Voodoo vs. Science:

The Practical Application of Bioremediation Techniques as a Removal Response Option at Oil Spill Sites in the Northwestern Pennsylvania Oil Patch

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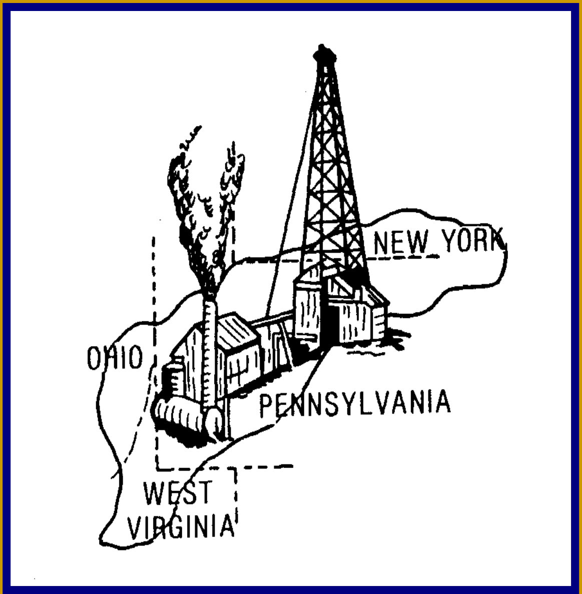


April 2004

Background

- Since the 1970's, oil contaminated soil and debris generated during federal removal response activities at oil spills in northwestern Pennsylvania was disposed of off-site, generally transported to a landfill.

- In the mid-1980's, local industry representatives vigorously debated the need for such off-site disposal, reasoning that if the oil-contaminated soil had not naturally attenuated or biodegraded, then the entire area would be covered with oil from the numerous oil spills that had occurred since oil was first discovered or produced in northwestern Pennsylvania.

- Local Industry also expressed concerns about bioremediation

Bioremediation of the Unknown Medium Oil Spill

Custer City, McKean County, PA

- PIC #1-6-0006

PIC #1-6-0006

Pre Removal Conditions

PIC #1-6-0006

Post Bioremediation

-NW PA Major Oil Spill Project (1985-1987)

-Bar Room Brawls and Back Alley Debates

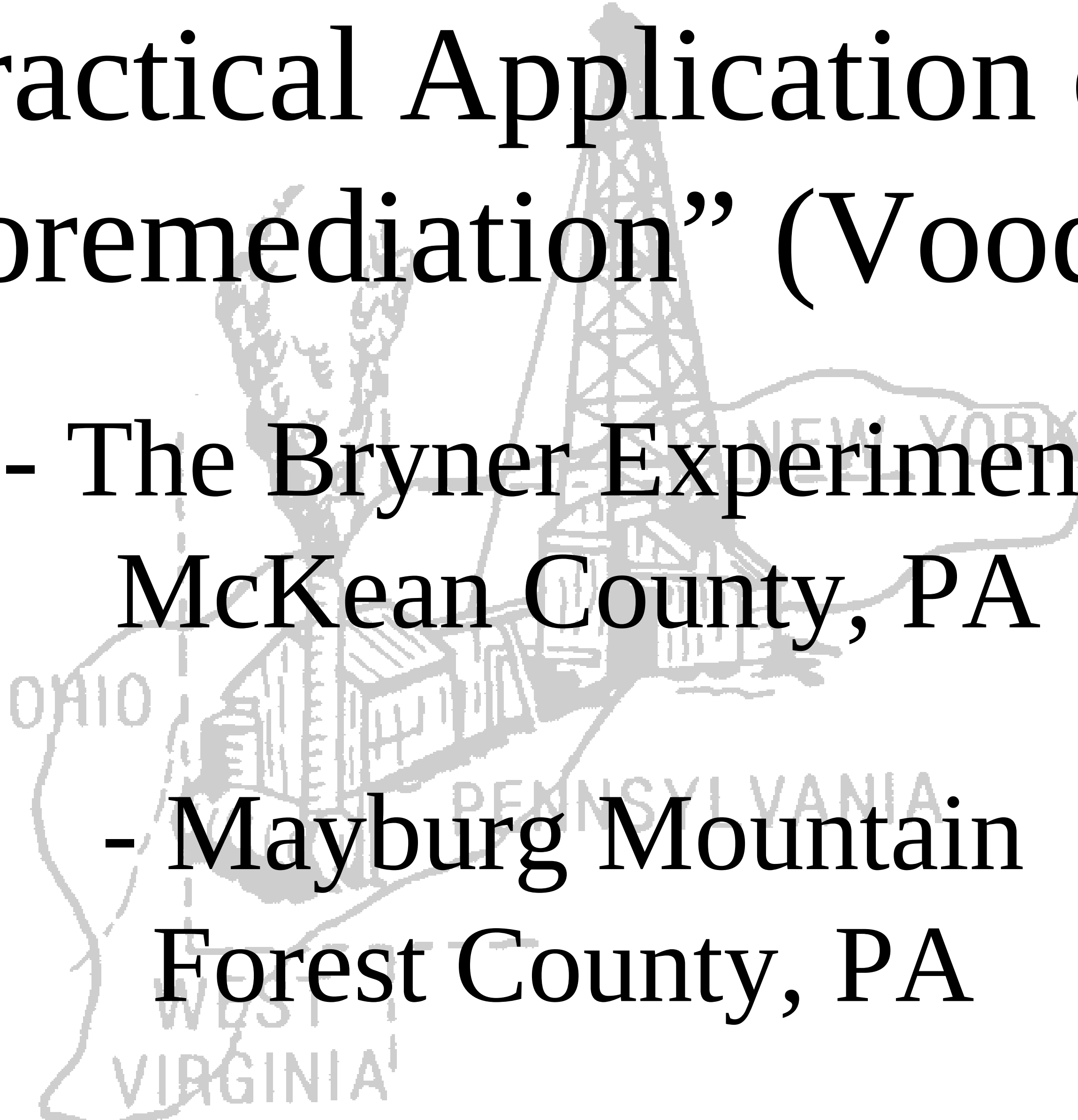
-Voodoo versus Science

Natural Attenuation

"Bioremediation"

