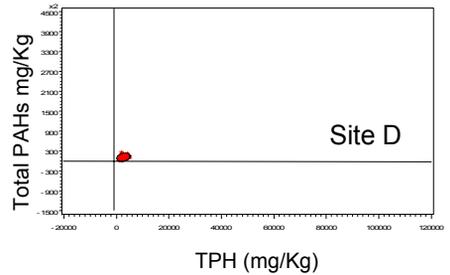
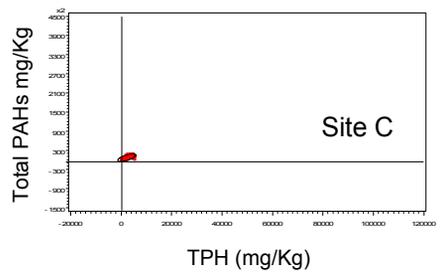
- Between locations
  - Original composition of contaminants
  - Previous degradation
  - Climate
- Within locations
  - Spatial variation
    - some accounting for in blocking of experiments
  - Time, Depth, and Treatment effects
  - Management Decisions
- Within samples
  - Sample heterogeneity
  - Analytical Variation
    - Instrumentation
    - Laboratory Procedures

## 95% Confidence Ellipses for RTDF Data



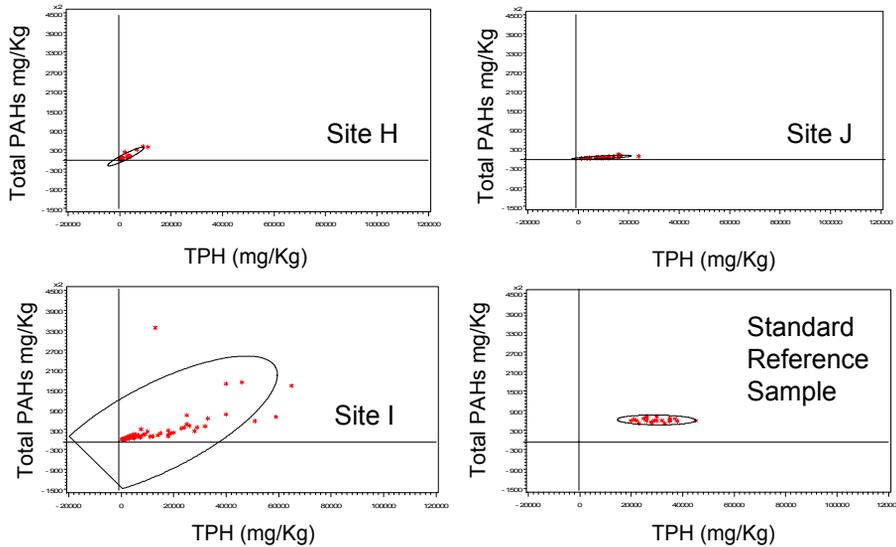
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## 95% Confidence Ellipses for RTDF Data



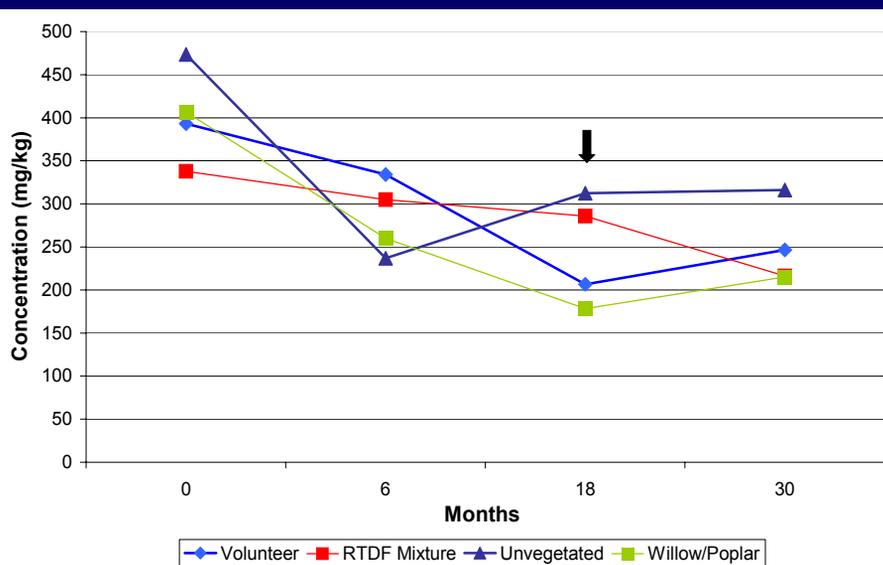
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## 95% Confidence Ellipses for RTDF Data



