Oil Spill Chemistry, Laboratory Analysis, and Field Screening

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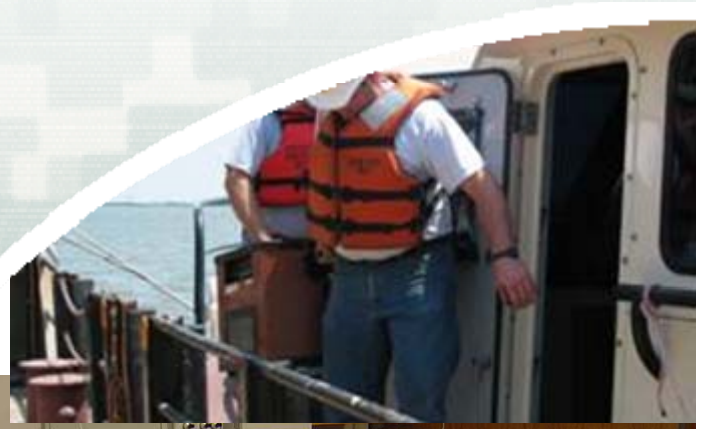

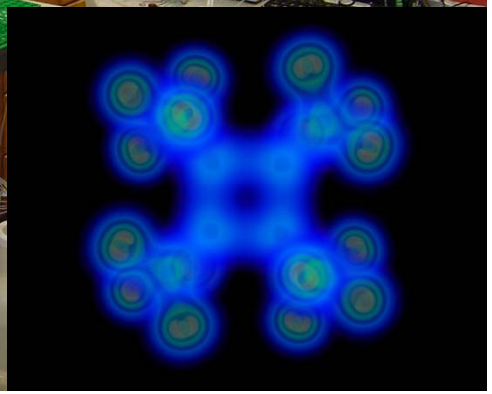

US Army Corps of Engineers

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Outline

- ‘Historical’ efforts
  - Initial work dates back to 2008
    - MVN, SPN – Both started as DOTS responses
    - Decades of experience with PAHs
      - More recently Alkylated-PAHs
- Laboratory Analysis
  - Methods
  - Characterization of source and weathered oil
    - PAHs and Alkylated PAHs
    - GRO/DRO/ORO
    - Degradation/Photolysis
- Field Analysis
  - Portable GC-MS instruments
  - Screening test kit / Demonstration

2008 Efforts

- 2008 Events
  - ► Oil spill in San Francisco Bay (December, 2007)
    - Initial ERDC response options included field portable GC-MS
    - Slow startup due to holidays and shipping instrument to CA
    - SPN used Pom-Poms
  - ► Lower MS River Barge Sinking
    - Same Field Instrumentation Response Option
      - ▷ Coupled to laboratory analysis of samples
    - Faster Deployment
    - In-Field ‘discovery’ of colorimetric oil determination
      - ▷ Subsequent laboratory optimization
      - ▷ Later developed into current fluorescence based method

Techniques

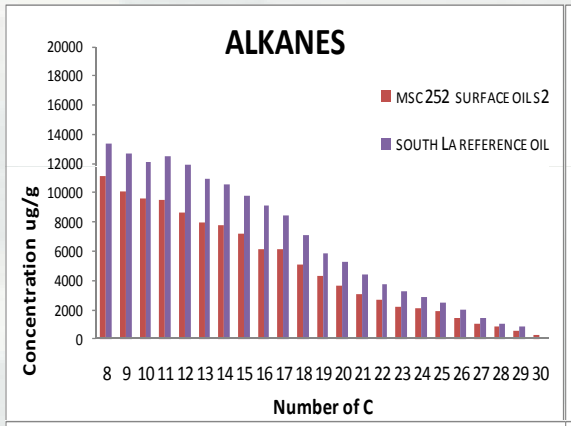
- GC-MS
  - Polycyclic Aromatic Hydrocarbons – 8270
  - Alkylated PAHs – 8272 / Modified 8270
  - Alkanes (C8 to 40) – Modified 8015
  - Volatiles (GRO, BTEX) – 8260
- GC-FID
  - Alkanes – 8015
- Other
  - Oil and Grease – 1664
  - Metals – 6020