- EPA recommends the natural attenuation processes be evaluated when assembling an appropriate removal action plan for a site with petroleum contaminated soils. While natural attenuation processes include biodegradation, sorption, dispersion, and volatilization, numerous studies have indicated that the natural, in-situ biodegradation process, often called intrinsic bioremediation, is a primary mechanism for the attenuation of petroleum hydrocarbons. Biodegradation is the only natural attenuation mechanism that has the potential to destroy the contaminants in-situ with nontoxic inorganic end products.

Practical Application of “Bioremediation” (Voodoo)



- The Bryner Experiments
McKean County, PA

- Mayburg Mountain
Forest County, PA

Practical Application of "Bioremediation" (voodoo) at Removal Response Actions

- North Fork OPA Site
Allegheny National Forest
McKean County, Pennsylvania

North Fork
Wellsite pre-removal

North Fork

Wellsite pre-removal

North Fork
Post plugging

North Fork
Bio-ops

-Rototilling
-Organic load

North Fork

Bio-ops: Rototilling

North Fork
Wellsite restoration

North Fork
Post Bio-ops
Wellsite
Restoration

VOODOO – SO WHAT?

- Although qualitative observations, such as the restoration of vegetative growth, indicated that the oil-contaminated soil had naturally attenuated or bioremediated and confirmed the success of this voodoo, no analytical data had been gathered to support the observations and certain Regional managers (“scientists”) strongly suggested data be gathered.

- Therefore, since 1995, the qualitative observations depicting the success of “voodoo bioremediation” have been substantiated by science (quantitative analytical analysis) at oil spill sites in northwestern Pennsylvania. The "bio-pods" are periodically sampled to obtain scientific data and monitor the concentration of total petroleum hydrocarbons (TPH). It has been observed the once the TPH concentrations are reduced to approximately 10,000 mg/kg, soil conditions improve sufficiently to support various micro and macro organisms and the "bio-pods" can sustain vegetative growth.

- ARARs

Passive Remedial Approach (Natural Attenuation)

- Aerobic Biodegradation
- Anaerobic Biodegradation
- Dispersion
- Volatilization
- Adsorption

Aggressive Removal Approach ("Unnatural Attenuation")

- Aerobic Biodegradation
- Solidification
- Dispersion
- Volatilization
- Organic amendment
- Nutrient amendment
- Moisture amendment
- Composting
- Land farming
- Anaerobic biodegradation

Unnatural Attenuation

Practical Application of "Bioremediation" as a Removal Response Option 1995- present

Park & Hungiville OPA Site, McKean County, PA

Allegro Oil and Gas Inc. OPA Site, Potter County, PA

Melvin Farm OPA Site, McKean County, PA

Avery Farm OPA Site, McKean County, PA

Hess Farm OPA Site, McKean County, PA

Onofrio Estate OPA Site, McKean County, PA

Barrett Wells OPA Site, McKean County, PA

McCracken Farm OPA Site, McKean County, PA

Johnston and Matthews OPA Site, McKean County, PA

Strick Farm OPA Site, McKean County, PA

Bryner-Fox OPA Site, McKean County, PA

AUGUST 1994
≈ 105,800 mg/kg

PARK & HUNGIVILLE
BIOPOD #1
[SEE BIOPOD #3]

JULY 1997
≈ 44,150 mg/kg

MAY 1996
≈ 17,261 mg/kg

PARK & HUNGIVILLE BIOPOD #2

MAY 1997
≈ 3,975 mg/kg

JULY 1997
≈ 44,150 mg/kg

PARK & HUNGIVILLE
BIOPOD #3
[SEE BIOPOD #1]