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## Site F Treatment Means for Total PAHs for 0 to 15 cm Depth



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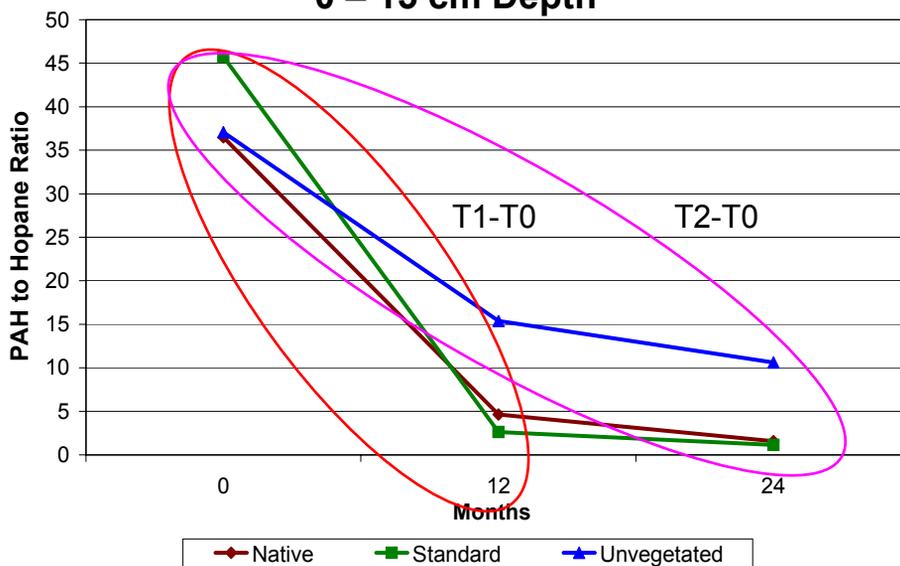
## Treatment Differences for 41 Normalized PAHs

>25% of PAHs different by ANOVA ( $P < 0.05$ )

Depth	Sampling Events							
	Time 0		Year 1		Year 2		Year 3	
	A	B	A	B	A	B	A	B
Site A					0.39		0.54	0.42
Site B								
Site C								
Site D								
Site E								
Site F								
Site G			0.46	0.71	0.56	0.80		
Site H								
Site I								
Site J								
Site K								
Site L								
Site M								

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## Site G – Hopane Normalized Total PAHs 0 – 15 cm Depth



