The Road to a Real-Time In Situ Monitoring System

Denise K. MacMillan
Engineer Research and Development Center
Environmental Laboratory
420 S 18th Street
Omaha, NE 68102

Conference on Accelerating Site Closeout, Improving Performance, and Reducing Costs Through Optimization

Long Term Monitoring Focus Area

- 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.
  - Sample collection and laboratory analysis
    - 70% of the total monitoring cost.
    - 50% of the total investigation cost.

Long Term Monitoring Focus Area

- Field analytical methods could reduce costs
  - Eliminate sample transport
  - Replace expensive fixed laboratory analytical costs

- Available field analytical methods may not be appropriate
  - Screening data produced
  - Delicate instrumentation unable to tolerate harsh conditions
  - Instrument operation requirements not compatible with field use
  - Inadequate for chemicals important to military

Focus Area Requirements

- **A(1.1.a) EQT Operational Requirements Document (EQT-ORD)**
  - Reduce LTM costs from 25 – 50%
  - Applicable to HMX, 1,3-DNB, NB, 3NT, 4NT, ClO_4^-, DU, propellants, pyrotechnics, and degradation products
  - Definitive data
  - 4 hour TAT
  - Portable or *in situ*
  - Easy to operate
  - Capable of remote operation
  - Comparable data to laboratory analysis
  - Meets requirements of & accepted for SW-846

Focus Area Project Delivery Team

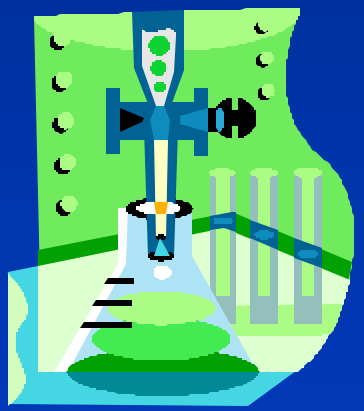
- ERDC - S&T (BA1-BA3)
  - Dr. M. John Cullinane – Manager for S&T effort.
  - Dr. Denise MacMillan - S&T Focus Area Manager
- AEC - T&E (BA4-BA6)
  - Mr. James Daniels - Manager for T&E effort
  - Mr. William Houser - T&E Focus Area Manager
- ERDC Principal Investigators
  - Environmental Laboratory
  - Cold Regions Research Laboratory
  - Construction Engineering Laboratory

