

PAH Phytodegradation & Habitat Restoration at a Historic Industrial Coke Oven Facility

Clayton Rugh

Michigan State University

Endang Susilawati

Michigan State University

Donald K. Russell

Ford Motor Company

Laura Carreira

Applied Phytogenetics

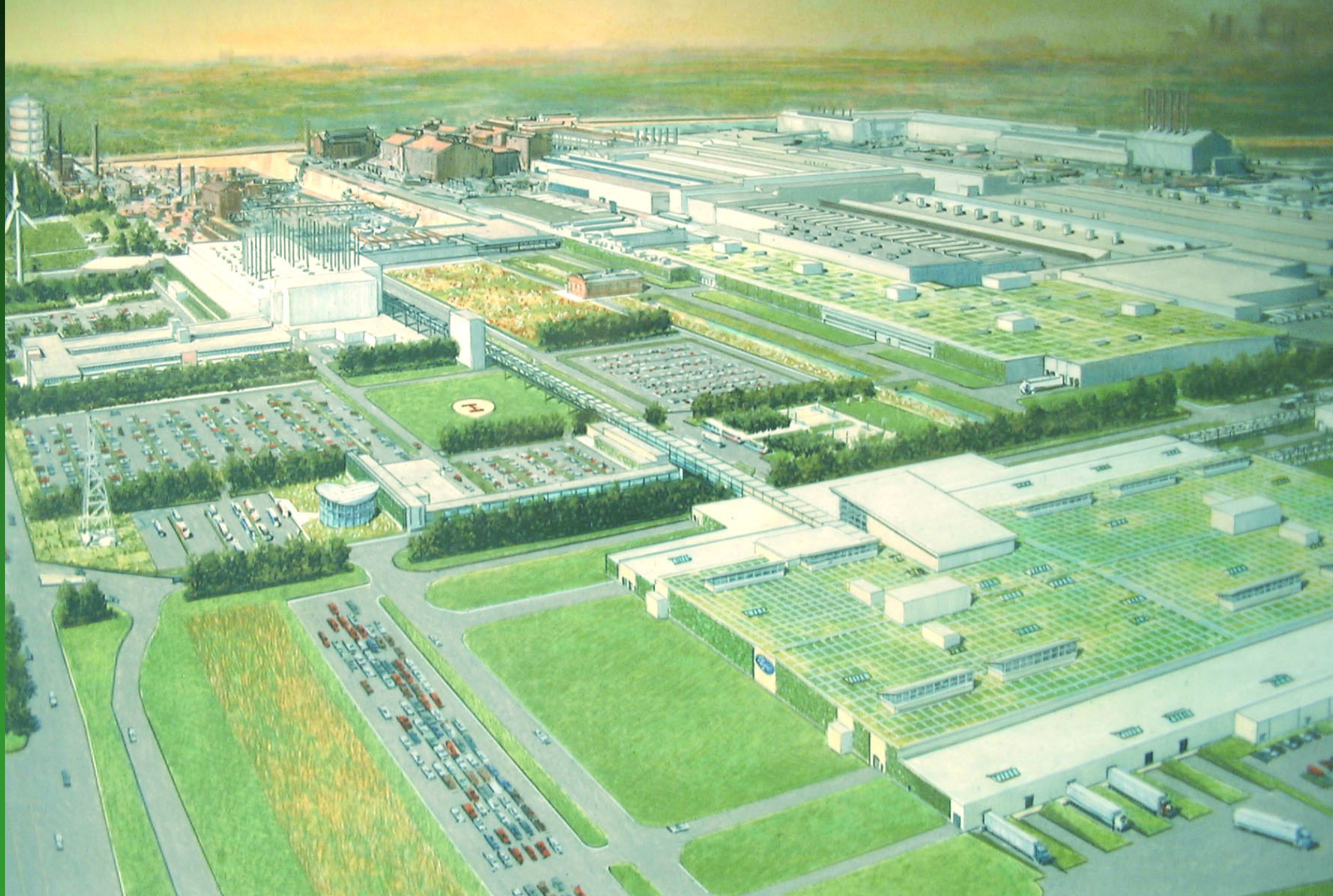
John C. Thomas

Univ of Michigan-Dearborn

Rouge Manufacturing Complex (Dearborn, MI)



Rouge Heritage Project – conceptualized by McDonough +Partners

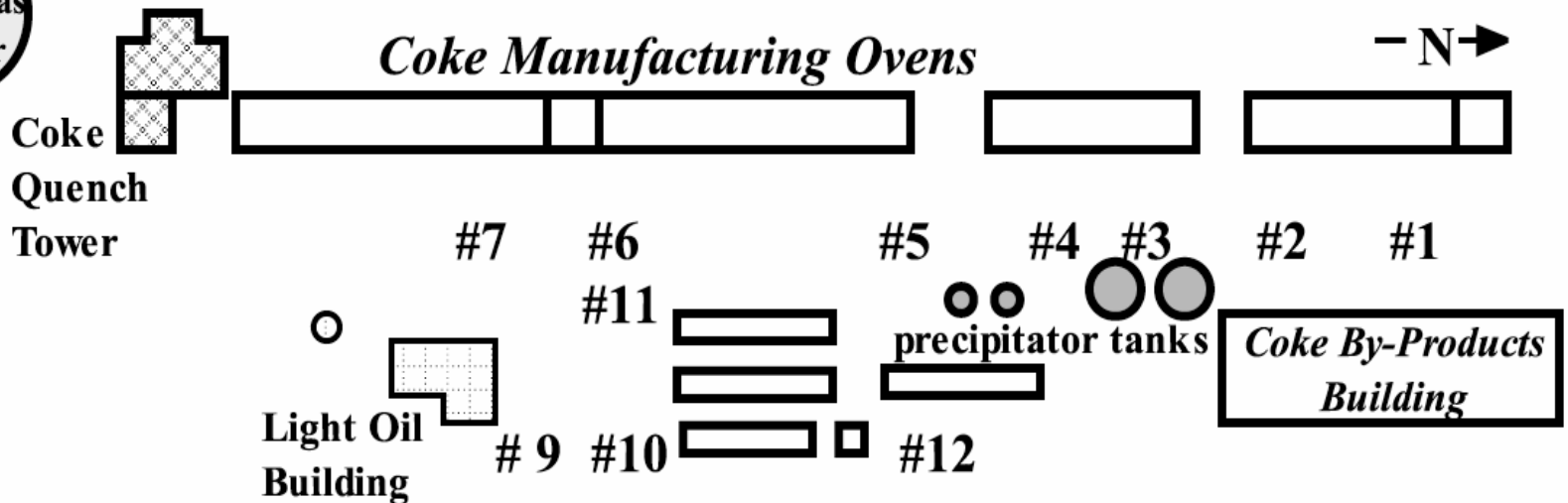


Rouge Manufacturing Complex – Coke Oven Area



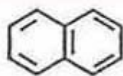
Coke Gas Holder

Soil collection locations from the Coke Oven Facility

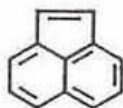


Polyaromatic Hydrocarbon (PAH) Chemical Structures

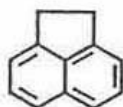
Naphthalene



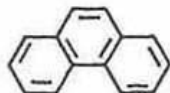
Acenaphthene



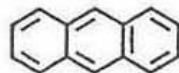
Acenaphthylene



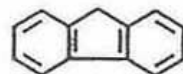
Phenanthrene



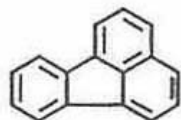
Anthracene



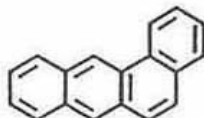
Fluorene



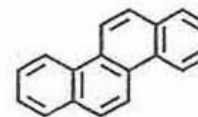
Fluoranthene



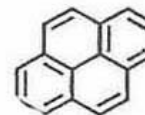
Benz(a)anthracene



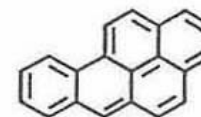
Chrysene



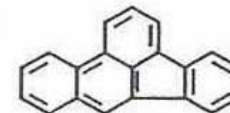
Pyrene



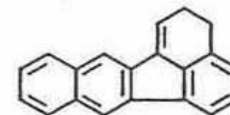
Benzo(a)pyrene



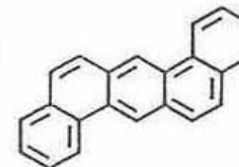
Benzo(b)fluoranthene



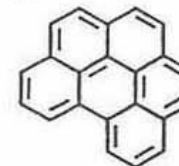
Benzo(k)fluoranthene



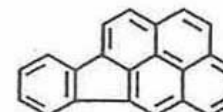
Dibenz(a,h)anthracene



Benzo(ghi)perylene



Indeno(1,2,3-cd)pyrene



Ecological or Intrinsic Phytoremediation

Use of managed, natural systems

Emphasis on sustainability

Regional native species + composts

Plant-Enhanced PAH Biodegradation

Rhizostimulation of bacterial dioxygenase activity

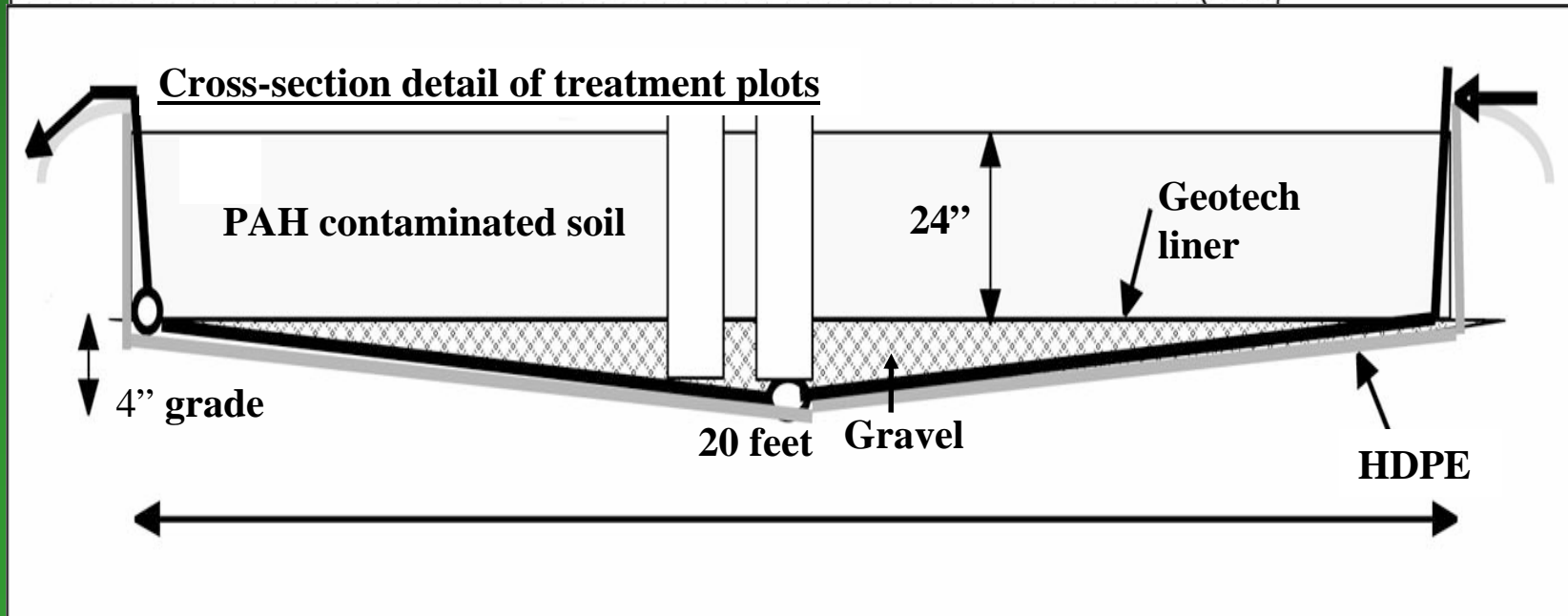
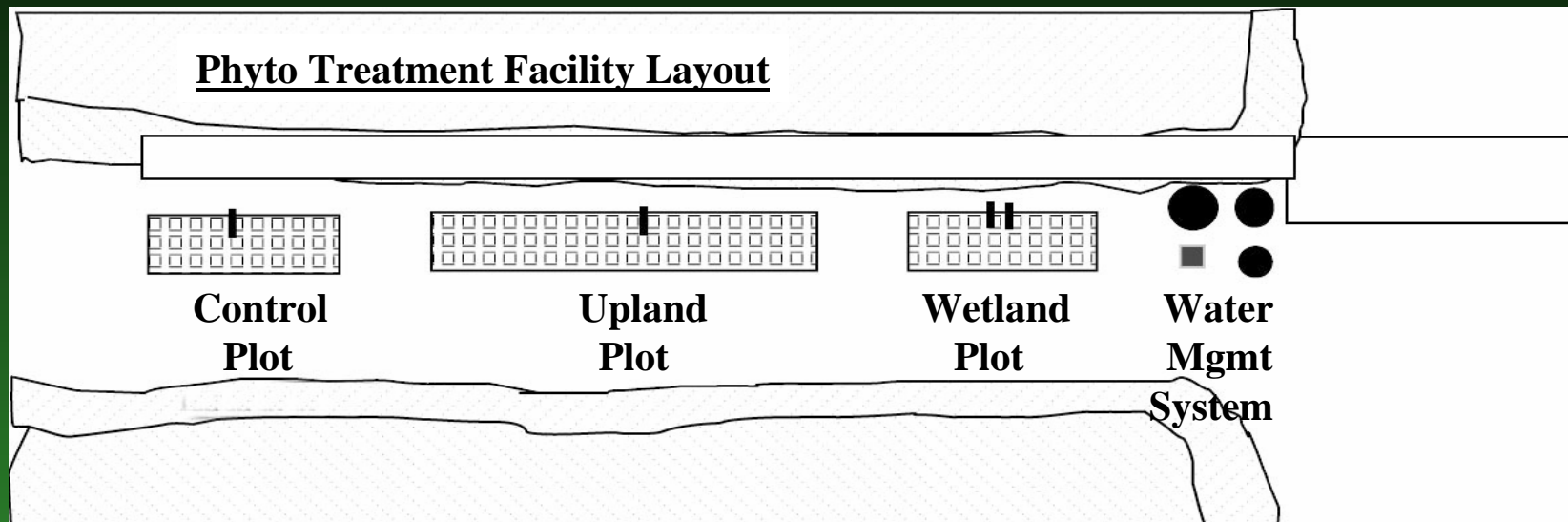
Root exudates as nutrients and co-metabolites

