The Road to a Real-Time In Situ Monitoring System

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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

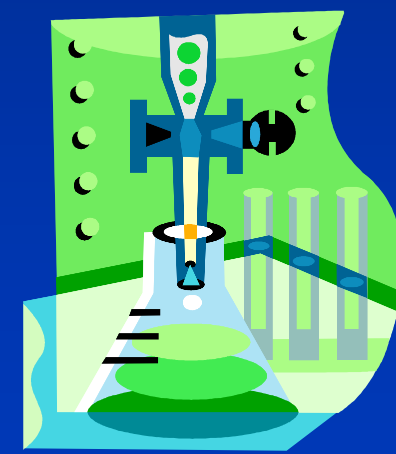
Focus Area Project Delivery Team

- 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

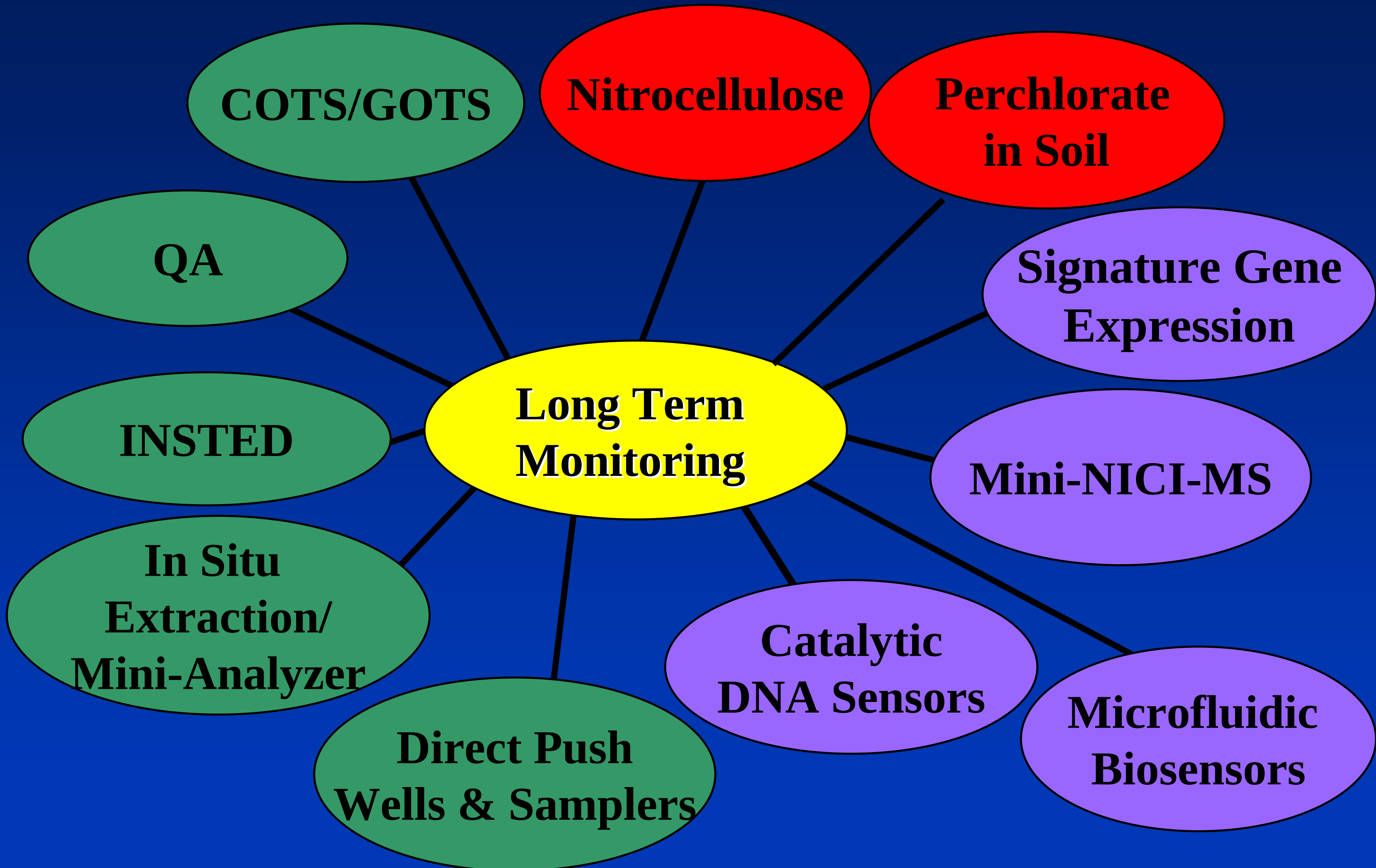
- ✓ **Interim Improvements**