Thrust Areas

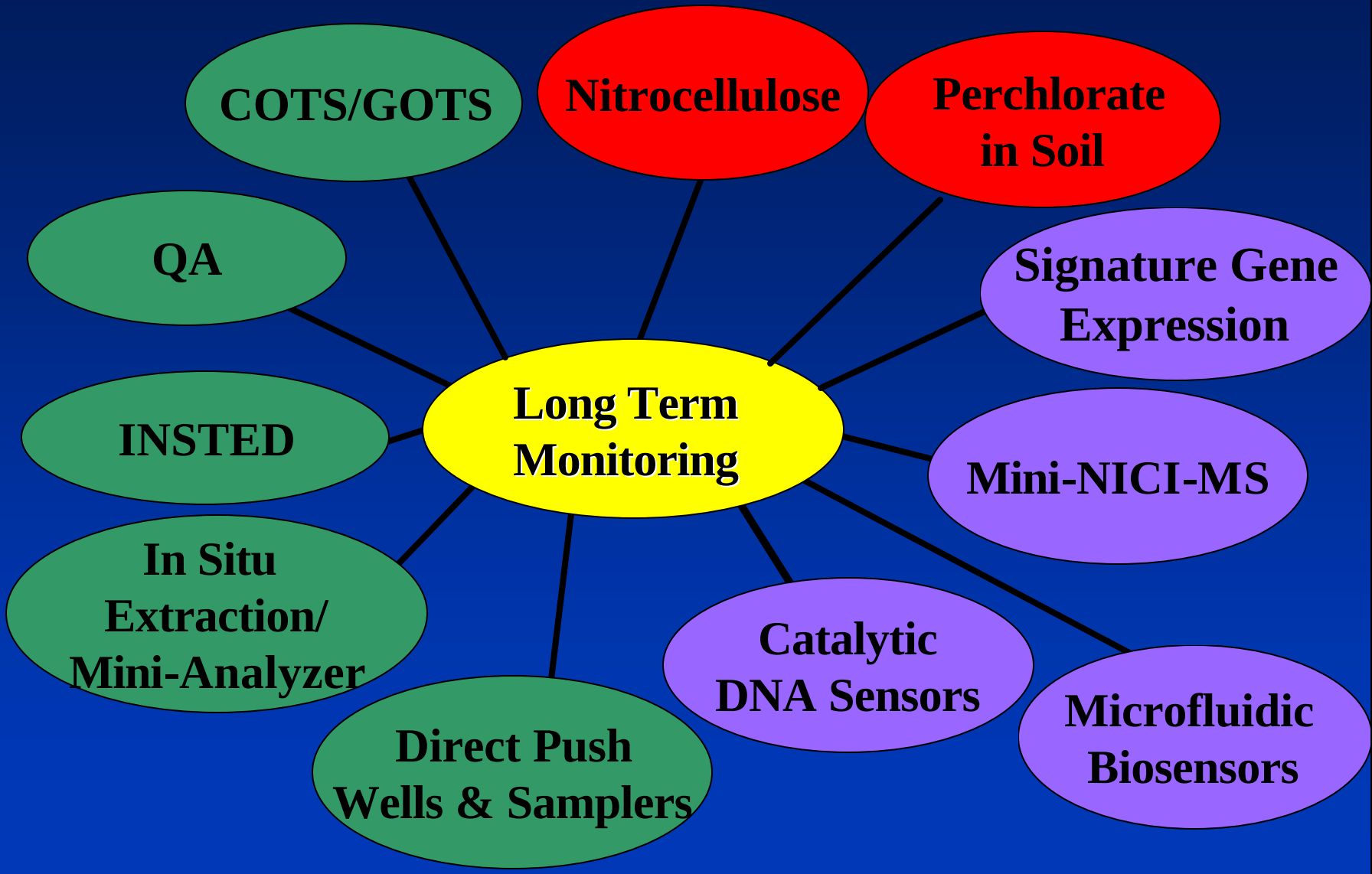
- ✓ Interim Improvements

- ✓ Leap Ahead Technologies

- ✓ Special Analytical Method Development



Long Term Monitoring Focus Area



COT/GOTS

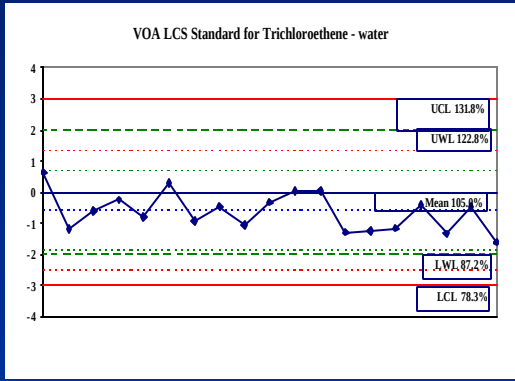
POC: Dave Splichal – EL, ERDC

- ✓ 2004 ERDC Technical Report
  - ✓ Sampling Devices
  - ✓ Field Instrumentation – GC/MS
  - ✓ Sensors

- ✓ Applicability to LTM
  - ✓ Detection Limits
  - ✓ Quality Control
  - ✓ Cost Savings

