The Use of Field Deployable Instrumentation for the Monitoring of Munitions Constituents in Groundwater

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## 10. ABSTRACT
Presented at the 2011 DoD Environmental Monitoring & Data Quality Workshop (EMDQ 2011), 28 Mar ? 1 Apr, Arlington, VA.
Introduction

- Long Term Monitoring of Groundwater
  - Can be required for 30+ years
    - Long after activities at a site have ceased
  - Regulatory approved methods/detection limits
  - Laborious and expensive process
    - Sample collection, overnight shipment under COC
      - Over $160/cooler shipping costs alone
    - Fixed laboratory analysis can be slow and expensive
      - 30-60 days, $225/sample for explosives

- Field analysis goals
  - Rapid (near real time)
  - Cheaper (no shipment costs)
  - Comparable results
    - Absolute detection, confirmation, and quantitation
  - NB, 1,3-DNB, 2,4-DNT, TNB, TNT, RDX
  - Demonstrated at 2 field sites, Louisiana and Milan AAPs
Field Portable = Minimal support services, i.e. power from a 5 kW generator, instrumentation fits in the same 4 m trailer the groundwater sampling supplies are transported in.

GC-MS is approximately 2’ cube, weighs 35 kg
Field Extraction Methods

- Solid Phase Extraction Cartridges
  - Method 3535A
  - Compared to direct water analysis (values in ppm)
  - Same analytical method, HPLC, 8330B
Field Instrument Performance

- **Instrument calibration range (SIM) 0.3 – 2.5 mg/L**
  - Ground water concentration range 1.5 – 12.5 μg/L (CF of 200)
  - $R^2 > 0.95$ for all analytes
  - Quantitation limit 1 μg/L
  - Yields an effective analysis at 2 μg/L with SPE extraction concentration factor (~200x)
  - Time from analysis to data reporting is ~9 minutes

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<th>0.001 ppm Verification</th>
<th>% REC</th>
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## Field Instrument LCS Recoveries

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LCS spike concentration 10 µg/L
## Field Instrument MS Recoveries

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<td>86</td>
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</tbody>
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MS spike concentration 10 \( \mu \text{g/L} \)
Laboratory-Field Comparison

- 28 groundwater samples collected from LAAP and MAAP
  - Additional ‘synthetic groundwater’ samples created by dilution of elevated samples with clean groundwater to make water samples with lower concentrations in a natural matrix
- Nitrobenzene (NB) was not detected in any groundwater sample by the field or laboratory methods
  - Limited comparison, but no false positives or negatives for the matrices tested
Laboratory-Field Comparison

- 1,3-DNB results show excellent agreement
  - Limited concentration range and dataset due to several non-detects
  - Ordinary least squares fit: \( F = 0.86L + 0.018 \)
  - Kendall-Theil (K-T) Line: \( F = 1.0 L + 0.00039 \)
Laboratory-Field Comparison

- 2,4-DNT results show excellent agreement
  - Limited concentration range and dataset due to several non-detects
  - Ordinary least squares fit: \( F = 0.88L + 0.0034 \)
  - Kendall-Theil (K-T) Line: \( F = 0.94L + 0.000042 \)

![Kendall's line for censored data](image URL)

\[
2,4\text{-DNT}_F = 0.000425 + 0.943765\times2,4\text{-DNT}_L
\]
Laboratory-Field Comparison

- TNB results show positive bias
  - Possibly owing to TNT interference
    - (similar mass signatures and little chromatographic separation)
  - TNT was often an order of magnitude or more higher than TNB
  - Ordinary least squares fit: \( F = 1.5L - 0.026 \)
  - Kendall-Theil (K-T) Line: \( F = 1.3L + 0.0019 \)
Laboratory-Field Comparison

- TNT results show excellent agreement
  - Screening level data below approximately 0.05 mg/L
  - Ordinary least squares fit: $F = 1.0L - 0.013$
  - Kendall-Theil (K-T) Line: $F = 0.87L + 0.00071$

![Kendall's line for censored data](image-url)
Laboratory-Field Comparison

- RDX results had significant scatter
  - Stability of RDX during thermal separation likely limits utility
    - GC-ECD by Method 8095 also has RDX/HMX issues
  - Screening level data by field GC-MS
  - Ordinary least squares fit: 
    \[ F = 1.3L - 0.11 \]
  - Kendall-Theil (K-T) Line: 
    \[ F = 0.69 L + 0.0013 \]

![Kendall's line for censored data](image)
Other Applications

- PAH analysis in dredged material to identify oil spill residue during dredging
  - Deployed to Dredge BE Lindholm in August 2008
  - Analyzed water and sediment during operations
  - Near real time data lead to dredging decisions being made on scientific data rather than observations of ‘sheen’

Conclusions

- Field portable instrumentation can provide near real time analysis of munitions constituents in water
  - Quantitative Agreement for Most Analytes
  - TNB was positively biased
    - Possibly due to elevated TNT
  - RDX is difficult by thermal separation methods
    - Limited to screening level data without further refinement
- Method development and instrument optimization are critical
Future Work

- **Delineation of PCB contamination at Anniston Superfund Site**
  - Near real time analysis of sediments
- **Other organic compounds**
  - Pesticides, Gulf Oil Spill/PAH Analysis
- **Further development of MIMS for direct analysis of water samples**
  - No sample preparation/extraction needed
Funding

- ESTCP
  - ER-0922
- Environmental Quality and Installation Long Term Monitoring
Questions?

Thank You

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David.E.Splichal@usace.army.mil
Laboratory-Field Cost Comparison

- Cost difference between the laboratory and field analysis
  - Breakeven point occurs at ~3.5 years
    - Assumes 12 5-day sampling trips/year and 25 samples analyzed per sampling trip. Total of 300 samples analyzed per year
  - Net present value (NPV) analysis
    - Savings of ~90K after 7 years (life expectancy of a field instrument)