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Long Term Groundwater Monitoring Program – Development of Field Analytical Technologies for the Detection of Military Unique Chemicals

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USACE - ERDC - EL

Environmental Chemistry Branch

DoD Environmental Monitoring and Data Quality

Reno, NV 2004

LTM Focus Area

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Long Term Monitoring (LTM) of groundwater:

- Required component of closure on many DoD sites undergoing restoration.
- All military services, other Federal agencies (e.g. DoE), states, and responsible parties share similar responsibility.
- Costs associated with sampling and laboratory analysis over 10 years estimated to approach $500M.
  - 70% of the total monitoring cost.
  - 50% of the total investigation cost.
- Generation of large quantities of waste material
- Long time periods from collection to data report

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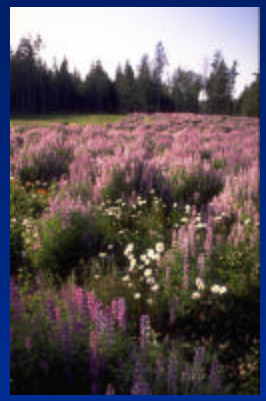
- Field analysis of sites for compounds of interest could significantly alleviate some of the issues facing LTM projects.
  - Eliminate sample transport
  - Replace expensive fixed laboratory analytical costs and reduce analysis time



- Available field analytical methods may not be appropriate for military unique compounds (MUCs)
  - Quality of data obtained (screening)
  - Delicate instrumentation unable to tolerate field conditions
  - Instrumentation operational requirements not compatible with field use
  - Inadequate instrumentation and/or technologies for detection of MUCs

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LTM Focus Area

The mission of the LTM Groundwater Program of the Engineering Research and Development Center (ERDC) of the US Army Corps of Engineers is to develop effective field analytical technologies that are acceptable to all levels of the regulatory community and also meet the stewardship and fiscal needs of the Army.

LTM - Requirements

Technologies that are being developed within the LTM program will address the following according to the A(1.1.a) EQT Operational Requirements Document (EQT-ORD)

- **Applicable to MUCs such as explosive, DU, propellants (e.g. ClO_4^-), pyrotechnics, and degradation products.**
- **Quick analytical turnaround time (<4hrs)**
- **Cost reductions of 25-50% compared to traditional laboratory analysis**
- **Portability, Remote and *In Situ* Operation**
- **Detection of MUCs at levels of concern with defensible data generation**
- **Acceptability to all level of regulatory community (meet requirements of & accepted for SW-846)**