QA Processes & Protocols

POC: Denise MacMillan – EL, ERDC

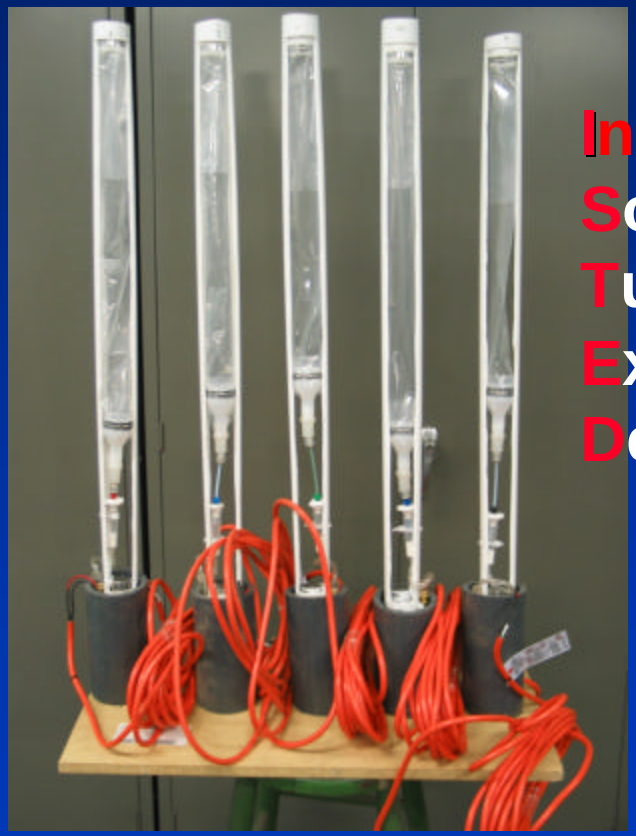


Key Component of LTM Technologies is Ability to Generate Definitive Data

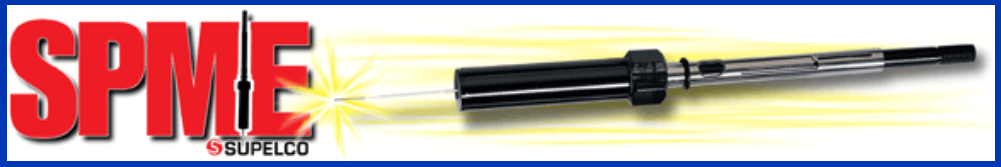
- ✓ Identify Essential QA/QC for Field Analytics
- ✓ Identify Reduced Cost Steps for Fixed Lab
- ✓ Evaluate Proposed Processes & Protocols
- ✓ 2004 ERDC Technical Report