Phyto Field Trial - Selected Upland Plant Species

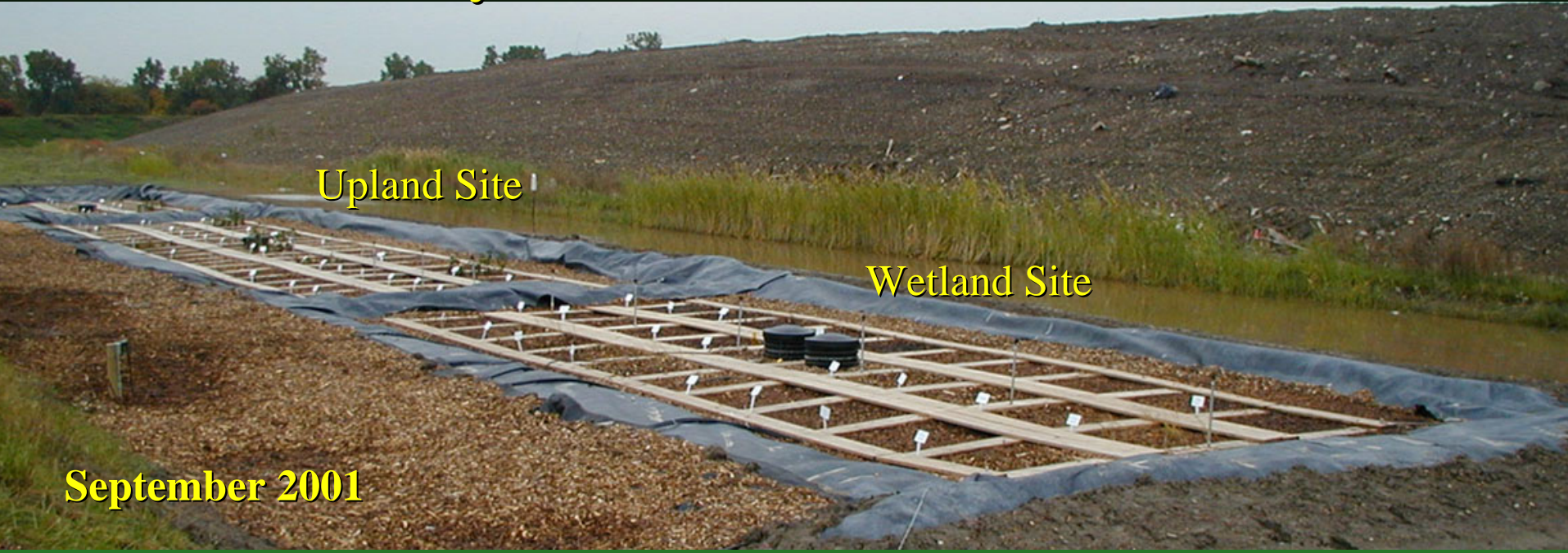
	Scientific Name	Common Name
Grasses	<i>Andropogon gerardii</i>	Big Bluestem
	<i>Andropogon scoparius</i>	Little Bluestem
	<i>Hystrix patula</i>	Bottlebrush Grass
	<i>Spartina pectinata</i>	Prairie Cordgrass
Sedges	<i>Carex sprengeii</i>	Sprengel Sedge
	<i>Scirpus atrovirens</i>	Bulrush
Herbaceous	<i>Amorpha canescens</i>	Leadplant
	<i>Aster novae-angliae</i>	New England Aster
	<i>Cirsium discolor</i>	Pasture Thistle
	<i>Eupatorium perfoliatum</i>	Boneset
	<i>Eupatorium purpureum</i>	Joe-Pye Weed
	<i>Geum triflorum</i>	Prairie Smoke
	<i>Lobelia cardinalis</i>	Cardinal Flower
	<i>Silphium teribinthinaceum</i>	Prairie-dock
Shrubs	<i>Ceanothus americanus</i>	New Jersey Tea
	<i>Physocarpus opulifolius</i>	Common Ninebark
	<i>Spirea alba</i>	Meadowsweet
	<i>Viburnum dentatum</i>	Arrowhead Viburnum

Phytoremediation Demonstration Plots

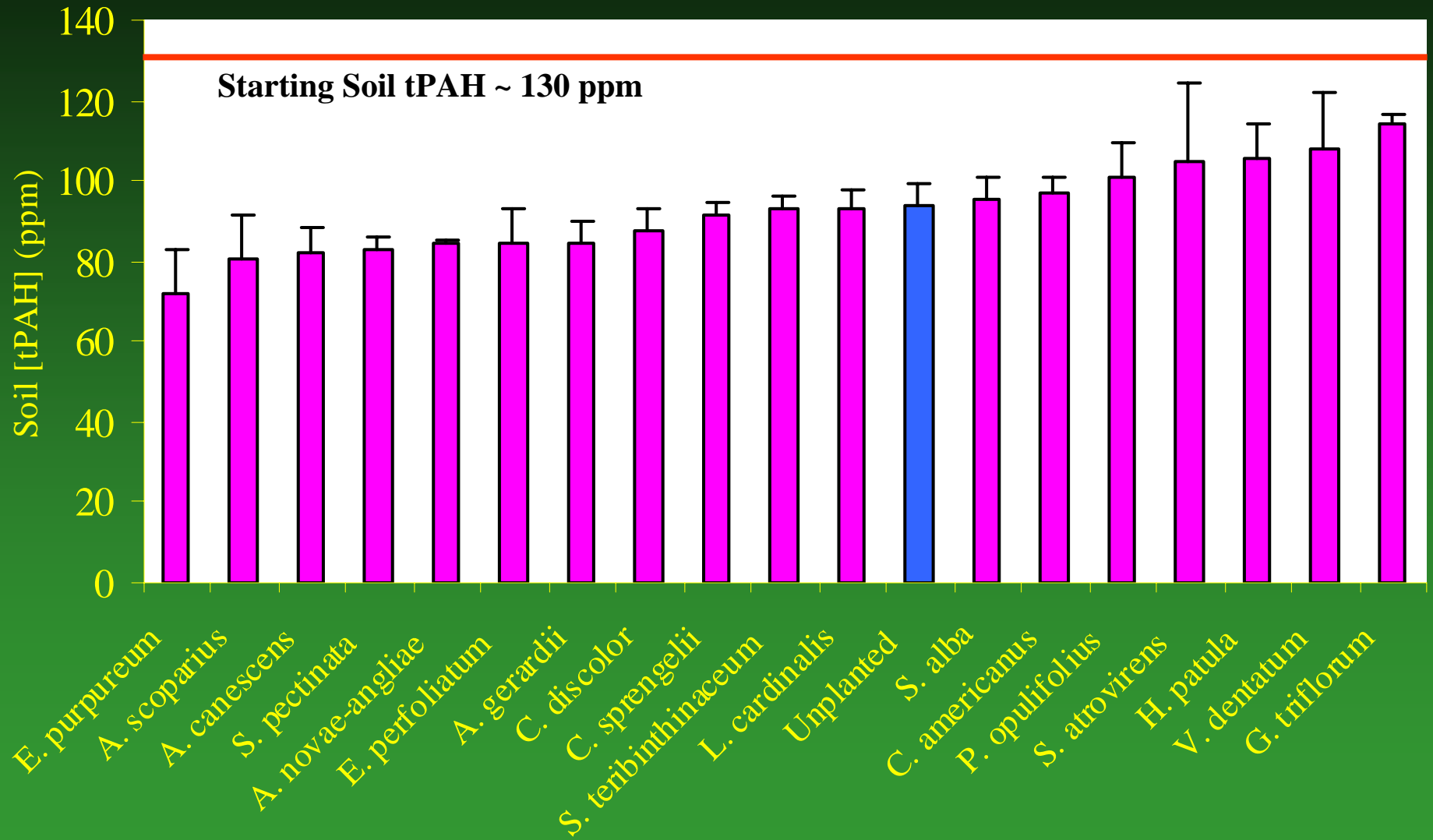
Constructed at Allen Park Clay Mine Landfill by URS Corp.