- ✓ **Leap Ahead Technologies**



- ✓ **Special Analytical Method Development**

Long Term Monitoring Focus Area



COT/GOTS

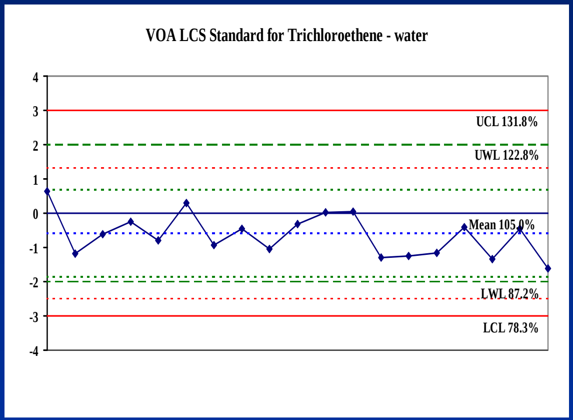
POC: Dave Splichal – EL, ERDC

- ✓ 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



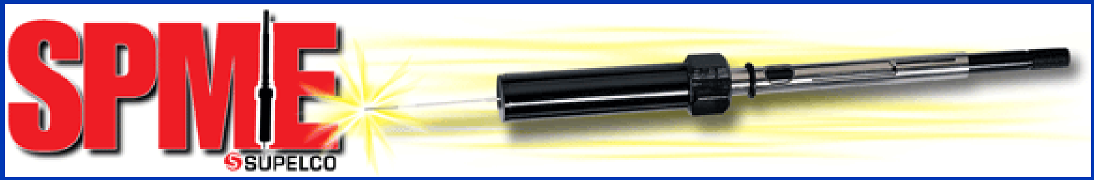
Key Component of LTM Technologies is Ability to Generate Definitive Data