In Situ Extraction Technologies

POC: Dave Splichal – EL, ERDC



In Situ
Solid Phase
Tubular
Extraction
Device



In Situ Extraction Technologies

INSTED with Spiked Standards

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

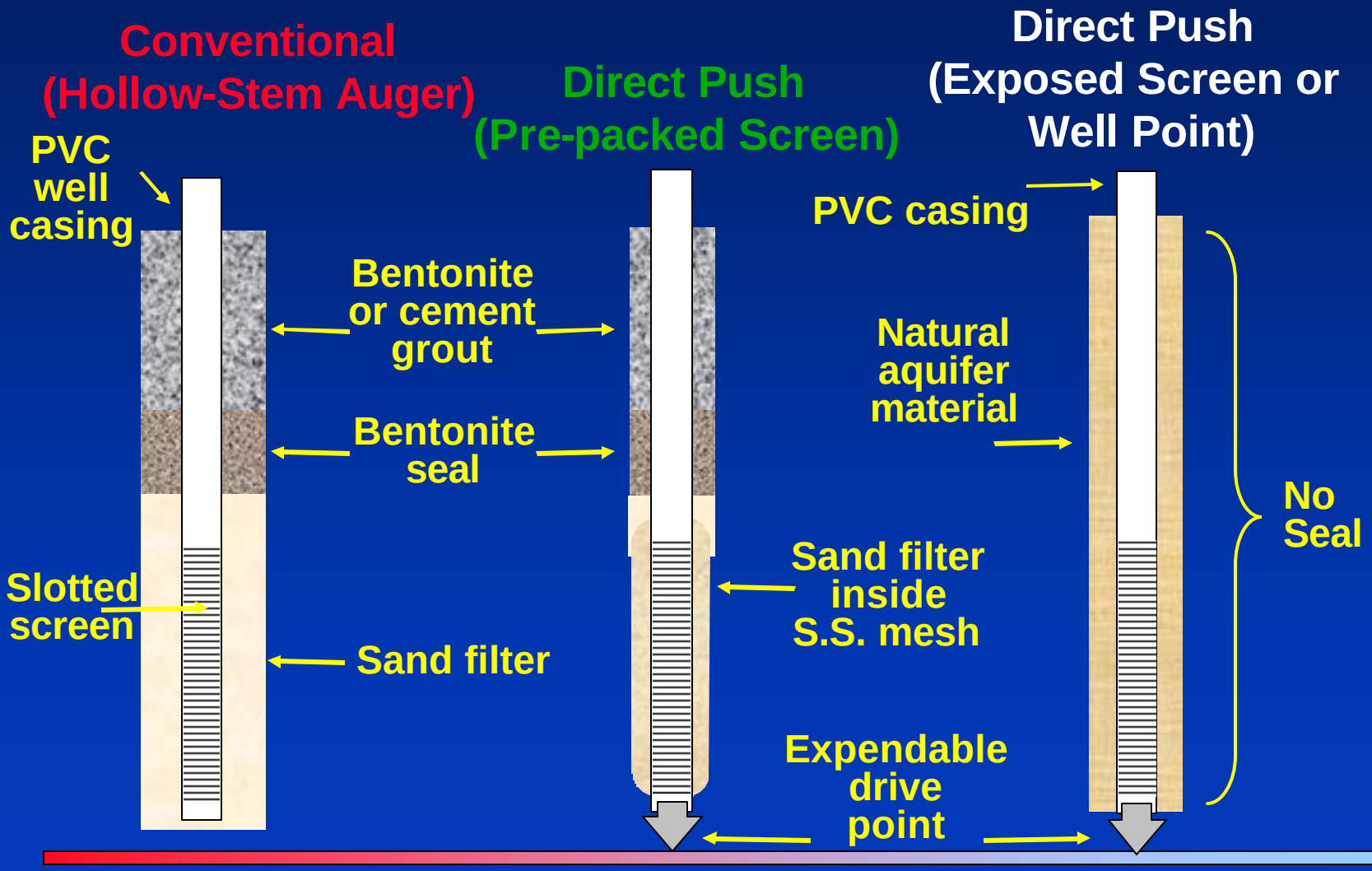
In Situ Extraction Technology

INSTED with Real World Samples

Analyte	INSTED ug/L	Method 8330 ug/L	% Diff
RDX	153	159	3.8
HMX	21.4	21.6	0.93
MNX	1.99	2.26	13
4-A-DNT	1.53	1.49	2.6

Direct Push Wells & Samplers

POC: Louise Parker – CRREL, ERDC



Jar-Type Sampler Study

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
TNT	2.32	2.32	0.1
2,4-DNT	0.080	0.078	-2.6

Snap Sampler

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

In Situ Extraction/ Mini-Analyzer

POC: June Mirecki & Dave Splichal – EL, ERDC

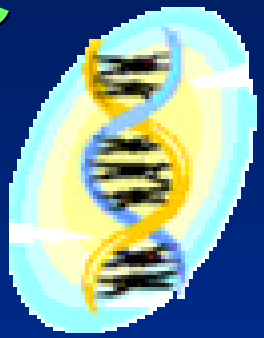
- ✓ Develop Field Analytical Capability for Twister™ & SPME
- ✓ Perform Lab & Field Studies for Explosives Detection
  - ✓ Characteristic Spectra (GC/MS)
  - ✓ Sensitive and Precise
  - ✓ Quality Control

Minotaur 400s

Catalytic DNA Sensors

POC: Don Cropek – CERL, ERDC

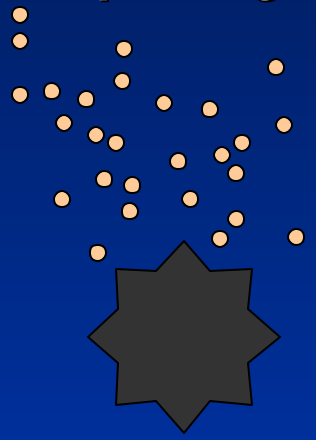
Collaboration with Dr. Yi Lu, University of Illinois



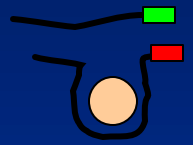
- ✓ **Specific – Reacts with a single chemical, reliable without false positives**
- ✓ **Sensitive – Ultra-low concentration**
- ✓ **Flexible – Detector for many different compounds**
- ✓ **Convenient – Fast, small sensor array**

Catalytic DNA Sensors

Contaminated Water or Vapor Signature

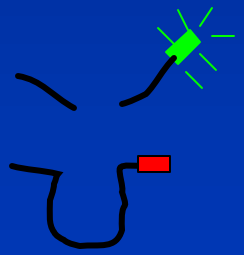


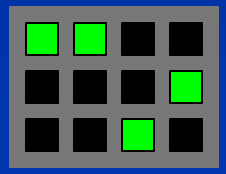
Explosive-sensitive DNA



DNA reacts with vapor signature

Reaction cleaves the DNA, causing detectable fluorescence.