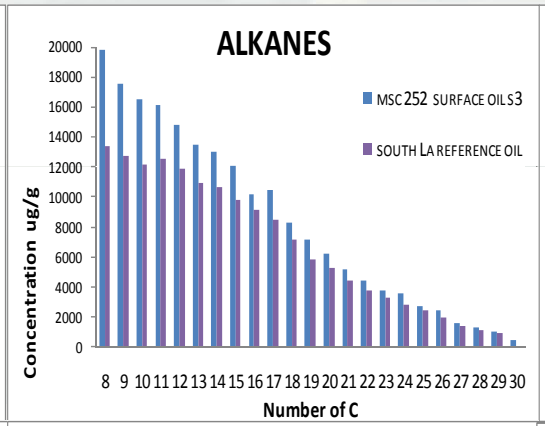
Sample Analysis

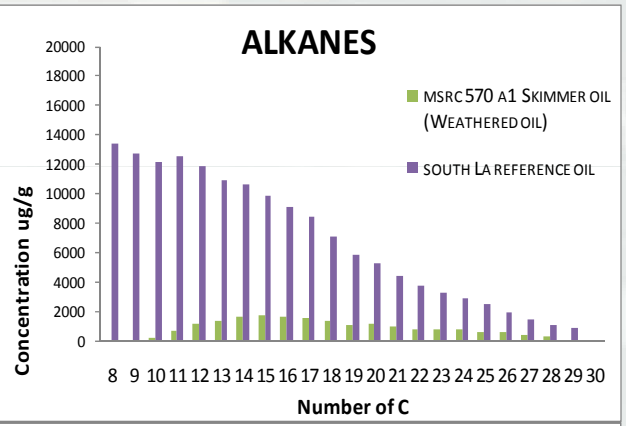
- Background
  - ► Five Soil and Five water samples collected by ERDC/USGS
    - Very Low Levels or non-detects
    - <0.02 μg/L in water, 4.1-74 μg/kg Benzo (a) pyrene, Chrysene/Fluorene in 2 samples
  - ► Surface Oil Samples provided by MVN
  - ► Source Oil and weathered sample provided by MVN from BP
  - ► Alabama Geological Survey shoreline groundwater samples
- Standard Analyte List
  - ► GRO/DRO/ORO
  - ► PAHs, Alkylated-PAHs
  - ► Oil and Grease

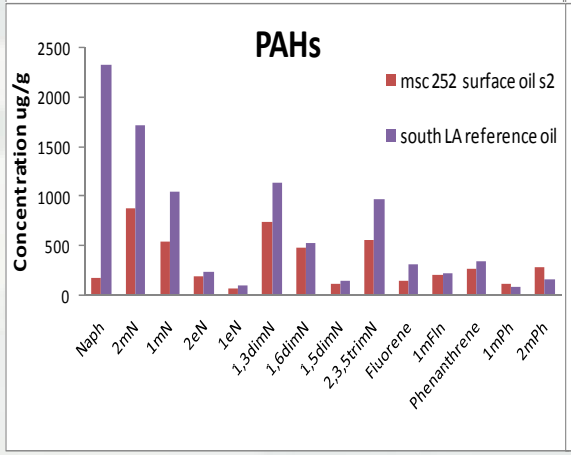
Characterization

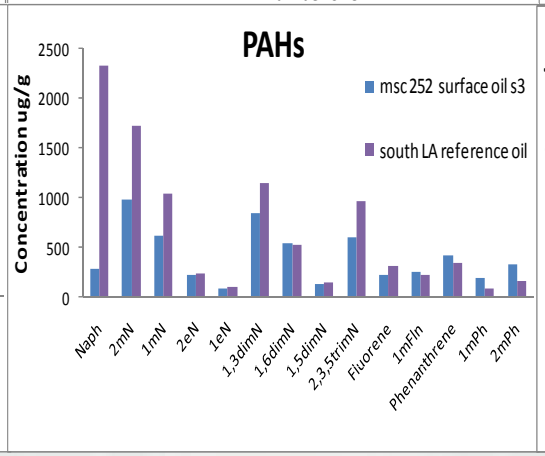
- South Louisiana Crude
  - Commercially available standard from Fisher Scientific
  - Compared to field collected samples provided by MVN