- ✓ **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

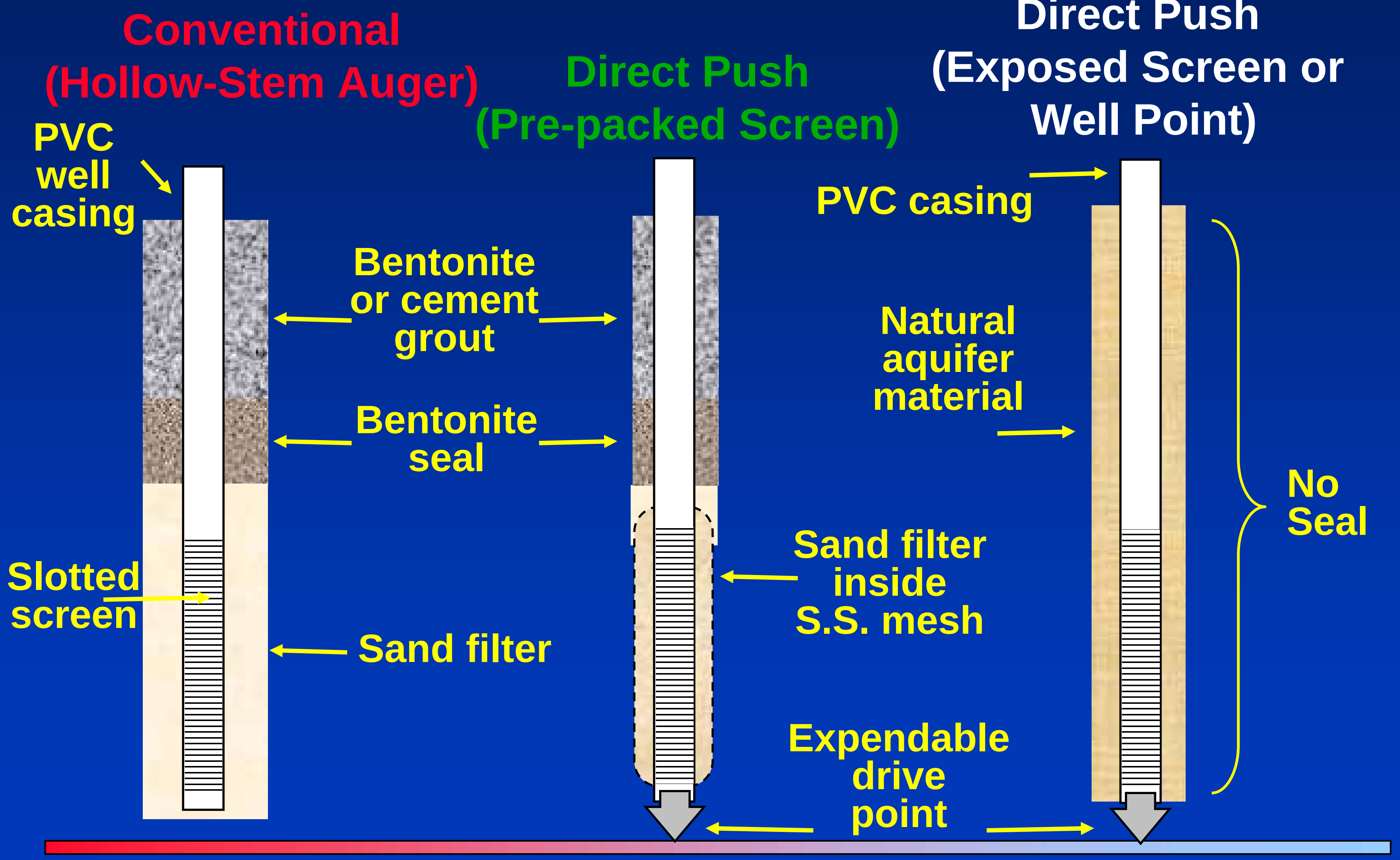
In Situ Extraction Technology

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

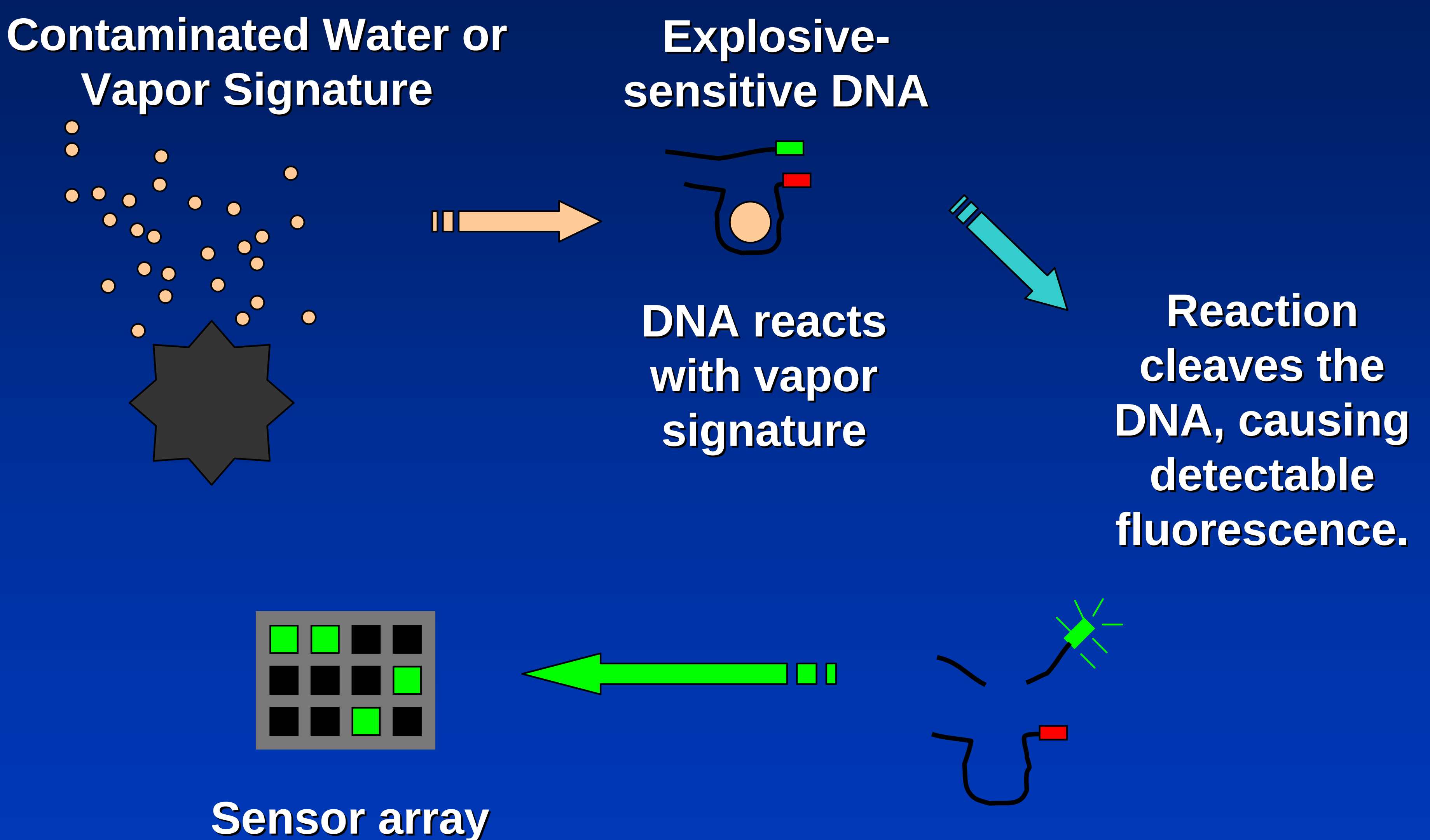
Catalytic DNA Sensors

POC: Don Cropek – CERL, ERDC