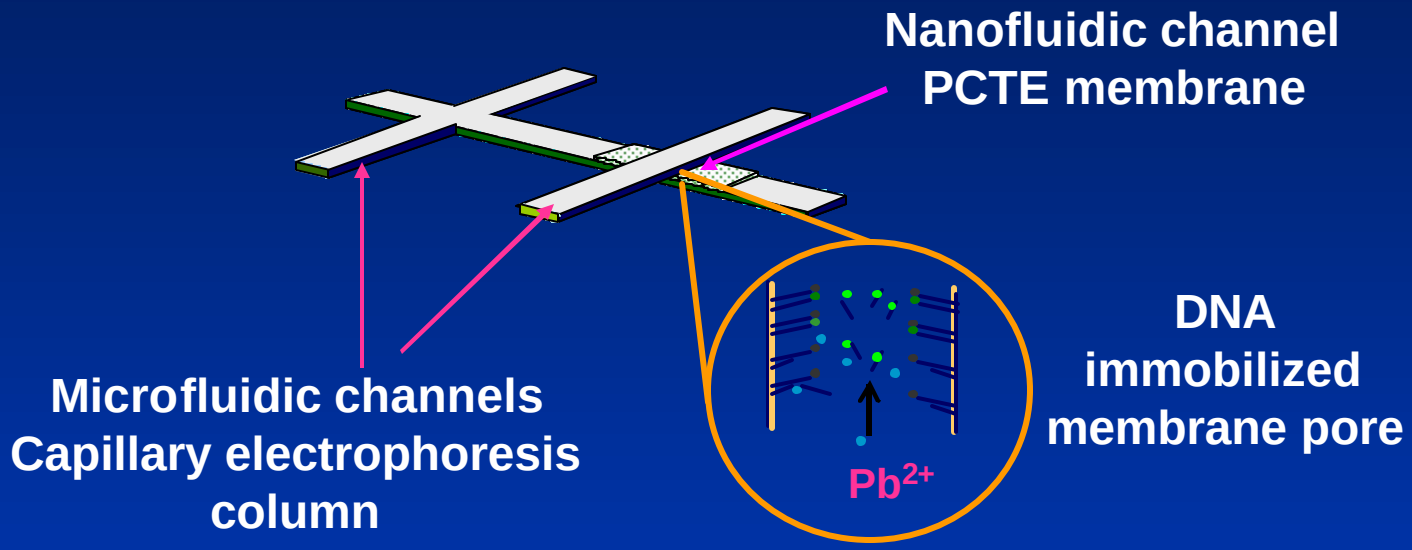


Sensor array

Land Mine

Catalytic DNA Sensors

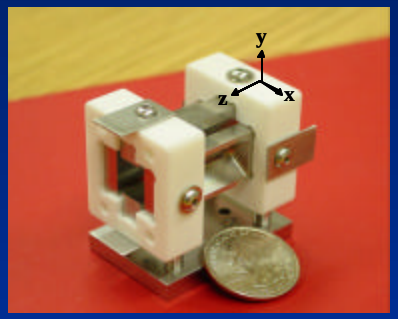
Nanofluidic Molecular Gate Membranes



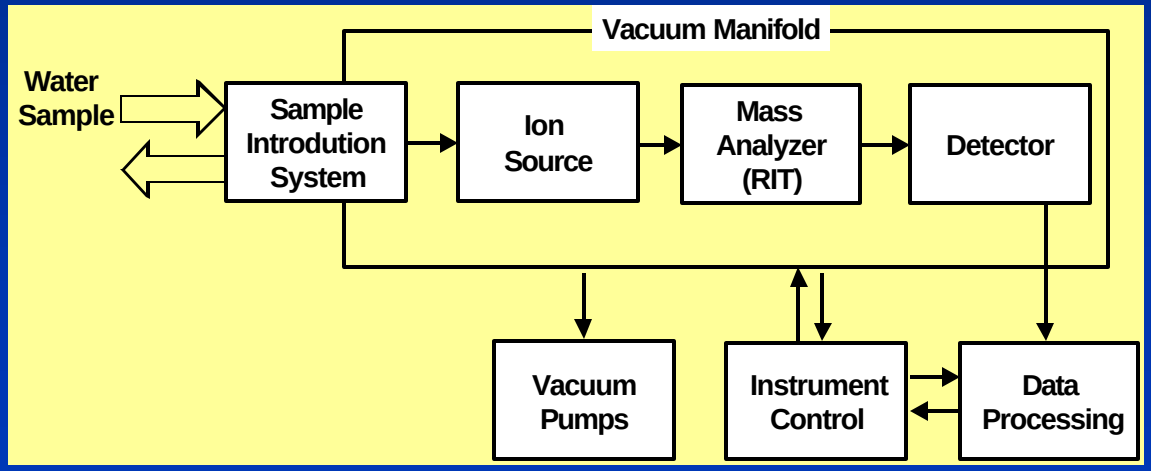
Expanded view of the microfluidic channels and the nanofluidic molecular gate membrane

Miniature Mass Spectrometer

POC: Denise MacMillan – EL, ERDC



Collaboration with Dr. Graham Cooks, Purdue University



Microfluidic Biosensors

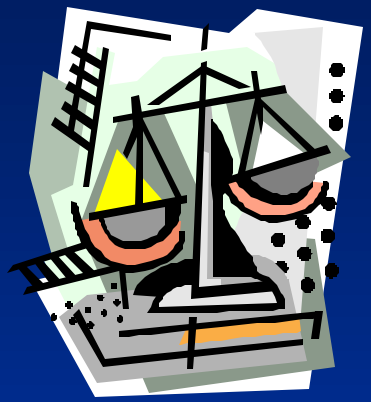
POC: Shana Dalton & Denise MacMillan – EL, ERDC

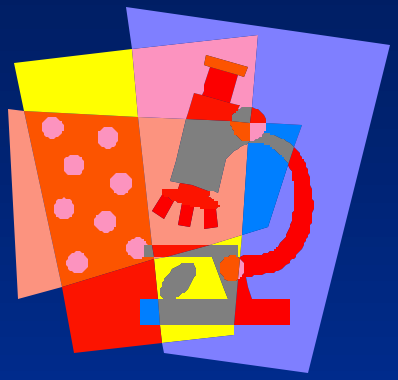
Biosensor: Sensor that uses biochemicals to detect chemicals

