Field-Based Analytical Methods for Explosive Compounds

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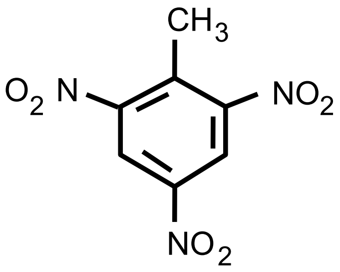
Outline of Presentation

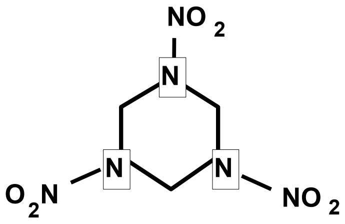
- Important properties of nitroaromatic (TNT) and nitramine (RDX) explosives
- Accepted laboratory methods for explosives chemicals
- Detection criteria for explosives-related chemicals
- Why should you consider using on-site methods?
- Sampling considerations for explosives in soil and water
- Verified methods for on-site determination of explosives in soil and water
- Advantages / disadvantages of various on-site methods

Overview of topics to be covered in the presentation.

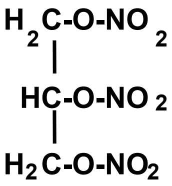
Nitroaromatic
(TNT)



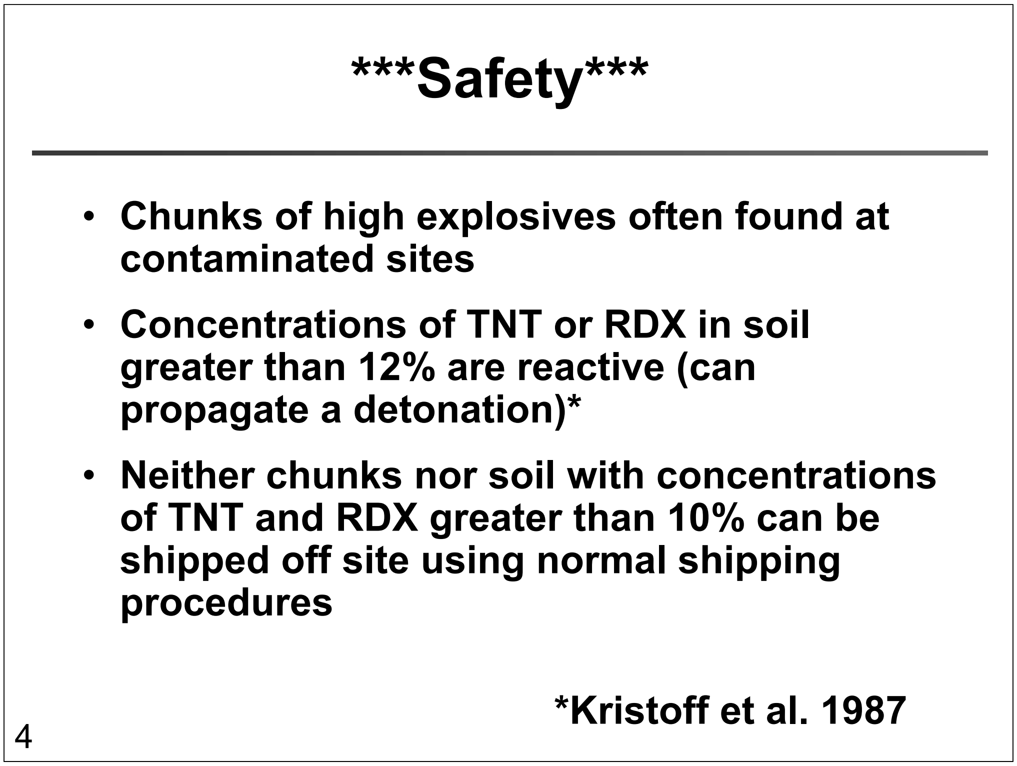
Nitramine
(RDX)



Nitrate Ester
(NG)



$$\begin{array}{l} H_2C\text{-}O\text{-}NO_2 \\ \quad | \\ HC\text{-}O\text{-}NO_2 \\ \quad | \\ H_2C\text{-}O\text{-}NO_2 \end{array}$$



Safety

- **Chunks of high explosives often found at contaminated sites**
- **Concentrations of TNT or RDX in soil greater than 12% are reactive (can propagate a detonation)***
- **Neither chunks nor soil with concentrations of TNT and RDX greater than 10% can be shipped off site using normal shipping procedures**

***Kristoff et al. 1987**

The most important property of all is the ability of these compounds to detonate if they are subjected to the right type of stimulus (spark, shock).

This is one of the major reasons why on-site analysis is so important for explosives.

Kristoff, F.T., T.W. Ewing and D.E. Johnson (1987) Testing to Determine Relationship Between Explosive Contaminated Sludge Components and Reactivity. USATHAMA Report No. AMXTH-TE-CR-86096, Aberdeen Proving Ground, Maryland.

Physical and Chemical Properties of Explosive Chemicals

- Most are solids at environmental temperatures
- Sources often particulate at soil surface
- Low aqueous solubilities, slow rates of dissolution
- Surface contamination persists for long periods (50-100 years)
- Once dissolved, RDX can migrate rapidly through vadose zone
- TNT readily biotransforms
- Relatively non-volatile
- Thermally labile

Except for nitroglycerin, all of the major explosives are solids at environmental temperatures.

Because they are thermally labile, it has been difficult to develop robust methods using GC where a heated injector is necessary. Recent advances in columns and injector materials have made it possible, however.

EPA SW846
Standard Laboratory Methods for Nitroaromatic and Nitramine Explosives in Soil and Water

- **Sample preparation**
  Water: Salting-out or solid-phase extraction
  Soil: Ultrasonic extraction with acetonitrile
- **Determination**
  SW846 Method 8330 (RP-HPLC)
  SW846 Method 8095 (GC-ECD) (Draft)

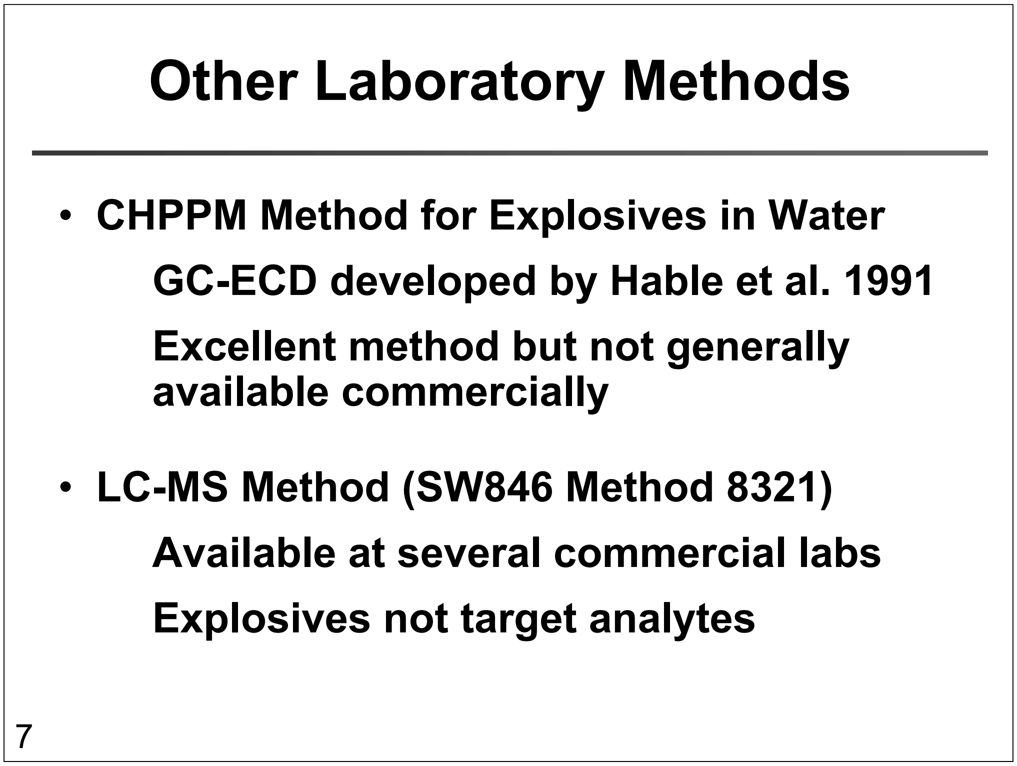
While this course emphasizes on-site methods, a subset of samples are often sent to off-site laboratories for analysis and we wanted to provide an overview of the methods that are used along with some of the advantages and disadvantages of each.

Under the SW846 program, there are two methods that specify explosives as target analytes. Both use the same sample preparation.

Method 8330 has been the industry standard for many years.

Method 8095 has not been promulgated yet, but the draft method has been accepted by the organics work group at the EPA Office of Solid Waste.

RP-HPLC Reversed Phase High Performance Liquid Chromatography
GC-ECD Gas Chromatography-Electron Capture Detector



Other Laboratory Methods

- CHPPM Method for Explosives in Water
  - GC-ECD developed by Hable et al. 1991
  - Excellent method but not generally available commercially
- LC-MS Method (SW846 Method 8321)
  - Available at several commercial labs
  - Explosives not target analytes

The CHPPM (US Army Center for Health Promotion and Preventive Medicine, Aberdeen Proving Ground, MD) method is excellent and in their hands has been quite a good method. Unfortunately it is not generally used in contract labs.

The LC-MS (Liquid Chromatography-Mass Spectrometry) method is offered by several commercial labs, but explosives are not target analytes of the published method so we don't have any performance data for this approach.

Hable et al. 1991 - Hable, M., C. Stern, C. Asowata and K. Williams (1991) Determination of nitroaromatics and nitramines in ground and drinking water by wide-bore capillary gas chromatography. Journal of Chromatographic Science, 29: 131-135.

Target Analytes for SW846 Methods 8330 and 8095

	Method	
	8330	**8095**
Nitroaromatics		
TNT, TNB, DNB, 2,4-DNT, 2,6-DNT, tetryl, nitrobenzene, o-,m-,and p-nitrotoluene	√	√
Nitramines		
RDX, HMX	√	√
Aminodinitrotoluenes		
2-ADNT, 4-ADNT	√	√
3,5-dinitroaniline		√
Nitrate esters		
NG, PETN		√

An advantage of Method 8095 is that it can provide analysis of nitrate esters in the same determination as the nitroaromatics and nitramines. Only if a diode array detector is used with Method 8330, can nitrate esters be determined using Method 8330 since these analytes do not absorb in the UV region at he normal wave length (254 nm) used by this method.

