In-Situ Chemical and Biological Remediation of Munitions Constituents from Point Source Emitters in Marine Environment

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The Problem

- Dumped munitions are found in both marine environments and lakes
- Underwater dumped munitions have been located in shallow and deep water
- Some have cracked and are leaking
- Leaking munitions pose ecotoxicological risks
- There is need for cost-effective, in-situ and non-explosive destruction of some of the underwater dumped munitions

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FY2007 U.S. Defense Authorization Act –Research on Effects of Ocean Disposal of Munitions

- Sampling and analysis of ocean waters and sea beds adjacent to munitions disposal sites
- Examine long-term effects of exposure and impacts to ocean environment
- Investigate feasibility of removal / remediation
- Develop safety measures for underwater UXO

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Purpose

- Advance new ways of developing in-situ technologies for remediation of underwater ordinance in deep and shallow water
- Begin to identify specific in-situ chemical and biologically technologies that have great potential for success

Underwater Disposal Technologies

- Demolition Technologies
  - High order blow-in-place (BIP)
  - Low order BIP
  - Consolidate and blow
- Abrasive water jet cutting
- Entombment

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If this piece of corroded munition is leaching its toxic constituents into the marine water column, can we degrade its constituents in-situ?

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Can we adapt in-situ chemical treatment technologies for terrestrial application in underwater environment?

- Engineering challenges
  - Mode of delivery
  - Rate of reaction
  - pH effect

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In-situ chemical treatment of munitions constituents in soil
Visual Comparison, 5 hours