AUGUST 1998
≈ 10,031 mg/kg

AUGUST 2001
≈ 11,200 mg/kg

PARK & HUNGIVILLE BIOPOD #4

OCTOBER 2001
≈ 1,070 mg/kg

MAY 1997

≈ 550,500 mg/kg

ALLEGRO OIL & GAS BIOPOD #1163

SEPTEMBER 1999

≈ 5,300 mg/kg

MAY 1997
≈ 891,500 mg/kg

ALLEGRO OIL & GAS
BIOPOD #1672

SEPTEMBER 1999
≈ 440 mg/kg

NOVEMBER 1997
≈ 618,000 mg/kg

ALLEGRO OIL & GAS
BS BIOPOD

SEPTEMBER 1999
≈ 5,700 mg/kg

AUGUST 1998
≈ 65,700 mg/kg

ALLEGRO OIL & GAS
BS II BIOPOD

SEPTEMBER 1999
≈ 4,800 mg/kg

APRIL 1998
≈ 568,000 mg/kg

MELVIN FARMS BIOPOD

REFERRED TO ERT FOR PHYTOREMEDIATION IN SPRING 2002

OCTOBER 2001
≈ 32,600 mg/kg

MAY 1999
≈ 126,200 mg/kg

AVERY BIOPOD

REFERRED TO ERT FOR PHYTOREMEDIATION IN SPRING 2002

OCTOBER 2001
≈ 23,100 mg/kg

APRIL 1999
≈ 130,700 mg/kg

HESS BIOPOD

REFERRED TO ERT FOR PHYTOREMEDIATION IN SPRING 2002

OCTOBER 2001
≈ 9,400 mg/kg

APRIL 1999
≈ 409,000 mg/kg

ONOFRIO BIOPOD

SEPTEMBER 2002
≈ 18,000 mg/kg

JULY 2000
≈ 80,500 mg/kg

BARRETT BIOPOD

OCTOBER 2000
≈ 4,060 mg/kg

JUNE 2001
≈ 219,730 mg/kg

McCRACKEN BIOPOD #1

OCTOBER 2003