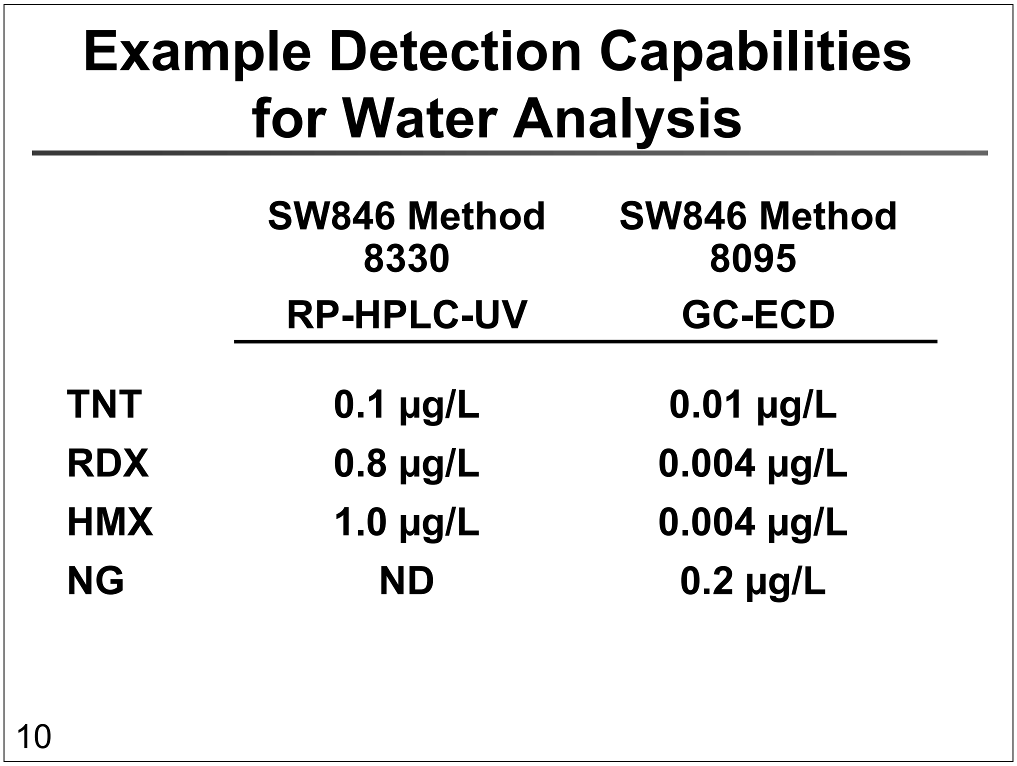
TNT	2,4,6-Trinitrotoluene
TNB	1,3,5-Trinitrobenzene
DNB	1,3-Dinitrobenzene
2,4-DNT	2,4-Dinitrotoluene
2,6-DNT	2,6-Dinitrotoluene
Tetryl	2,4,6-trinitrophenylmethylnitramine
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
2-ADNT	2-Amino-4,6-dinitrotoluene
4-ADNT	4-Amino-2,6-dinitrotoluene
NG	Nitroglycerin
PETN	Pentaerythritoltetranitrate

Detection Capabilities for Soil Analysis

	SW846 Method 8330	SW846 Method 8095
	RP-HPLC-UV	GC-ECD
TNT	80 µg/kg	0.45 µg/kg
RDX	740 µg/kg	3.4 µg/kg
HMX	1300 µg/kg	25 µg/kg
NG	ND	13 µg/kg

Detection limits for Method 8330 were adequate for use at contaminated manufacturing facilities and depots, but for testing and training range samples, the lower detection capability of method 8095 may be needed.

ND Non-detect



Example Detection Capabilities for Water Analysis

	SW846 Method 8330	SW846 Method 8095
	RP-HPLC-UV	GC-ECD
TNT	0.1 µg/L	0.01 µg/L
RDX	0.8 µg/L	0.004 µg/L
HMX	1.0 µg/L	0.004 µg/L
NG	ND	0.2 µg/L

Lifetime Health Advisories are set at 2 µg/L for TNT and RDX, 400 µg/L for HMX, and 5 µg/L for NG.

Method 8330 vs. Method 8095

SW846 Method 8330 RP-HPLC-UV	SW846 Method 8095 GC-ECD
more rugged in routine use	lower detection capability
requires less stringent QA program	simultaneous determination of nitroaromatics, nitramines, and <u>nitrate esters</u>

Most commercial labs are set up to do Method 8330 but not Method 8095. GC-ECD equipment is generally available.

When explosives are determined using Method 8330, it is accomplished while the analytes remain in solution and thus they are not subjected to the high temperatures of the an injection port. This is one of the main reasons for the ruggedness of the HPLC method. In the GC method, as solids are deposited in the injection port liner, some losses of explosives analytes can occur. Surveillance of this potential problem must be a goal of a more stringent QA program.

Sampling Studies

Investigated traditional sampling approaches for explosives site characterization

Surface soils

Groundwater

Several studies have investigated the use of traditional sampling approaches for characterization of groundwater and soil samples for explosives.

Sampling Problem for TNT in Groundwater

- First observed by Goerlitz and Franks (1989) at Hawthorne AAP
- Concentration of TNT increased from 2.0 to 32.0 µg/L after 60 gal of water bailed
- Observation confirmed by Pennington et al. (1999) at Louisiana AAP
- Low flow (minimal drawdown) protocol by Puls and Barcelona (1996)

Biological activity degrades TNT to its daughter products. Biological activity can be enhanced in the portion of the aquifer next to a well due to the altered conditions (such as gas and nutrient availability) induced by the well.

Therefore the TNT (and daughter product) concentrations in the water next to the well may be very different from the concentrations in the formation farther away from the well. If the purpose of sampling for TNT (and daughter products) is to establish drinking water safety, sampling should be representative of the pumping conditions used to draw the drinking water. For some (many? all?) wells, low-flow purging prior to sample collection may be more representative than a rapid 3 well-volume purge.

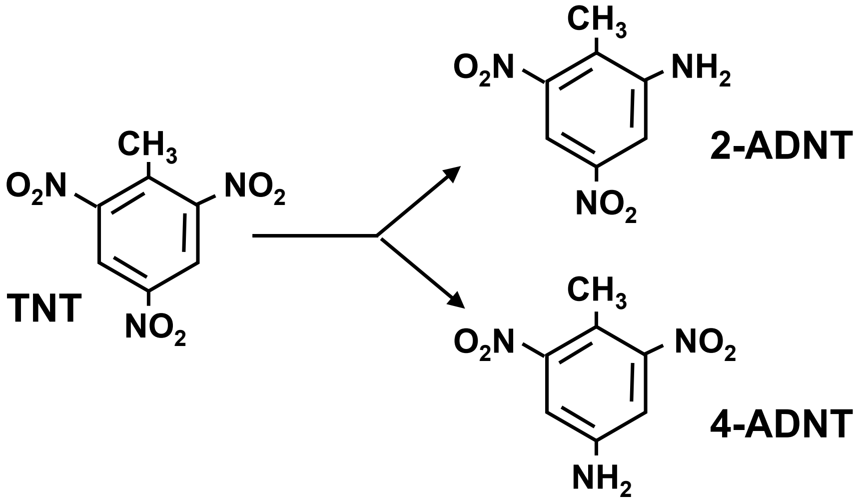
As always, an appropriate project-specific sampling and analysis plan will evaluate sampling procedures in light of the purpose of sampling in order to ensure that sample collection will be representative and relevant to the intended use of the data.

Goerlitz and Franks 1989 - Goerlitz, D.F., and Franks, B.J., 1989, Use of on-site high performance liquid chromatography to evaluate the magnitude, extent and transport of organic contaminants in aquifers: Ground Monitoring Review, v. 9, no. 2, p. 122-130.

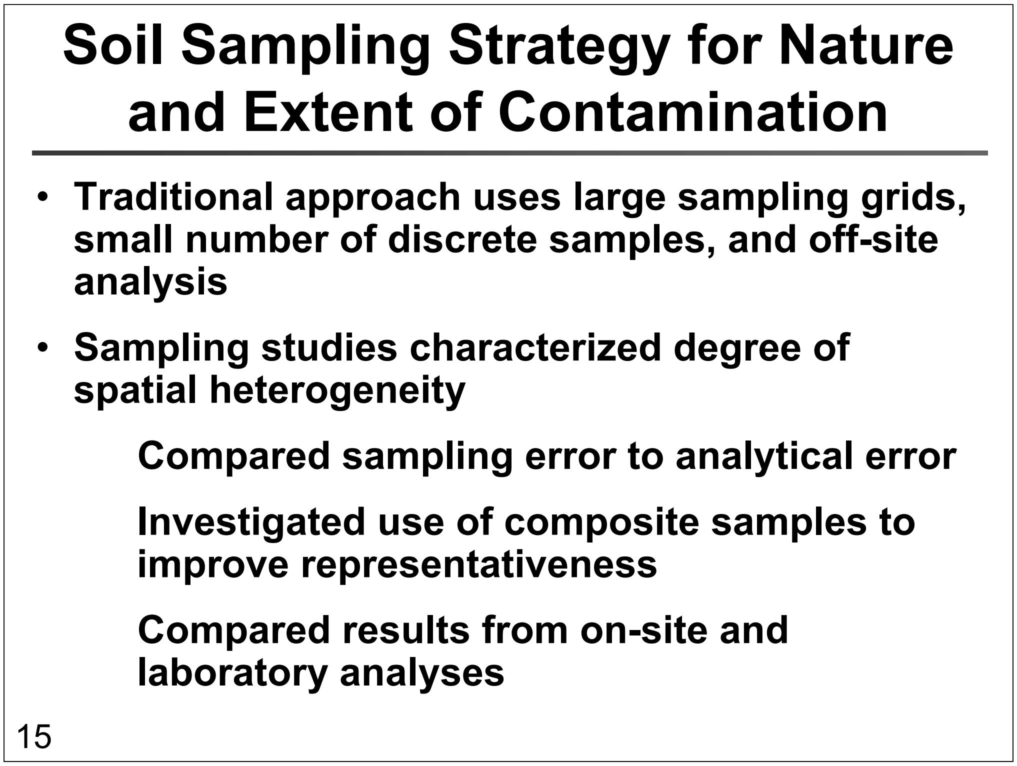
Pennington et al. 1999 Natural Attenuation of Explosives in Soil and Water Systems at Department of Defense Sites: Final Report," Technical Report SERDP-99-1. http://www.wes.army.mil/el/elpubs/pdf/trserdp99-1.pdf

Puls and Barcelona 1996 Low-flow (Minimal Drawdown) Ground-water Sampling Procedures (EPA 540-S-95-054) http://www.epa.gov/tio/tsp/download/lwflw2a.pdf

Microbiological Transformation of TNT



TNT can be converted to two isomers of monoaminodinitrotoluene both biologically and chemically.

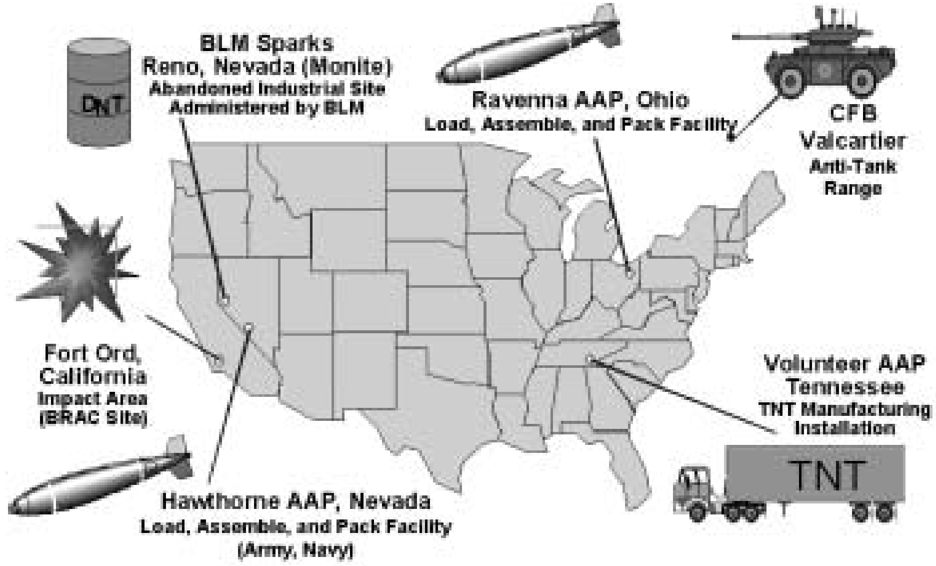


Soil Sampling Strategy for Nature and Extent of Contamination

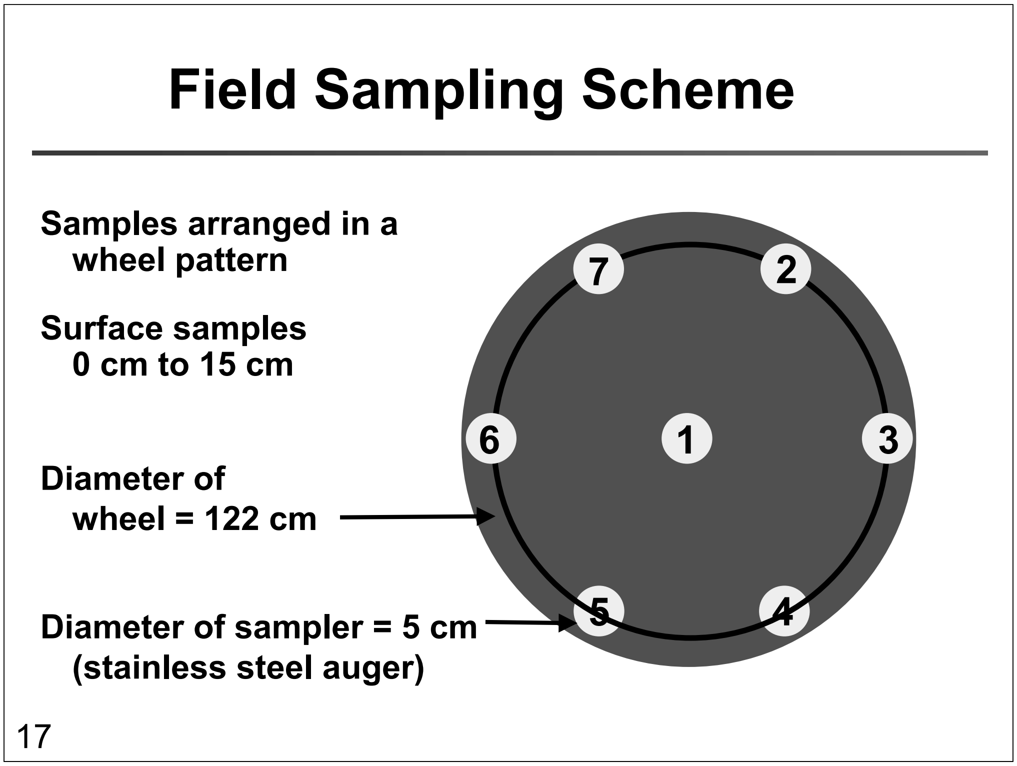
- Traditional approach uses large sampling grids, small number of discrete samples, and off-site analysis
- Sampling studies characterized degree of spatial heterogeneity
  - Compared sampling error to analytical error
  - Investigated use of composite samples to improve representativeness
  - Compared results from on-site and laboratory analyses