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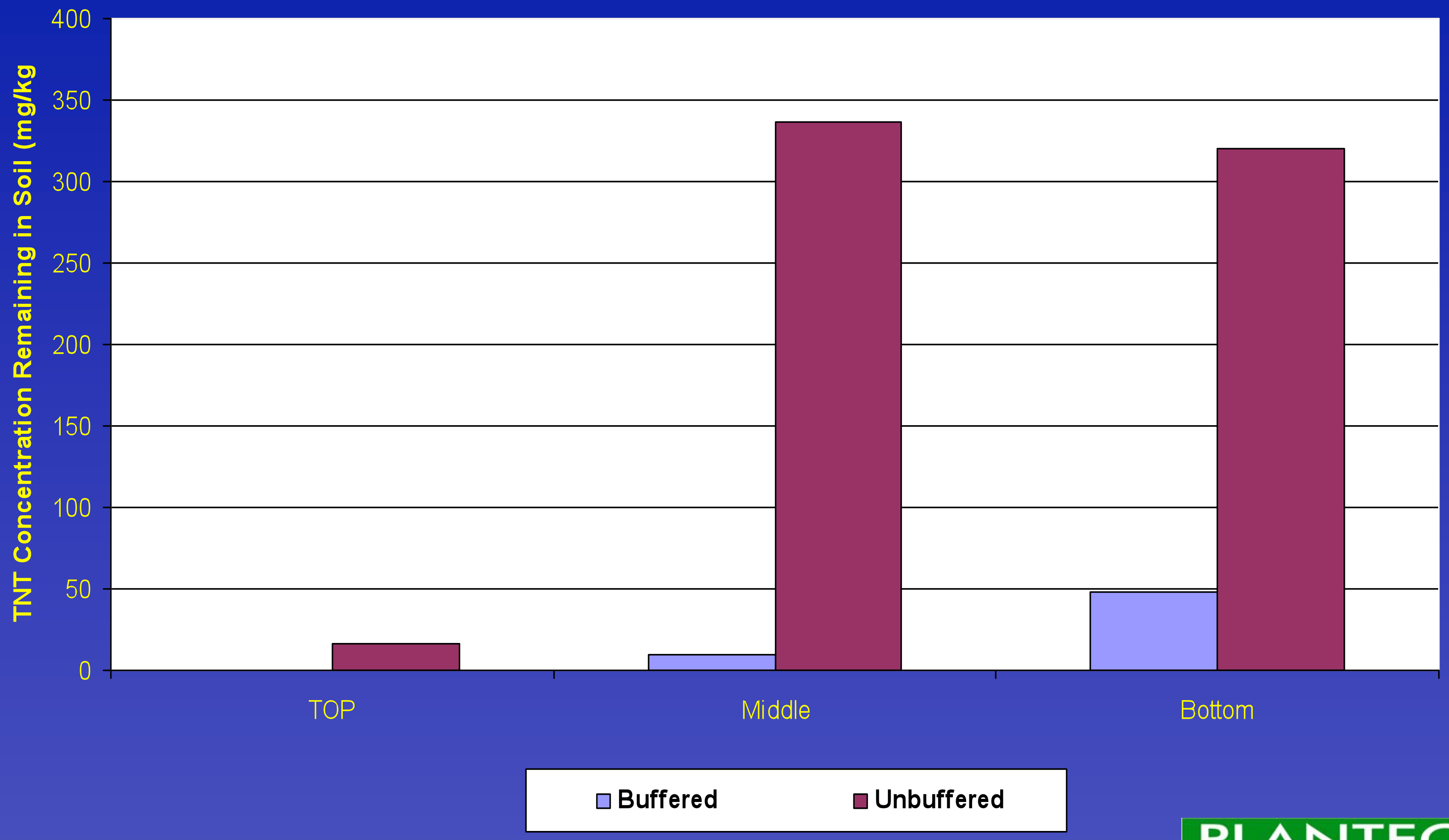
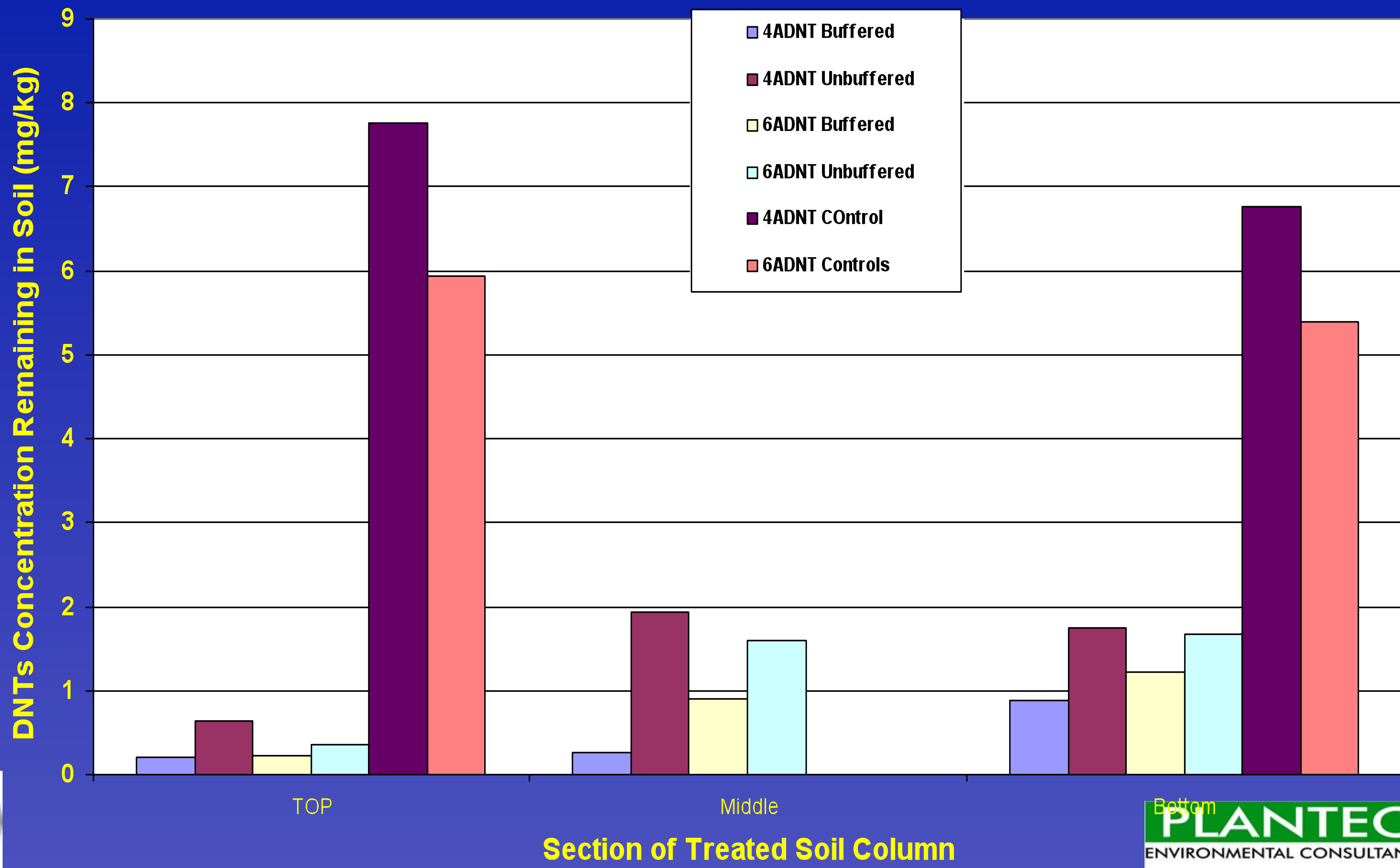
New Discovery at the University of Georgia
In-situ chemical treatment of TNT in Packed Soil Columns using a bulk reductant
30 cm long column; 24 hours reaction time



In-situ chemical treatment of DNTs in packed soil columns 30 cm long column; 24 hours reaction time



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What are the breakdown products of the munitions constituents?