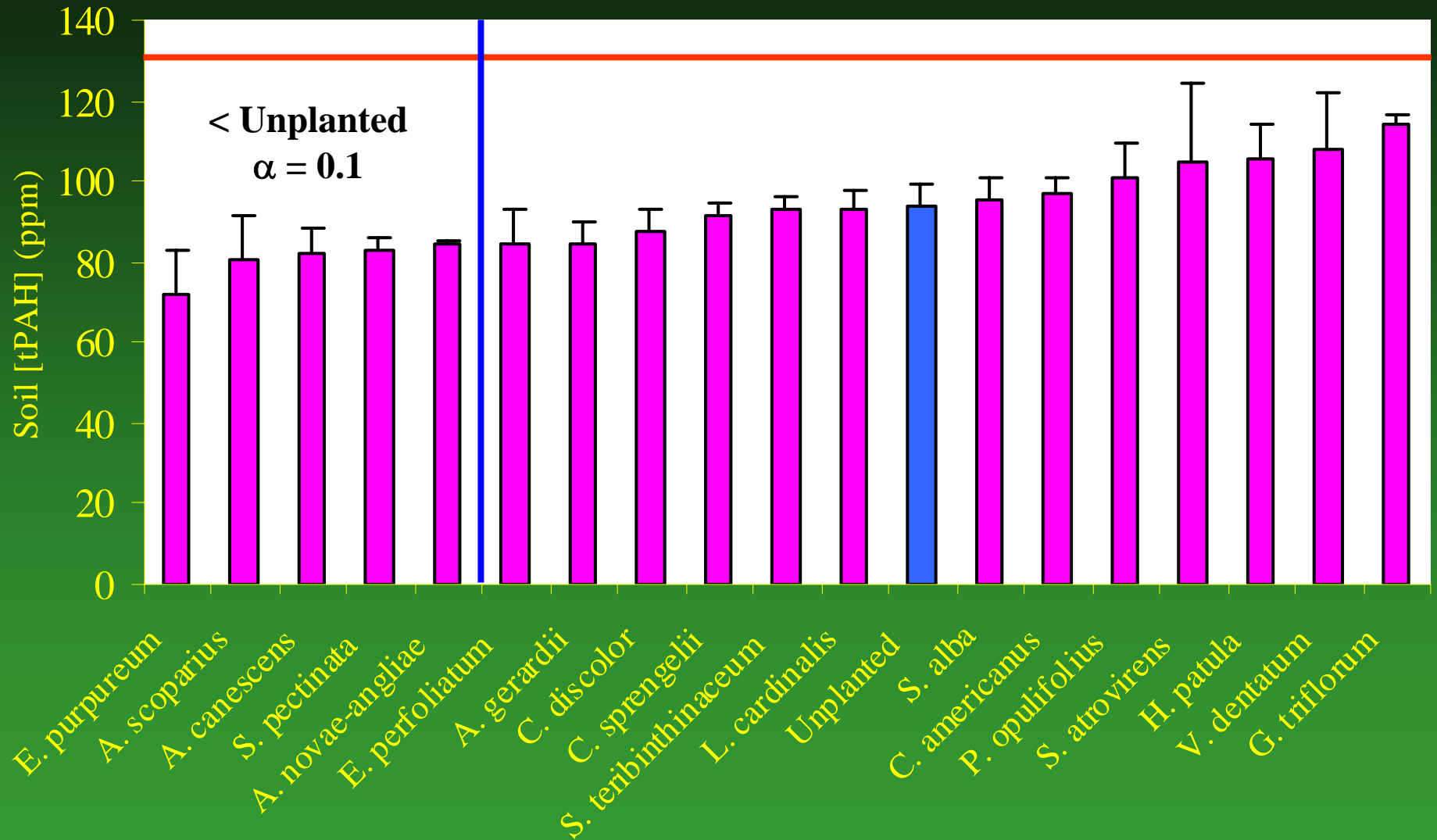
Ford Phytoremediation Field Trial Plots



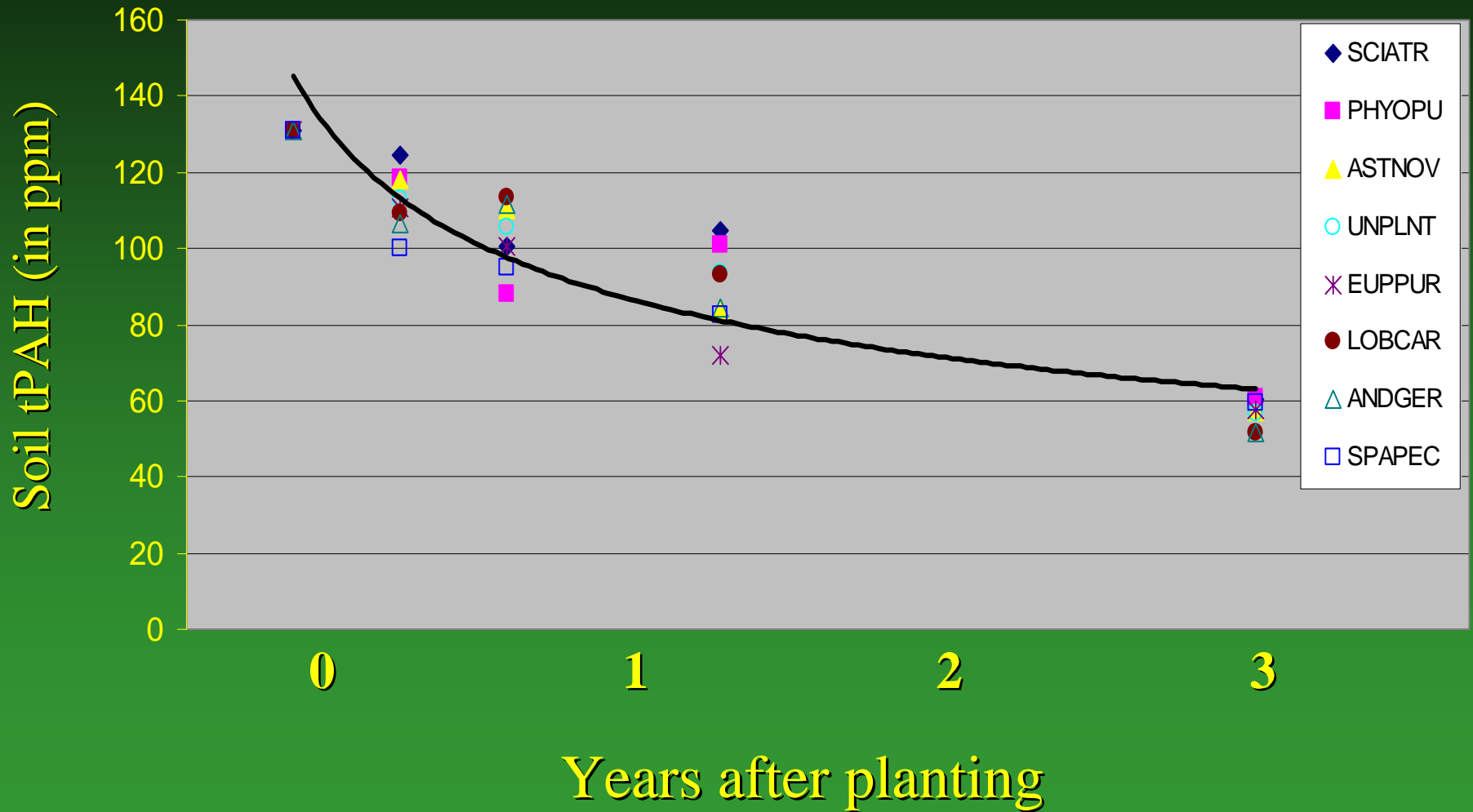
Upland Plot Soil [tPAH] - Sept 2001 (Yr 1)



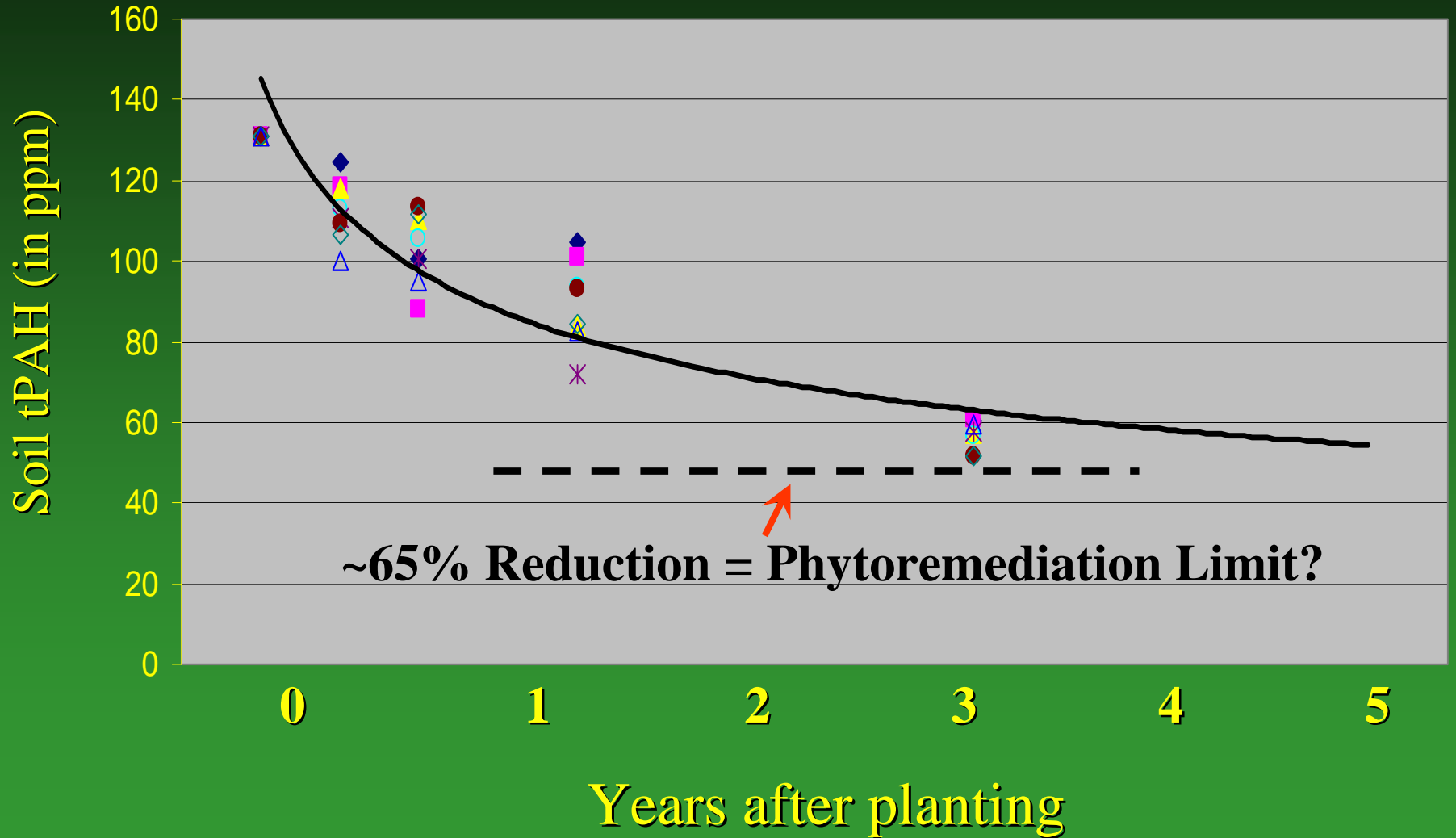
Upland Plot Soil [tPAH] - Sept 2001 (Yr 1)



Final Soil tPAH Concentration for Selected Treatments



Projected Soil tPAH Concentration for Phyto Treatments



Solubility Properties of Selected POPs

<u>PCBs</u>	<u>log(K_{ow})</u>	<u>PAHs</u>	<u>log(K_{ow})</u>
Biphenyl	4.1	Benzene (C ₆ H ₆)	2.1
2-CBP (1 Cl)	4.5	Naphthalene (C ₁₀ H ₈)	3.4
4-CBP (1 Cl)	4.4	Phenanthrene (C ₁₄ H ₁₀)	4.5
4,4'-CBP (2 Cl)	5.2	Anthracene (C ₁₄ H ₁₀)	4.5
2,4,5-CBP (3 Cl)	5.7	Chrysene (C ₁₈ H ₂₂)	5.6
2,3,'4,4'-CBP (4 Cl)	6.3	Benzo(a)pyrene (C ₂₀ H ₁₂)	6.5
Decachloro-BP (10 Cl)	8.2	Benzo(g,h,i)perylene (C ₂₂ H ₁₂)	7.2

Hydrophobicity is measured as solubility in Octanol divided by Aqueous Solubility

Ex. Phenanthrene has a $\log K_{ow} = 4.46$

...which equals 28840.32X more Phen in octanol phase than in aqueous

Particle-Scale Understanding of the Bioavailability of PAHs in Sediment.
Talley, Ghosh, Tucker, Furey, Luthy. 2002. ES&T 36:477-483

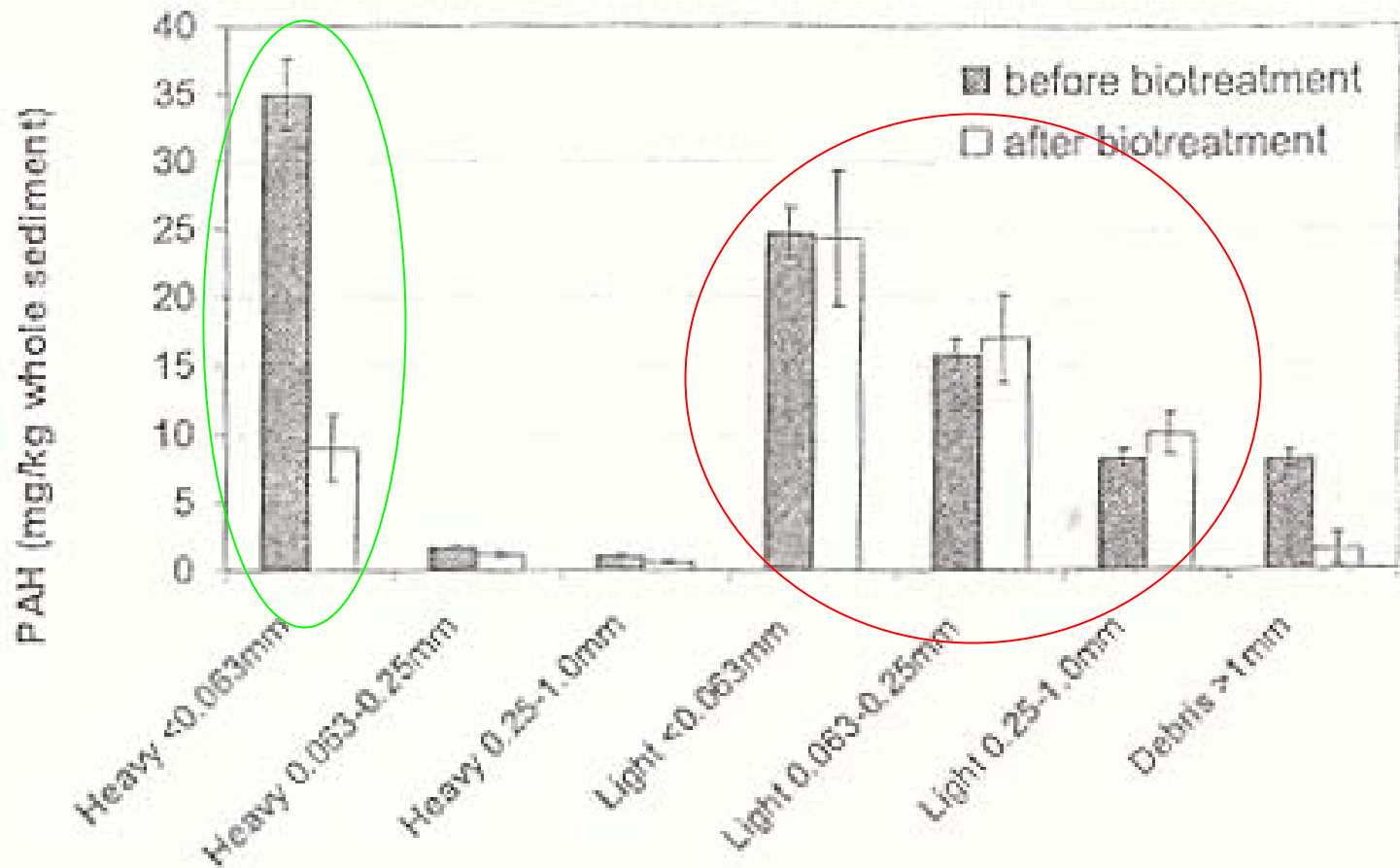
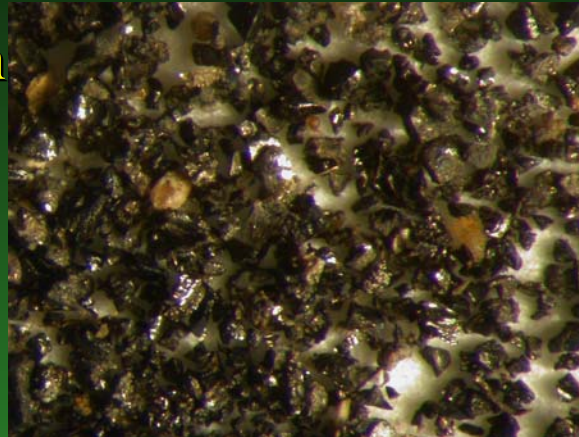