Traditional approach assumes that representative samples can be obtained by taking a very small number of discrete samples. Each sample represents a fairly large area. The assumption is that analytes are homogeneously distributed spatially.

Locations for Sampling Studies



Sampling studies conducted at a number of installations with a variety of contamination scenarios.



Field Sampling Scheme

Samples arranged in a wheel pattern

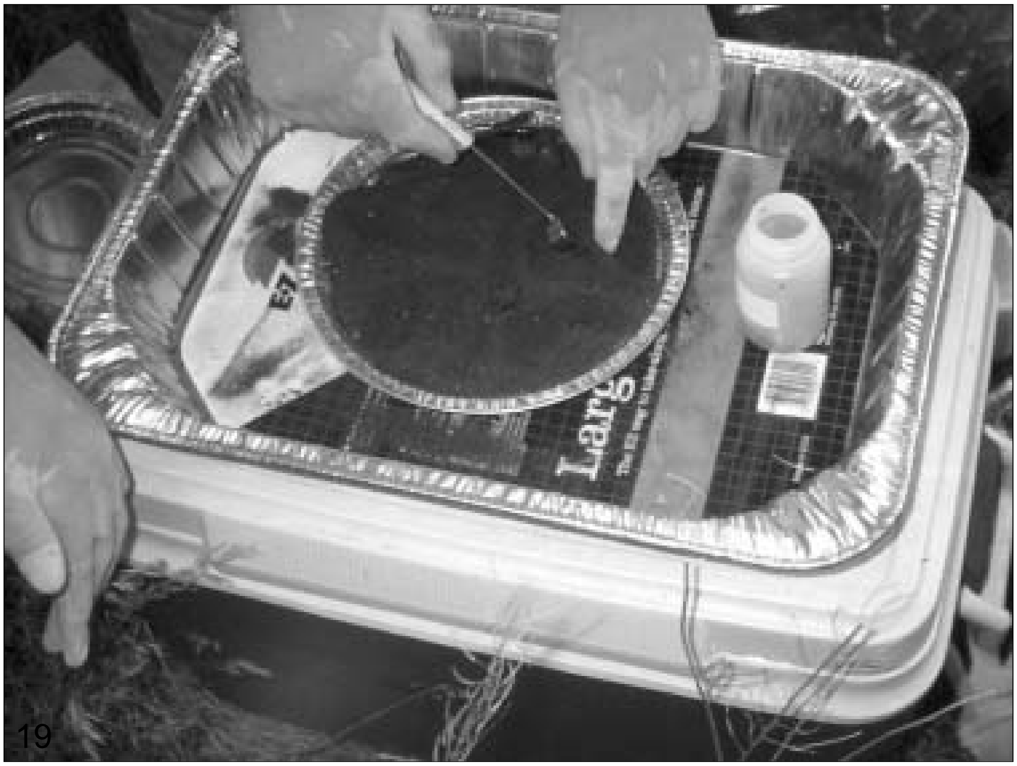
Surface samples 0 cm to 15 cm

Diameter of wheel = 122 cm

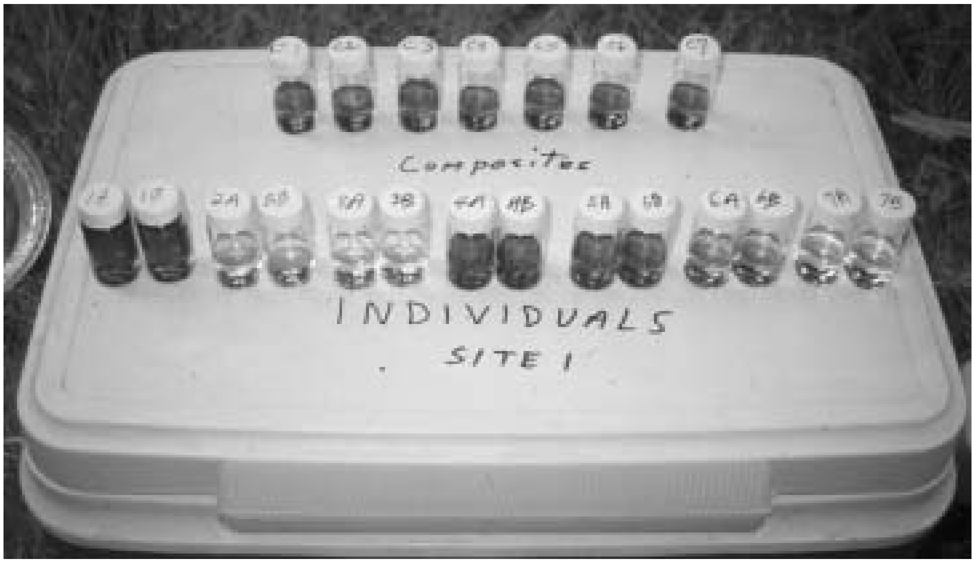
Diameter of sampler = 5 cm (stainless steel auger)

The objective of the sampling scheme shown was to examine the sampling error associated with the use of discrete samples to estimate the average concentration over a small region. At each location a set of seven surface samples were collected in a wheel pattern simulating a 2 foot triangular grid.

Template used for sample collection.



Each discrete sample was homogenized on site and replicate samples collected for both on-site and off-site analysis.

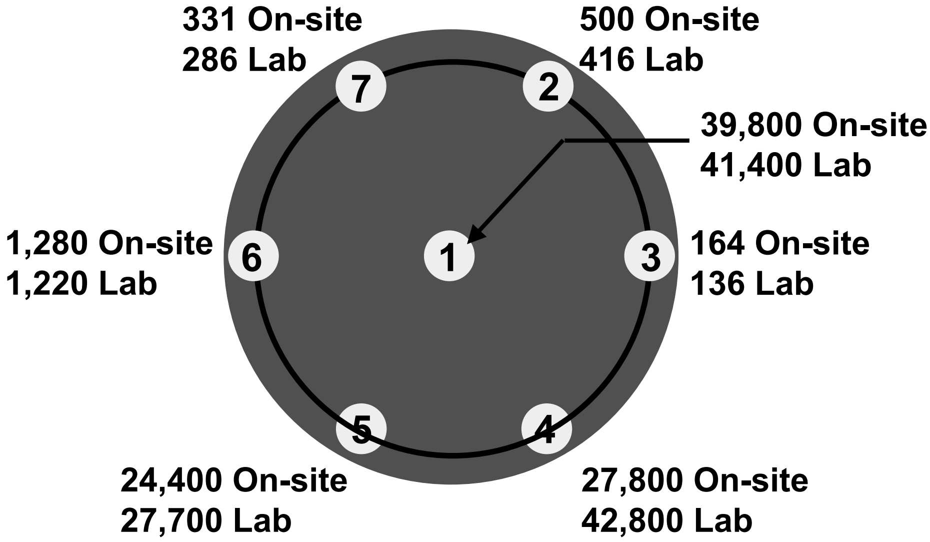


This is a photo of the filtered extracts that resulted from the seven samples collected at the Monite site near Sparks, NV. Notice there are seven sets of duplicates in the front row and seven composites in the back row. The color comes from phototransformation products of TNT and the intensity of color parallels the concentrations of TNT that we will show in a later slide.

The colors of the duplicates agree, but the intensity of color is very different from discrete sample to discrete sample. The color of the composites are an average of the discretes.

The colors are quite similar to the beer sampler that was observed that night at a local brew pub.

Monite Site, Sampling Location #1
Major Analyte: TNT (mg/kg)



These are the results of the analysis of the set of seven discrete samples from Monite.

Note the agreement of the on-site colorimetric (EnSys Colorimetric Test Kits; EPA SW-846 Methods 8515 and 8510) and off-site analytical results.

Note the differences in the results among the seven samples.

Conclusion: spatially the concentrations of TNT was very heterogeneous and because any one of these discrete samples would be a legitimate sample by the traditional approach, this approach does not provide representative samples to characterize this site.

We found the same situation at every site we sampled.

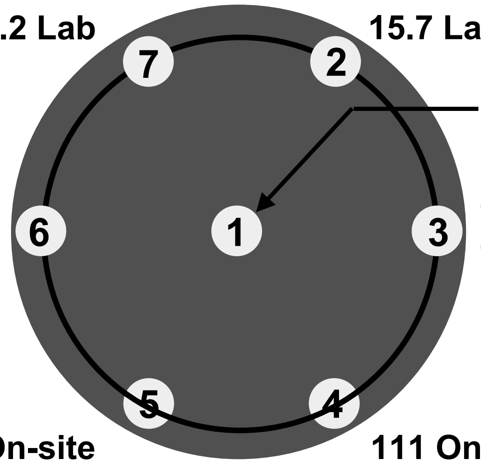
A very different decision regarding the need for remediation might be made if the location for sample collection was at position number 1 or position number 7!

Photo of sampling investigation at an antitank firing range at Canadian Force Base Valcartier in Quebec.

24

Photo of a ruptured antitank rocket. Rocket contains octol which is made up of 70% HMX and 30% TNT.

Valcartier ATR, Sampling Location #10
Major Analyte: HMX (mg/kg)



54.0 On-site
75.2 Lab

16.0 On-site
15.7 Lab

100 On-site
111 Lab

324 On-site
325 Lab

183 On-site
190 Lab

321 On-site
328 Lab

111 On-site
142 Lab

Results of on-site and off-site of wheel samples from the Valcartier antitank range.

Again note the agreement of the on-site colorimetric results with the off-site laboratory analyses.

Note the differences in concentration from location to location.