LTM - Thrust Areas

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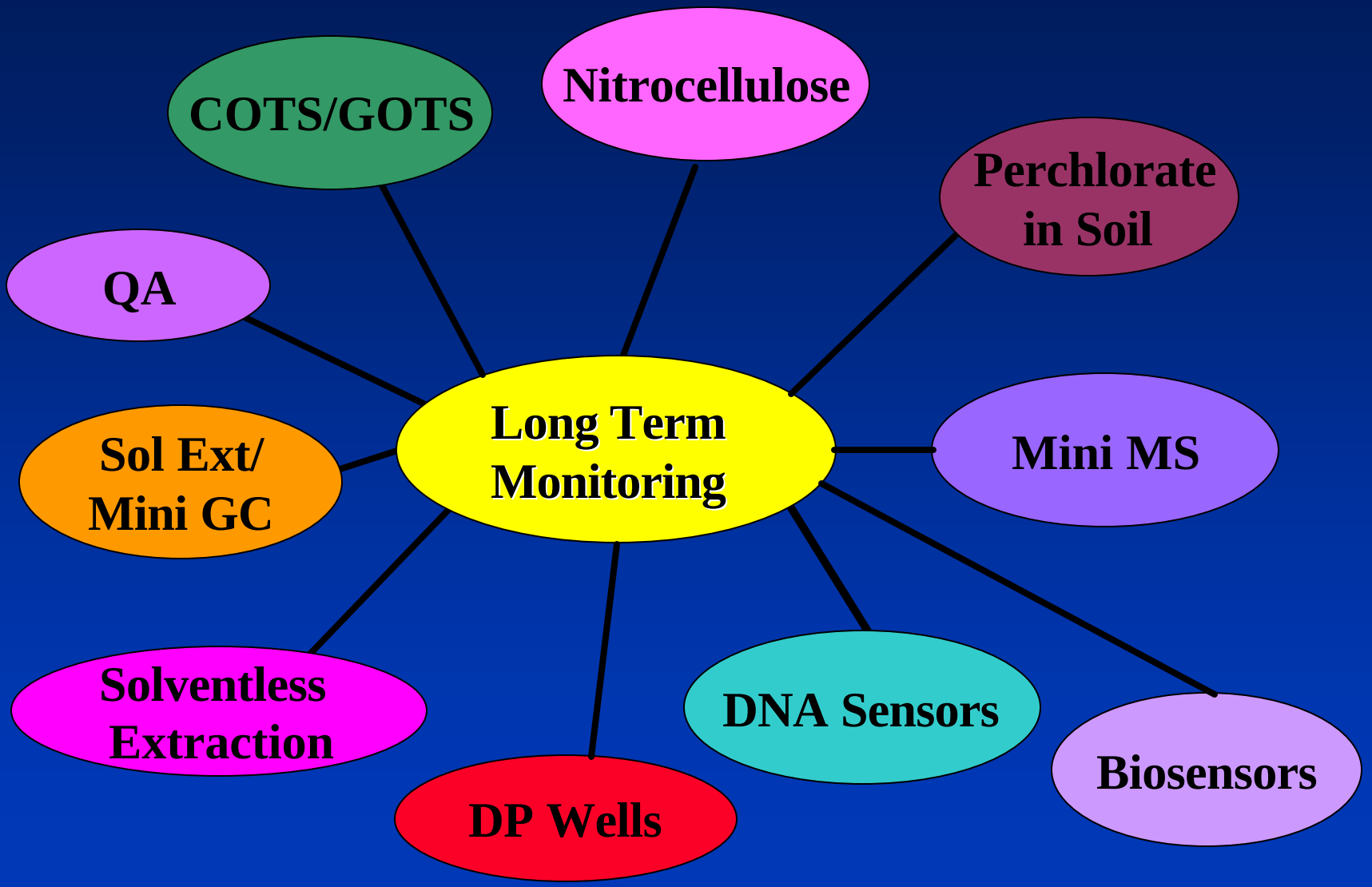
- Interim Improvements

- Leap Ahead Technologies

- Special Analytical Method Development

Long Term Monitoring Focus Area



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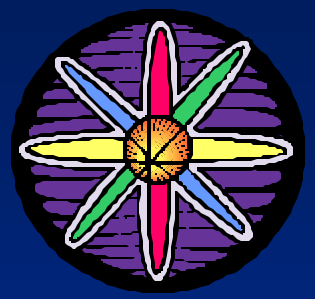
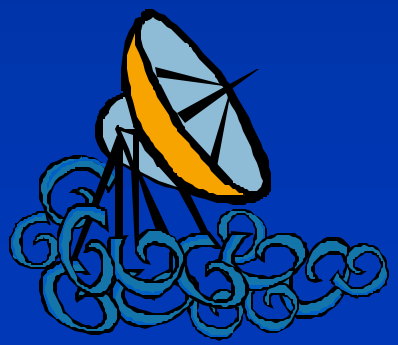
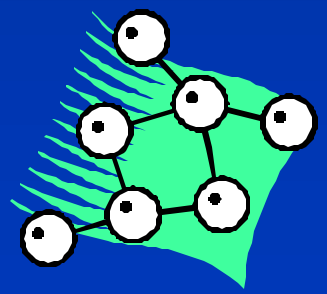
LTM - Interim Improvements

- QA Processes & Protocols
- COTS/GOTS
- Direct Push Wells & Samplers
- Solventless Extraction Technologies
- Solventless Extraction Technologies Interfaced to Miniature GC







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LTM - Interim Improvements

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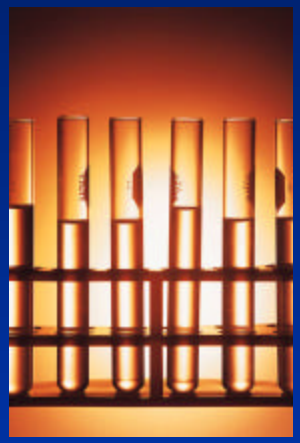