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## Treatment Differences

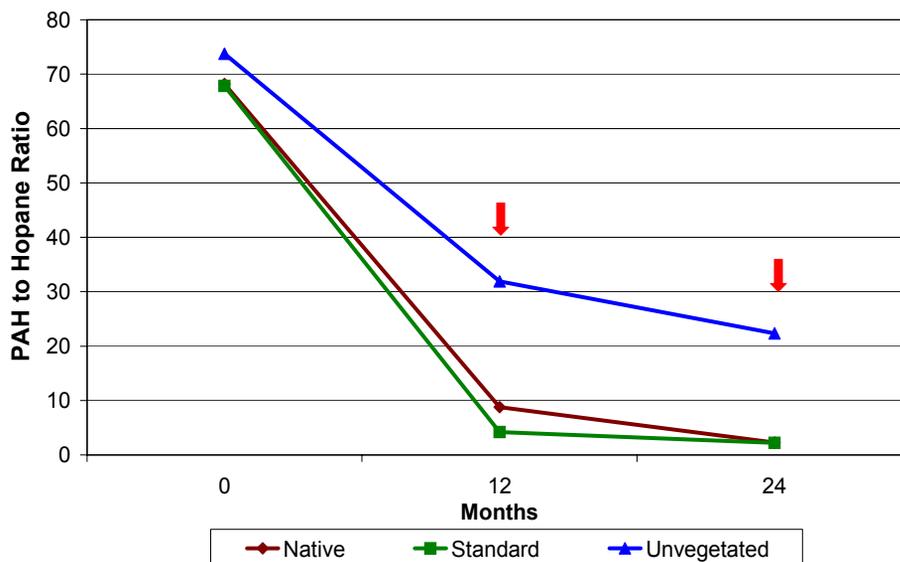
### Change in 41 Normalized PAHs

>25% of PAHs different by ANOVA (P<0.05)

Depth	Interval							
	Time 1-Time 0		Time 2-Time 0		Time 3-Time 0		Time 3-Time 1	
	A	B	A	B	A	B	A	B
Site A		0.29	0.39		.37	.42	.49	0.56
Site B								
Site C								
Site D				0.53				
Site E								
Site F							0.34	
Site G	0.44	0.44	0.46	0.51				
Site H								
Site I								
Site J								
Site K								
Site L								
Site M								

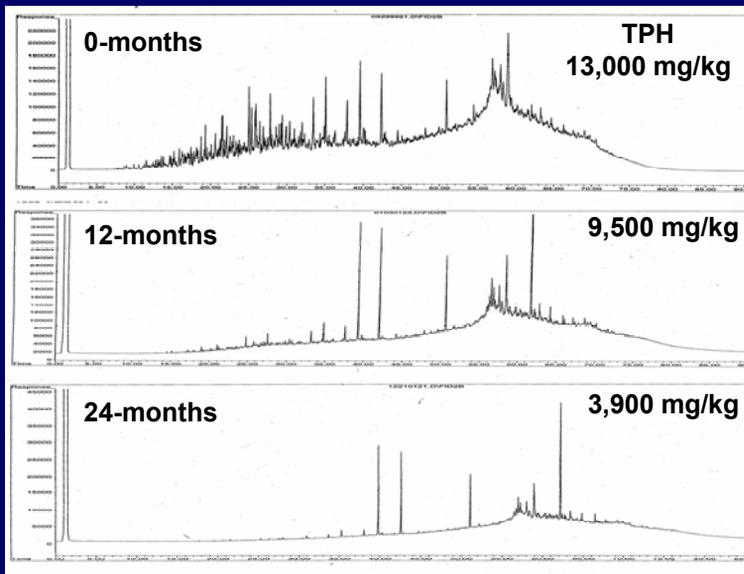
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### Site G – Hopane Normalized Total PAHs 15 – 45 cm Depth



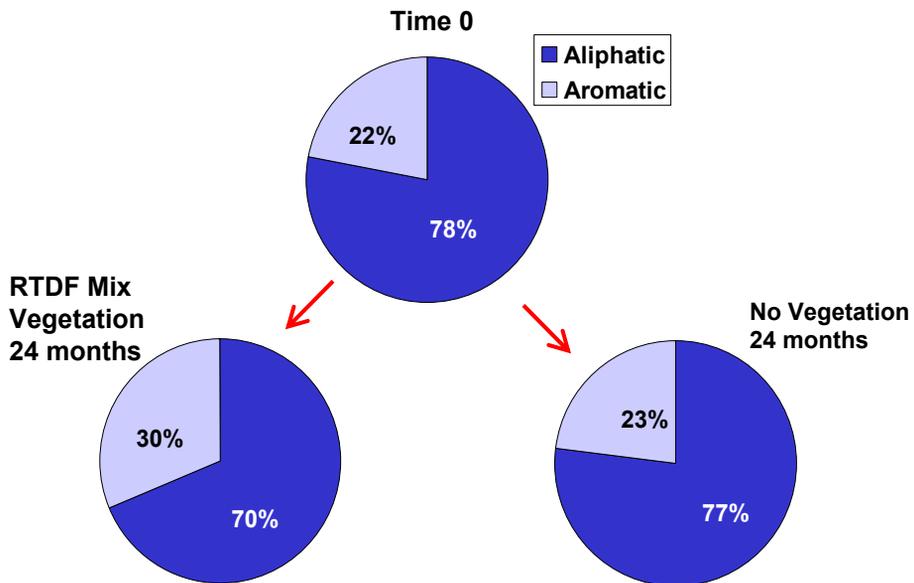
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## Total Petroleum Hydrocarbons -- Plot G11, 0-15 cm Depth