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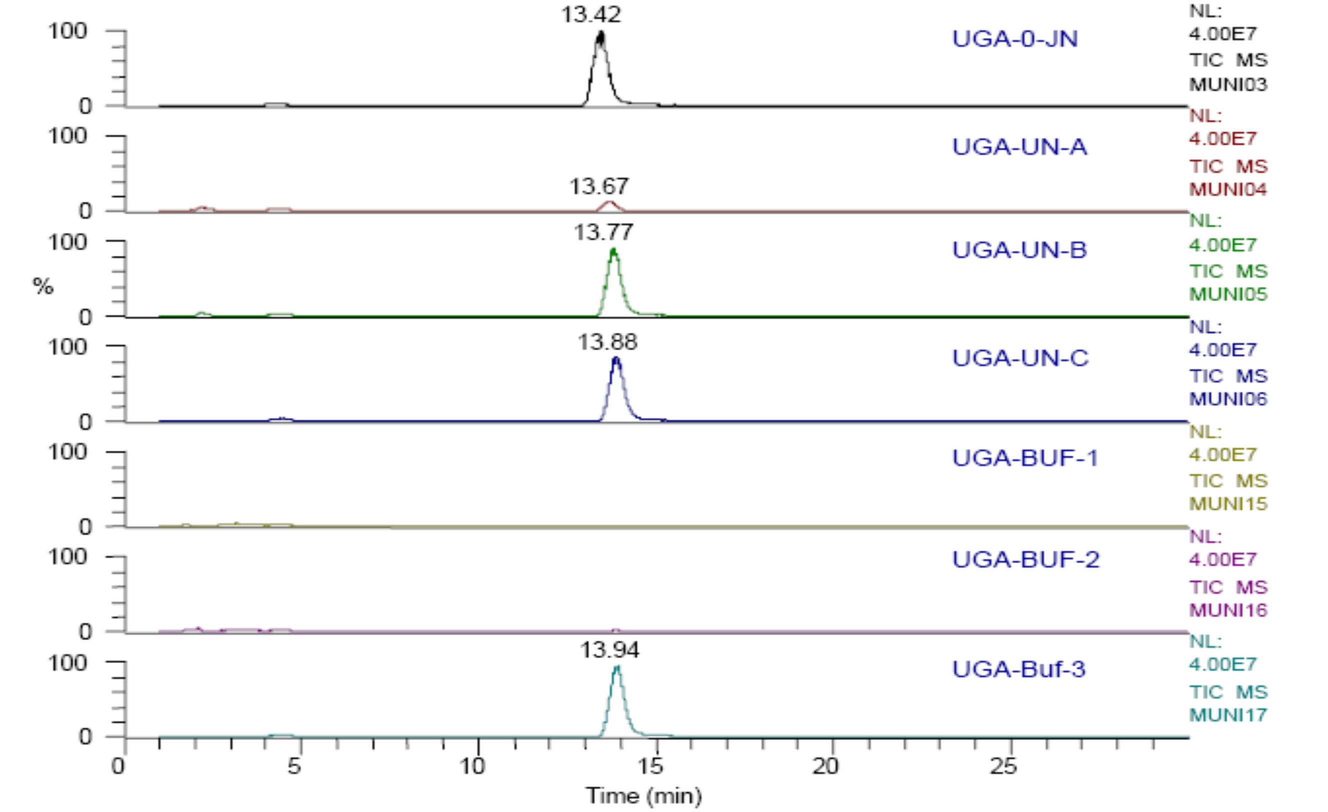
LC/MS analysis of UGA Samples – W07017

Daniel Snow, David Cassada, and Teyona Damon
Water Sciences Laboratory - April 2007

Figure 1. TIC of soil samples extracts. TNT retention time ~ 13.5 min. Differences in the retention times o
TNT between analyses are most like due to column equilibration over the analysis run.