QA Processes & Protocols

POC: Rich Meyer – Environmental Laboratory, ERDC

- Identify Essential QA/QC for Field Analytics
- Identify Reduced Cost Steps for Fixed Lab
- Evaluate Proposed Processes & Protocols
- 2004 ERDC Technical Report

Key Component of LTM Technologies is Ability to Generate Definitive Data

LTM - Interim Improvements

COTS/GOTS

POC: Dave Splichal – Environmental Laboratory, ERDC

- 2004 ERDC Technical Report
  - Sampling Devices
  - Field Instrumentation – GC/MS
  - Sensors
- Applicability to LTM
  - Detection Limits
  - Quality Control
  - Cost Savings

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LTM - Interim Improvements

Solventless Extraction Technologies

POC: Dave Splichal & Denise MacMillan
- Environmental Laboratory, ERDC

- Identify & Develop Solventless Extraction Technologies
- Perform Lab & Field Studies
- Investigating use of Twister and SPME for MUCs
- Evaluation of Potential for On-Site Extraction

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LTM - Solventless Extraction

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Preliminary Results for On-Site Extraction of Explosives

Analyte	% Recovery	Method 8330 Control Chart, % Recovery
HMX	100	39-126
RDX	72	35-119
Tetryl	131	14-120
TNT	92	71-117
2,4-DNT	99	76-110

LTM - Interim Improvements

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Solventless Extraction Technologies Interfaced to Miniature GC

POC: June Mirecki & Dave Splichal – Environmental Laboratory, ERDC

- Develop Field Analytical Capability for Twister & SPME
- Perform Lab & Field Studies for Explosives Detection
  - Characteristic Spectra (GC/MS)
  - Sensitive and Precise
  - Quality Control

LTM - Interim Improvements

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Direct Push Wells & Samplers

POC: Louise Parker – Cold Regions Research Laboratory, ERDC

LTM - Direct Push Wells

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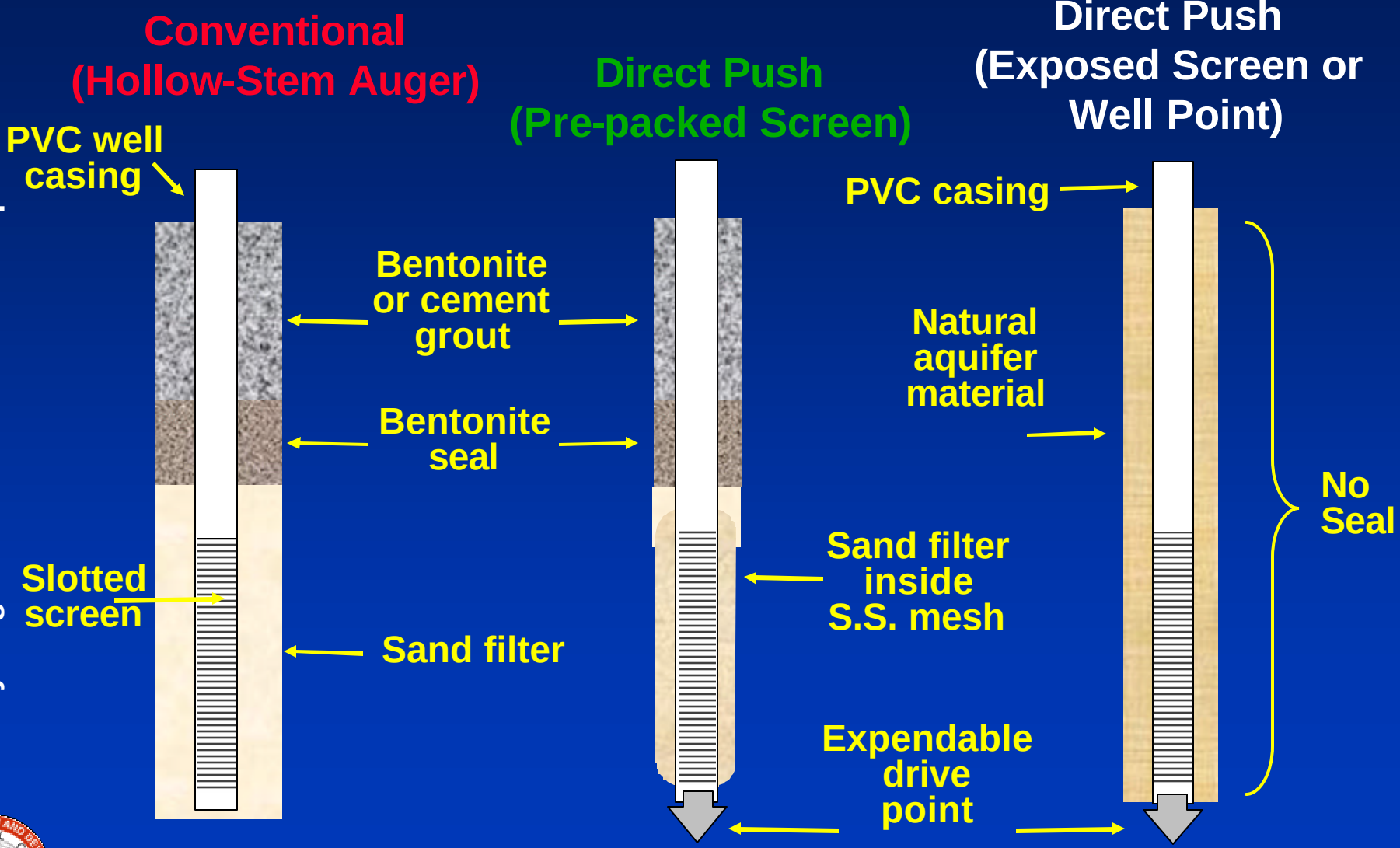