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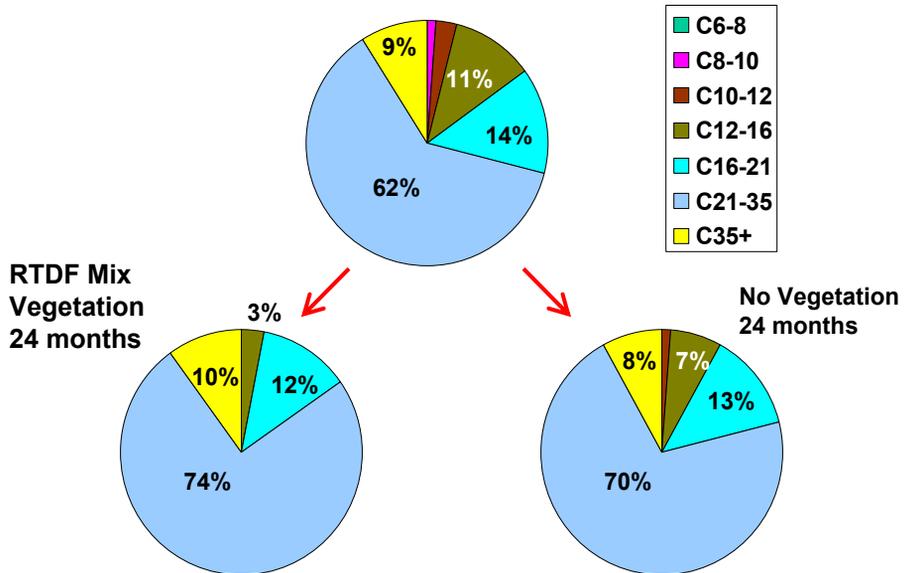
## Site G – 0 to 15 cm Depth



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## Site G – 0 to 15 cm Depth