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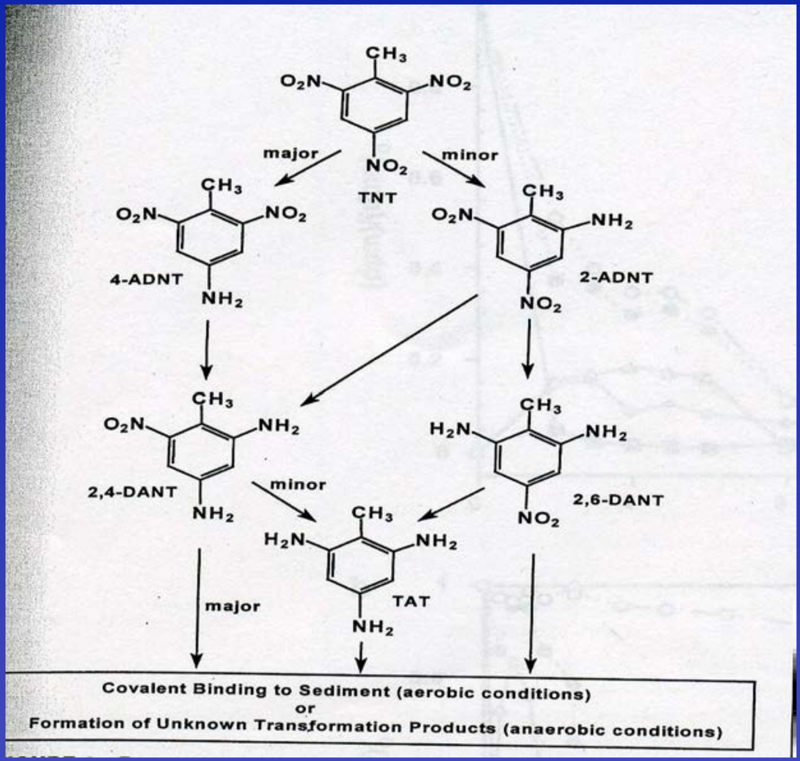
Example: TNT Reductive Degradation

- **Step-wise reductive degradation**
  - Transfer of electron to the nitro substituents
  - Reduction from nitro group to amino group
  - Amino Dinitrotolune Isomers (ADNTs)
  - DiaminoNitrotolune Isomers (DANTs)
  - Triaminotolune (TAT)
  - TAT sorbs irreversibly to soils
  - Specific intermediate products not well understood
    - Anilines
    - Amines
    - hydroxyamines



Source: Elowitz and Weber, 1999

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Our reagent also immobilizes/precipitates redox sensitive metals

Cd, Cr, Fe, U, Pb, Pu, As, Tc etc.

Cr(VI) reduction/immobilization

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Proposed delivery mechanisms of our reagents

- Use solid reagents

- Adapt detergent tablets concept – need a carrier?
  - Encapsulate reagents in slow release tablets
  - Coat reagent with slow decay polymer

- All constituents must already exist in marine environment, e.g., alginate, silica, clay nanocomposites, etc.

- Cover decaying UXO with encapsulated reagent

Example: SOLUBLON® Water Soluble Packaging for Easy Delivery at Point Source. http:// www.solublon.com/soap_leaves.htm

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New Breakthrough Configurations in PVA Water Soluble bags for** both **Powders and Liquids by** Gowan Milling**.

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In-Situ Bioremediation Approach for Underwater Application

Let us think Green – Microbial Mats

- Dominated by *Cyanobacteria* (Blue-Green Algae)
  - 3.5 Billion Years
- Photosynthetic – "solar powered"
- Bacterial Communities
  - sulfur reducers, purple bacteria, *rhodopseudomonas*, etc.
- Can Inhabit Fresh or Saline Water