Collaboration with Dr. Yi Lu, University of Illinois

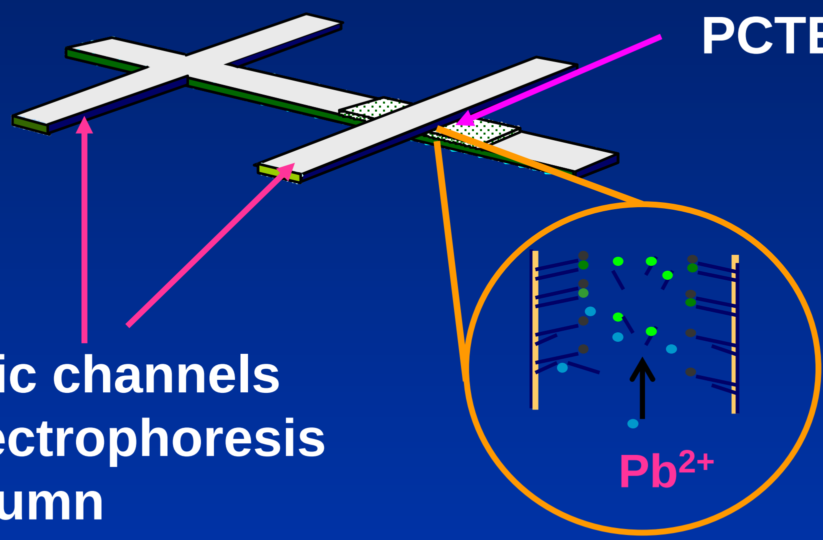
- ✓ **Specific – Reacts with a single chemical, reliable without false positives**
- ✓ **Sensitive – Ultra-low concentration**
- ✓ **Flexible – Detector for many different compounds**
- ✓ **Convenient – Fast, small sensor array**