Promising Discrete-Interval Devices

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Diffusion Sampler – Membrane Varies

- Goal is to find a membrane/device that works for explosives
- Initial studies have focused on a jar-type sampler with open end covered with Nylon membrane
- Developed by Don Vroblesky (USGS)

Jar-Type Sampler Study

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Day 7	Control	Sampler	Difference
HMX	1.63	1.55	-4.8
TNB	14.6	14.2	-2.7
RDX	9.20	8.90	-3.3
1,3-DNB	0.635	0.619	-2.4
TNT	2.66	2.58	-3.2
2,4-DNT	0.095	0.092	-2.8
Day 35			
HMX	1.46	1.46	0
TNB	13.3	13.1	-1.5
RDX	8.18	8.22	+0.5
1,3-DNB	0.564	0.564	0.0
TNT	2.32	2.32	0.1
2,4-DNT	0.080	0.078	-2.6

Re-designed Hydrasleeve

VOC Testing

and

Turbidity Evaluations

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Snap Sampler

- Spring activated
- No sample transfer
- VOCs, explosives & pesticides

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LTM - Leap Ahead Technologies

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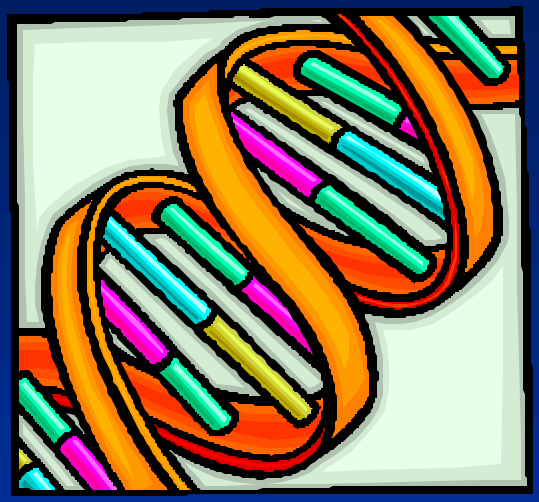
Catalytic DNA Sensors



POC: Don Cropek – Construction Engineering Research Laboratory, ERDC

Collaboration with Dr. Yi Lu, University of Illinois

- Specific - Reacts with a single chemical, reliable without false positives
- Sensitive - Ultra-low concentration
- Flexible - Detector for many different compounds
- Convenient - Fast, small sensor array

LTM - Catalytic DNA Sensors

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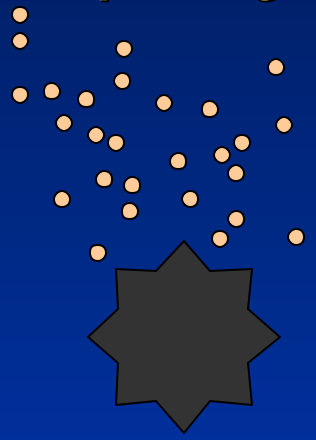
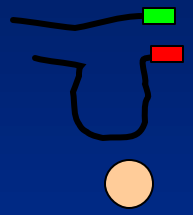
Contaminated Water or Vapor Signature