≈ 8,200 mg/kg

JULY 2001
≈ 112,485 mg/kg

McCRACKEN BIOPOD #2

REFERRED TO ERT FOR
PHYTOREMEDIATION IN SPRING 2002

OCTOBER 2001
≈ 9,385 mg/kg

AUGUST 2001
≈ 79,890 mg/kg

JOHNSTON & MATTHEWS BIOPOD

OCTOBER 2003
≈ 35,000 mg/kg

JUNE 2002
≈ 180,000 mg/kg

STRICK FARM BIOPOD

OCTOBER 2003
≈ 24,000 mg/kg

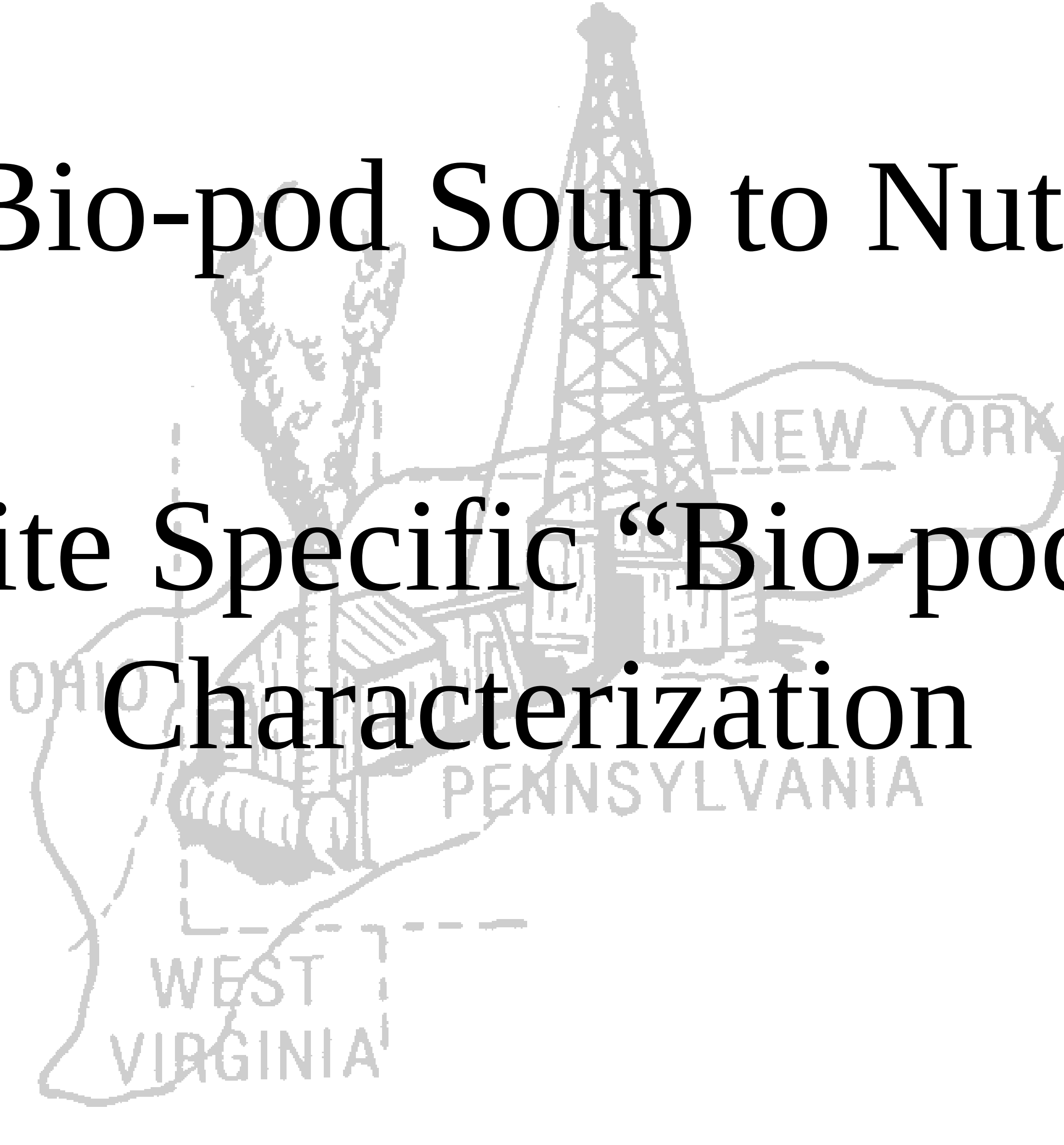
JUNE 2002
≈ 520,000 mg/kg

BRYNER-FOX BIOPOD

OCTOBER 2003
≈ 40,000 mg/kg

Bio-pod Soup to Nuts

Site Specific “Bio-pod” Characterization



Pre-removal

Solidification

Solidification

Solidification

Configuring Bio-pod

Addition of BS

Solidification of BS

Solidification/Organic Load

Rototilling

Biopod Sampling

Biopod Sampling

Current Conditions

Blinded by Science

Bioremediation of Crude Oil Contaminated Soils in Pennsylvania*

Environmental
Science &
Technology

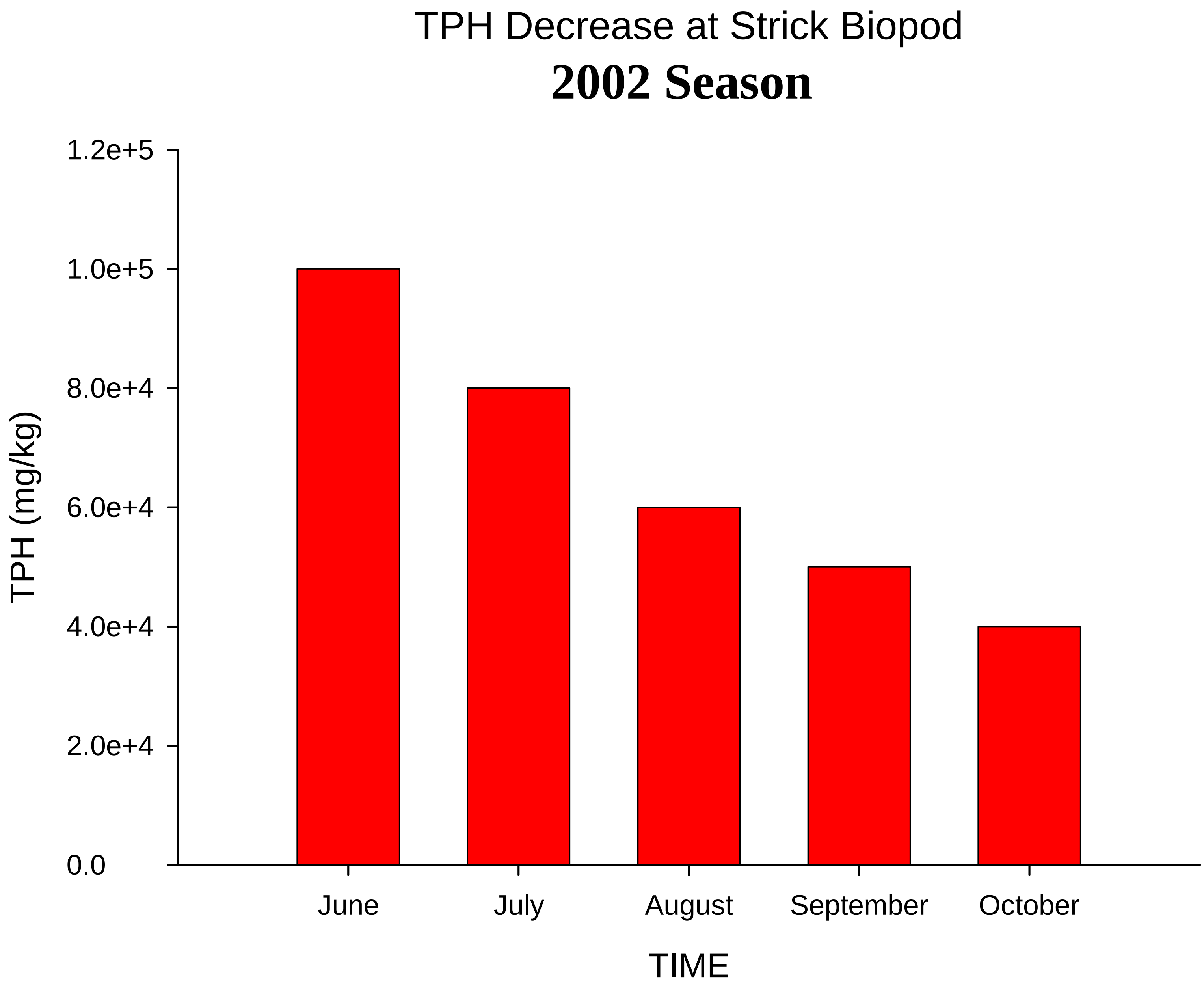
Clean Water Team

Hank Edenborn
Research Microbiologist
NETL - Pittsburgh Lab

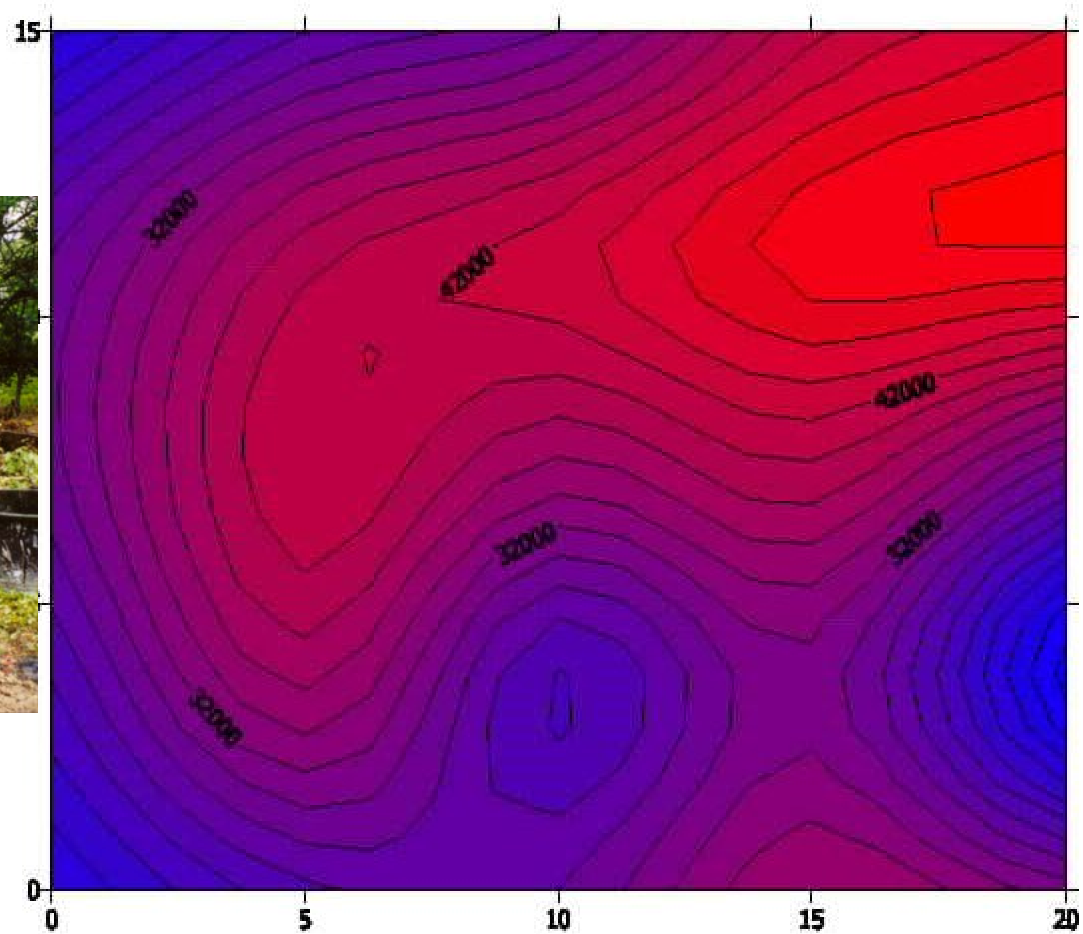
***As adapted for Freshwater Spills Symposium 2004**