Data Analysis from Sampling Studies

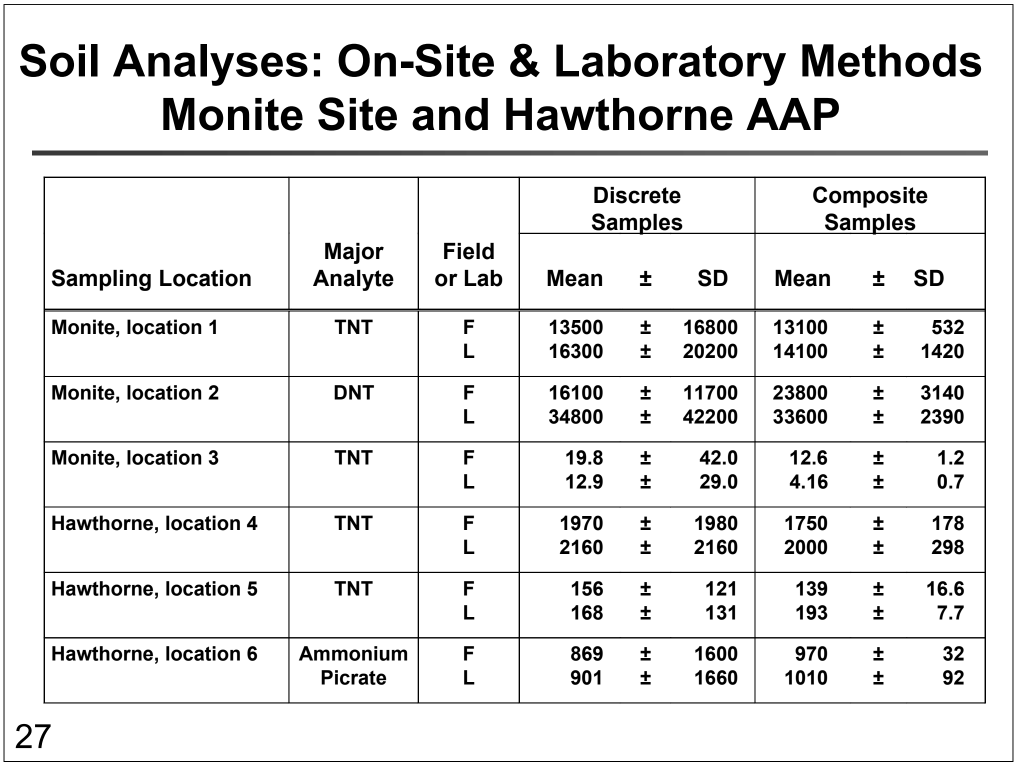
Analytical error for each type estimated by:
reproducibility of duplicate on-site and laboratory analyses

Sampling error estimated by:
differences in mean values between sampling locations

Accuracy of on-site methods estimated by:
comparison of mean values between on-site and laboratory analyses

The sampling study was conducted so that variances could be partitioned into sampling error and analytical error.

A comparison of the on-site colorimetric method with the lab method (Method 8330) was obtained by regression analysis of paired results from the same samples.



Soil Analyses: On-Site & Laboratory Methods Monite Site and Hawthorne AAP

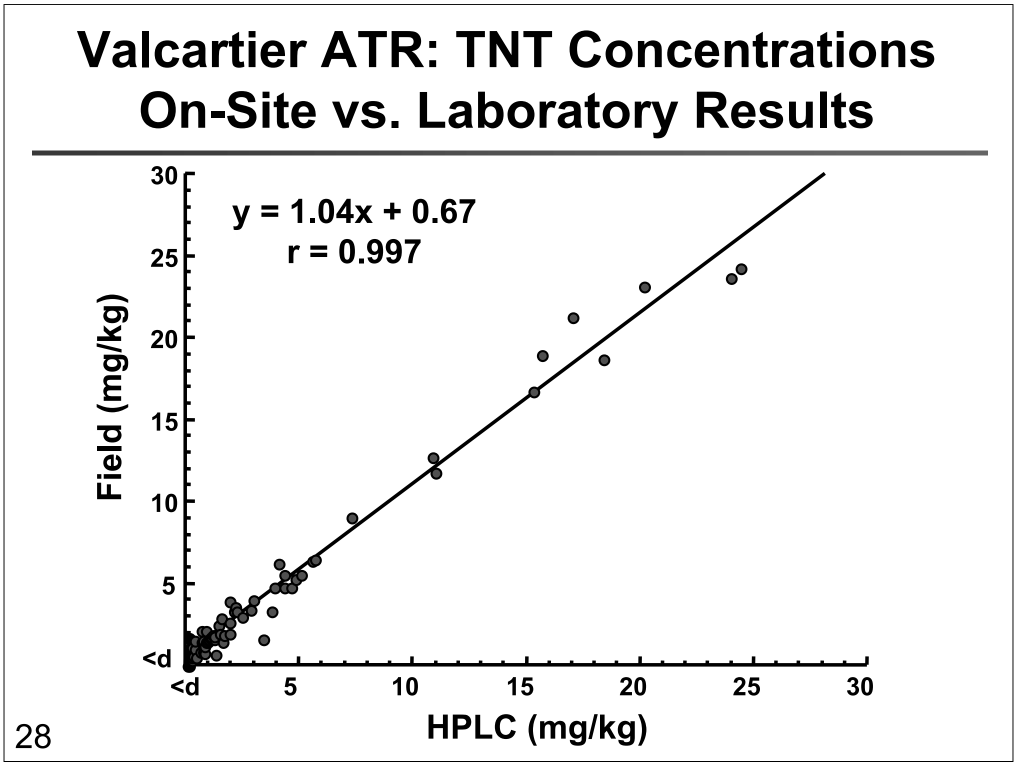
			Discrete Samples			Composite Samples		
Sampling Location	**Major Analyte**	**Field or Lab**	**Mean**	**±**	**SD**	**Mean**	**±**	**SD**
Monite, location 1	**TNT**	**F**	**13500**	**±**	**16800**	**13100**	**±**	**532**
		L	**16300**	**±**	**20200**	**14100**	**±**	**1420**
Monite, location 2	**DNT**	**F**	**16100**	**±**	**11700**	**23800**	**±**	**3140**
		L	**34800**	**±**	**42200**	**33600**	**±**	**2390**
Monite, location 3	**TNT**	**F**	**19.8**	**±**	**42.0**	**12.6**	**±**	**1.2**
		L	**12.9**	**±**	**29.0**	**4.16**	**±**	**0.7**
Hawthorne, location 4	**TNT**	**F**	**1970**	**±**	**1980**	**1750**	**±**	**178**
		L	**2160**	**±**	**2160**	**2000**	**±**	**298**
Hawthorne, location 5	**TNT**	**F**	**156**	**±**	**121**	**139**	**±**	**16.6**
		L	**168**	**±**	**131**	**193**	**±**	**7.7**
Hawthorne, location 6	**Ammonium Picrate**	**F**	**869**	**±**	**1600**	**970**	**±**	**32**
		L	**901**	**±**	**1660**	**1010**	**±**	**92**

This table provides a great deal of information.

F represents the on-site method (colorimetric) results; L is the laboratory results using Method 8330. Point out that both the means and standard deviations of the two methods are very similar.

Point out that for the discrete samples, the standard deviations are about the same magnitude as the means. Thus the variability among the seven discrete samples is very large in each case and it would fortuitous if a single discrete sample accurately represented the mean concentration.

Point out that the values for the composite samples are very similar to that of the discretes but that the standard deviations are much lower (generally the RSD is about 10%). Thus a singe composite sample is much more representative of the sampled area than a single discrete sample.

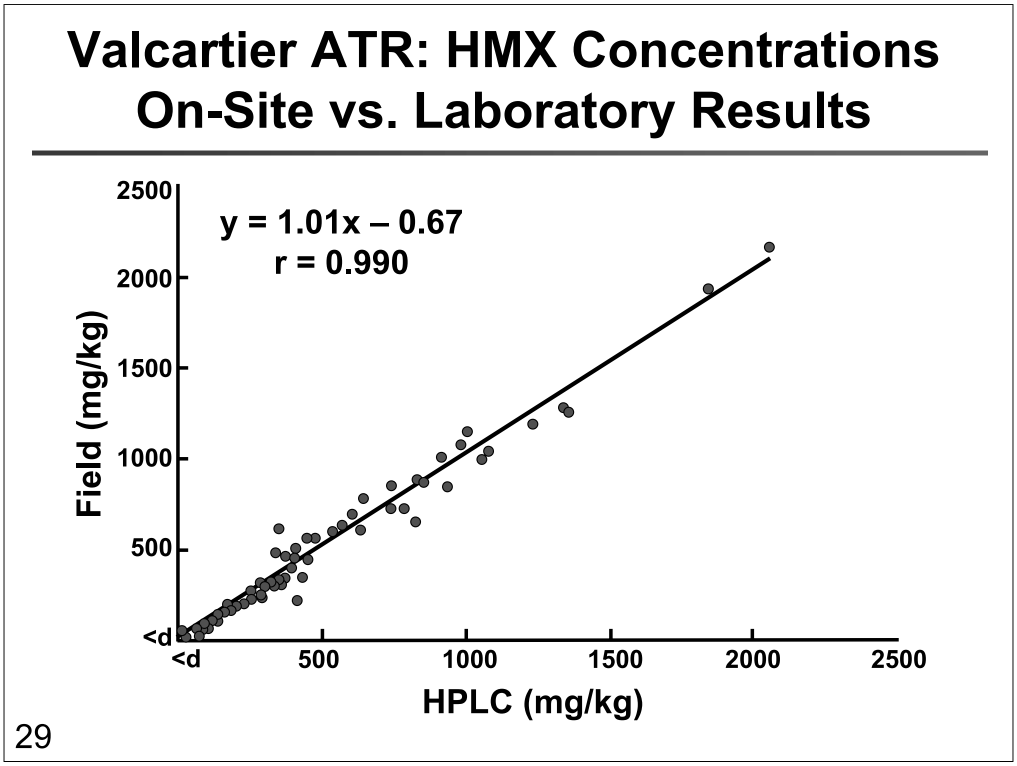


Valcartier ATR: TNT Concentrations On-Site vs. Laboratory Results

This is the result of regression analysis of the TNT results from the on-site colorimetric method vs. the laboratory HPLC method (Method 8330).

Note the slope is very close to 1 (indicating that the on-site method provides essentially the same level of accuracy as the lab method).

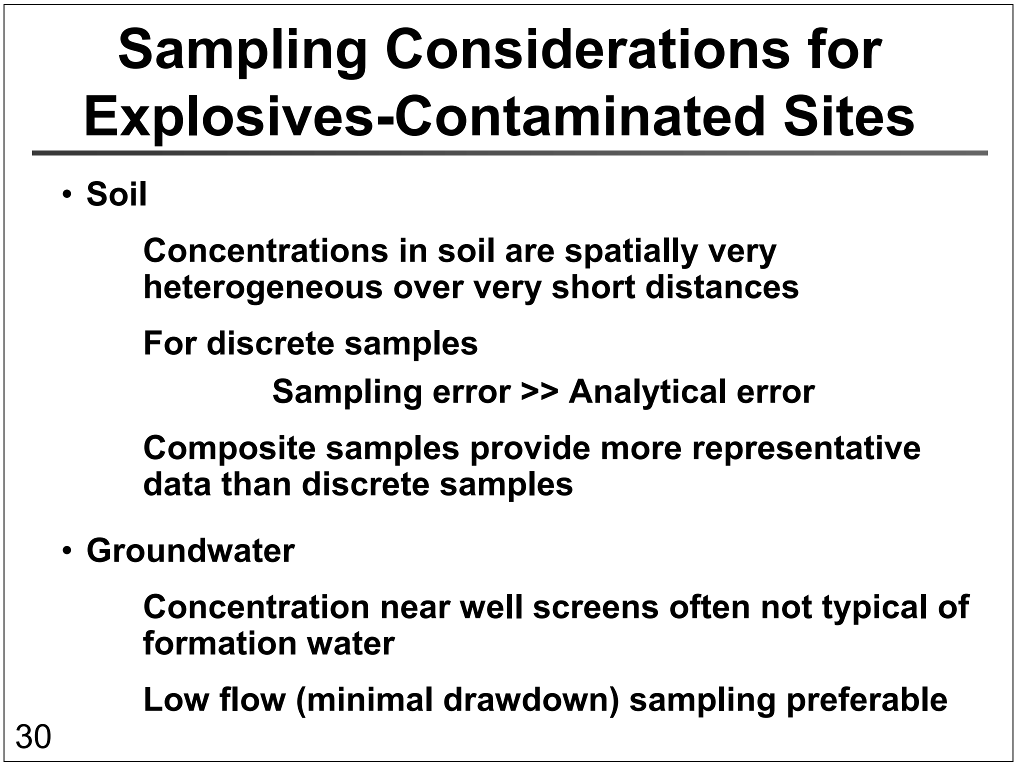
Note also the very high correlation coefficient and low value for the intercept.



Valcartier ATR: HMX Concentrations On-Site vs. Laboratory Results

This is a similar regression analysis of HMX results using the on-site colorimetric vs. the lab (HPLC) method.