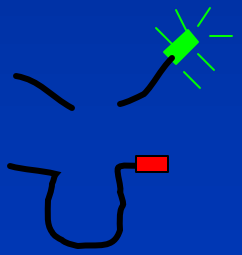


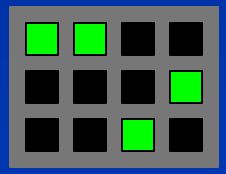
Explosive-sensitive DNA



DNA reacts with vapor signature

Reaction cleaves the DNA, causing detectable fluorescence.





Sensor array

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LTM - Catalytic DNA Sensors

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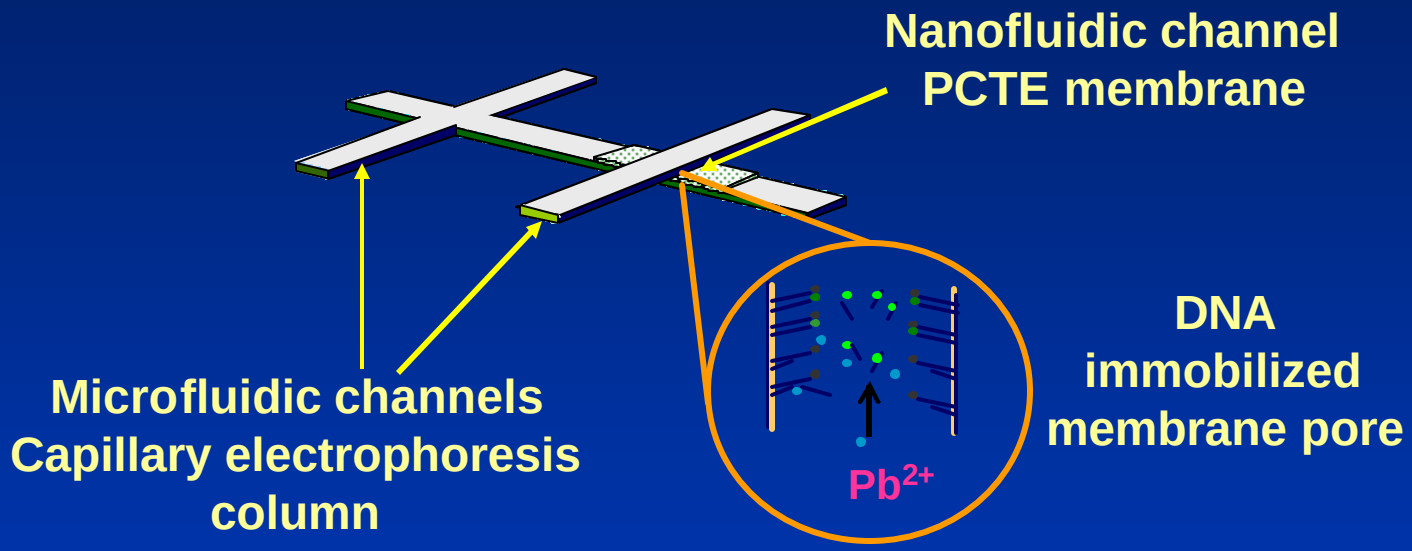
Nanofluidic Molecular Gate Membranes



Expanded view of the microfluidic channels and the nanofluidic molecular gate membrane.