FIGURE 3. PAH reduction in sediment fractions before and after bioslurry treatment. These values are based on the contribution of each fraction to the total PAH concentration of 90 mg/kg as measured by GC-FID. Error bars indicate ± 1 SD based on analysis of four reactors.

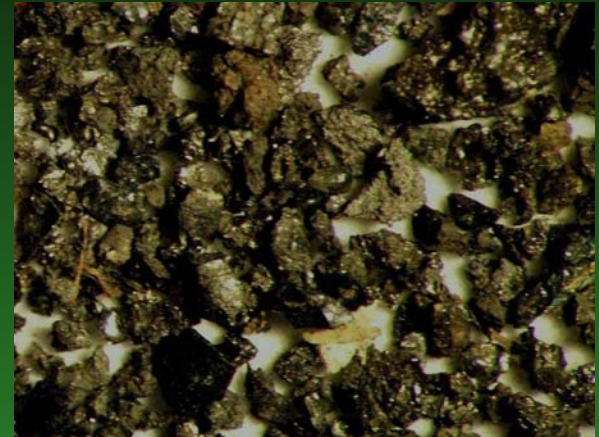
Particle Fractionation of Rouge Soil (Luthy lab, Stanford Univ.)

Size Separation @ 250 μ & Density Separation @ 1.8 g/ml (sat'd CsCl)

Soil Organic Fraction
21% w/w

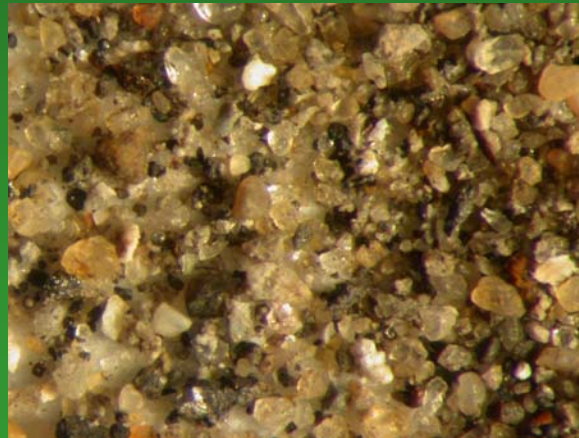


Light Soil (63-250 μ)

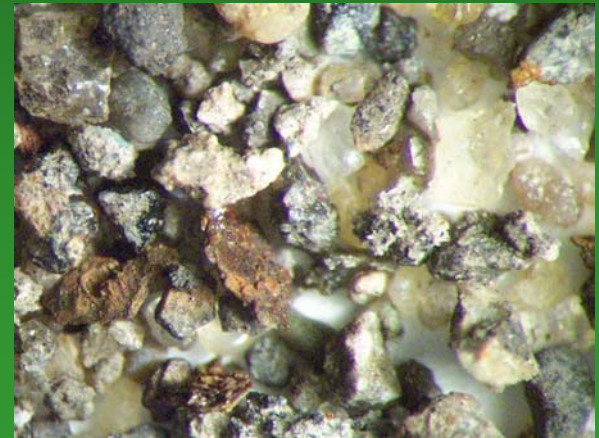


Light Soil (250-1000 μ)

Soil Mineral Fraction
79% w/w



Heavy Soil (63-250 μ)

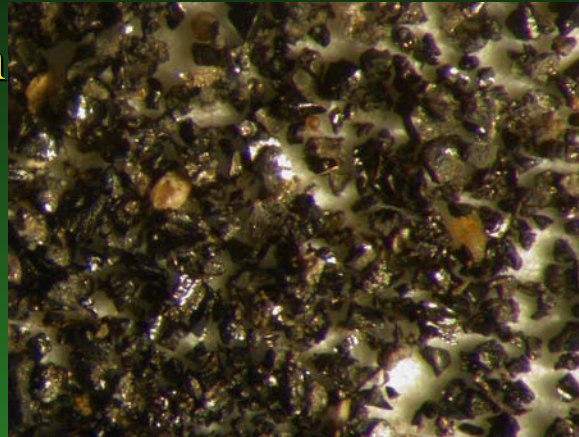


Heavy Soil (250-1000 μ)

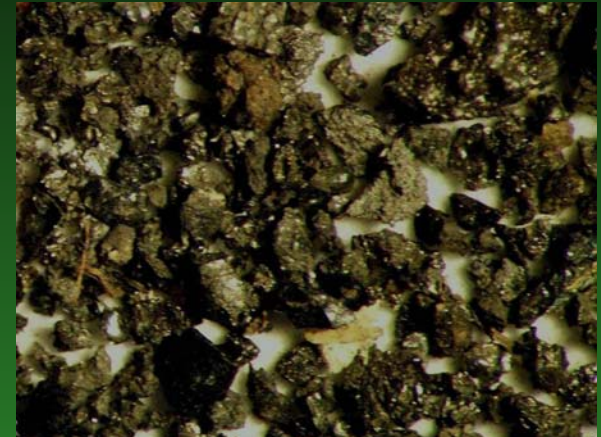
Particle Fractionation of Rouge Soil (Luthy lab, Stanford Univ.)

Size Separation @ 250 μ & Density Separation @ 1.8 g/ml (sat'd CsCl)

Soil Organic Fraction
21% w/w
75% tPAH content

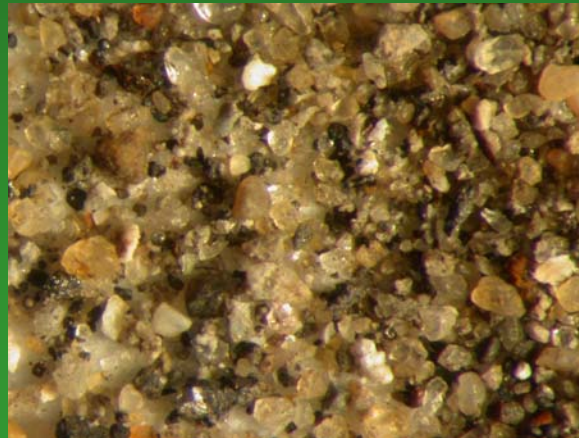


Light Soil (63-250 μ)

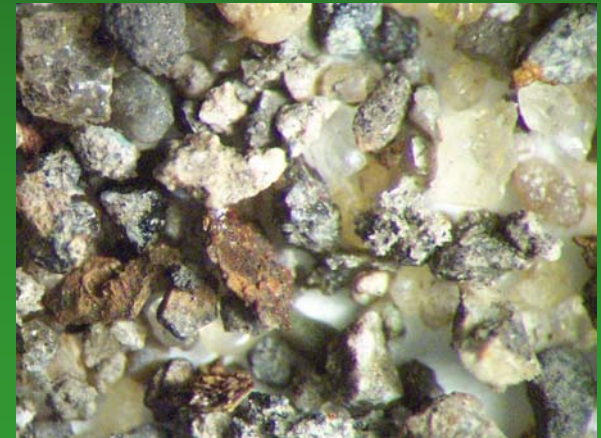


Light Soil (250-1000 μ)

Soil Mineral Fraction
79% w/w
25% tPAH content

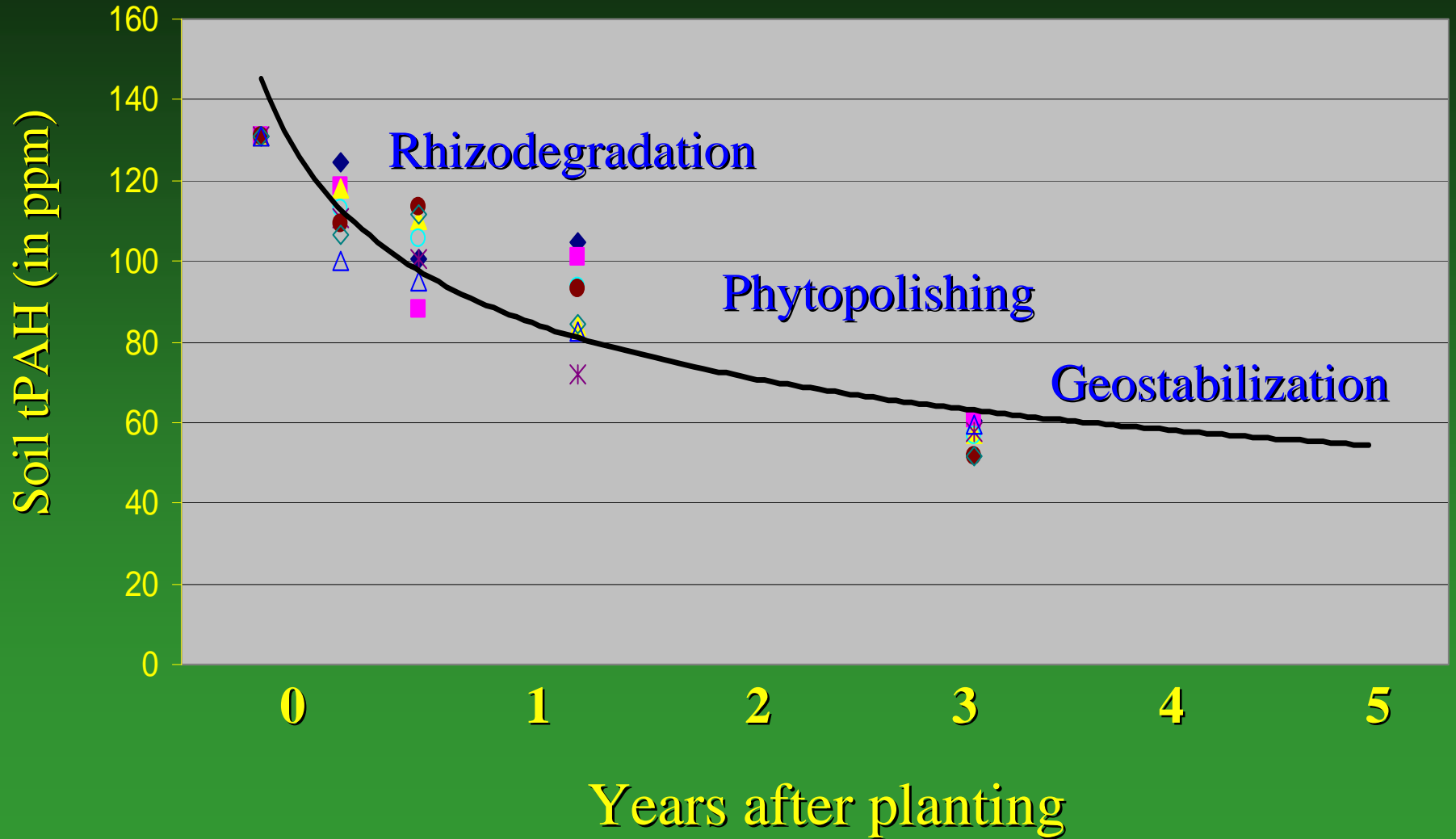


Heavy Soil (63-250 μ)