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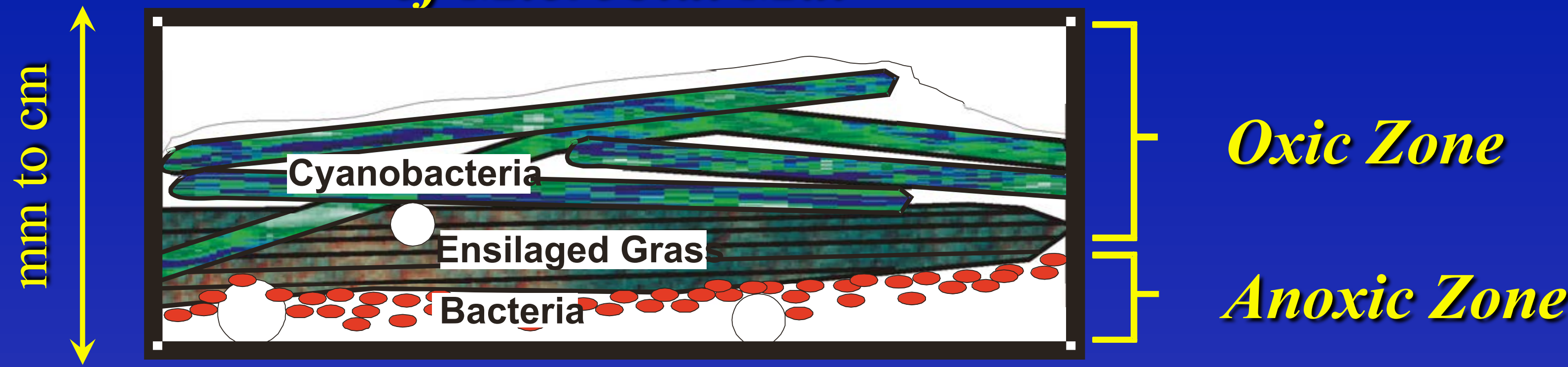
Schematic Cross-Section of Microbial Mat



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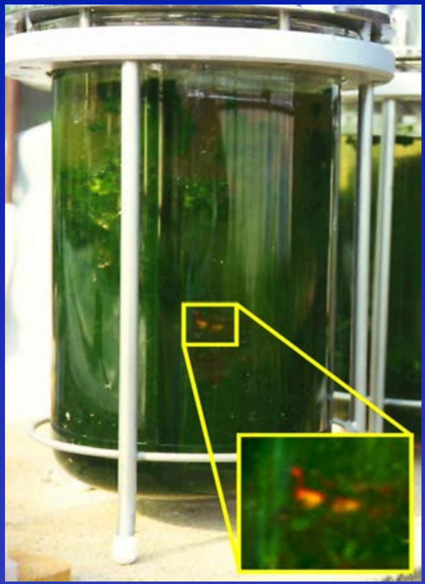
Properties of Microbial Mats



- Non-toxic
- Highly oxic and anoxic zones
- Rapid growth rate
- Ability to survive harsh environmental conditions (cold weather, saline water, low pH, etc.)
- Remove or degrade organics, sequesters metals and other inorganics

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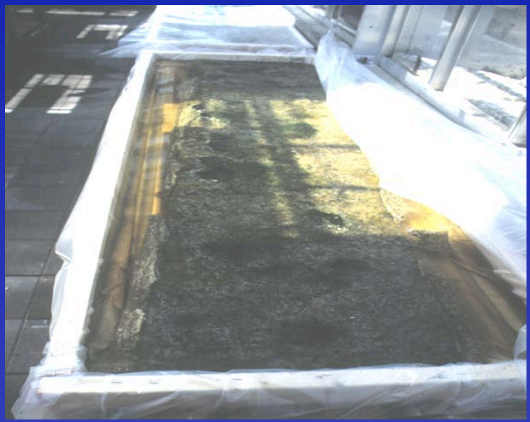
Contaminants Treated Using Biomats®

- Metal Sequestering & Reduction:
  - Ag, As, Cd, Co, Cr^{+6}, Cs, Cu, Fe, Mn, Ni, Pb, Se^{+6}, Zn
- Sequester of Radionuclides:
  - $Co^{58, 60}$, $Cs^{134, 137, 138}$, Mn^{54}, $Sb^{124, 125}$, U^{238}
- Remediation of Mixed Contaminants:
  - TCE + Zn, Chrysene + Zn, and TNT + Pb
- Degradation of:
  - Hexadecane, Naphthalene, Phenanthrene, Chrysene, RDX, HMX, TNT, DNT, Carbofuran, Chlorodane, PCB, Gasoline (BTEX): benzene, mineralized pulp & paper mill effluents, trichloroethylene (TCE), tetrachloroethylene (PCE), and perchlorate



