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

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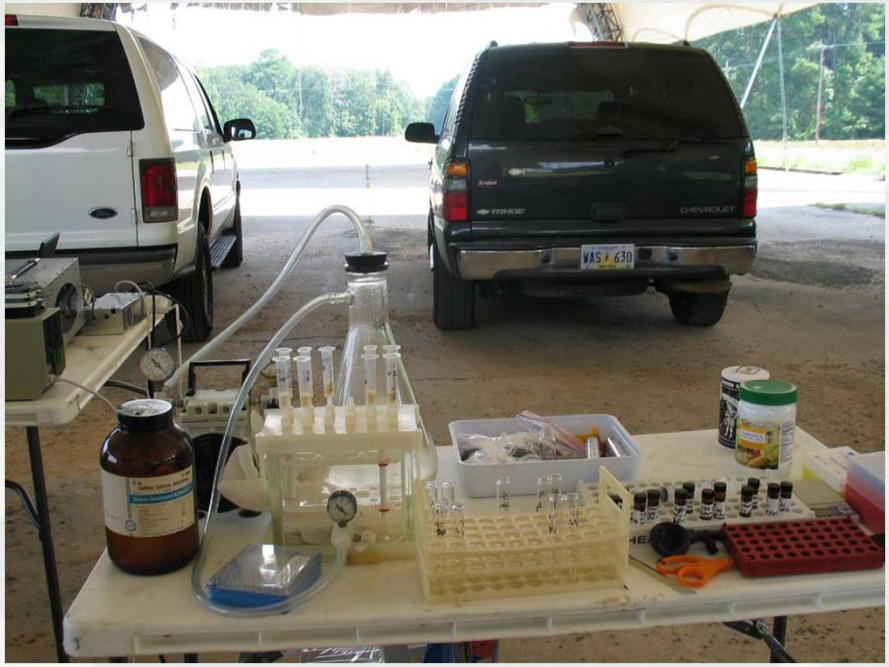
Introduction