Bradford Biopods
(McCracken #1 & Bryner-Fox)

Bradford Biopods
(Onofrio & Strick)


TPH Decrease at Strick Biopod
2002 Season
1.2e+5
1.0e+5
8.0e+4
6.0e+4
4.0e+4
2.0e+4
0.0
TPH (mg/kg)
June
July
August
September
October
TIME

McCracken Biopod Oil Sludge Distribution

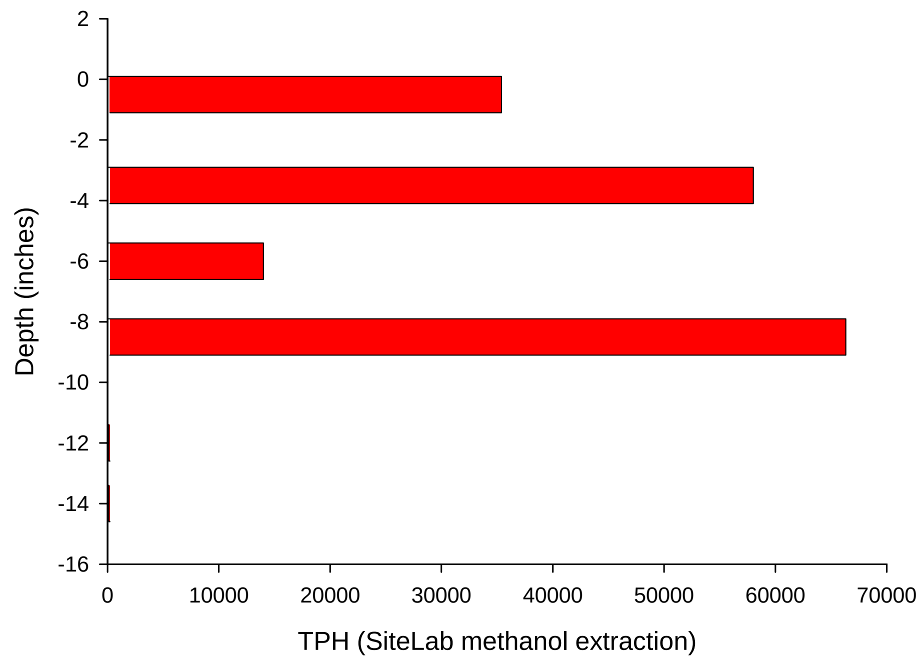


Strick Biopod

- Calculated "ideal" fertilizer requirement based on estimated amount of added crude oil
- Analyzed numerous chemical and biological variables since 6/18/02
- Monitoring soil quality using biotoxicity assays

North Fork Site

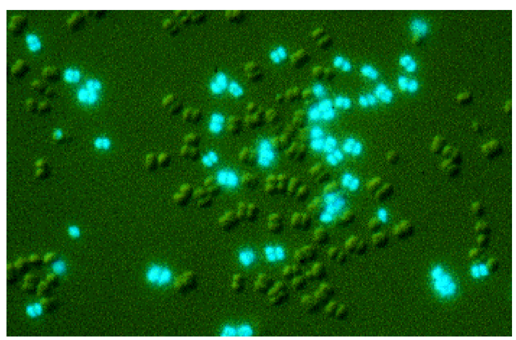
October 8, 2002



NETL Research Objectives

- Provide objective scientific data to agencies operating in PA
- Determine environmental impact (toxicity) of remediated soils
- Help establish protocols for PA crude oil bioremediation in soil
- Demonstrate potential effectiveness of biodegradation as treatment option
- Validate or dismiss the use of specific remedial practices in PA