Result even better than for TNT.



Sampling Considerations for Explosives-Contaminated Sites

- Soil
    - Concentrations in soil are spatially very heterogeneous over very short distances
    - For discrete samples
        - Sampling error >> Analytical error
    - Composite samples provide more representative data than discrete samples
- Groundwater
    - Concentration near well screens often not typical of formation water
    - Low flow (minimal drawdown) sampling preferable

Thus if sampling is conducted using discrete samples, the sampling error overwhelms analytical error in every case that we investigated.

Sampling error is minimized using composite samples.

For ground water, low flow sampling eliminates the problem of potentially misrepresenting the actual concentrations in the formation water of interest.

Advantages of Using Composite Samples

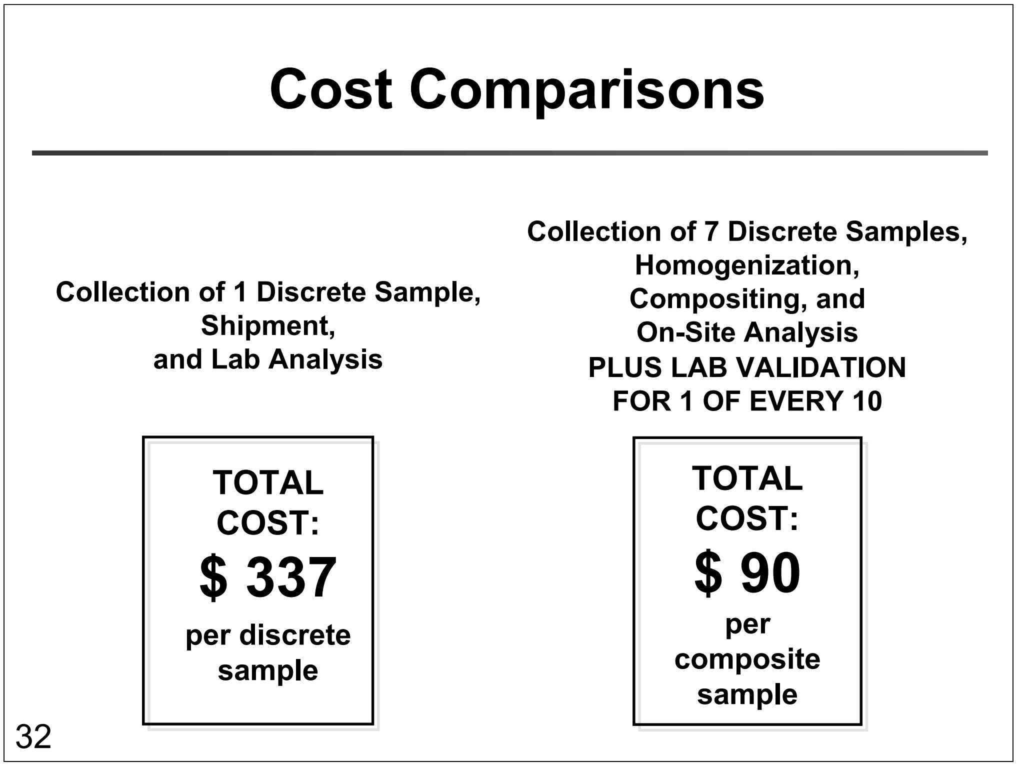
- **Physical averaging process**
- **Vastly improves representativeness of samples**
- **Allows a reduction in samples analyzed while improving characterization**
- **Provides a greater degree of statistical confidence than a comparable set of discrete samples**

Jenkins et al. 1996

If the objective of the sampling plan is to estimate mean concentration, then composite sampling yields a much better estimate of the mean than that provided by an equal number of discrete samples. The following is a quote from Soil Screening Guidance: User's Guide (U.S. EPA 1996)

"As explained in the Supplemental Guidance to RAGS: Calculating the Concentration Term (U.S. EPA, 1992d), an individual is assumed to move randomly across an exposure area (EA) over time, spending equivalent amounts of time in each location. Thus, the concentration contacted over time is best represented by the spatially averaged concentration over the EA. Ideally, the surface soil sampling strategy would determine the true population mean of contaminant concentrations in an EA. Because determination of the "true" mean would require extensive sampling at high costs, the maximum contaminant concentration from composite samples is used as a conservative estimate of the mean."

Jenkins, T.F., C.L. Grant, G.S. Brar, P.G. Thorne, and T.A. Ranney (1996) Assessment of sampling error associated with collection and analysis of soil samples at explosives-contaminated sites. USA Cold Regions Research and Engineering Laboratory, Special Report 96-15.



Cost Comparisons

**Collection of 1 Discrete Sample,
Shipment,
and Lab Analysis**

TOTAL COST:

$ 337

per discrete sample

**Collection of 7 Discrete Samples,
Homogenization,
Compositing, and
On-Site Analysis
PLUS LAB VALIDATION
FOR 1 OF EVERY 10**

TOTAL COST:

$ 90

per composite sample

This assessment was conducted several years ago using the CRREL colorimetric method, but the conclusion should be the same. Not only is the using of composite sampling and on-site analysis cheaper, but it provides representative data.

Conclusions in Verse

Seven sites were sampled that contained some TNT,
One Ammonium Picrate, and another DNT.

Very heterogeneous were these explosives as they lay,
Differing by ten times ten, though two short feet away,

Statistical calculations proved conclusively, did they not?
That sampling error far exceeded analytical by a lot!

Thus our recommendations to improve the sampling scheme
Are simple and effective and are not at all extreme:

Homogenize your soil cores as soon as they're removed,
Composite them together and analysis is improved.

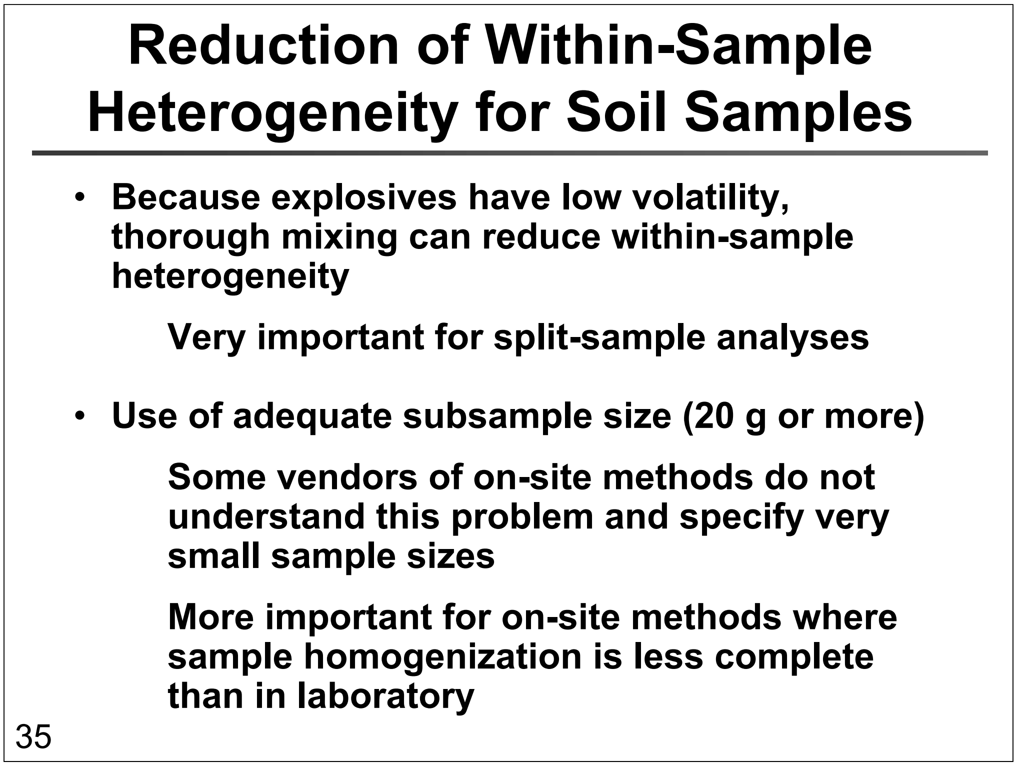
Finally, to preclude the chance of wrong interpretation,
Each sample must provide us with an accurate representation.

Jane G. Mason, CRREL

The Effect of Grinding on Laboratory Subsampling Error of Soil from a Hand Grenade Range


Soil prior to grinding.

Rep	TNT Conc. mg/kg Not Ground	TNT Conc. mg/kg Ground	RDX Conc. mg/kg Not Ground	RDX Conc. mg/kg Ground
1	0.25	2.03	1.68	4.75
2	1.81	2.04	1.77	4.71
3	0.37	2.00	1.46	4.80
4	1.48	2.03	3.80	4.73
5	7.93	1.97	7.83	4.67
6	0.56	2.00	1.81	4.66
7	0.35	1.90	2.35	4.62
8	0.75	2.02	2.51	4.62
9	0.56	1.97	2.08	4.64
10	0.35	1.98	1.98	4.69
11	0.62	1.90	1.68	4.66
12	5.62	1.91	13.0	4.60
mean	1.72	1.98	3.50	4.68
std dev	2.46	0.051	3.47	0.057
RSD	143%	2.57%	99%	1.23%



Reduction of Within-Sample Heterogeneity for Soil Samples

- Because explosives have low volatility, thorough mixing can reduce within-sample heterogeneity
  - Very important for split-sample analyses
- Use of adequate subsample size (20 g or more)
  - Some vendors of on-site methods do not understand this problem and specify very small sample sizes
  - More important for on-site methods where sample homogenization is less complete than in laboratory

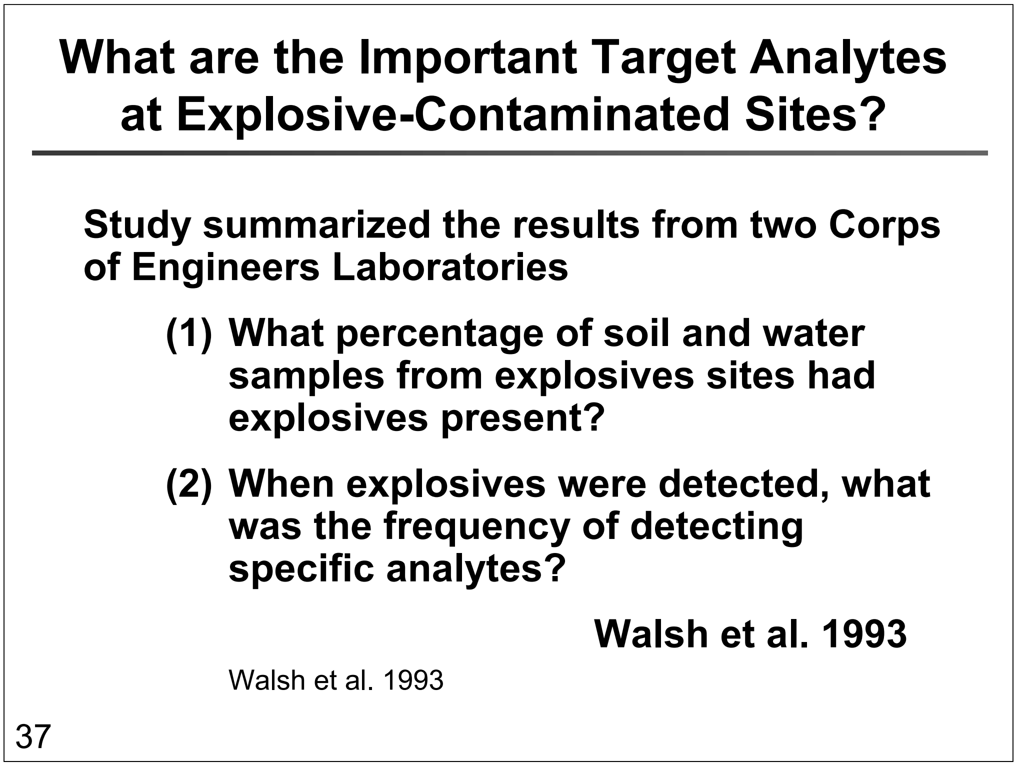
Ramsey, Charles and Jennifer Suggs (2001) Improving laboratory performance through scientific subsampling techniques. Environmental Testing and Analysis. 10(2):13-16.