- 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

Deployable Mass Spectrometer

Field Extraction Equipment



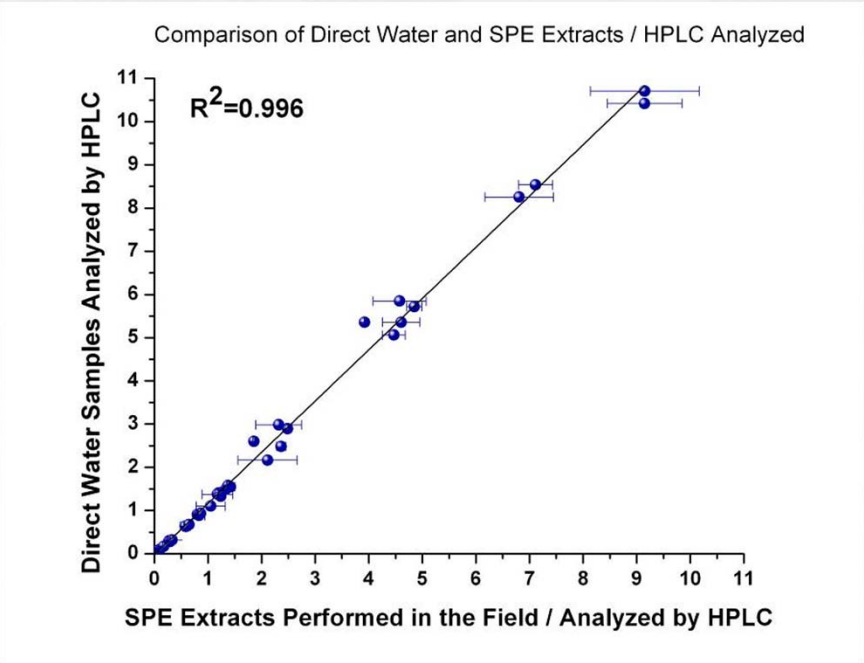
ICx Griffin 400 and 450

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

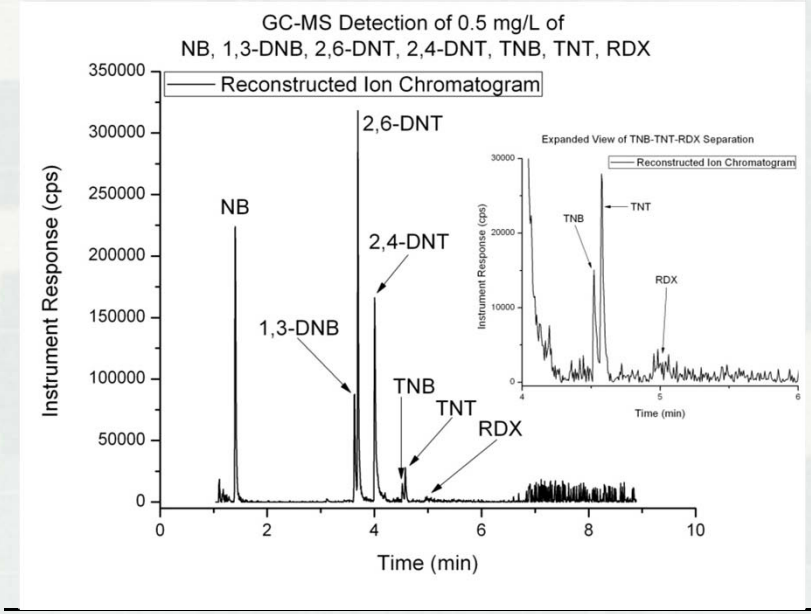
Field Extraction Methods

- 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



Analyte	MDL	0.001 ppm Verification	% REC
NB	0.0026	0.0012	120.0
1,3-DNB	0.0005	0.0011	110.9
2,4-DNT	0.0006	0.0008	75.8
TNB	0.0003	0.0005	52.2
TNT	0.0003	0.0013	133.2
RDX	0.0016	0.0012	117.0

Field Instrument LCS Recoveries

	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
DoD QSM Limits	50-140	45-160	60-135	65-140	50-145	50-160
LAAP Day 1	78	73	82	83	74	57
LAAP Day 2	58	47	60	73	59	**33**
LAAP Day 3	110	65	96	91	83	69
MAAP Day 1	100	98	91	81	82	55
MAAP Day 2	110	93	100	72	67	**41**
MAAP Day 3	99	100	110	**62**	70	57
MAAP Day 4	77	110	100	79	88	110

LCS spike concentration 10 μg/L

Field Instrument MS Recoveries

	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
DoD QSM Limits	50-140	45-160	60-135	65-140	50-145	50-160
LAAP Day 1	96	86	91	74	63	**45**
	100	74	120	100	92	**38**
LAAP Day 2	92	**180**	**170**	**7000**	**3600**	**-2200**
	99	**240**	**200**	**5300**	**2200**	**-3800**
LAAP Day 3	80	72	73	75	72	54
	96	100	93	88	81	**49**
MAAP Day 1	120	110	110	66	55	**9.8**
	120	77	96	79	58	**26**
MAAP Day 2	110	68	100	**59**	54	**260**
	120	99	120	89	81	**200**
MAAP Day 3	**160**	110	110	**22**	61	**20**
	140	93	110	**23**	66	**37**
MAAP Day 4	70	99	94	66	86	**33**
	98	130	100	76	96	**34**