Heavy Soil (250-1000 μ)

Progressive Mechanism of Soil Phyto Treatments



Part II. Rhizosphere Ecology Influences

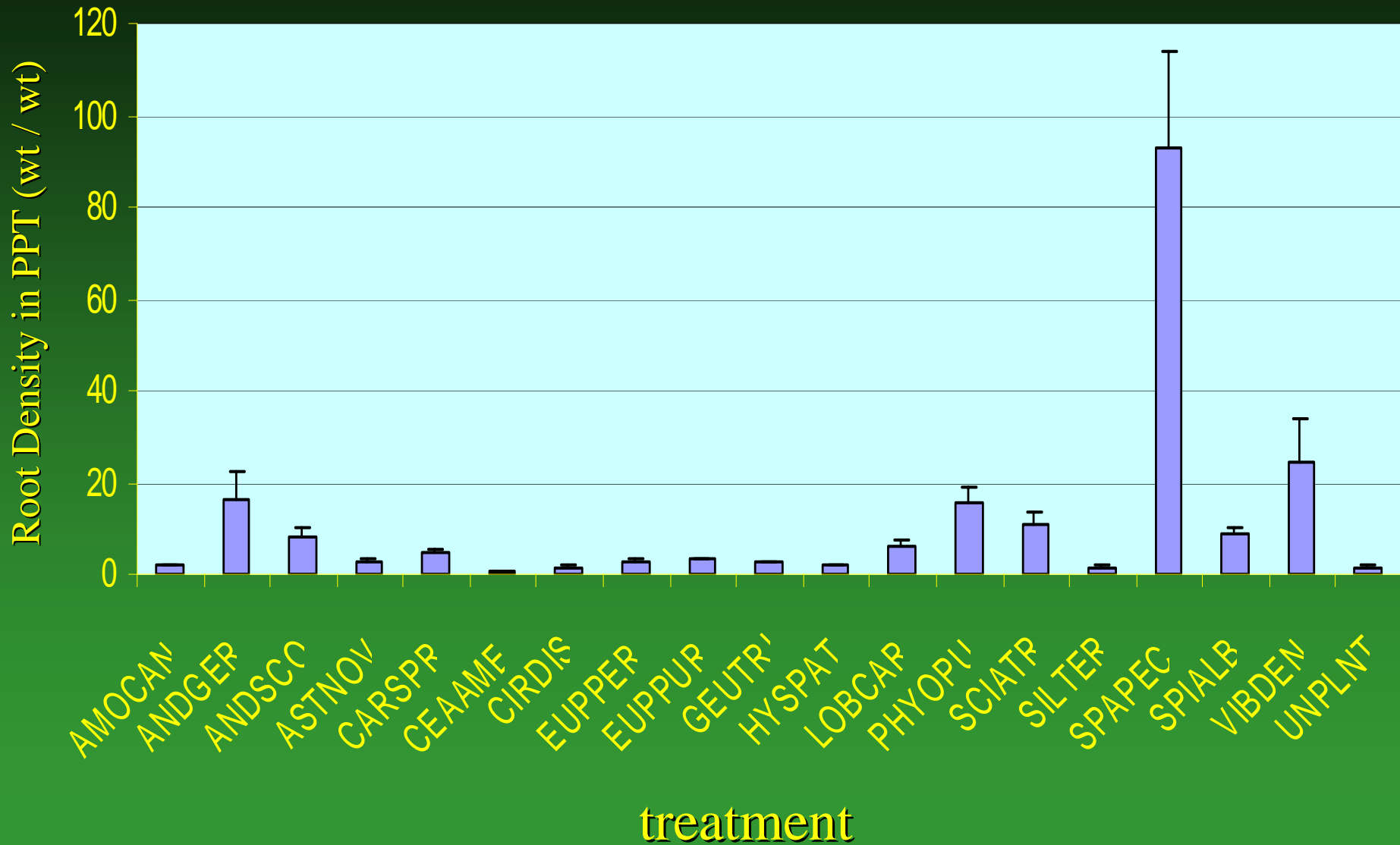
- **Root Quantification and Density**

Excavation and isolation of root biomass

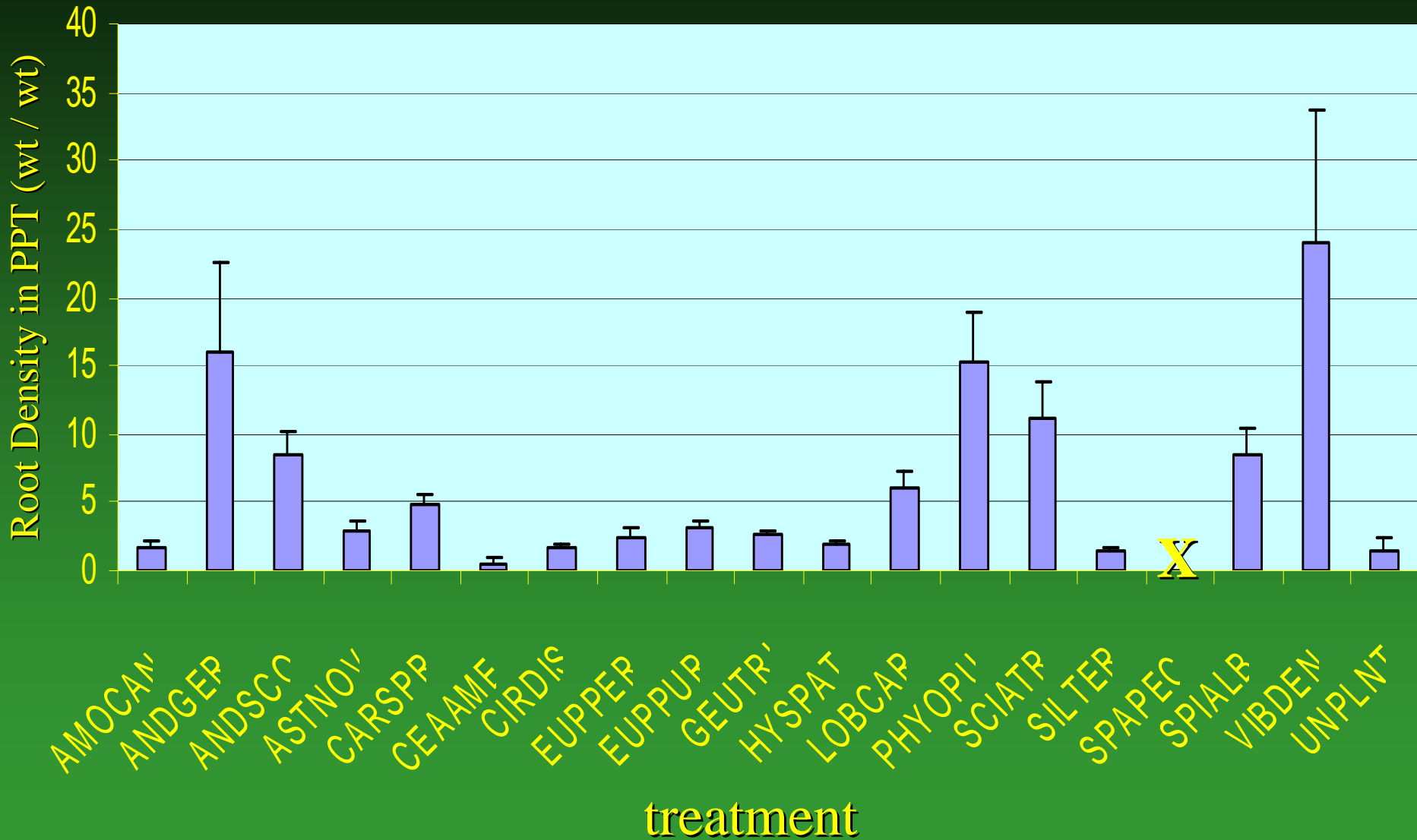
What is a “rhizosphere”?

- **“The area of the soil influenced by root systems...”**
 - estimated to be as much as 3% of soil volume
(J. Fletcher, Univ. of Oklahoma)
 - soil that “stays attached to roots after shaking”

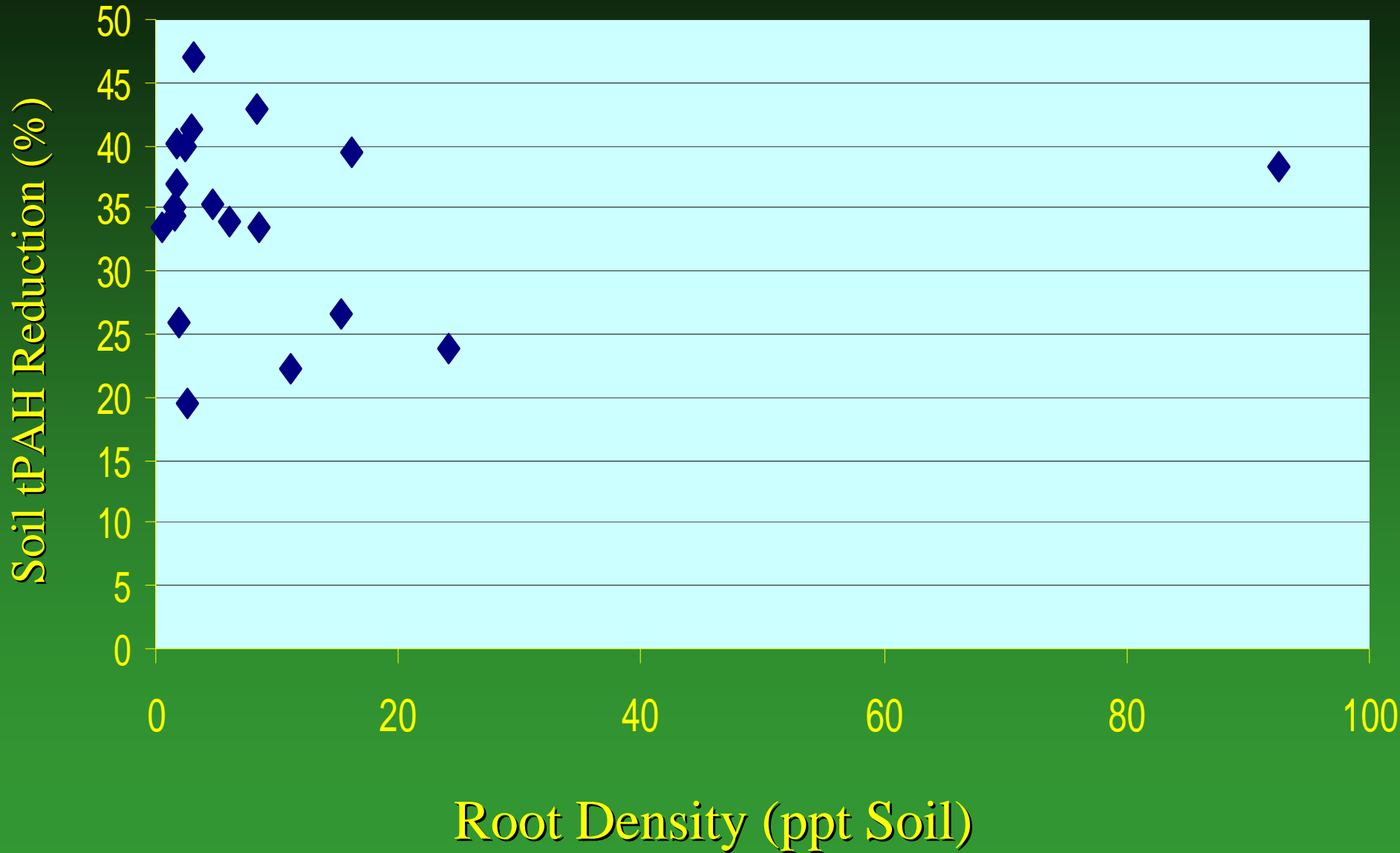
Root Biomass Density relative to Soil (cu. yd.)