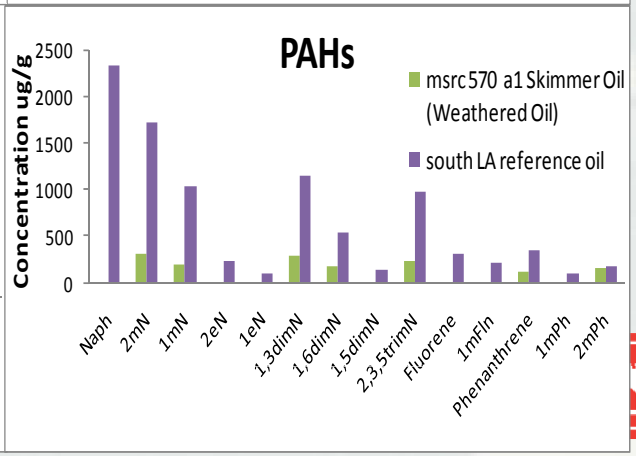






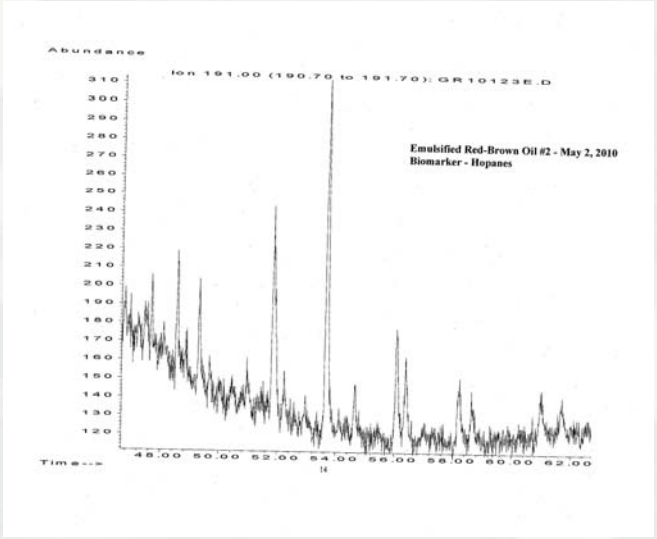


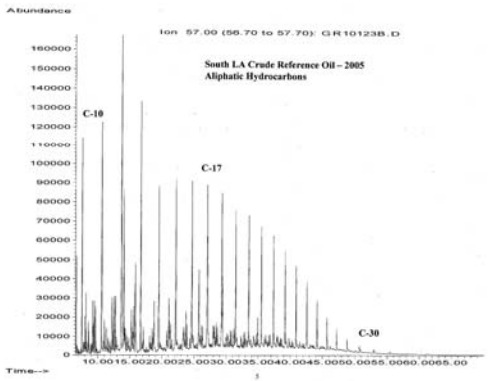


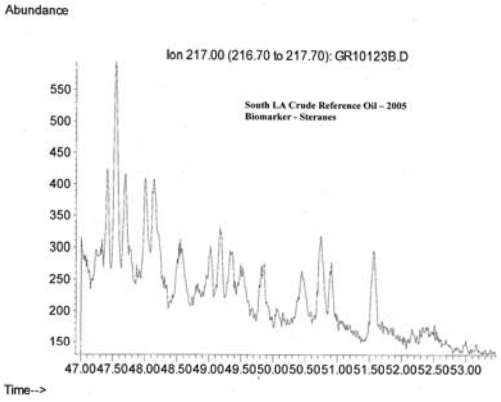


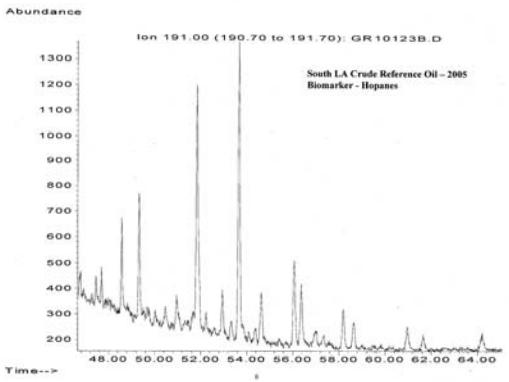
Fingerprinting Analysis

- Specific organic compounds/patterns
  - Aliphatic Hydrocarbons
  - PAHs and Alkylated-PAHs
  - Large Aromatics/Biomarkers