Sample Processing / Holding Times

- Nitroaromatics are subject to microbiological transformation and photodegradation
- Soil and water samples should be kept cold in the dark
- Water samples can be preserved using acidification to extend holding times*
- Official holding times are 7 days to extraction

*Jenkins et al. 1995

Jenkins et al. 1995 Evaluation of Clean Solid Phases for Extraction of Nitroaromatics and Nitramines from Water
http://www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/SR95_22.pdf



What are the Important Target Analytes at Explosive-Contaminated Sites?

Study summarized the results from two Corps of Engineers Laboratories

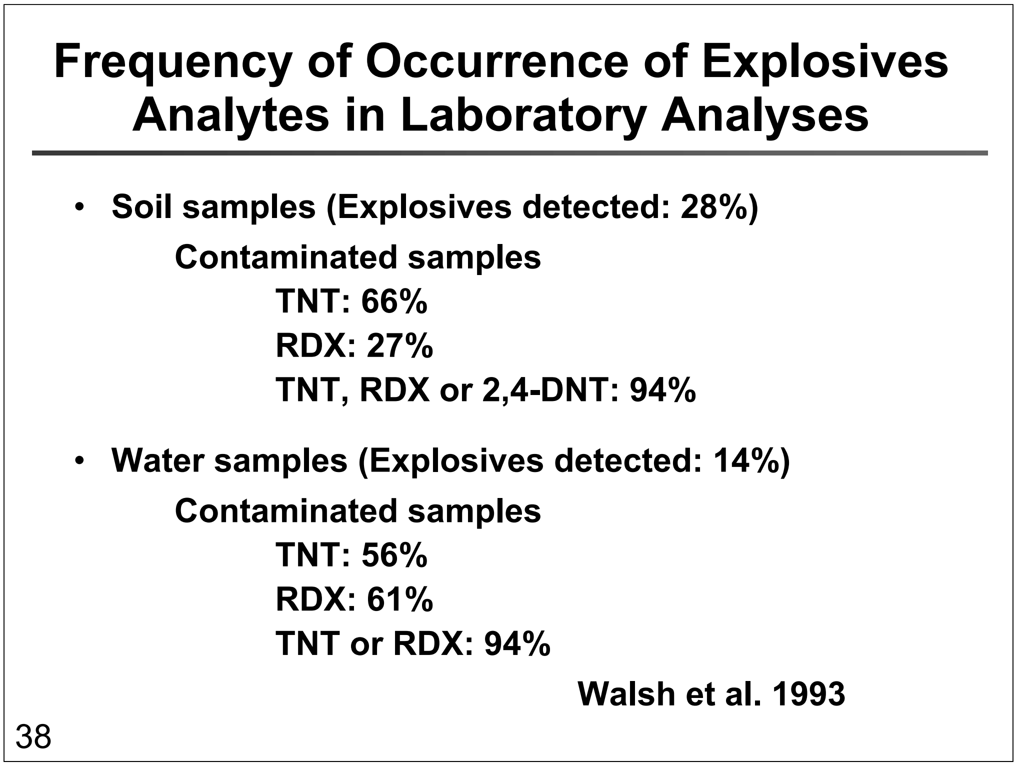
(1) What percentage of soil and water samples from explosives sites had explosives present?

(2) When explosives were detected, what was the frequency of detecting specific analytes?

Walsh et al. 1993

Walsh et al. 1993

Walsh, M.E., T.F. Jenkins, P.S. Schnitker, J.W. Elwell, and M.H. Stutz (1993) Evaluation of analytical requirements associated with sites potentially contaminated with residues of high explosives. USA Cold Regions Research and Engineering Laboratory, Special Report 93-5.



Frequency of Occurrence of Explosives Analytes in Laboratory Analyses

- **Soil samples (Explosives detected: 28%)**
  - **Contaminated samples**
    - **TNT: 66%**
    - **RDX: 27%**
    - **TNT, RDX or 2,4-DNT: 94%**
- **Water samples (Explosives detected: 14%)**
  - **Contaminated samples**
    - **TNT: 56%**
    - **RDX: 61%**
    - **TNT or RDX: 94%**

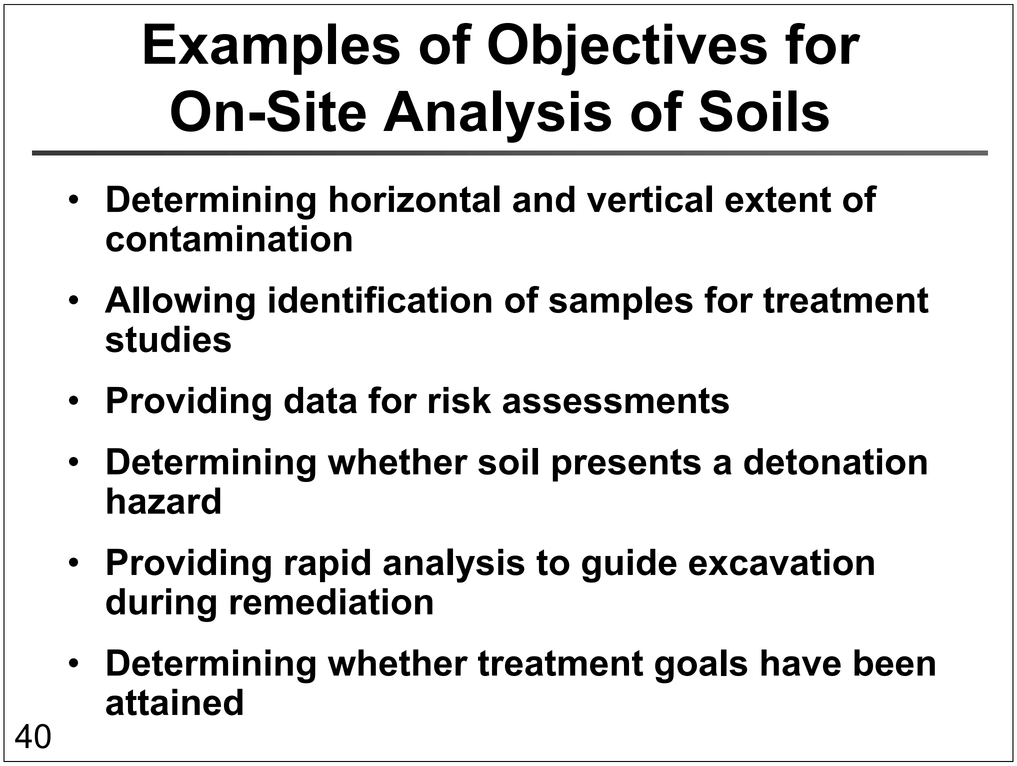
Walsh et al. 1993

Walsh, M.E., T.F. Jenkins, P.S. Schnitker, J.W. Elwell, and M.H. Stutz (1993) Evaluation of analytical requirements associated with sites potentially contaminated with residues of high explosives. USA Cold Regions Research and Engineering Laboratory, Special Report 93-5.

Most Important Analytes for On-Site Characterization of Explosives Contamination

TNT

RDX

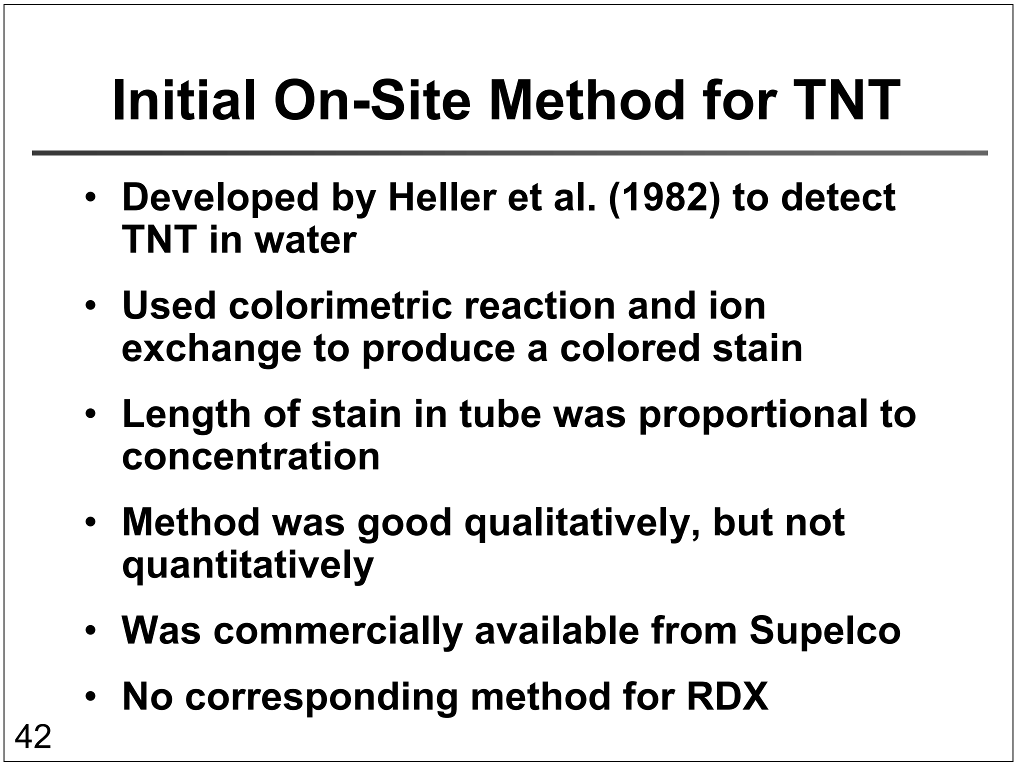


Examples of Objectives for On-Site Analysis of Soils

- Determining horizontal and vertical extent of contamination
- Allowing identification of samples for treatment studies
- Providing data for risk assessments
- Determining whether soil presents a detonation hazard
- Providing rapid analysis to guide excavation during remediation
- Determining whether treatment goals have been attained

Examples of Objectives for On-Site Analysis of Water

- Rapid analysis of well-water samples
- Evaluation of contamination in seeps and surface waters
- Routine assessment of treatment efficiency of pump-and-treat systems



Initial On-Site Method for TNT

- Developed by Heller et al. (1982) to detect TNT in water
- Used colorimetric reaction and ion exchange to produce a colored stain
- Length of stain in tube was proportional to concentration
- Method was good qualitatively, but not quantitatively
- Was commercially available from Supelco
- No corresponding method for RDX

Heller, C.A. S.R. Grenl and E.E. Erickson (1982) Field detection of 2,4,6-trinitrotoluene in water by ion-exchange resins. Analytical Chemistry, 54:286-289.

Currently Available On-Site Technologies for Explosives

- **EXPRAY Kit (Plexus Scientific)**
- **EnSys Colorimetric TNT and RDX/HMX Kits (SDI)**
- **DTECH Enzyme Immunoassay Kits (SDI)**
- **Fast 2000 (Research International)**
- **GC-Ionscan (Barringer Instruments)**
- **GC-TID (SRI Instruments)**
- **SPREETA TNT Sensor (Texas Instruments)***
- **RIDASCREEN TNT Kit (Accurate Chemical & Sci.)**

***Not commercially available at present**

We will be discussing each of these methods.

EXPRAY Kit

- **Simplest screening kit (Colorimetric)**
- **Useful for surfaces and unknown solids**
- **Can be used to provide qualitative test for soils**
- **Kit contains three spray cans**
  - **EXPRAY 1 - Nitroaromatics (TNT)**
  - **ESPRAY 2 - Nitramines (RDX) and Nitrate esters (NG)**
  - **EXPRAY 3 - Black powder, ANFO**
- **Spray cans used sequentially**

This is a qualitative tool but is very helpful and easy to use. Even if you are using an on-site quantitative method, it is very useful to have this kit on site as well to test suspicious solids.

Available from:

Plexus Scientific

12501 Prosperity Drive, Suite 401
Silver Spring, MD 20904

(Tel. 301-622-9696)
(FAX 301-622-9693)

Cost is $130 / kit

This is a photo of the EXPRAY kit containing three spray cans.