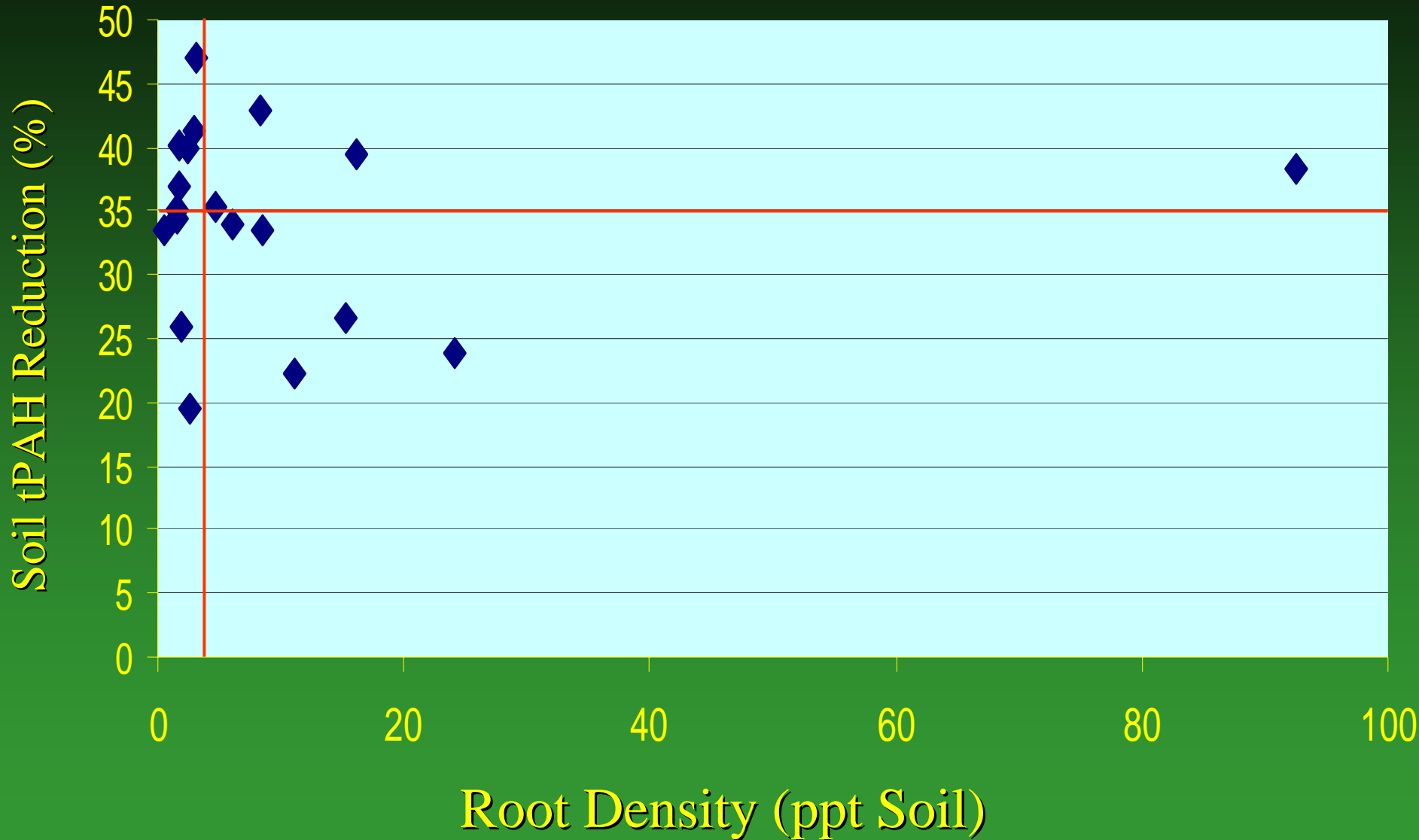
Root Biomass Density relative to Soil (cu. yd.)



Root Biomass Influence on PAH Reduction



Root Biomass Influence on PAH Reduction



Root-Microbe Ecology Interactions

- **Bacterial Rhizostimulation**

Root-enhanced bacteria cell density

Enrichment of PAH biodegraders via cometabolism

- **Bacterial Metabolic Enrichment**

Expansion of bacterial metabolic capabilities

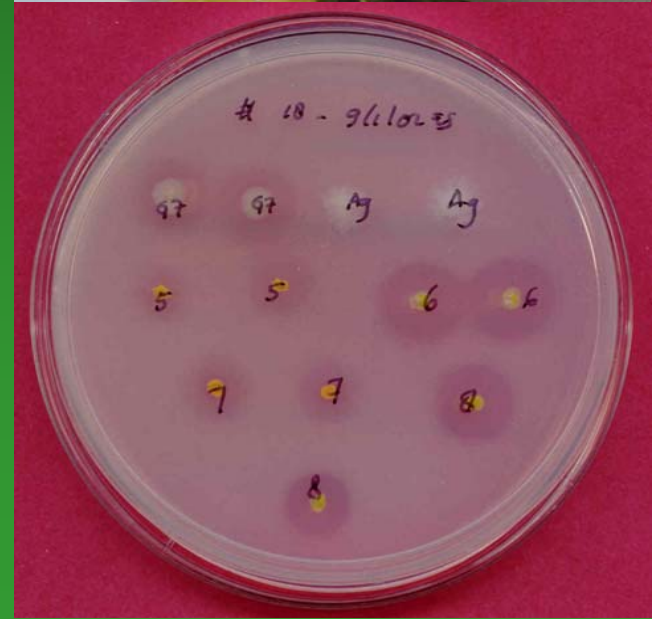
PAH Metabolism Spray Plate Assay

Specific PAH biodegrader assay

Soil extracts plated for CFUs

Phenanthrene residue applied

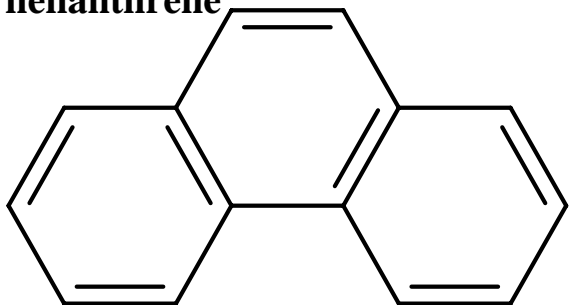
Clear zones = biodegraders = ZFUs



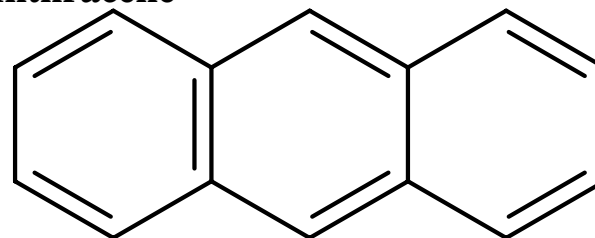
Bacterial Phenanthrene-Degrading Isolates

Spray-Tested against Multiple PAHs

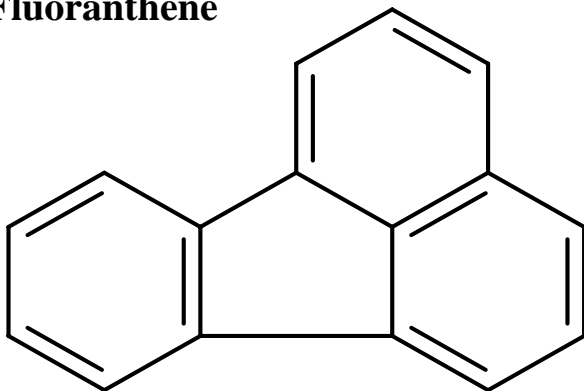
Phenanthrene



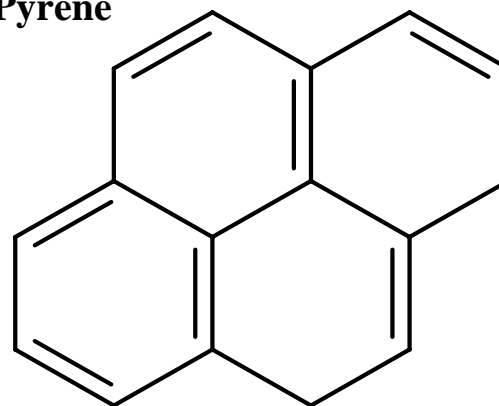
Anthracene



Fluoranthene



Pyrene

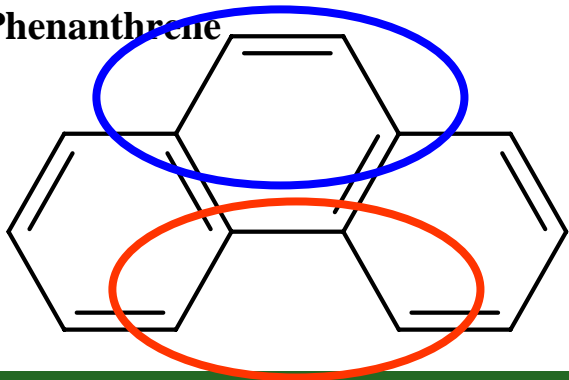


Bacterial Phenanthrene-Degrading Isolates

Spray-Tested against Multiple PAHs

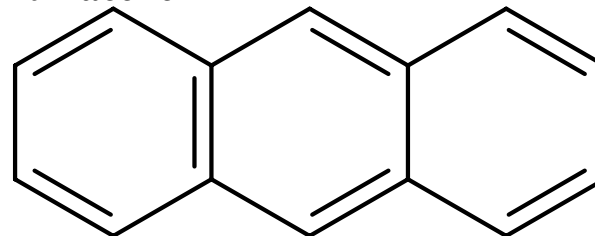
k-region

Phenanthrene

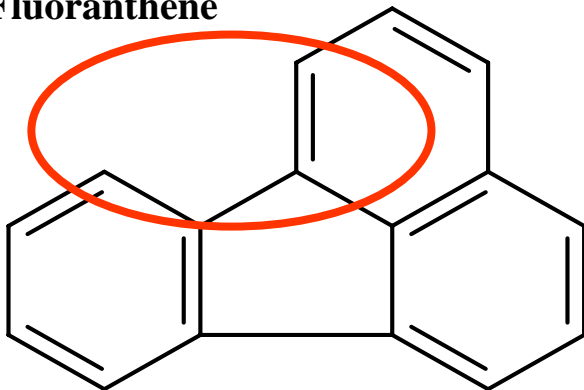


Bay-region

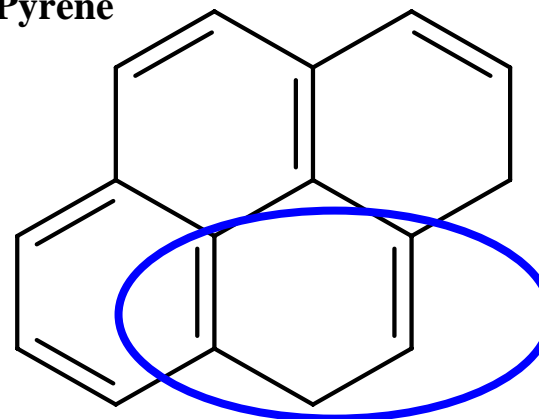
Anthracene



Fluoranthene



Pyrene

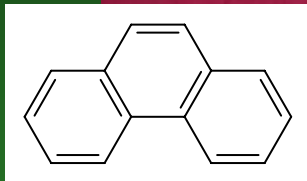


Bacterial Isolates Tested against Multiple PAHs

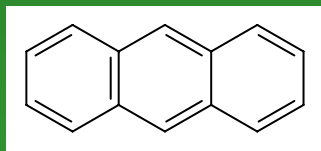
Over 2100 Phenanthrene Degraders Isolated

~110 isolates from each Phyto treatment including untreated soils

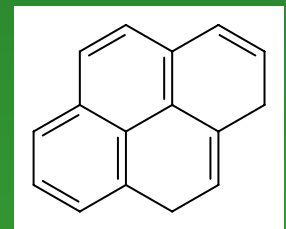
Phen^D isolates Spray-Tested against other PAH compounds