    - Dibenzothiophene
    - Hopanes
    - Steranes
  - LSU GC-MS analysis of South Louisiana Crude
    - Initial samples were a slightly weathered surface oil



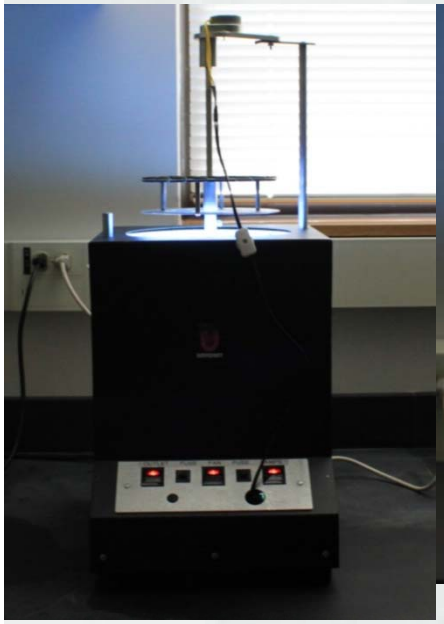






Degradation

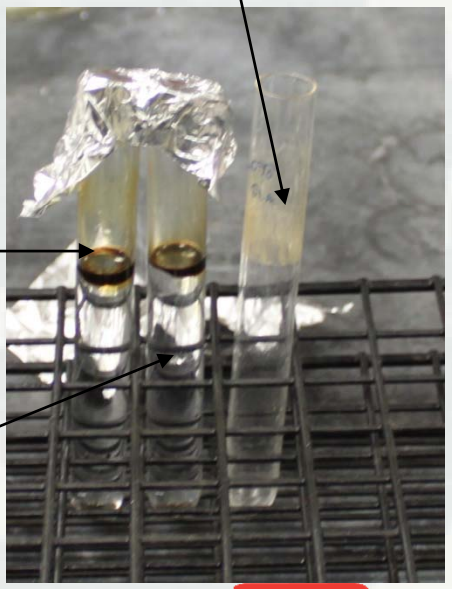
- Losses due to volatilization
  - Biological Degradation
  - Photolysis