Use of EXPRAY Kit

- **For surfaces or unknown solid**
  - **Wipe surface with sticky collection paper**
  - **Spray paper with EXPRAY**
- **For soil**
  - **Place soil on top of two filter papers**
  - **Soak soil with acetone**
  - **Spray the bottom filter paper with EXPRAY reagents (Spray cans used sequentially)**
- **Detection limit - 20 ng**

Sampling a piece of partially detonated ordnance for residual explosive. Color shows explosives present.

EnSys Colorimetric Test Kits
EPA SW846 Methods 8515 and 8510

- **Initial TNT method developed by CRREL 1990* (8515)**
- **Initial RDX method developed by CRREL 1991** (8510)**
- **Commercialized by EnSys, now SDI**
- **Colorimetric methods for TNT and RDX / HMX**
- **Successfully used at variety of explosives sites**
- **Results correlate well with Method 8330**
- **TNT kits cost $410 for 20 tests ($20.50 / sample)**
- **RDX kits cost $500 for 20 tests ($25 / sample)**

*** Jenkins 1990; **Walsh and Jenkins 1991**

Commercial kits available from:

Strategic Diagnostics Inc. (SDI)
128 Sandy Dr.
Newark, DE 19713-1147

(phone: 302-456-6789)
(FAX: 302-456-6770)

Spectrophotometer available from:

Hach Company
P.O. Box 608
Loveland, CO 80539-0608
(phone: 800-227-4224)
(FAX: 970-669-2932)

Jenkins, T.F. (1990) Development of a Simplified Field Method for the Determination of TNT in Soil. U. S. Army Cold Regions Research and Engineering Laboratory Special Report 90-38, Hanover, New Hampshire.

Walsh, M.E. and T.F. Jenkins (1991) Development of a Field Screening Method for RDX in Soil. U. S. Army Cold Regions Research and Engineering Laboratory Special Report 91-7, Hanover, New Hampshire.

Characteristics of Colorimetric Kits

- TNT and RDX / HMX tests produce reddish colored solutions
- Concentrations are proportional to intensity of color
- TNT test also responds to 2,4-DNT, Tetryl, TNB
- RDX / HMX test also responds to NG, PETN, NC, Tetryl
- TNT test is subject to interference from yellow color produced from reaction with humic substances and molecular sulfur (EnSys only)
- RDX/HMX test is subject to interference from nitrate ion unless the optional ion exchange step is used

These kits have been around and number of years and have been used successfully at a wide variety of sites.

This photo shows the portable spectrophotometer. The reddish colored extract is indicative of a positive hit.

Closer view of spectrophotometer and reddish colored solution that forms after addition of reagents to soil extract when TNT is present.

Advantages / Disadvantages of Colorimetric Methods

Advantages

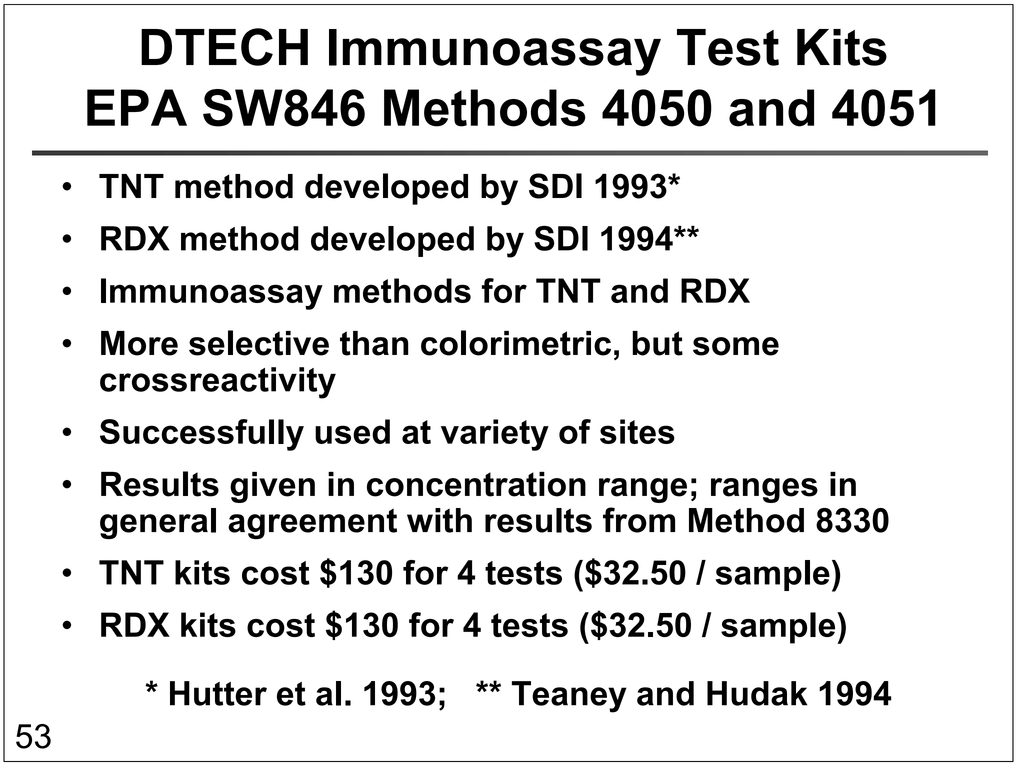
- Easy to use in the field
- Good quantitative agreement with laboratory results
- Dilutions do not require use of an additional kit
- Screens for presence of non-targeted explosives
- Successfully used at many contaminated sites
- Good method to assess reactivity of soil prior to shipping

Disadvantages

- Requires some experience with chemical analysis
- Class specific but not analyte specific
- Yellow color from humics can interfere with TNT test
- Use for water samples requires preconcentration (SPE)

A major advantage of using the two colorimetric tests is that it screens for the presence of nearly all of the explosives analytes that might be present.

SPE = Solid Phase Extraction



DTECH Immunoassay Test Kits
EPA SW846 Methods 4050 and 4051

- **TNT method developed by SDI 1993***
- **RDX method developed by SDI 1994****
- **Immunoassay methods for TNT and RDX**
- **More selective than colorimetric, but some crossreactivity**
- **Successfully used at variety of sites**
- **Results given in concentration range; ranges in general agreement with results from Method 8330**
- **TNT kits cost $130 for 4 tests ($32.50 / sample)**
- **RDX kits cost $130 for 4 tests ($32.50 / sample)**

*** Hutter et al. 1993; ** Teaney and Hudak 1994**

These kits have also been around a long time and have been used successfully at a number of sites.

They are more specific for TNT and RDX than the colorimetric kits.

Available from:

Strategic Diagnostics Inc. (SDI)

128 Sandy Dr.
Newark, DE 19713-1147

(phone: 302-456-6789)
(FAX: 302-456-6770)

Hutter, L., G.Teaney and J.W. Stave (1993) A novel field screening system for TNT using EIA, p 472 in Field Screening Methodsfor Hazardous Wastes and Toxic Chemicals, Vol. 1, Proceedings of the 1993 USEPA/AWMA International Symposium.

Teaney, G.B., and R.T. Hudak (1994) Development of an enzyme immunoassay-based field screening system for the detection of RDX in soil and water. In Proceedings of 87th Annual Meeting and Exhibi-tion, Air and Waste Management Association. Cincinnati, Ohio, 19–24 June 1994, 94-RP143.05.

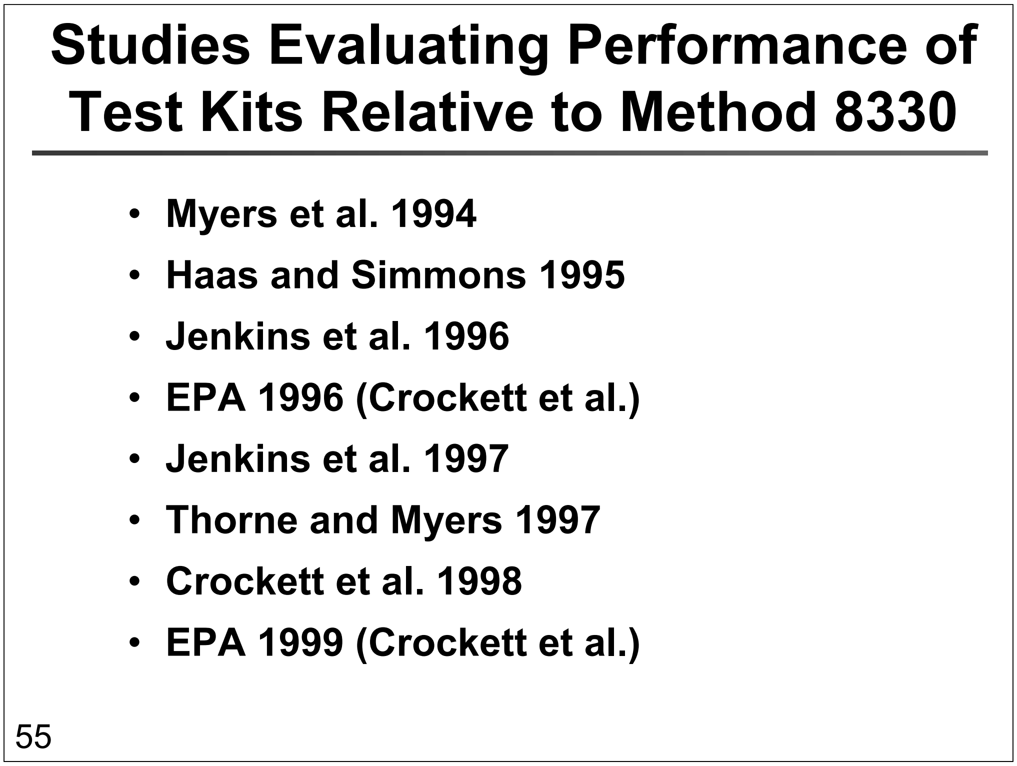
Advantages / Disadvantages of DTECH Immunoassay Methods

Advantages

- Configured for ease of use in the field
- Requires less training / experience
- Relatively specific for TNT and RDX
- Successfully used at many contaminated sites
- No preconcentration required for water analysis

Disadvantages

- Fair quantitative agreement with laboratory results
- Provides only concentration range
- Provides no information on non-target analytes
- Dilutions require use of additional kit



Studies Evaluating Performance of Test Kits Relative to Method 8330

- **Myers et al. 1994**
- **Haas and Simmons 1995**
- **Jenkins et al. 1996**
- **EPA 1996 (Crockett et al.)**
- **Jenkins et al. 1997**
- **Thorne and Myers 1997**
- **Crockett et al. 1998**
- **EPA 1999 (Crockett et al.)**

A number of studies have been conducted to assess the performance of the EnSys and DTECH kits. In general, they have been shown to be very useful in delineating areas of contamination and often the results have correlated well with laboratory results.

Myers, K.F., E.F. McCormick, A.B. Strong, P.G. Thorne, and T.F. Jenkins (1994) Comparison of commercial colorimetric and enzyme immunoassay field screening methods for TNT in soil. USA Corps of Engineers, Waterways Experiment Sta-tion, Technical Report IRRP-94-4.

Haas, R.A. and B.P. Simmons (1995) Measurement of TNT and RDX in soil by enzyme immunoassay and high performance liquid chromatography (EPA 8330). California Environmental Protection Agency, Department of Toxic Substances Control, Hazardous Materials Laboratory.