Phenanthrene

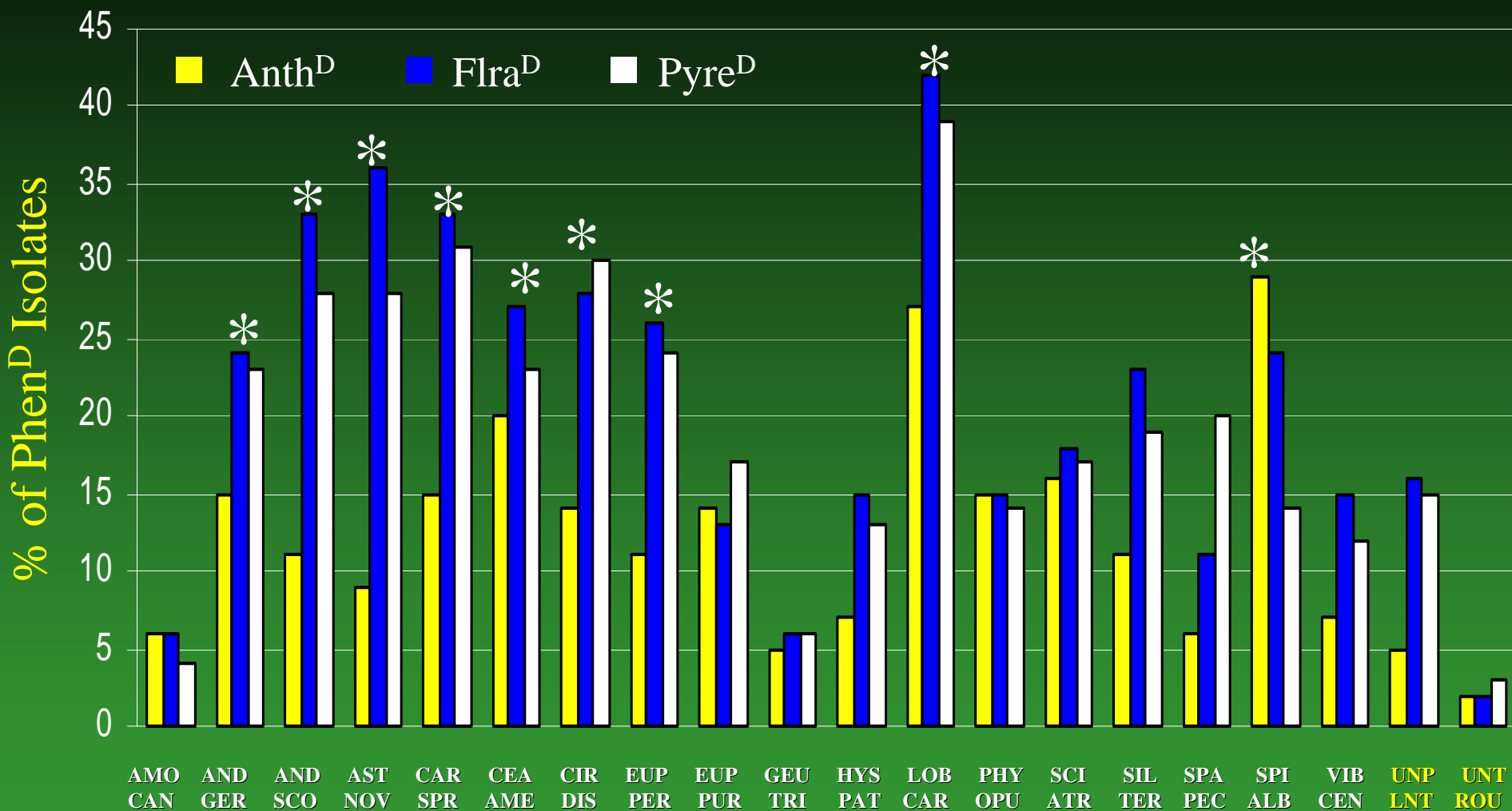


Anthracene



Pyrene

Phenanthrene Degraders tested on other PAHs



* $\alpha = 0.10$

Soil Treatment
(plant spp abbr)

Part III. Community Ecology Influences

- **Vegetated Community Persistence**

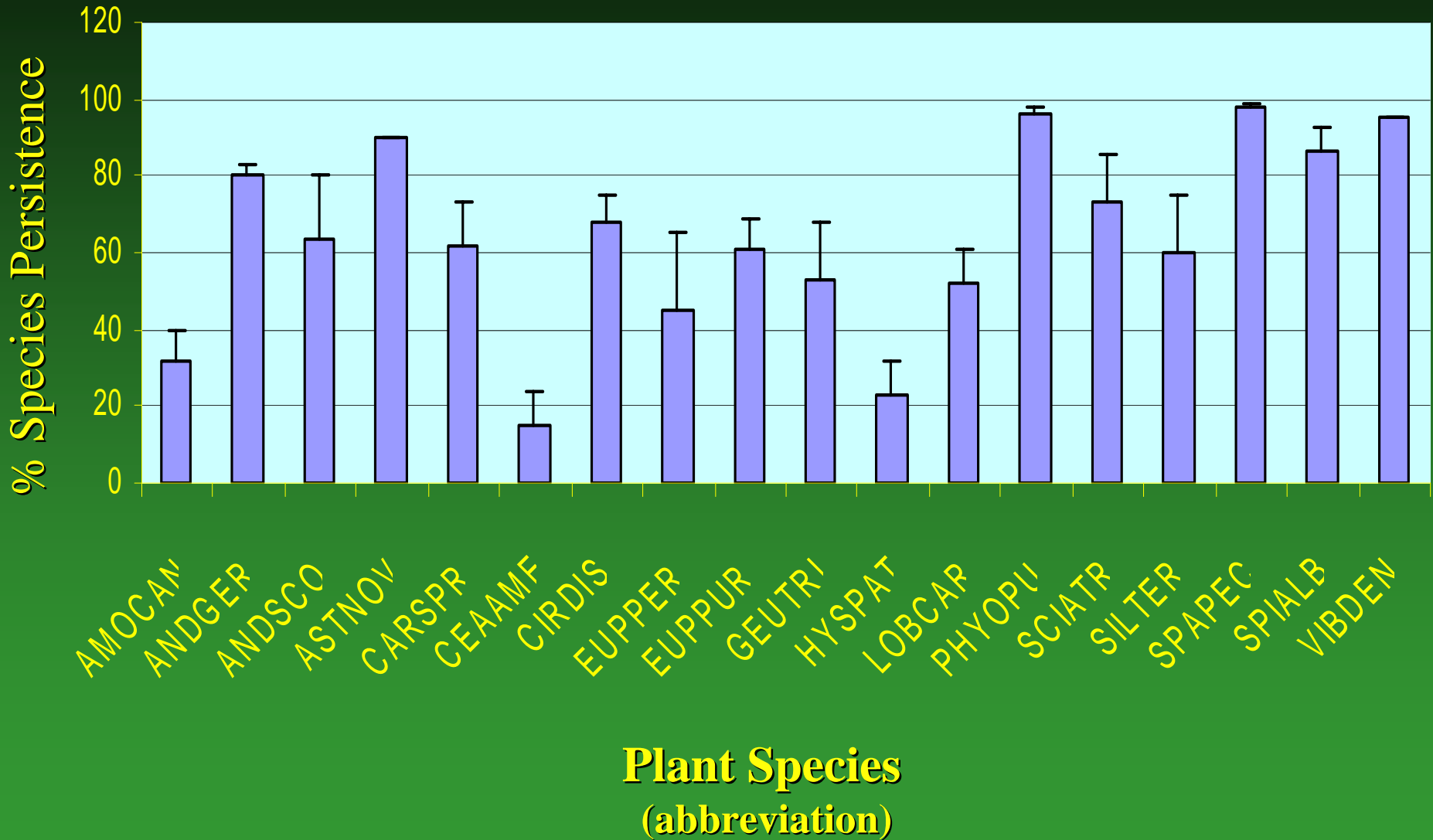
Field installation strategy

Susceptibility to herbivores, disease, encroachment

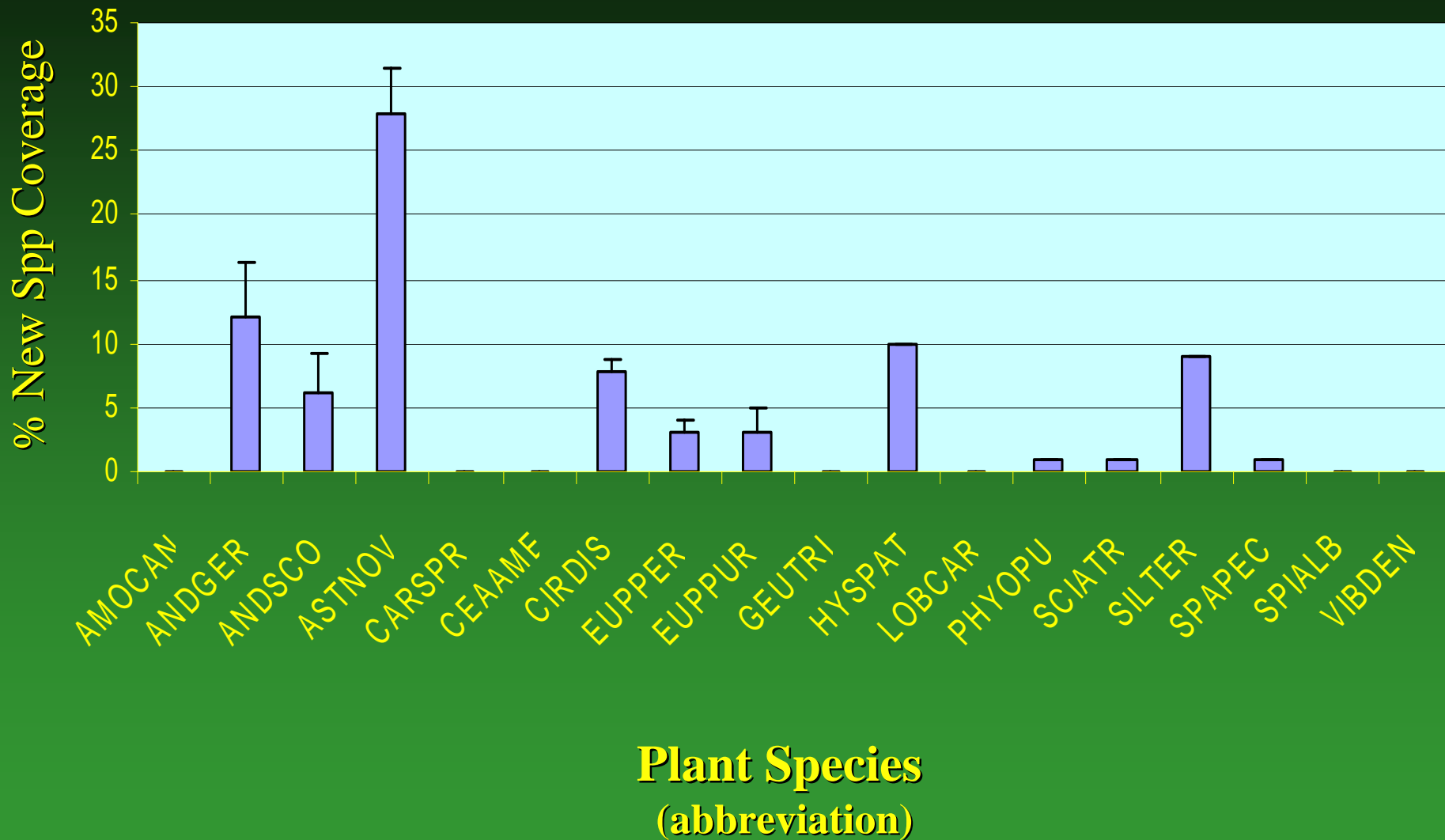
- **Vegetated Community Expansion**

Self-propagation and competitiveness

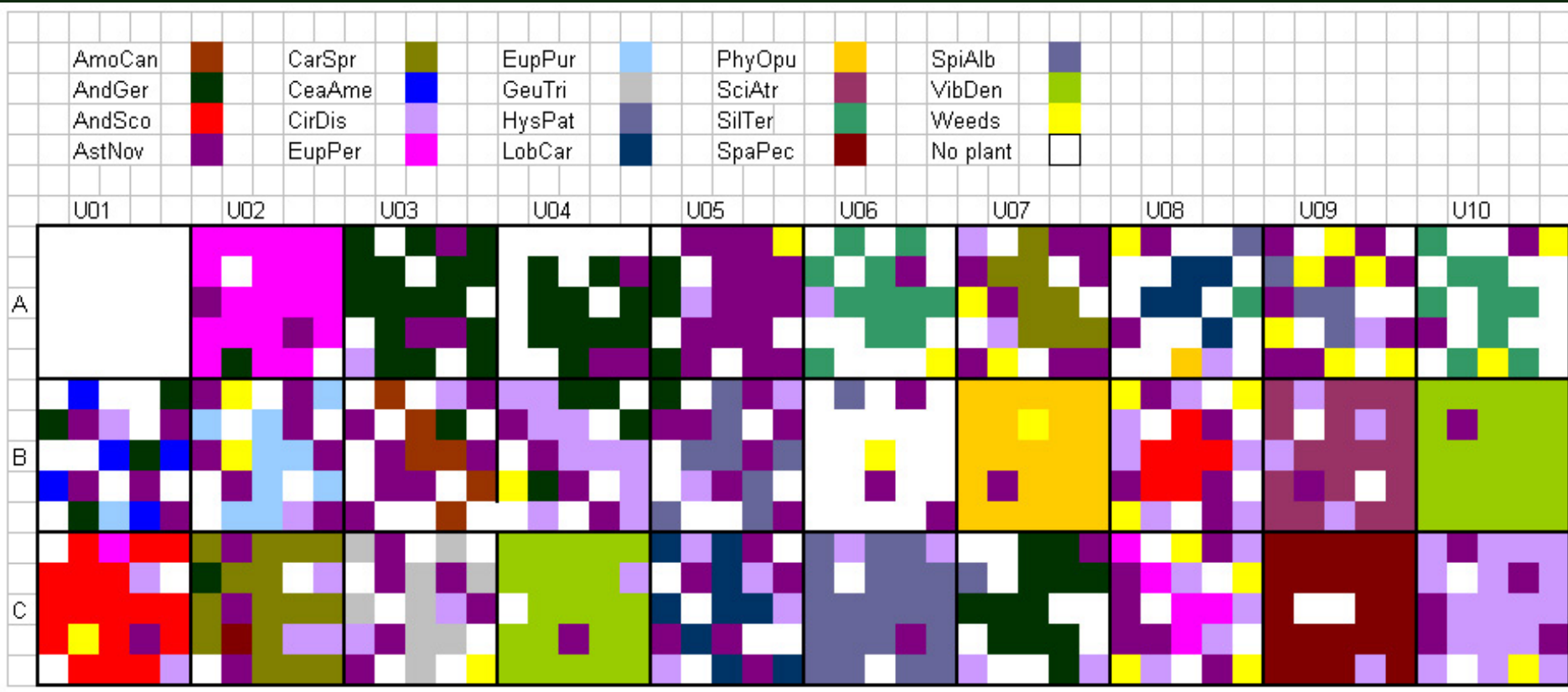
Persistence of Planted Phyto Species (3rd Yr)