Hexane Insoluble Residue After Photolysis

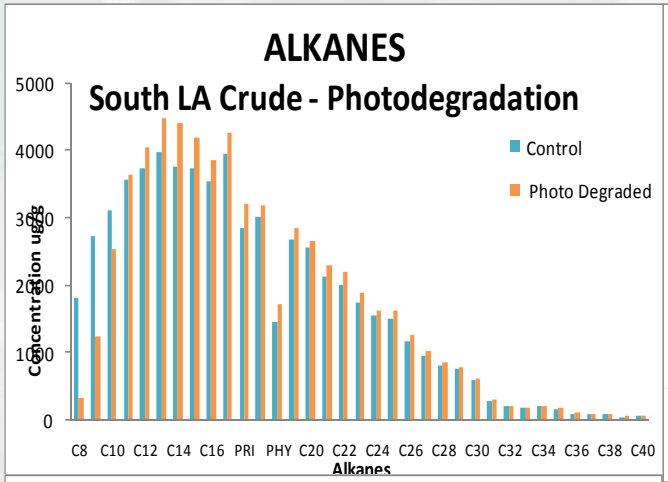
BP Source Oil After Photolysis

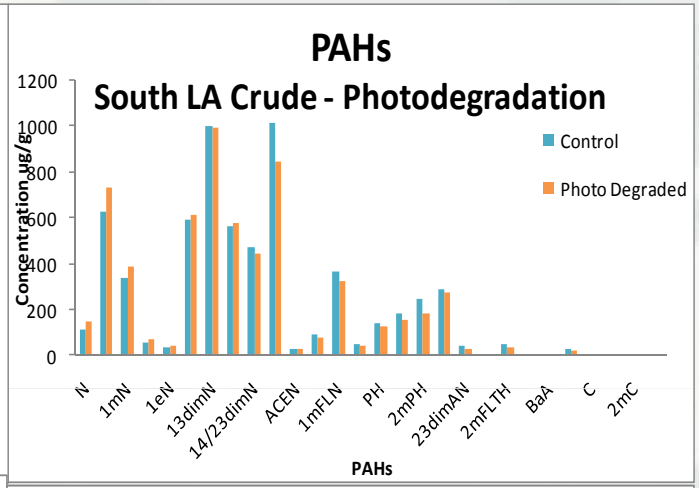
South La Oil After Photolysis

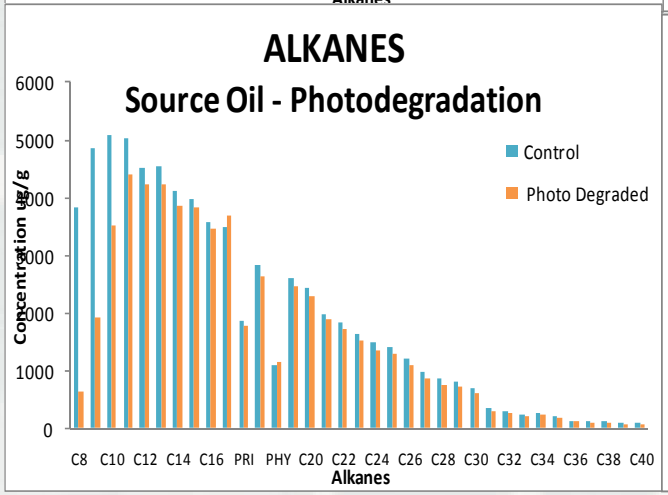


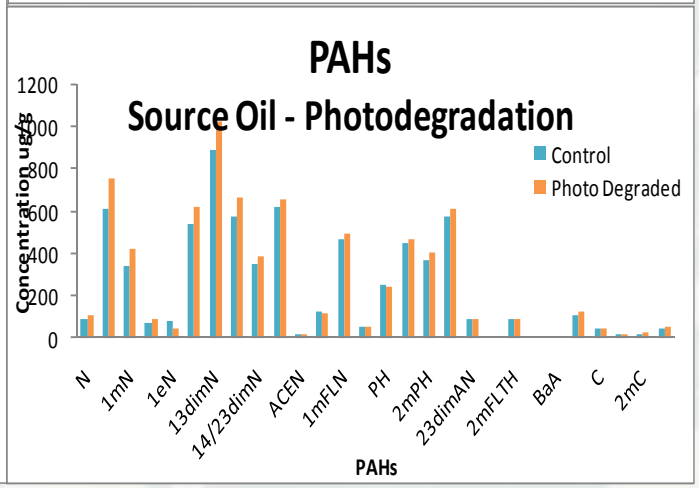
Characterization/Degradation

- BP Crude
  - Source Oil
  - UV Weathering
    - 6 hours, 300nm



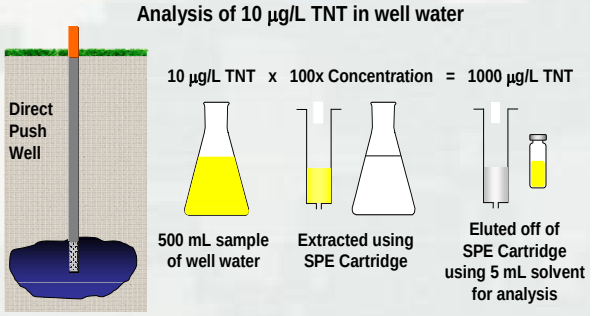


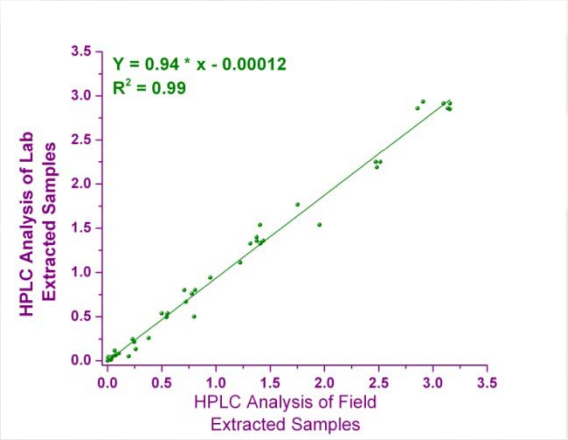




Field-Portable GC-MS

- Originally Developed for Explosives





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2008 MS River Deployment

- Analysis of PAHs in Dredged Material