LTM - Leap Ahead Technologies

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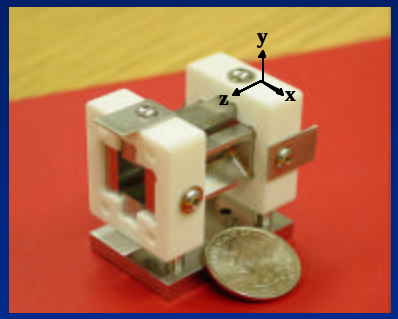
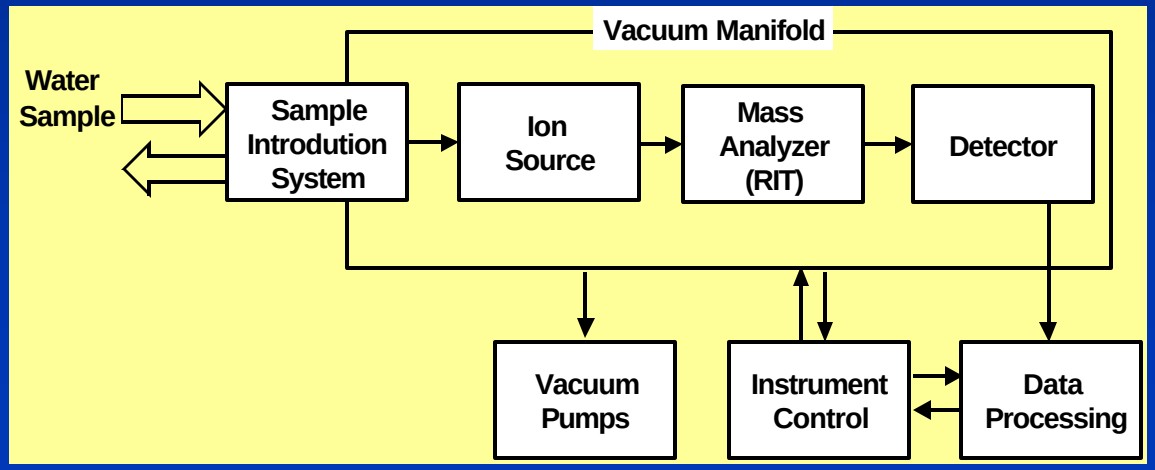


Miniature Mass Spectrometer

POC: Denise MacMillan – Environmental Laboratory, ERDC

Collaboration with Dr. Graham Cooks, Purdue University



LTM - Leap Ahead Technologies

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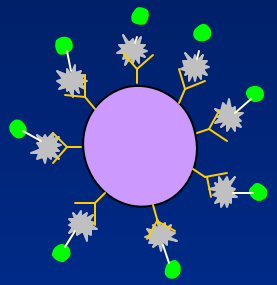
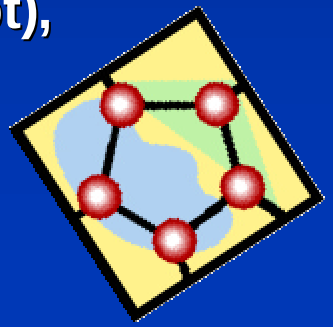
Microfluidic Biosensors

POC: Shana Dalton – Environmental Laboratory, ERDC



- **Develop Sensitive & Selective *In Situ* Detection Capability for Military Unique Compounds with Antibody Capture Technology (Immunoassay)**
  - **Rapid (minutes), Sensitive (ppb or ppt), Specific, Small**
- **Fluorescent-linked detection**



LTM - Microfluidic Biosensors

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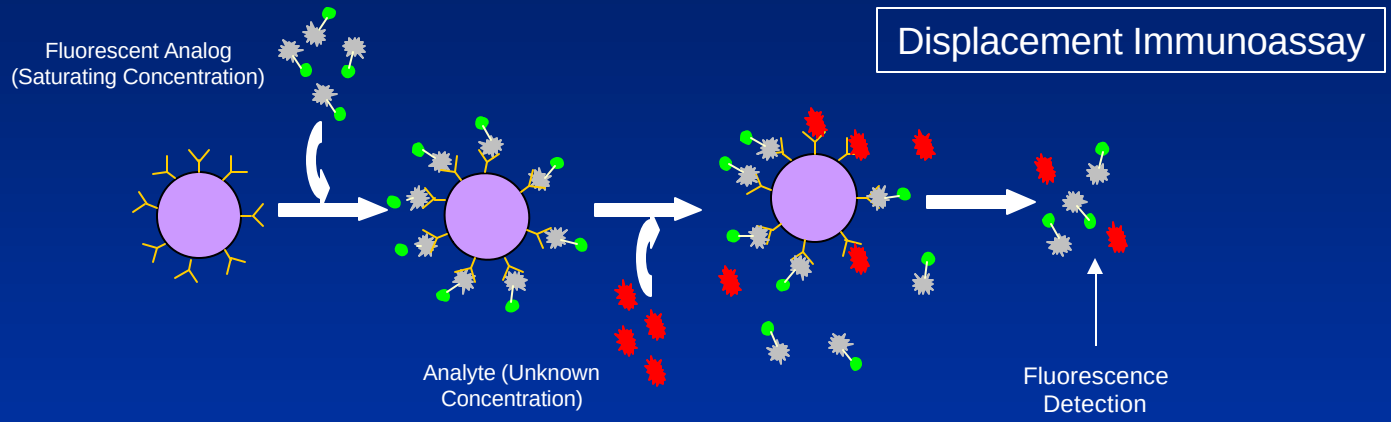
- Immunoassays with commercially available RDX and TNT antibodies immobilized on magnetic beads