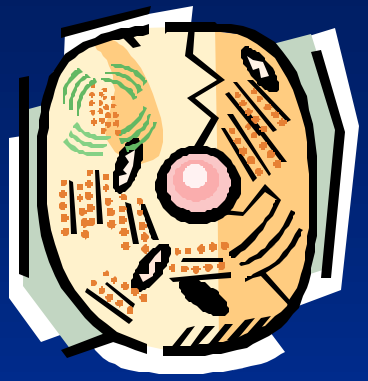
Bioprobe: Sensor that detects biochemicals

- ✓ **Develop Sensitive & Selective in situ Detection Capability for Explosives with Antibody Capture Technology**
- ✓ **Identify & Develop Biosensor Technology for Perchlorate**

Microfluidic Biosensors





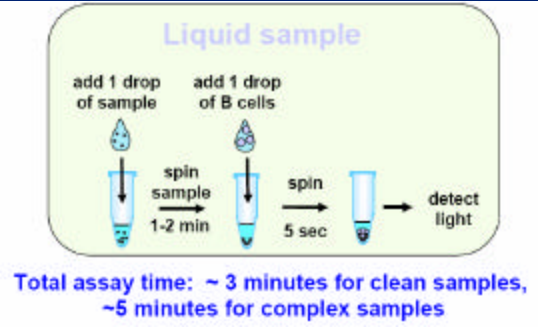


- ✓ Immunoassays with commercially available RDX and TNT antibodies immobilized on magnetic beads
- ✓ Expand the number of antibodies to MUCs
  - ✓ Developing antibodies to HMX and 2, 4-DNT with Strategic Biosolutions (~ 9 months / analyte)
- ✓ Collaborate with other laboratories currently developing immunoassay-based technologies