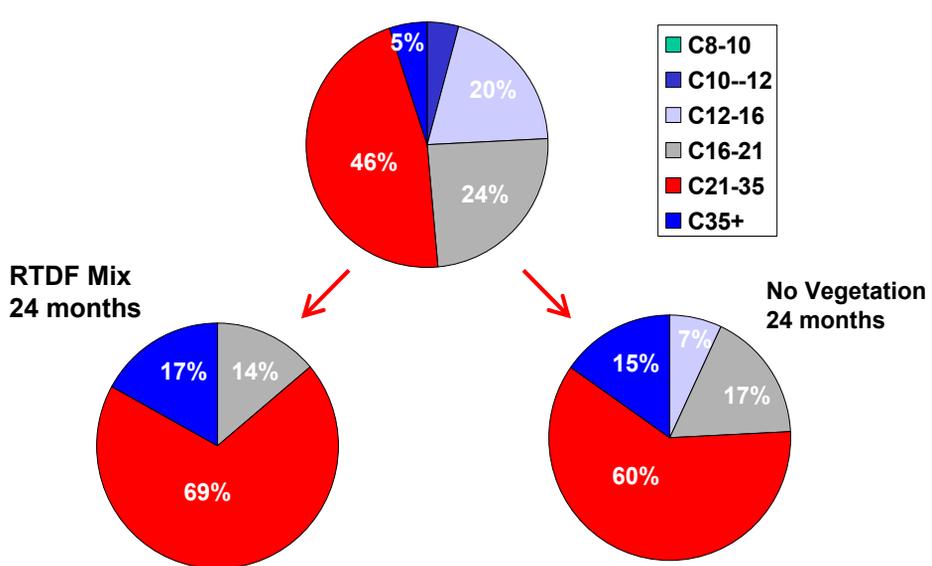
### Aliphatic Fractions Time 0



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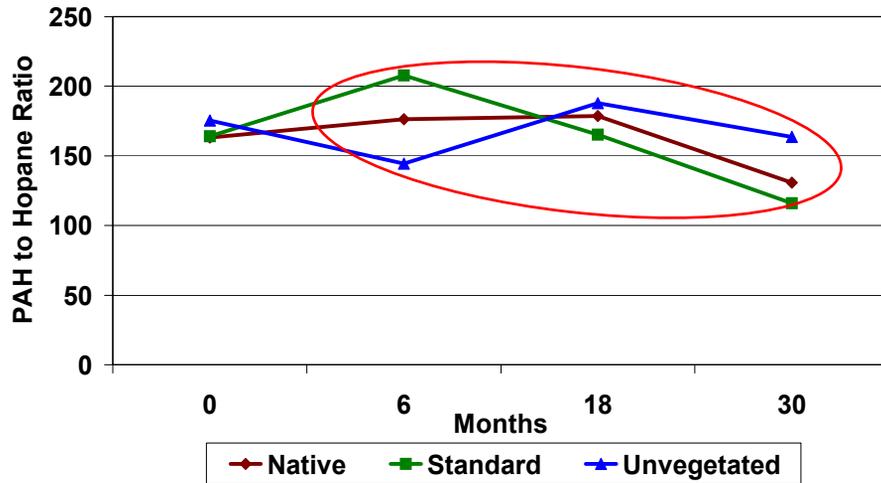
## Site G – 0 to 15 cm Depth

### Aromatic Fractions Time 0



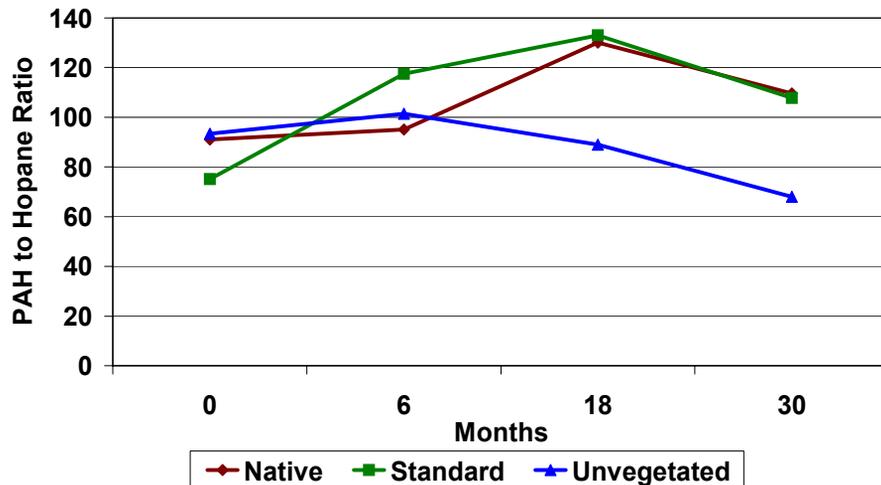
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RTDF Trial Site A -- Hopane Normalized Total PAHs  
15 to 45 cm