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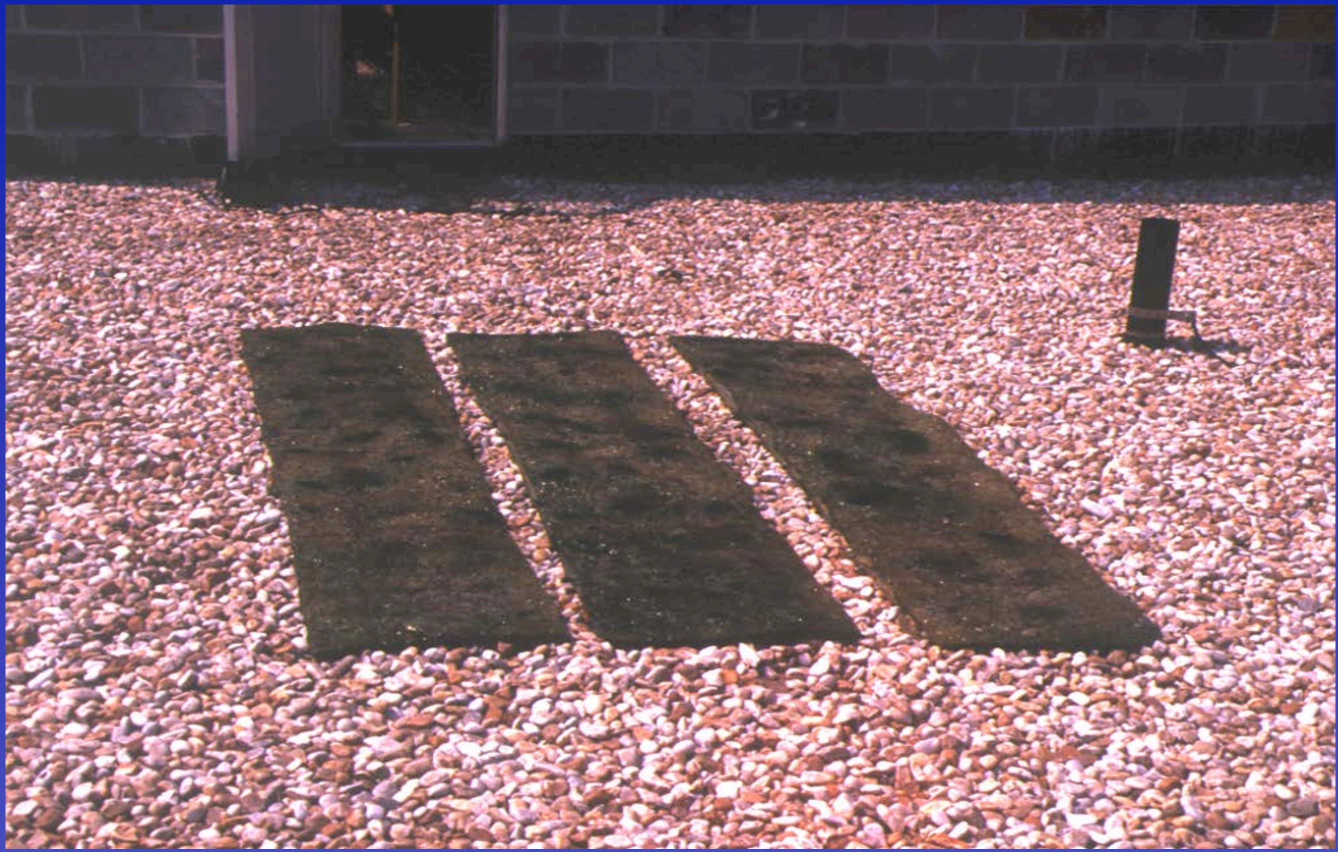
Microbial Mats Grown on Coconut Fiber

The dried mats can be packaged in many forms for field use, e.g., bagged or blankets



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Bench Scale Tests

Studying the effects of microbial mat in sea water

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Monitoring the effects of microbial mats on sea water quality at the bench scale