  - ► Laboratory based GC-MS is standard PAH analysis method
    - Samples taken during active dredging operations
  - ► Field instrument provides near real time analysis



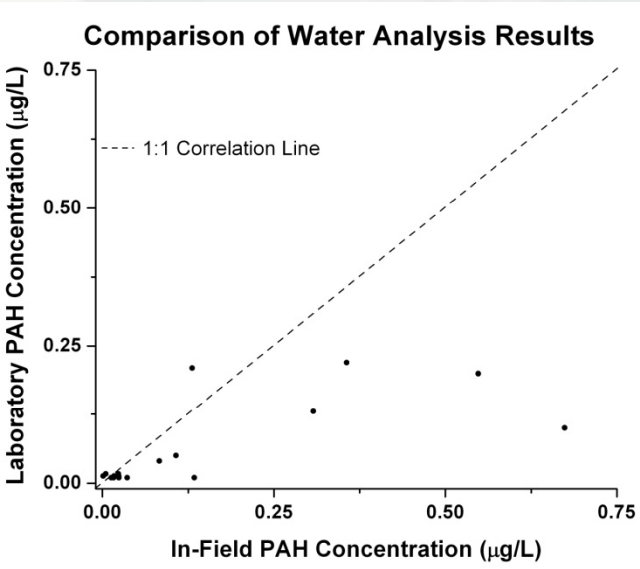
2008 MS River Deployment

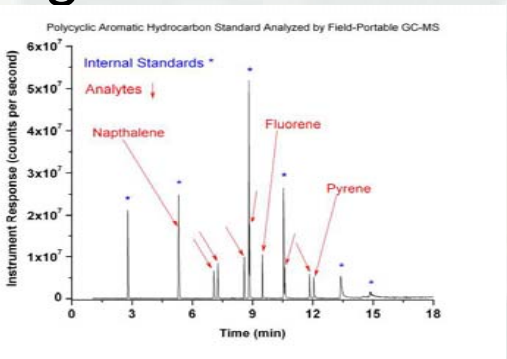
- Similar ‘laboratory’ set-up as field explosives analysis
  - Solids extraction by hexane using sonication
  - Liquid extraction by methylene chloride using separatory funnel

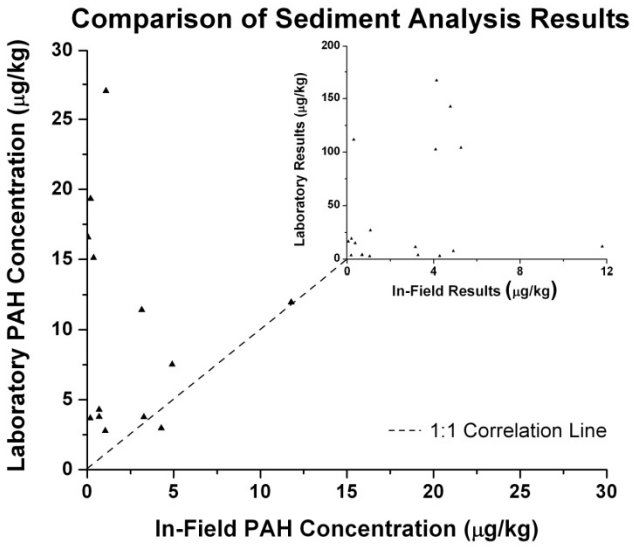


In-Field Analysis Comparison

- PAHs in Dredged Material
  - PAHs below action limits, allowed dredging to continue