Phyto Species Expansion within Plot (3rd Yr)



Relative Density Map of Phyto Community Species



Selected Phyto Species should be perennial, competitive and prolific

Results Summary

Planted treatments were typically more effective at reducing soil PAHs than unplanted treatments

Different plant species had different effects on bacterial biodegrader community

Plants generally enriched broad-range bacterial PAH metabolic capabilities

Varied plant community dynamics among species – some more suitable for stable habitat restoration

Rouge Manufacturing Complex Phytoremediation Trials

Dearborn, MI – May 2003



Planted Fall 02 with ~24,000 Individual Plants

Rouge Phyto Exhibit – Plant Community Subplots

Sp A = Large Shrubs

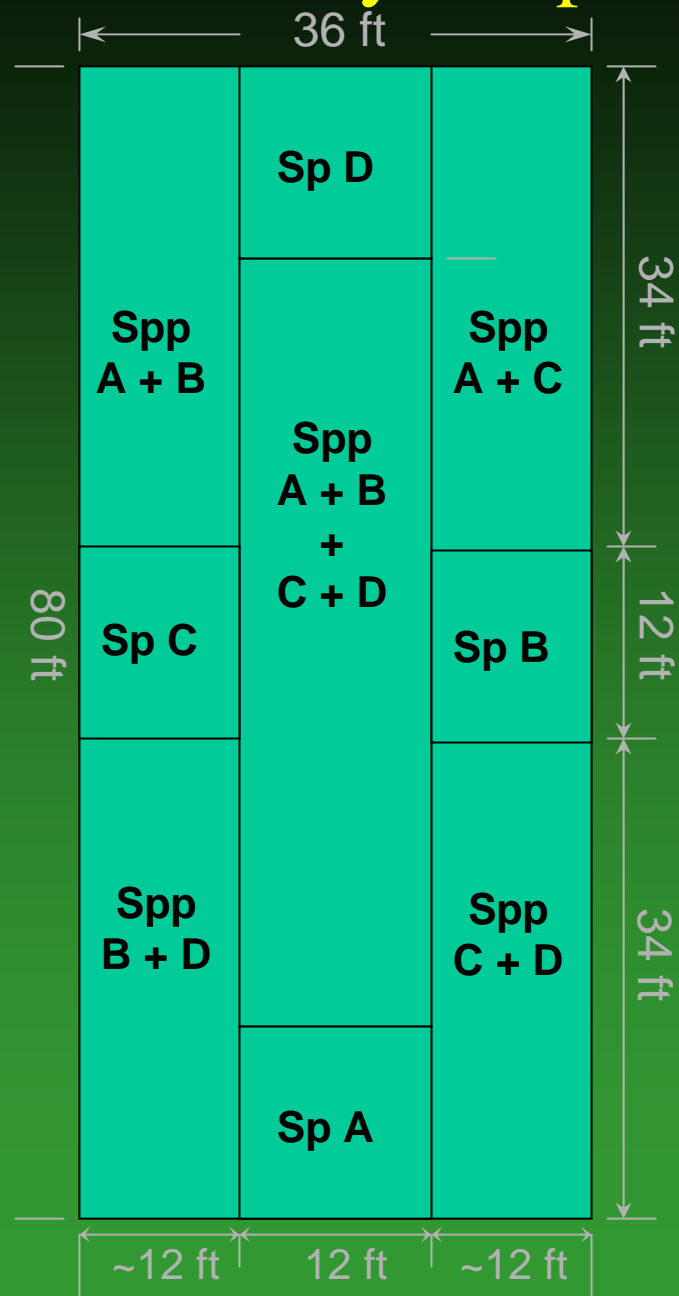
Sp B = Short Grasses

Sp C = Low Shrubs

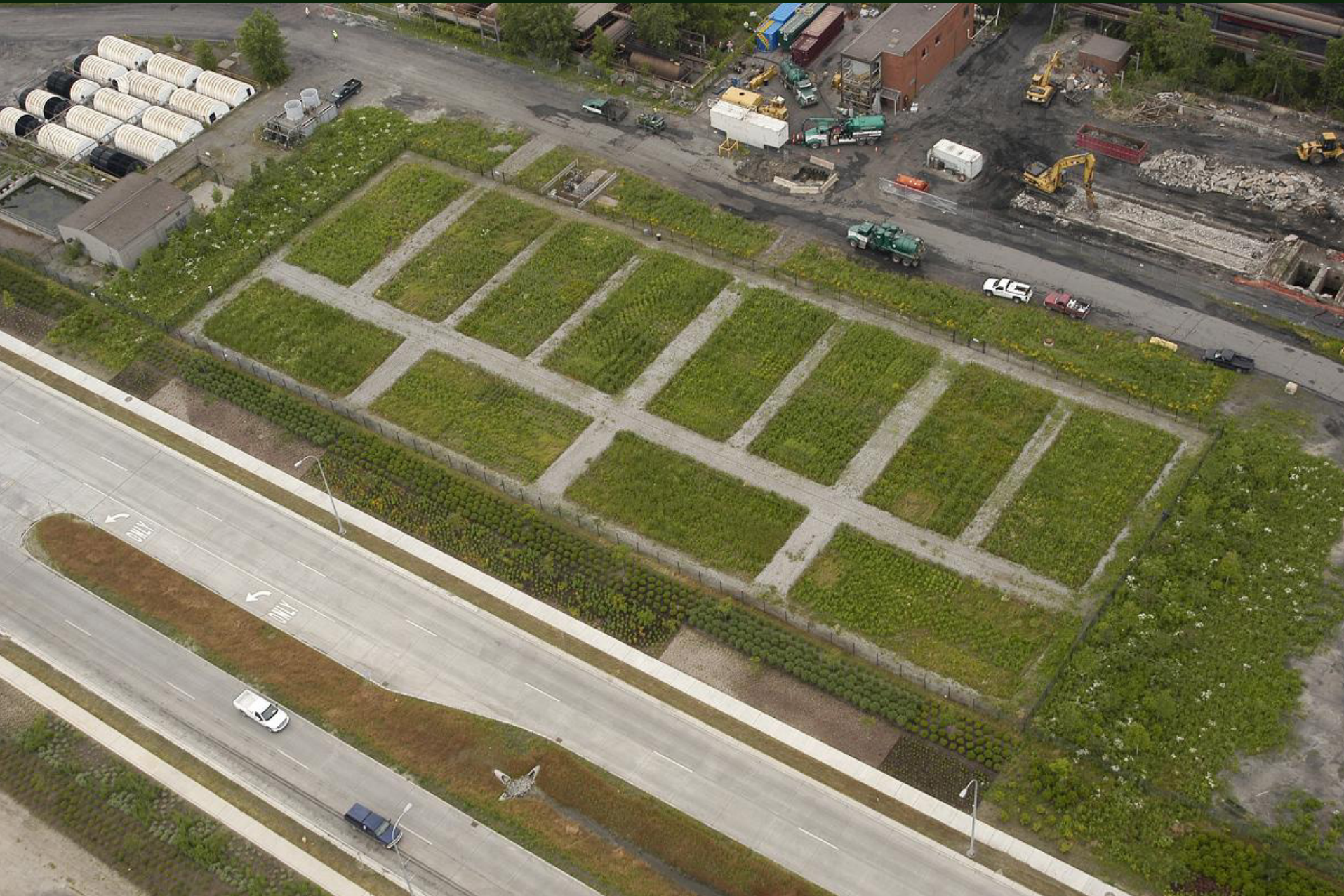
Sp D = Tall Grasses or Trees

12 Plots X 9 Subplots =

108 plant spp combinations



Rouge Phyto Exhibit – June 2004 - Aerial Overview





**Rouge Complex Phytoremediation Installation Exhibit
July 2004 – 2nd Season**

Wildlife Recovery at the Industrial Brownfield

Protected
Species and
Pollinators



Hummingbird Moth

Blue-Flag Iris

Wildlife Recovery at the Industrial Brownfield

Protected
Species and
Pollinators



Hummingbird Moth

Blue-Flag Iris

Habitat and
Beneficial
Species



New England Aster

Praying Mantis

Wildlife Recovery at the Industrial Brownfield

Protected
Species and
Pollinators



Hummingbird Moth

Blue-Flag Iris

Habitat and
Beneficial
Species

Urban
Mammal
Migration



New England Aster

Praying Mantis



Big Bluestem

Junkyard Dog
Canus detroitii

Recommended Phyto Species:

Phyto and Weed-resistance rating: * = ok, ** = good, * = excellent**

Habitat: U = upland, W = wetland (low-land),

Type: G = grass, H = herbaceous

<u>Species</u>	<u>Common Name</u>	<u>Phyto</u>	<u>Weed-R</u>	<u>Habitat</u>	<u>Type</u>
<i>Andropogon gerardii</i>	Big Bluestem	***	*	U	G
<i>Aster novae-anglicae</i>	New England Aster	***	***	U or W	H
<i>Carex sprengeii</i>	Sprengel Sedge	**	***	U or W	G
<i>Eupatorium perfoliatum</i>	Boneset	**	***	U or W	H
<i>Eupatorium purpureum</i>	Joe-pye Weed	***	*	U	H
<i>Hystrix patula</i>	Bottlebrush Grass	**	***	U	G
<i>Panicum virgatum</i>	Switchgrass	***	***	U	G
<i>Physocarpus opulifolius</i>	Ninebark	**	***	U	H
<i>Scirpus atrovirens</i>	Green Bulrush	***	***	U or W	G
<i>Solidago patula</i>	Swamp Goldenrod	**	***	U or W	H
<i>Spartina pectinata</i>	Prairie Cordgrass	**	***	U or W	G
<i>Spirea alba</i>	Meadowsweet	***	***	U	H
<i>Viburnum dentatum</i>	Arrowwood Viburnum	**	***	U	H

Potential PARAPHYTOREMEDIATION Species:

Phyto and Weed-resistance rating: * = ok, ** = good, * = excellent**

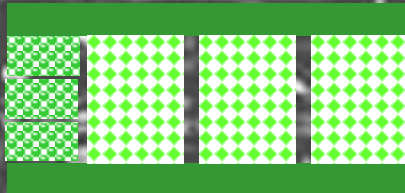
Habitat: U = upland, W = wetland (low-land),

Type: G = grass, H = herbaceous

<u>Species</u>	<u>Common Name</u>	
<i>Andropogon gerardii</i>	Big Bluestem	<u>BIOMASS RECOVERY</u>
<i>Aster novae-anglicae</i>	New England Aster	
<i>Carex sprengeii</i>	Sprengel Sedge	<u>Biocomposite Plastics</u> – replacement for fossil fuel-derived products
<i>Eupatorium perfoliatum</i>	Boneset	
<i>Eupatorium purpureum</i>	Joe-pye Weed	
<i>Hystrix patula</i>	Bottlebrush Grass	<u>Bioenergy Crops</u> – pelletized high-energy
<i>Panicum virgatum</i>	Switchgrass	
<i>Physocarpus opulifolius</i>	Ninebark	<u>Cellulose Feedstocks</u> – ethanol, etc.
<i>Scirpus atrovirens</i>	Green Bulrush	
<i>Solidago patula</i>	Swamp Goldenrod	Collaboration with:
<i>Spartina pectinata</i>	Prairie Cordgrass	Ford Research Labs
<i>Spirea alba</i>	Meadowsweet	MSU Composite Materials Center
<i>Viburnum dentatum</i>	Arrowwood Viburnum	

Potential Site Redevelopment / Rehabilitation Plan

Phyto &
Biomass
Studies



Tree Row – Wind Break

Phyto Meadow

Tree Row – Wind Break

30 Acre Remediation / Rehabilitation Challenge

Sustainable plant community for site stabilization and intrinsic bioremediation

~\$8,000 - \$20,000 per acre not including labor costs

Optional industrial, site restoration, and educational opportunities

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