Catalytic DNA Sensors



Catalytic DNA Sensors

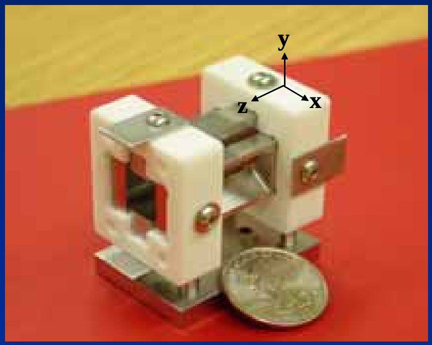
Nanofluidic Molecular Gate Membranes



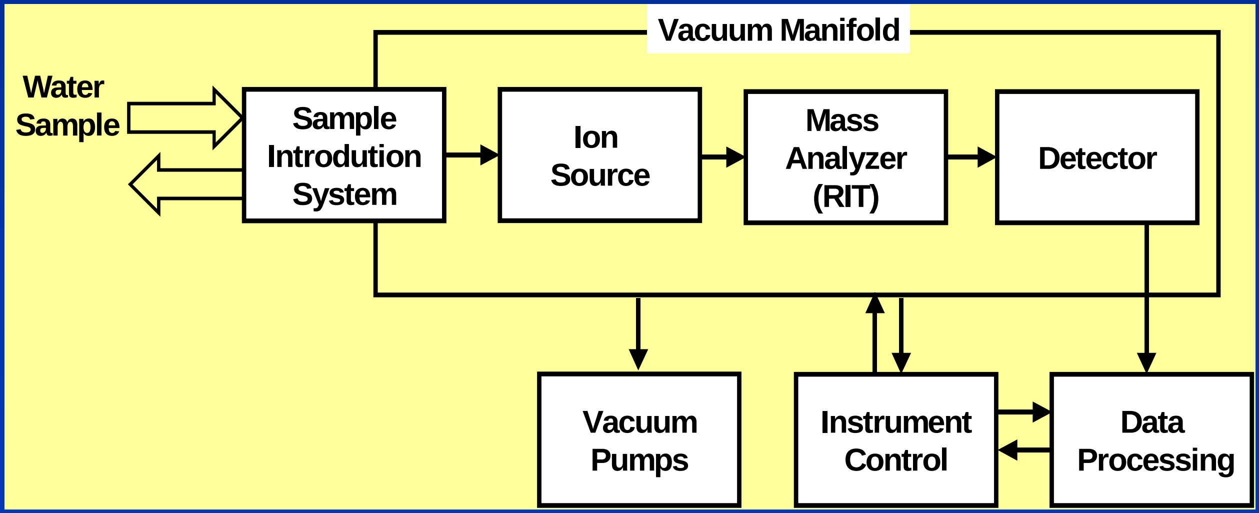
Expanded view of the microfluidic channels and the nanofluidic molecular gate membrane

Miniature Mass Spectrometer

POC: Denise MacMillan – EL, ERDC



Collaboration with Dr. Graham Cooks, Purdue University



Microfluidic Biosensors

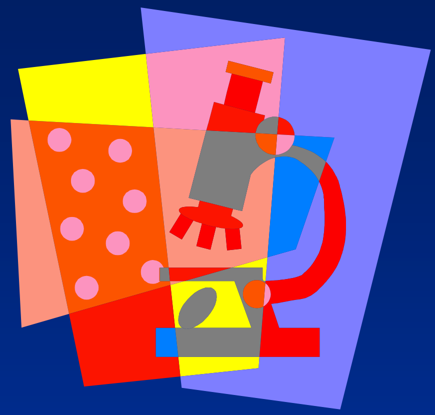
POC: Shana Dalton & Denise MacMillan – EL, ERDC

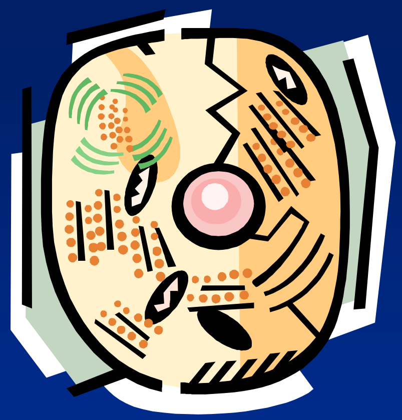
Biosensor:* *Sensor that uses biochemicals to detect chemicals