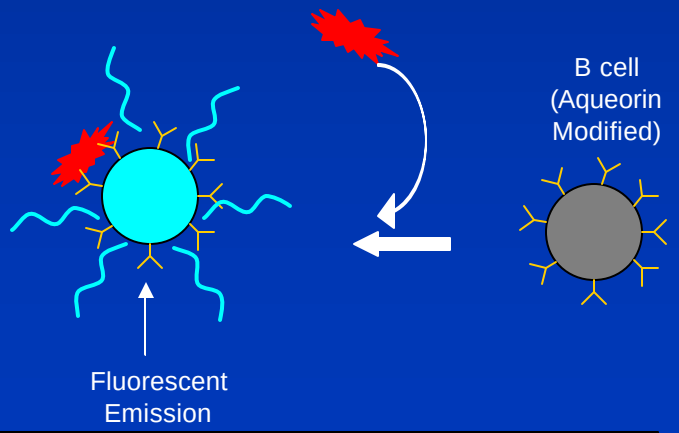
Microfluidic Biosensors

CANARY
(Cellular Analysis & Notification of Antigen Risk & 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 – Developmental Stage

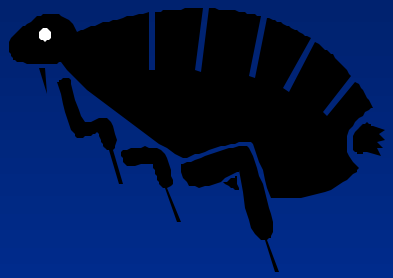


CANARY Bioassay



Signature Gene Expression

POC: Ed Perkins – EL, ERDC



- ✓ Expose *Daphnia* to contaminant
- ✓ Characterize signature gene response
- ✓ Immobilize *Daphnia* in microchip flow cell
- ✓ Mixture separation by micro-chromatography
- ✓ Amplify signal with micro-PCR

Special Analytical Methods

Nitrocellulose

- ✓ Gun cotton, pyroxilin, ~12% N
- ✓ Occurs with NG at firing points
- ✓ Differential solubility method & pyrolysis method

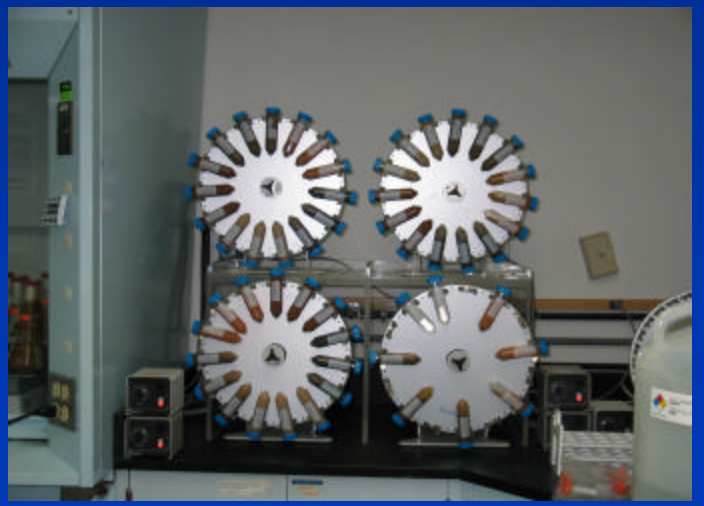
- ✓ Used primarily as a solid rocket fuel
- ✓ Through soils with little, if any, adsorption occurring
- ✓ Little literature evidence to support hypothesis
- ✓ Competes with iodine in thyroid – low action level expected