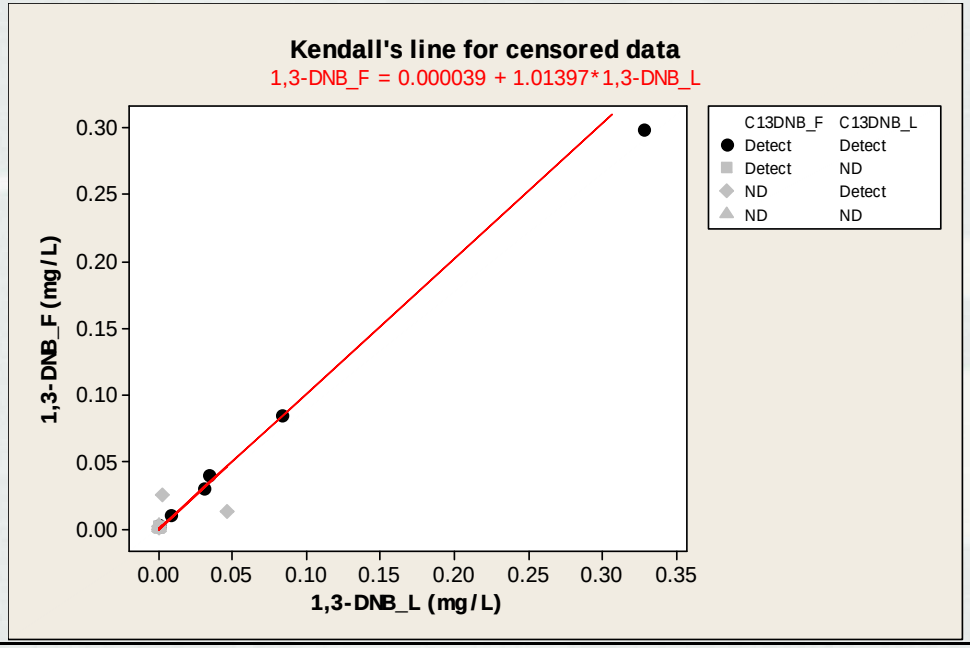
MS spike concentration 10 μg/L

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

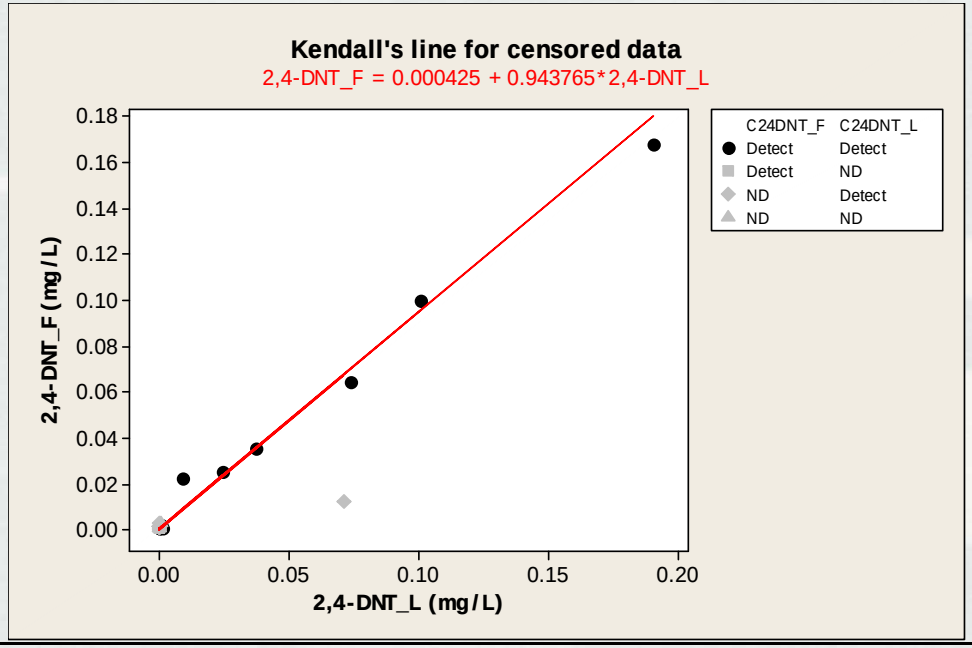
Laboratory-Field Comparison