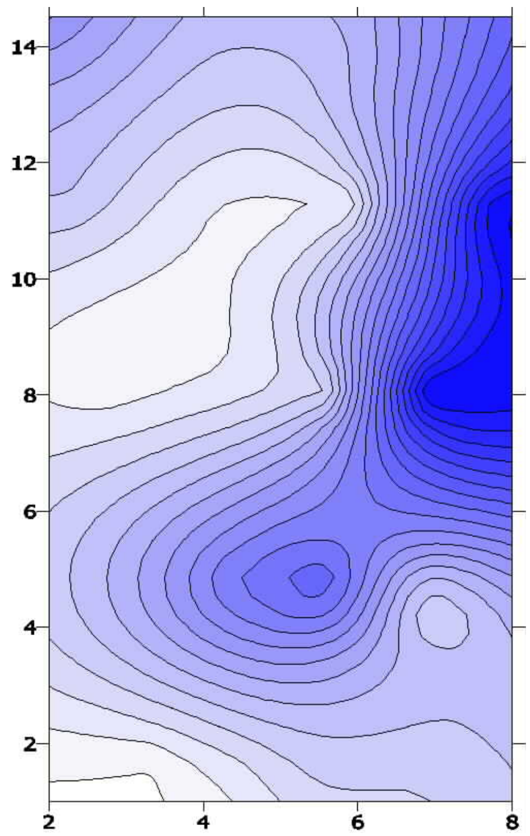
Biotoxicity Assays



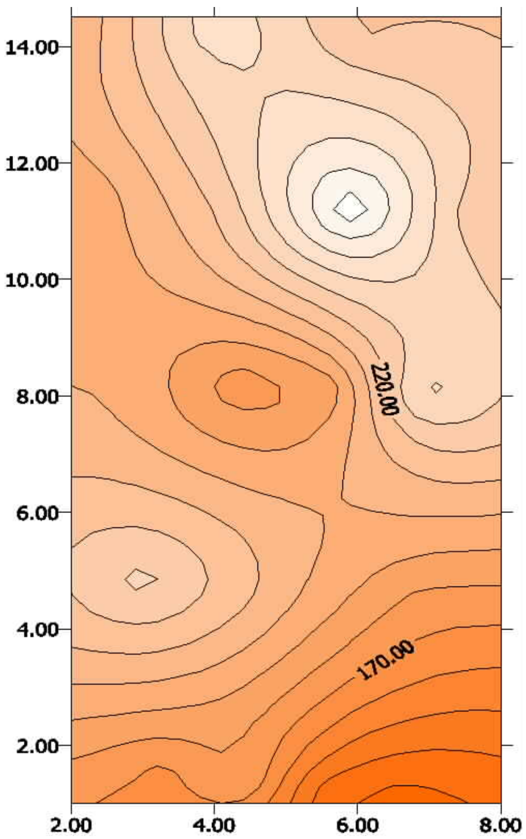
- Earthworm survival
- Lettuce and switchgrass germination
- Microtox (luminescent bacteria)

Mapping of Biological Variables

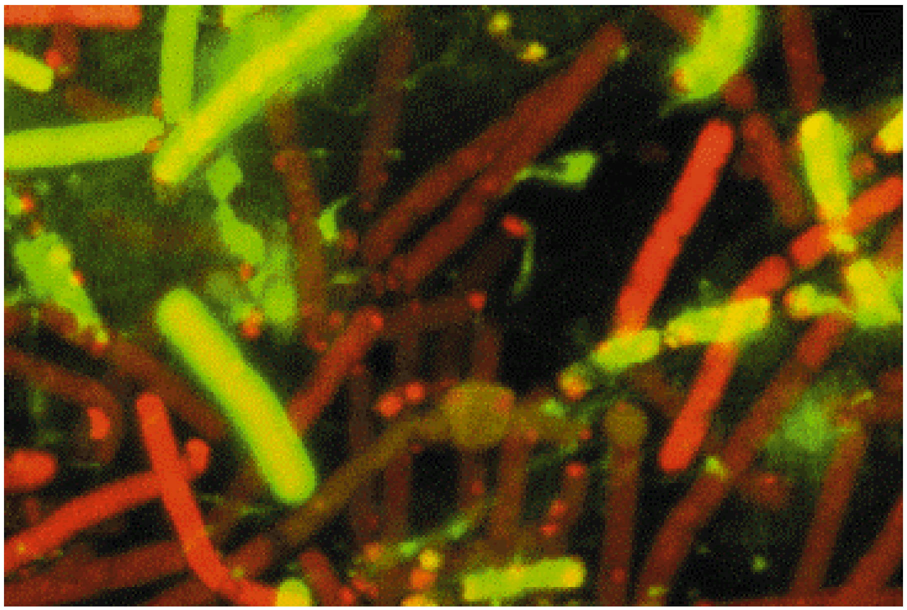
Bacterial CFU



FDA Hydrolysis



Pittsburgh NETL DOE Lab Microbiology Resources



- complete microbiology laboratory - 1400 sq. ft
- molecular biology equipment (DGGE, etc.)
- fluorometer; Microtox
- chemiluminescence system
- field sampling equipment

Bioremediation of Crude Oil Contaminated Soils in Pennsylvania

Harry M. Edenborn, Ph.D., U.S. Department of Energy
National Energy Technology Laboratory, Pittsburgh, PA

✘ Dr. Hank provided recommendations to optimize fertilizer amendments for bioremediation of crude oil at various NW PA OPA Sites based upon bench-scale treatment studies

✘ Dr. Hank's microbiological research at various NW PA OPA Sites revealed a greater bacterial abundance, but lower total species diversity in soil, consistent with the proliferation of specific oil-degrading bacteria

✘ Dr. Hank's research found that the NW PA OPA Site bio-pod soils were "severely hydrophobic" before and after bioremediation, with the adjacent control soils minimally hydrophobic

✘ Dr. Hank's tests of indigenous Pennsylvania grasses as indicators of soil toxicity shows

- conventional lettuce seed germination was unaffected by crude oil contamination
- native blackwell switchgrass was more sensitive to crude oil contamination

Bioremediation of Crude Oil Contaminated Soils in Pennsylvania

- ✘ Dr. Hank provided recommendations to immobilize copper at one NW PA OPA Site (Melvin Farm) where the bio-pod was found to have high concentrations of total copper, and thus exhibited poor bioremediation.