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



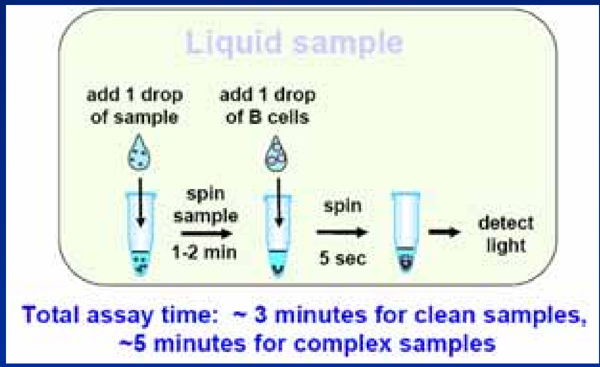


- ✓ Immunoassays with commercially available RDX and TNT antibodies immobilized on magnetic beads
- ✓ Expand the number of antibodies to MUCs
  - ✓ Developing antibodies to HMX and 2, 4-DNT with Strategic Biosolutions (~ 9 months / analyte)
- ✓ Collaborate with other laboratories currently developing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

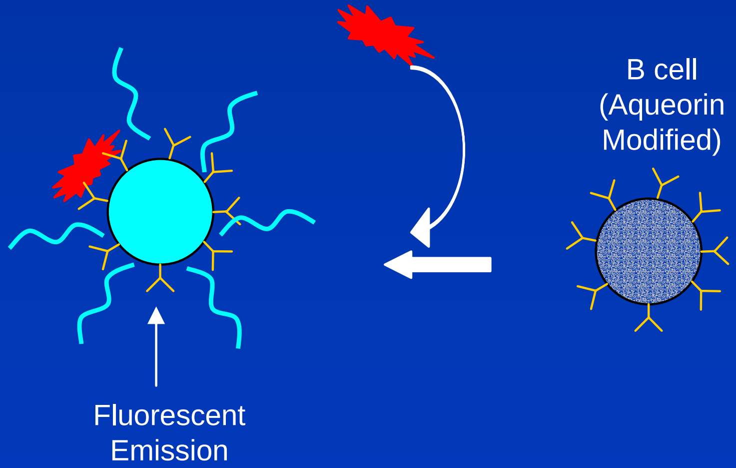
Microfluidic Biosensors

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

Perchlorate

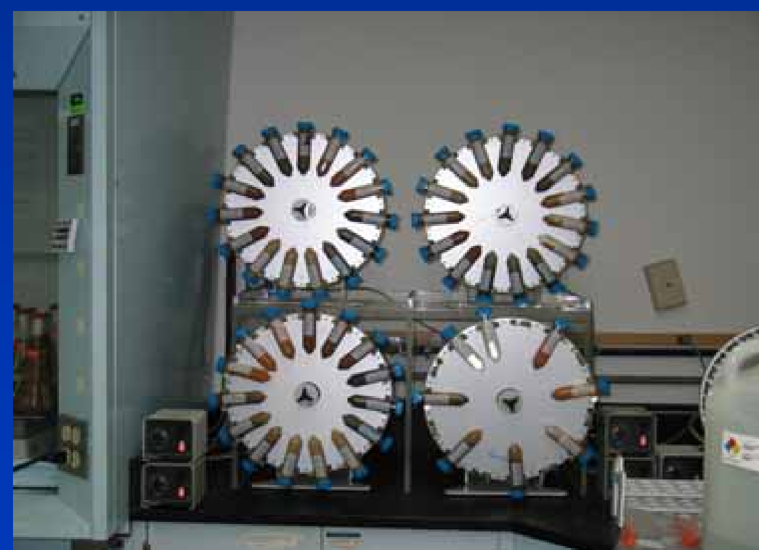
- ✓ Used primarily as a solid rocket fuel
- ✓ Through soils with little, if any, adsorption occurring
- ✓ Little literature evidence to support hypothesis
- ✓ Competes with iodine in thyroid – low action level expected

Special Analytical Methods

- ✓ Soils utilized in the project
  - ✓ "Average" Soil
  - ✓ Sandy Soil
  - ✓ High Iron Soil
  - ✓ High pH Soil
  - ✓ High Total Organic Soil