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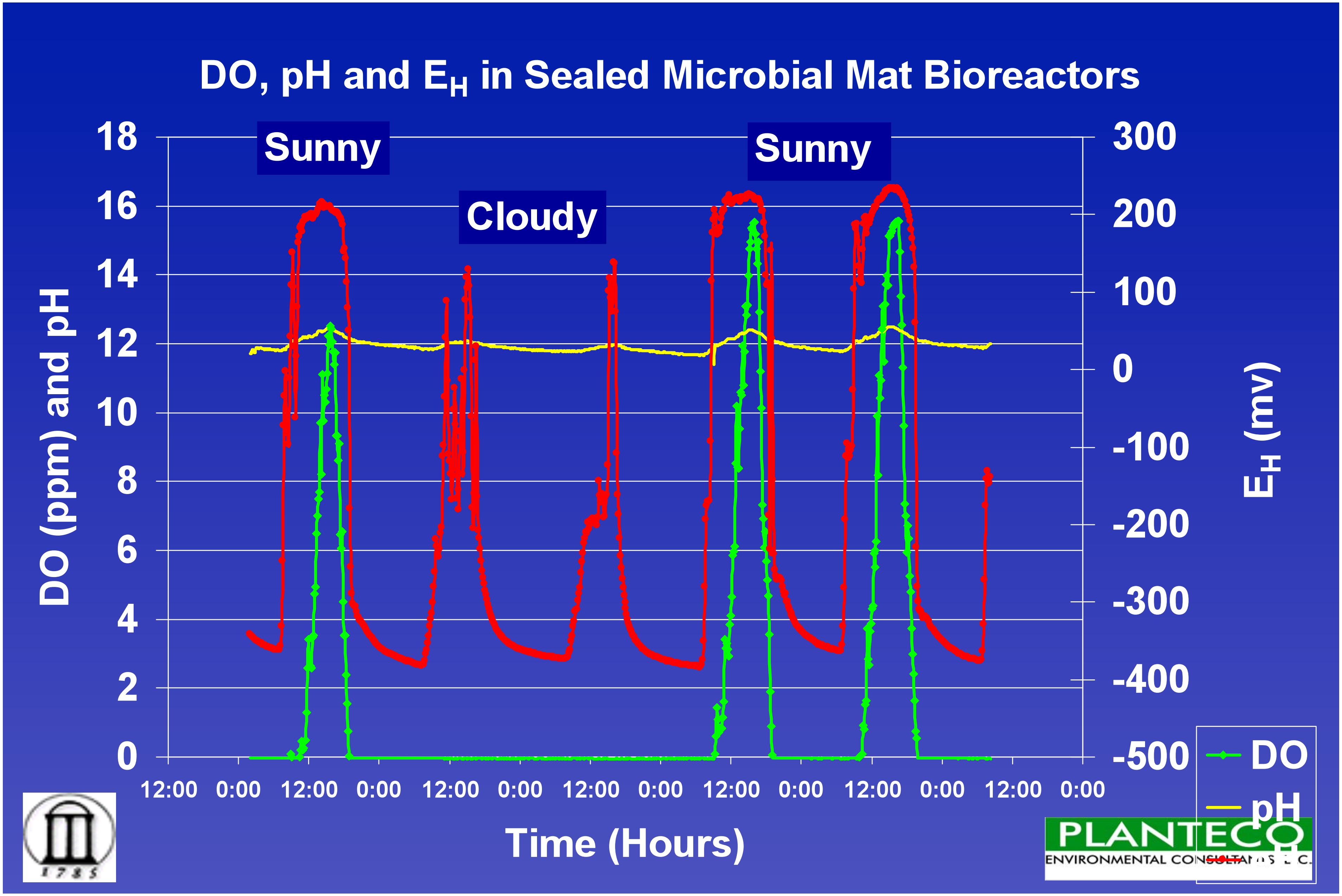

DO, pH and E_H in Sealed Microbial Mat Bioreactors
Sunny
Cloudy
Sunny
DO (ppm) and pH
E_H (mv)
Time (Hours)
18
16
14
12
10
8
6
4
2
0
300
200
100
0
-100
-200
-300
-400
-500
12:00
0:00
DO
pH
E_H
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Suitable site conditions

- Protected environment without storm
- Shallow water
- Lots of munitions

Mode of Application in underwater environment

- Construct “bagged mat” or Microbial mat blanket
- Cover the decaying/leaching point source emitter with microbial mat blanket
- Weigh down the mat blankets with sand and staked to anchor down
- Microbial mats will be left in place as a sink for carbon in the aquatic environment

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Salps are transparent, tubular, jelly-like animals that live in all oceans but are seldom seen. Feeding on microscopic plants, salps remove significant quantities of organic (carbon-containing) material from upper ocean waters. The brown spots are the salps' stomachs.

Richard.Black (BBC , UK)(Image L.Madin/WHOI)

Salp pellets take carbon to the floor of the ocean

Richard.Black (BBC , UK)

- Microbial mats sequester carbon dioxide and other green house gases
- Their use in underwater UXO bioremediation equally sequesters carbon while biodegrading pollutants

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Benefits

- In-situ treatment translates to low-cost
- Removal of nitrogen means reduction in hypoxia and algae blooms
- Reduces nitrogen emission into water column
- Increases dissolved oxygen content of water during daylight hours
- Decreases toxicity to aquatic life, which improves the health of our fisheries