- ✘ Dr. Hank's earthworm studies indicate that the soil in the bio-pods was extremely toxic after the initial introduction of oil contaminated soil and debris, but were essentially non-lethal when diluted to 50% total volume with clean soil (OSC's note: dilution is not the solution to pollution)

- ✘ Dr. Hank's biotoxicity studies of earthworm, Microtox and switchgrass germination all correlated negatively with crude oil contamination in soil

- ✘ Dr. Hank is currently undertaking a detailed study to determine the effectiveness of a field fluorometric method for the quantification of petroleum hydrocarbons which could provide an on-site, cost effective means of determining how clean is clean

- Dr. Harry Allen

"*A Phased Approach for Bioremediation of Petroleum Contaminated Soil Using Phytoremediation*"

Technology transfer to State and Industry

A Phased Approach for Restoration of Petroleum Contaminated Sites Using Plant-Mediated Bioremediation

What is Phased Treatment Bioremediation?

••**Phase I** is pretreatment with <u>either</u> Conventional Land Treatment <u>or</u> Plant-Mediated Bioremediation
••**Phase II** combines Plant-Mediated Bioremediation and Revegetation using <u>native plants</u>

Why Use Phased Treatment?

••Phased Treatment is preferred over either Conventional Land Treatment or Plant-Mediated Treatment alone; it is cost-effective, technically sound, and flexible.

What is the Technical Basis for the Phased Treatment Approach?

••**Phase I** lowers initial petroleum hydrocarbons (TPHs) in soil to levels tolerated by native grasses.
••**Phase II** uses native cool- or warm-season 'bunch' type grasses for both Plant-Mediated Bioremediation and Site Revegetation It is a passive, low-cost, low-maintenance process that reduces soil TPH to an acceptable risk level. The plant rhizosphere contains both large numbers of soil microorganisms, plant root exudates, and root decomposition products, all of which may enhance biodegradation of recalcitrant hydrocarbons.

What are the Phase I Treatment Options?

••Conventional Land Treatment Bioremediation with regular soil tillage; <u>**or**</u>
••Plant-Mediated Bioremediation using TPH tolerant plants such as annual ryegrass

What are the Advantages of Plant-Mediated vs Conventional Land Treatment Bioremediation?

••Lower cost ($10-$50/ton) than Conventional Land Treatment ($25-$75/ton)
••Aesthetic appeal
••Low exposure potential to soil contaminants during treatment
••Native plants contribute to site restoration, and may provide enhanced treatment

A Phased Approach for Restoration of Petroleum Contaminated Sites Using Plant-Mediated Bioremediation - Continued

What are the Disadvantages of Plant-Mediated Bioremediation?

••Time for treatment is longer than Conventional Land Treatment

When is Phase I Treatment Switched to Phase II?

.When soil TPH is low enough to support growth of native grasses; about 1% TPH

When Can Phase II Treatment be Used Directly?

.When soil TPHs are less than 1% and phytotoxic hydrocarbons are absent; and
.Soil quality is sufficient to support plant growth.

How Much Time is Needed for Closure Using Phased Treatment?

.Total treatment time can range from 2 to 5 years.
.Treatment endpoint can be estimated using a 28-day bioslurry test.

Harry L. Allen, Ph.D., Environmental Response Team, U.S. EPA, Edison, NJ
James L. Brown, Ph.D., Lockheed Martin/REAC, Edison, NJ

(special thanks to Royal J. Nadeau, Ph.D., Environmental Response Team, U.S. EPA, retired)

Use of Native Grasses in Site Restoration

Selection Criteria for Native Grasses

••Well adapted to soil and site conditions
••Easy to establish & maintain
••Rapid growth & fibrous root system
••Provide good soil cover to prevent soil erosion by wind and water
••Low maintenance
••Suitable for site restoration (long term stability)
••Provide cover and forage for wildlife
••Aesthetic value

No single plant species can fulfill all these criteria, but an initial mixture of cool and warm season grasses and legumes can. With time, desired warm-season native grasses will predominate. Once warm-season grasses become established, they require little or no maintenance, provide cover and forage for wildlife, and are aesthetically pleasing. The following is a summary of cool vs warm season grass characteristics.

<u>Cool Season Grasses</u> - quickly established, rapid top growth, grows in spring/fall (dormant in summer without water and nutrients), high nutrient requirement, rooting depth 6-12 inches, vigorous competitors under ideal conditions, but require high maintenance (i.e., mowing, supplemental irrigation during drought, and fertilizer). Best used in companion plantings with warm-season grasses for rapid initial plant cover.

<u>Warm Season Grasses</u> - slowly established (2 years), very deep rooted, ‘bunch’ grass type, tolerant of drought and low nutrient availability. Once established, warm season grasses require little or no maintenance and tolerate marginal soil conditions.

EPA’s Superfund Redevelopment Initiative
••Emphasis on beneficial reuse of sites
••Preference on use of native plants for revegetation/restoration following remediation; beneficial to wildlife
••More than 13,000 acres now in ecological or recreational use at former Superfund sites
••

What is the Best Mixture of Native Plants for Site Restoration?
••A mixture of noncompetitive cool-season grasses with native warm-season grasses and legumes is ideal. It provides rapid plant cover, low maintenance, and long term stability. Native forbs, trees and shrubs can also be added if desired.
••

Technical Support
••EPA has an interagency agreement with the Natural Resource Conservation Service (NRCS) of the U.S. Department of Agriculture for revegetation/restoration of Superfund sites. Support is provided through regional plant materials centers. Contact local NRCS office for locations, or EPA’s Environmental Response Team Center in Edison, New Jersey.