- Expand the number of antibodies to MUCs
  - Developing antibodies to HMX and 2, 4-DNT with Strategic Biosolutions (~ 9 months / analyte)
- Collaborate with other laboratories currently developing immunoassay-based technologies

LTM - Microfluidic Biosensors

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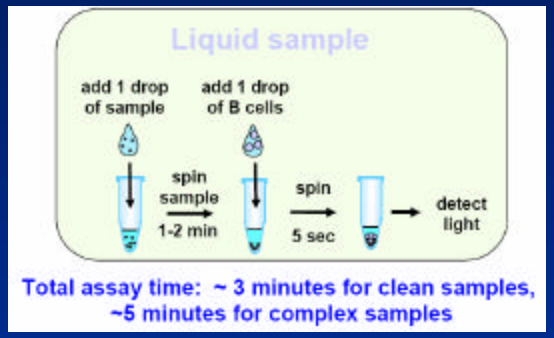
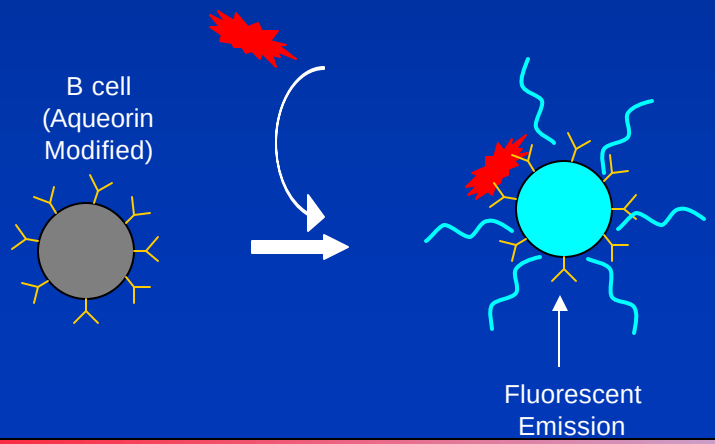
CANARY (Cellular Analysis and Notification of Antigen Risk and Yields)

- Developed at MIT-LL
- Excellent for Biological Agents
  - *Bacillus anthracus* (anthrax)
  - *Yersinia pestis* (plague)
  - FMD (Foot and Mouth Disease) virus
  - *E. coli*
- Highly sensitive response in seconds
- Detection of Toxins (Small Molecules)
  - Developmental Stage



Total assay time: ~ 3 minutes for clean samples, ~5 minutes for complex samples

CANARY Bioassay



Source: Presentation at Federal Bio-Chem Detection Conference, Oct. 2003 by Peter Emanuel, PhD, Critical Reagents Program Director, JPE-CBD

LTM - Special Analytical Methods

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Nitrocellulose:

- Gun cotton, pyroxilin, ~12% N
- Occurs with nitroglycerin at firing points
- Differential solubility method under development

Perchlorate:

- Used primarily as a solid rocket fuel
- Other sources include flares, airbags, fireworks, some nitrate-based fertilizers
- Competes with iodine in thyroid - low action level expected
- Through soils with little, if any, adsorption occurring
- Experiments designed & conducted to test ClO_4^- adsorption to soil under both oxic & anoxic conditions

Focus Area Project Delivery Team

- **Project Delivery Team: ERDC, AEC, and CEHNC**
  - Co-chaired by ERDC and AEC.
  - General oversight & dispute resolution by Environmental Technology Integrated Process Team (ETIPT).
- **ERDC - S&T (BA1-BA3)**
  - Dr. M. John Cullinane – Manager for S&T effort.
  - Dr. Denise MacMillan - S&T Focus Area Manager.
- **AEC - T&E (BA4-BA6)**
  - Mr. James Daniels Manager for T&E effort.
  - Mr. William Houser - T&E Focus Area Manager.
- **DOD Coordination Group**
  - Effort Managers.
  - Focus Area Managers.
  - Rep from CEHNC, JUXOCO, SERDP/ESTCP.
  - Rep from other service.