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Thank you

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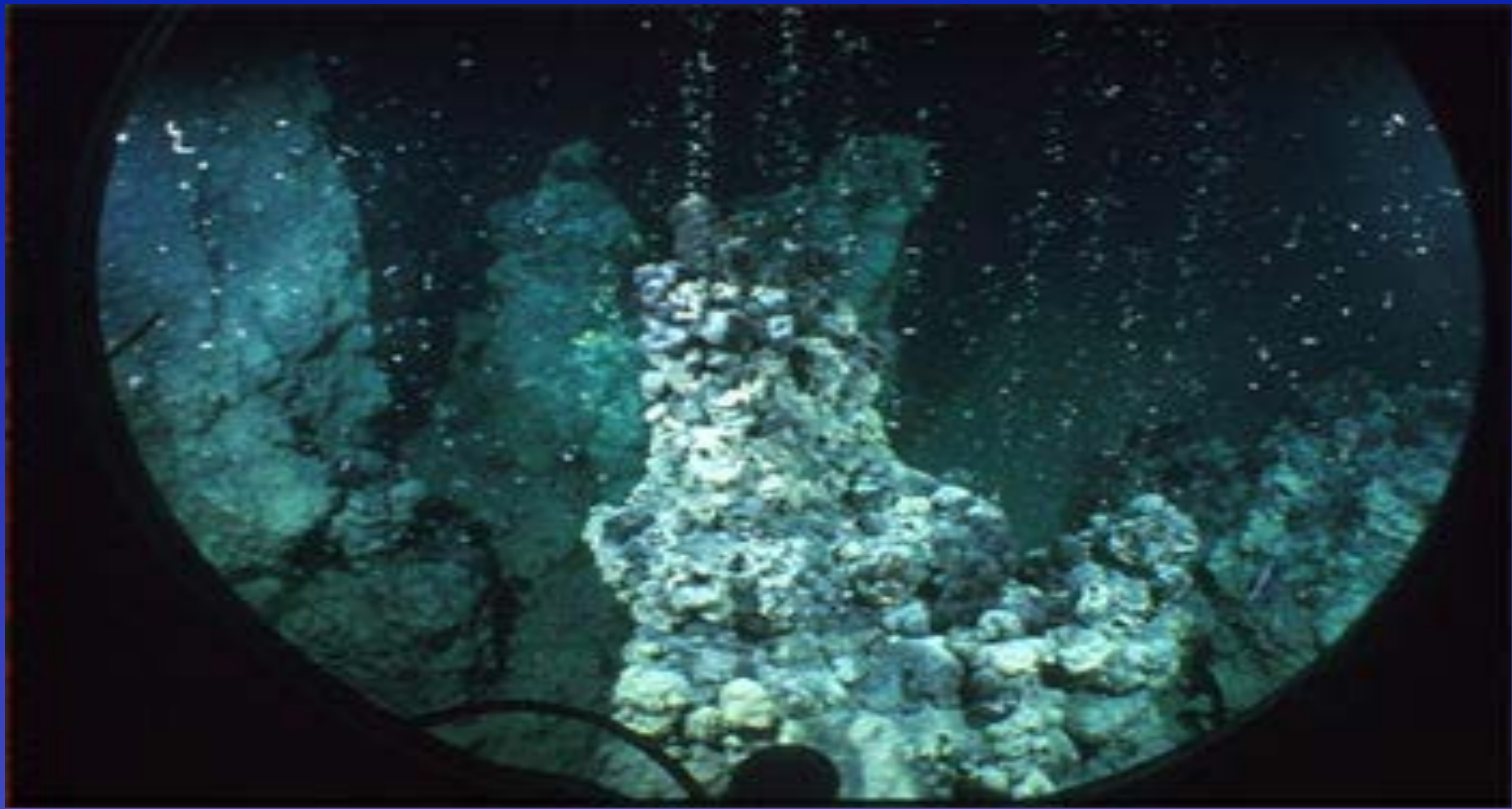
Without oxygen, microbes make a living off methane in Black Sea



Bubbles of free methane gas emanate from the tips of microbial mat reefs.

Courtesy Project Ghostdabs, University of Hamburg, Germany.

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Lovelock urges ocean climate fix
Richard Black

Environment correspondent, BBC News website

Writing in the journal Nature, Science Museum head Chris Rapley and Gaia theorist James Lovelock suggest looking at boosting ocean take-up of CO_2.

"And Professors Lovelock and Rapley suggest that the ocean pipes could also stimulate growth of algae that produce dimethyl sulphide (DMS), a chemical which helps clouds form above the ocean, reflecting sunlight away from the Earth's surface and bringing a further cooling….."

How then will regulators prevent the use of microbial mats for in-situ bioremediation of point sources of nitrogen emitter in underwater environments?

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