Perchlorate

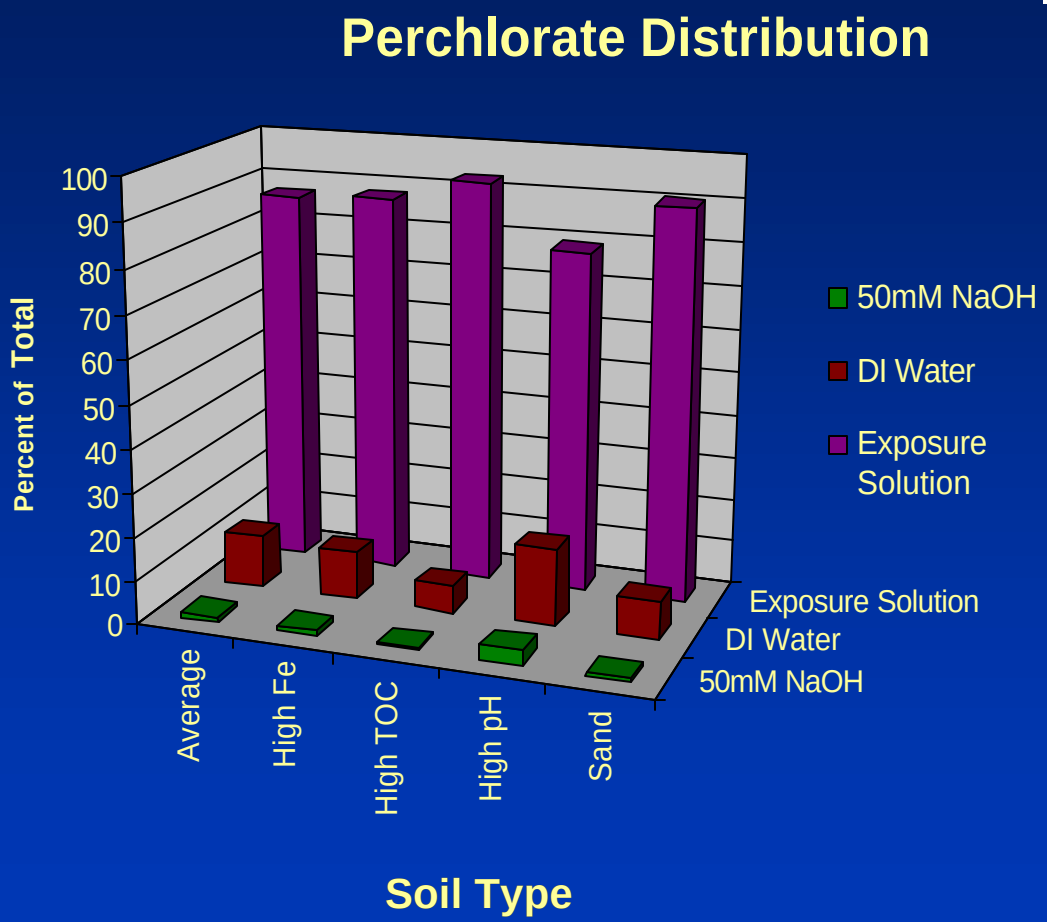
Special Analytical Methods

- ✓ Soils utilized in the project
  - ✓ "Average" Soil
  - ✓ Sandy Soil
  - ✓ High Iron Soil
  - ✓ High pH Soil
  - ✓ High Total Organic Soil
- ✓ Experimental Conditions
  - ✓ Oxic
  - ✓ Anoxic
  - ✓ Controls
    - ✓ No Soil
    - ✓ No Perchlorate

Soil Characteristic	Average Soil [WES Reference]	Sandy Soil [Ottawa Sand]	High Fe Soil [Telleco Loam]	High pH Soil [Crot Sandy Loam]	High TOC Soil
UCS Classification	Clay (CH), Brown	SP	Sandy Clay (CL), Red	Sandy Clay (CH) Grey	
Total Ca (mg/kg)	1440	<20	416	59500	
Total Fe (mg/kg)	21100	103	51600	13500	
Total Mg (mg/kg)	2090	<25	1050	15000	
TOC (mg/kg)	5320	13.85	6033	4746	
Percent sand	0.5	97.6	30.9	49.1	
Percent Fines	99.5	2.4	69.1	50.9	
pH of 20% Slurry	4.97	6.2	4.28	9.73	



Special Analytical Methods



Total (Perchlorate) = sum of the three different fractions

Preliminary Data

- Most ClO_4^- recovered from exposure solution; trace in NaOH wash
- No differences between soil type or O_2 conditions
- Results must be corrected for pore water

Future Plans

- ✓ Sensor arrays & additional analytes
- ✓ Robotics
- ✓ Data processing and communication
- ✓ Systems integration
- ✓ Dual use with Homeland Security
- ✓ Field evaluation
- ✓ Demonstration and validation

Acknowledgements

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