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Vicksburg, MS

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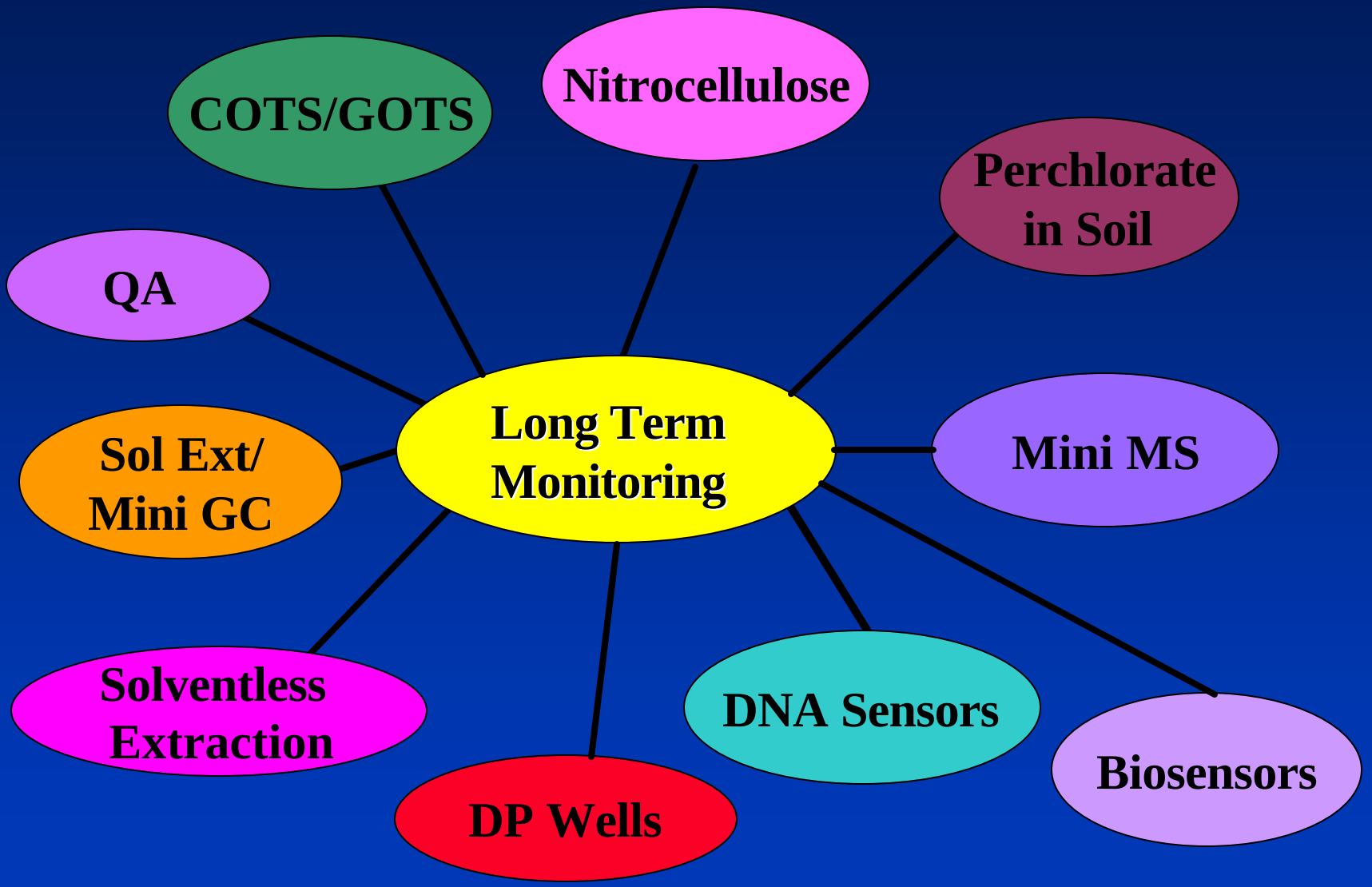
Lynn Escalon
Scott Waisner
Anne Weathersby

Long Term Monitoring Focus Area



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