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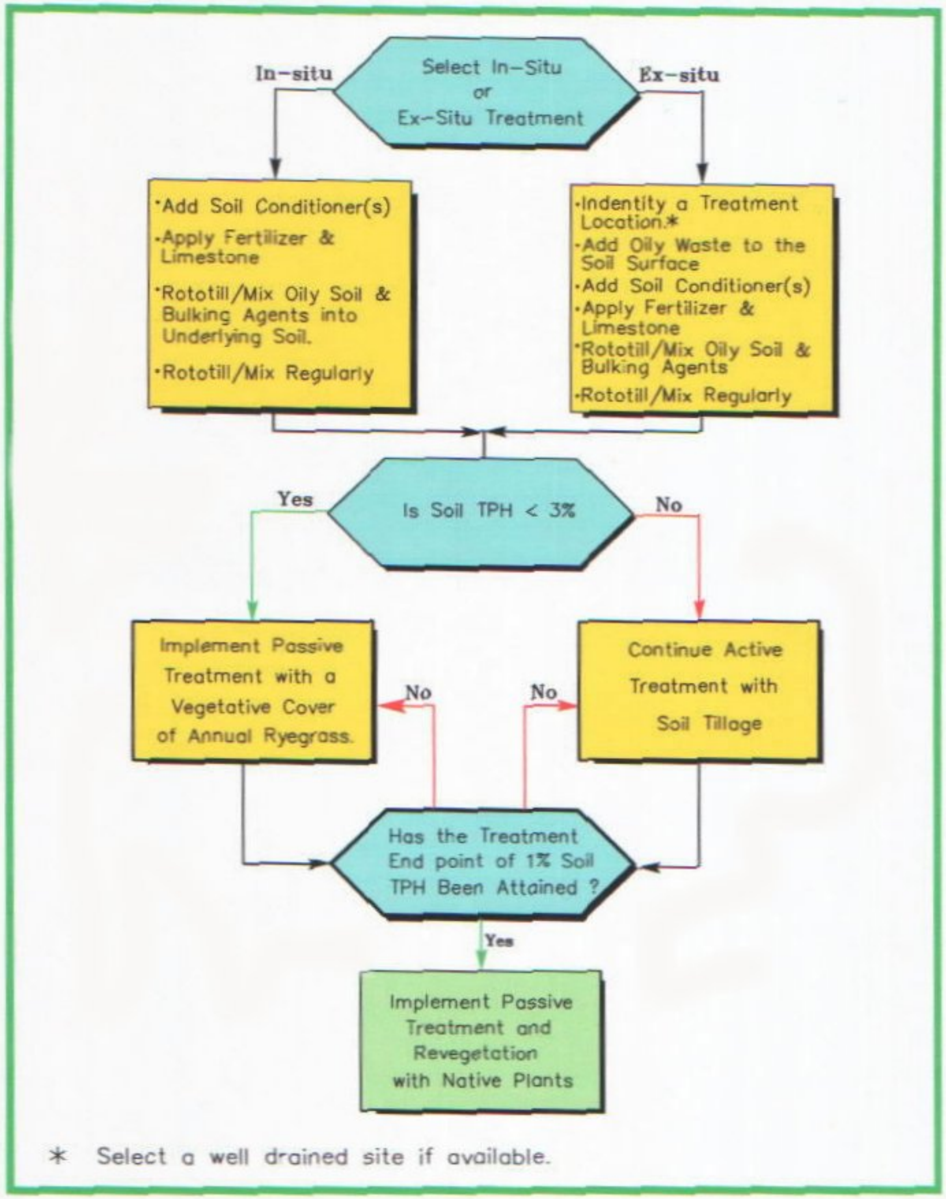
Restoration of Small Crude Oil-Contaminated Sites in Oil Well Fields of Pennsylvania Using Phased Bioremediation.



“Bioremediation” of Small Scale Oil-Contaminated Soil Sites

The United States Environmental Protection Agency (EPA) recommends that natural attenuation be evaluated by as a viable option when assembling an appropriate removal action plan for a site with petroleum-contaminated soils. Natural attenuation processes include biodegradation, adsorption, dispersion, and volatilization. Numerous studies have indicated that the natural, in-situ bio-degradation process, often called intrinsic bioremediation, is a primary mechanism for the attenuation of petroleum hydrocarbons. Bio-degradation is the only natural attenuation mechanism that has the potential to destroy the contaminants in-situ with nontoxic inorganic end products.

“Bioremediation” implemented as a removal response action at certain Oil Pollution Act (“OPA”) Sites in EPA Region III utilizes simple yet effective techniques and locally available equipment and materials to accelerate the process of intrinsic bioremediation, aggressively incorporating the natural attenuation processes of biodegradation, adsorption, dispersion and volatilization with solidification, aeration, organic loading, and composting of oil-contaminated soil and debris.

The following activities are recommended to implement “bioremediation” of oil-contaminated soil at oil spill sites that affect a relatively small surface area:

[1] Utilizing hand-tools (shovels, rakes) excavate the visibly oil-contaminated soil to solidify and aerate.

[2] Utilizing hand-tools, spread the solidified, aerated oil-contaminated soil to a depth of one to two inches deep.

[3] Utilizing hand-tools incorporate organic matter (composted leaf litter, manure) into the oil-contaminated soil. The incorporation of organic matter should almost double the volume of the oil contaminated soil. For example if the depth of the solidified/aerated oil-contaminated soil was one inch deep, then the depth should be approximately two inches deep after incorporation of organic matter.

[4] Apply a sufficient quantity of nutrient (10-10-10 fertilizer) to simply dust or coat the top of the oil-contaminated soil. Utilizing hand-tools, the nutrient can also be incorporated into the oil-contaminated soil.

[5] Apply seed to the top of the oil-contaminated soil.

If the seed sprouts, exhibits growth but then dies, repeat the procedures describe above, using the dead and dying vegetation as the organic matter.

Once the seed sprouts, exhibits growth and the vegetation persists, the process can be deemed complete. Typical Total Petroleum Hydrocarbon concentrations in the previously oil-contaminated soil may be expected to be at approximately 10,000 mg/kg at the time when a vegetative cover can successfully be reestablished using this practical “bioremediation” technique.

Should you have any questions concerning this “bioremediation” technique , please feel free to contact **Vincent Zenone, OSC at (215) 814-3267.**

QUESTIONS? ANSWERS? THE END?