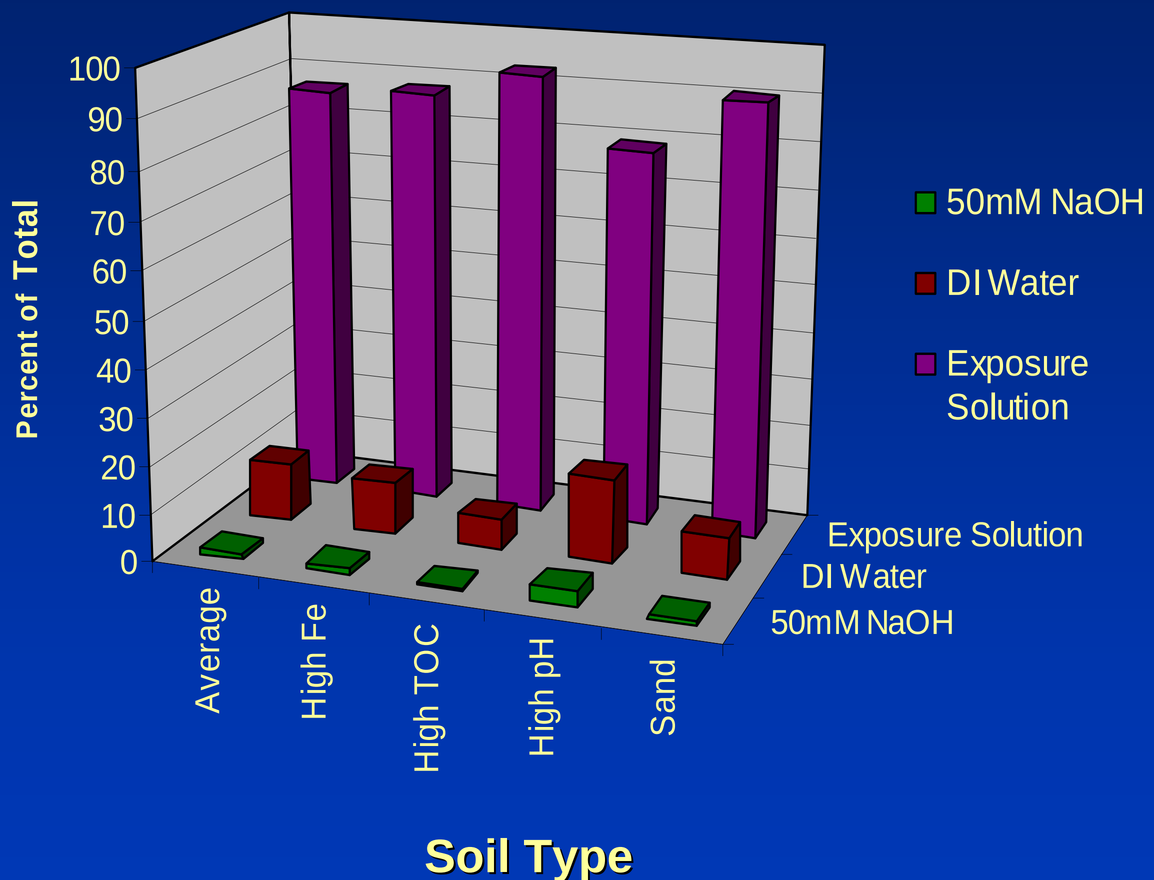
Soil Characteristic	Average Soil [WES Reference]	Sandy Soil [Ottawa Sand]	High Fe Soil [Telleco Loam]	High pH Soil [Crot Sandy Loam]	High TOC Soil
UCS Classification	Clay (CH), Brown	SP	Sandy Clay (CL), Red	Sandy Clay (CH) Grey	
Total Ca (mg/kg)	1440	<20	416	59500	
Total Fe (mg/kg)	21100	103	51600	13500	
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	

- ✓ Experimental Conditions
  - ✓ Oxic
  - ✓ Anoxic
  - ✓ Controls
    - ✓ No Soil
    - ✓ No Perchlorate



Special Analytical Methods

Perchlorate Distribution



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

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