- 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: $F = 1.0\ L + 0.00039$



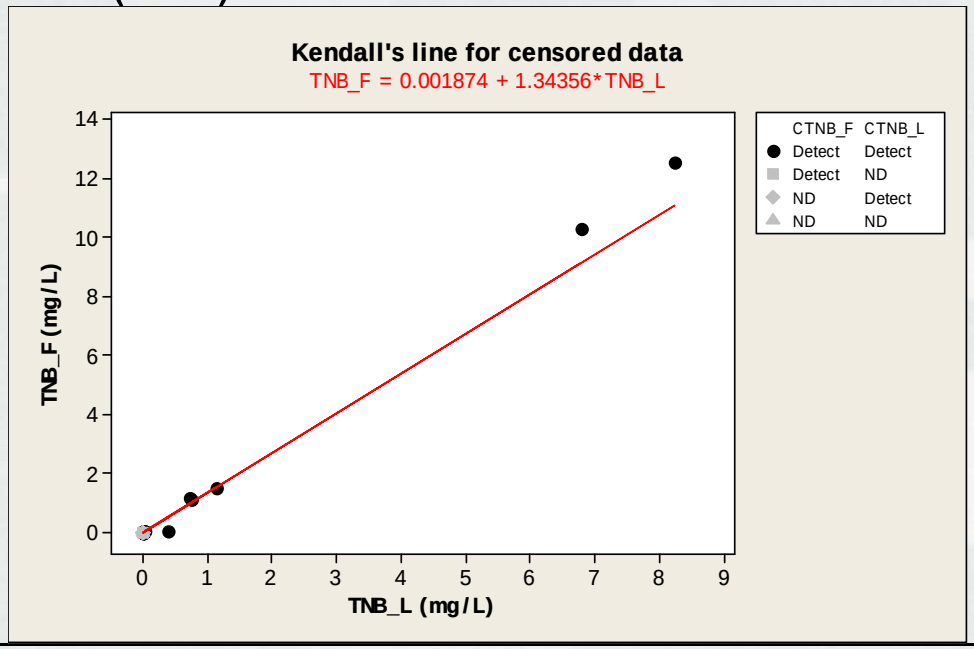
Laboratory-Field Comparison

- 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: $F = 0.94\ L + 0.000042$