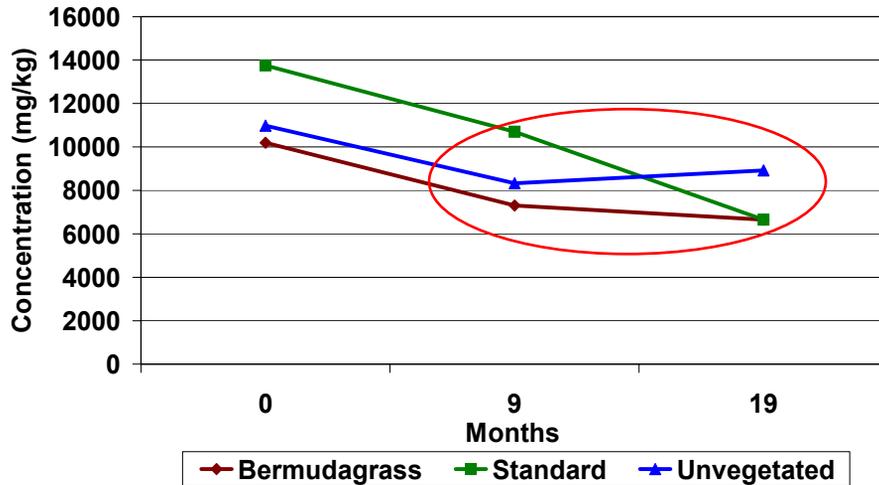
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RTDF Trial Site A -- Hopane Normalized Total PAHs  
0 to 15 cm



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RTDF Trial Site J -- Total Petroleum Hydrocarbons  
0 to 15 cm



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## Status of Project

- 75% data available
- 4 new datasets within next month
- 7 of 13 locations are finished
  - 5 have data for 3 growing seasons
    - Site F will continue for 3 more years
  - less than 3 growing seasons for 2 sites
- Additional results expected for 7 locations
- 2 new locations in Canada
- More data analysis

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## Primary Results to Date

Sites	Evidence
G	– strong evidence of positive vegetation effect - Highly degradable source, lower variation
J	– strong evidence of positive vegetation effect only with an alternative sampling method
A,D,F	– evidence of emerging vegetation effect - Needs confirmation over longer period
A	– evidence of negative vegetation effect in surface soil only

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## Preliminary Conclusions

- Is there evidence that vegetation enhances progress toward practical environmental management objectives for petroleum sites within 3 years?
- Yes, at some locations.
- Use site specific

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## Preliminary Conclusions

- Best locations -- Highly degradable source material with low to moderate hydrocarbon concentrations near risk-based levels.
  - Site characterization important
  - Net environmental benefits and cost may support use of phytotechnologies.

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## Preliminary Conclusions

- Highly weathered sites
  - Evidence of vegetation effect difficult to demonstrate.
  - High variability from multiple sources obscures potential treatment effects.
  - Initial composition and aging limits potential for further degradation.
  - Effects are long term and three years not always sufficient.
  - Vegetation has both positive and negative effects on bioavailability.

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## Preliminary Conclusions

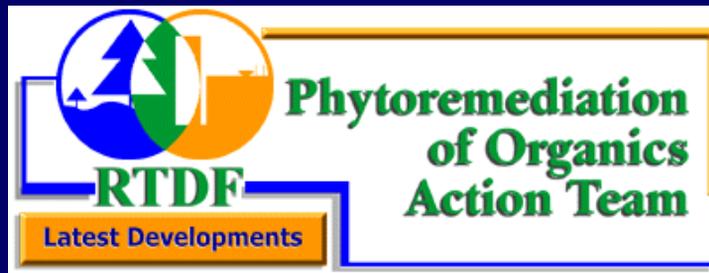
- Highly weathered sites
  - Phytotechnologies may be part of a long term ecological restoration strategy.
  - Phytorestoration that includes continued slow remediation and stabilization processes.
  - Need to understand bioavailability and risk.

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## The Future

- Improvements to the protocol
- Additional results and analyses
- Final report
- Results on RTDF website

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## TPH In Soil Subgroup

[www.rtdf.org](http://www.rtdf.org)