Field Screening Test Kit

- Hexane extraction of oil produces colored liquid solution
  - ► Colorimetric screening for heavy oil
  - ► Extraction based on Method 1664, Oil and Grease (HEM)

ERDC Field Fuel Oil Screening Kit – 2008

Test vials containing hexane extraction solvent and drying agent, and example extract solution

Scoop and Spatula for measuring and mixing

Blank to 100 mg/L

Calibration Solutions

Test Kit Modifications

- Modifications for 'Light Sweet' Crude – 2010
  - Fluorescence Detection
  - Field Fluorometer
    - 5 mg/L compared to 10 mg/L with heavy oil colored solution
  - Deployed by MVN and SAM in 2010

UV Fluorometer

Vials for Tests

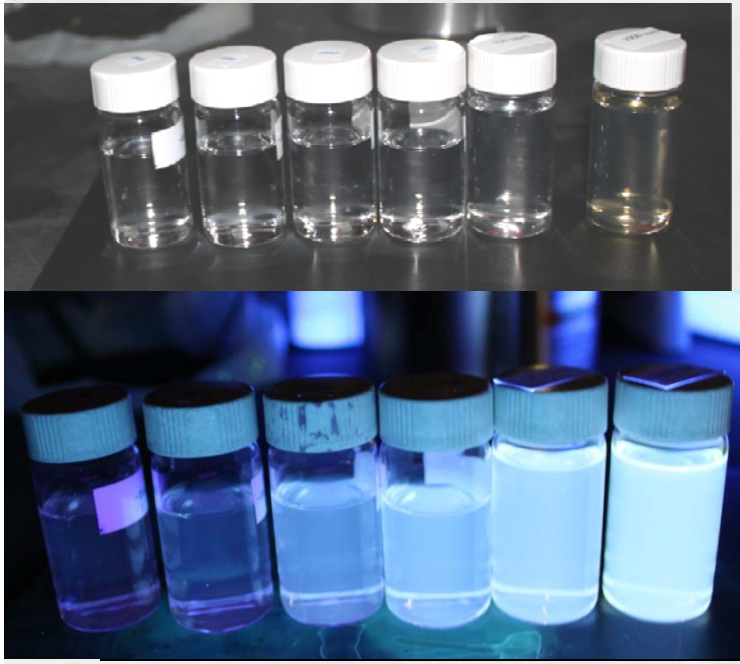
Comparison Solutions

Sample with Fluorescence

Hexane Blank, No Fluorescence

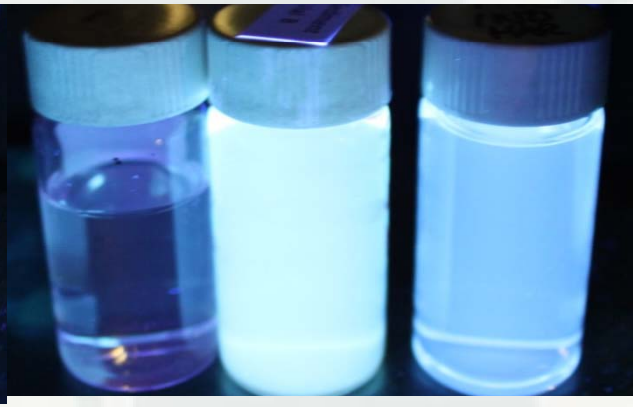
Test Kit Demonstration

- Standards from 5 to 1000 mg/L (and Blank)
  - Below 100 mg/L, Light Sweet Crude is not visible without fluorescence
  - Fluorescence is clear, particularly with little ambient light
- "Natural" Samples
  - Pond water and Indiana Harbor Sediment



Pond Water

Indiana Harbor- x2- x40



Questions

Thanks