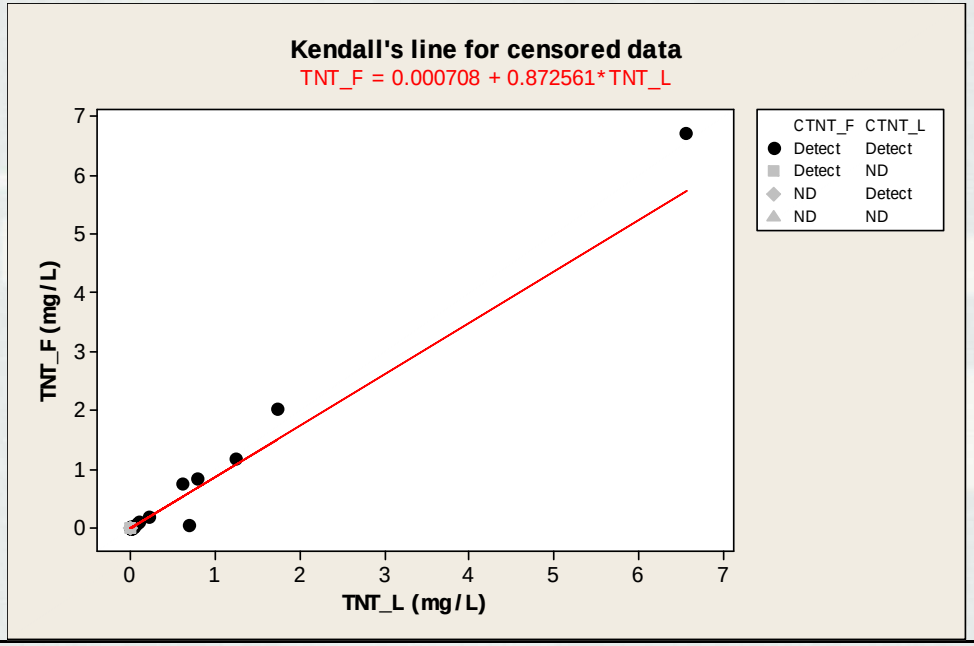
Laboratory-Field Comparison

- 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: $F = 1.3\,L + 0.0019$



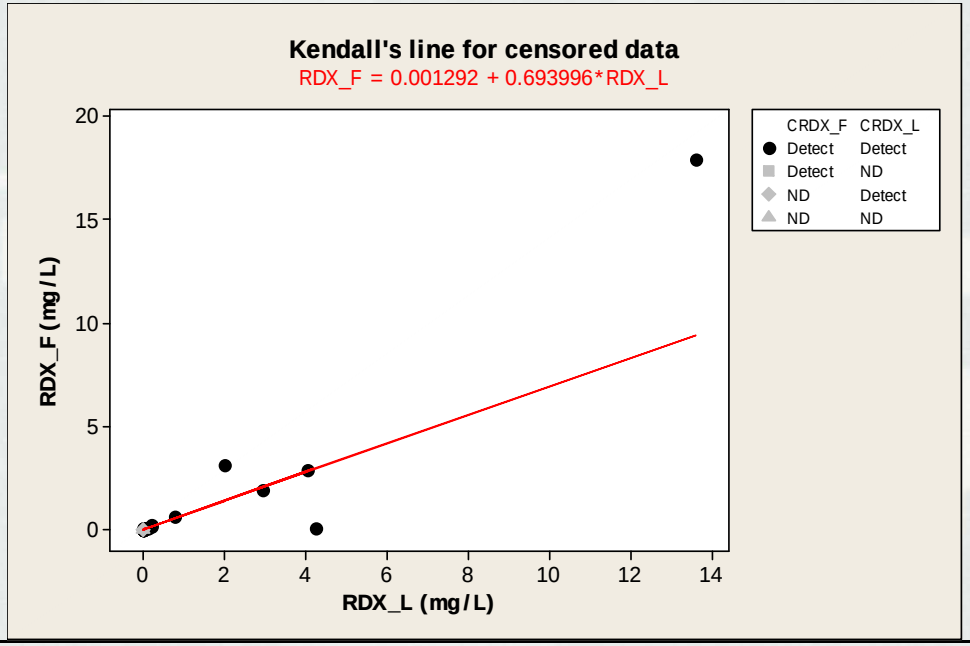
Laboratory-Field Comparison

- 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: $F = 0.87\ L + 0.00071$



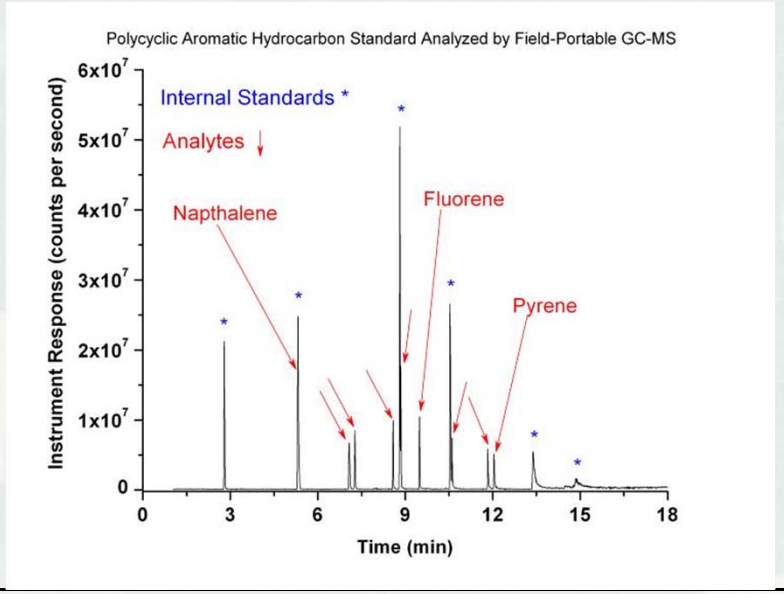
Laboratory-Field Comparison

- 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: $F = 0.69\,L + 0.0013$



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’



A.J. Bednar, R.A. Kirgan, J.M.Corbino and A.L. Russell; Analysis of Organic Contaminants in Dredged Material using a Field-Portable GC-MS; ERDC TN-DOER-E26 September 2009.

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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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)