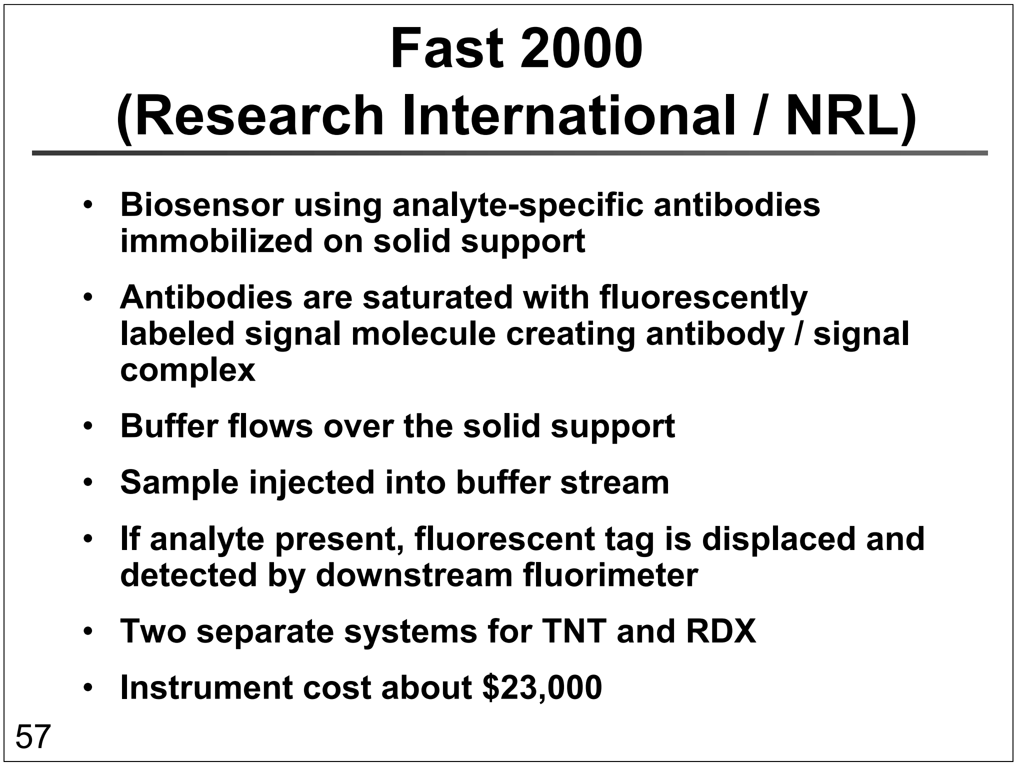
Jenkins, T.F., C.L. Grant, G.S. Brar, P.G. Thorne, and T.A. Ranney (1996) Assessment of sampling error associated with collection and analysis of soil samples at explosives-contaminated sites. USA Cold Regions Research and Engineering Laboratory, Special Report 96-15.

Crockett et al 1996 Field Sampling and Selecting On-site Analytical Methods for Explosives in Soil http://www.epa.gov/tio/tsp/download/explosiv.pdf

Environmental Technology Verification (ETV)

- **Conducted by Oak Ridge NL for EPA / DoD**
- **108 blind soil and 176 blind water samples**
- **Results compared to SW846 Method 8330**
- **1999 Demonstration (Results on web site)**
  - **Research International/NRL Fast 2000**
  - **Barringer GC-Ionscan**
- **2000 Demonstration (Results will be on web site)**
  - **SRI / CRREL GC-Thermionic**
  - **Texas Instruments SPREETA**

This program evaluated several on-site measurement technologies and was conducted by Oak Ridge National Laboratory over the past two years. I provided a number of blind samples to the technology developers to get an independent assessment of the performance of these methods under field conditions using real samples.



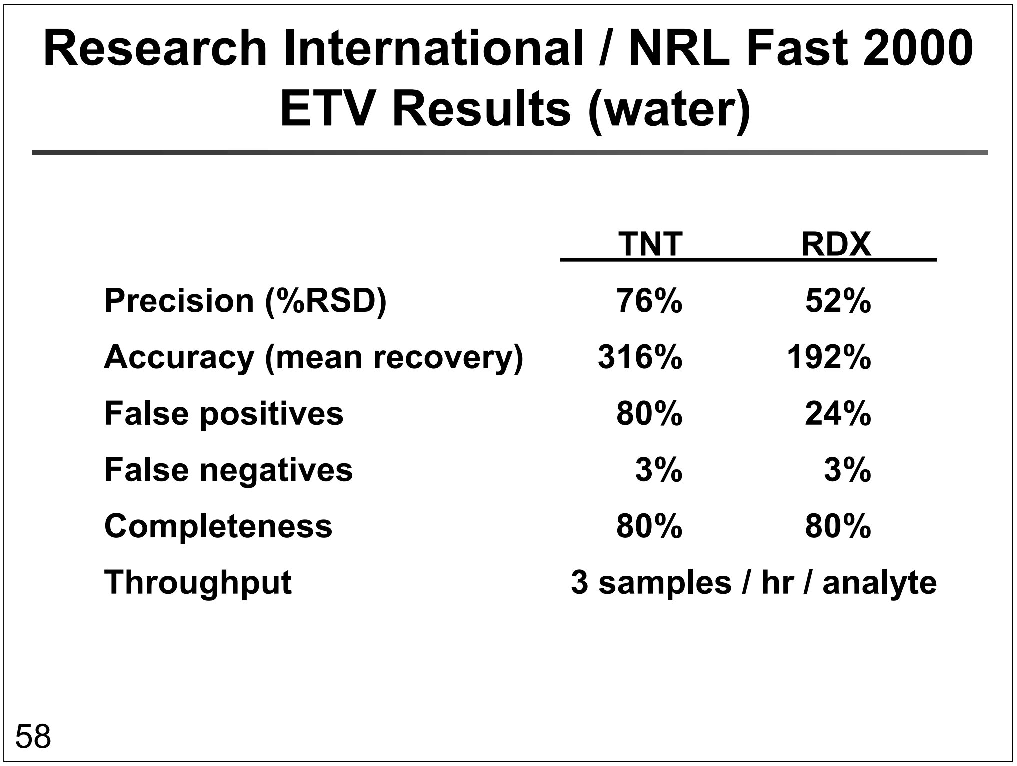
Fast 2000 (Research International / NRL)

- Biosensor using analyte-specific antibodies immobilized on solid support
- Antibodies are saturated with fluorescently labeled signal molecule creating antibody / signal complex
- Buffer flows over the solid support
- Sample injected into buffer stream
- If analyte present, fluorescent tag is displaced and detected by downstream fluorimeter
- Two separate systems for TNT and RDX
- Instrument cost about $23,000

This technology was developed by the Naval Research Laboratory and was licensed to Research International, Corp.

Instrument available from:

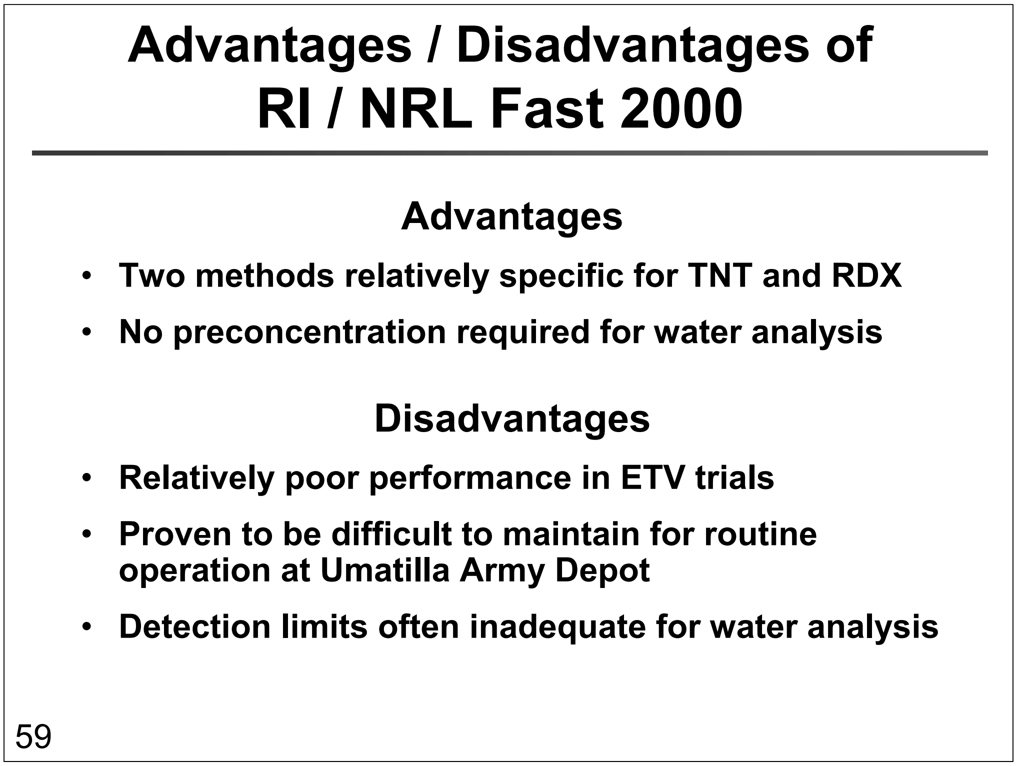
Research International, Inc.
18706 142nd Avenue NE
Woodinville, WA 98072-8523
(phone: 425-486-7831)
(FAX: 425-485-9137)



Research International / NRL Fast 2000 ETV Results (water)

	TNT	RDX
Precision (%RSD)	76%	52%
Accuracy (mean recovery)	316%	192%
False positives	80%	24%
False negatives	3%	3%
Completeness	80%	80%
Throughput	3 samples / hr / analyte	

These are the results of the ETV demonstration for water analysis.



Advantages / Disadvantages of RI / NRL Fast 2000

Advantages

- **Two methods relatively specific for TNT and RDX**
- **No preconcentration required for water analysis**

Disadvantages

- **Relatively poor performance in ETV trials**
- **Proven to be difficult to maintain for routine operation at Umatilla Army Depot**
- **Detection limits often inadequate for water analysis**

A new model, the Fast 6000 is now available but it has not been tested under the ETV program.

GC-Ionscan (Barringer Instruments)

- Extensive experience in explosives detection for anti-terrorism applications (Airport Security)
- Uses Ion Mobility Spectrometry (IMS)

  Very sensitive for most explosives
- Combination with GC allows multianalyte method
- Instrument well developed; minimum development for environmental methods (water)

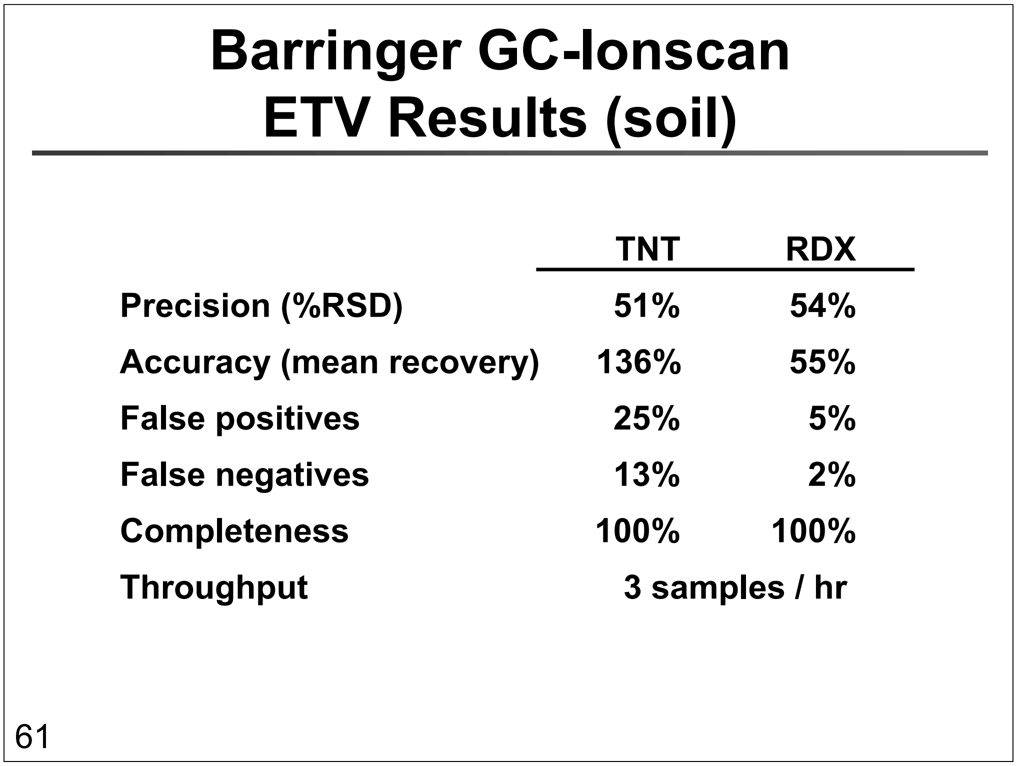
Barringer has many years of experience in explosives detection for security and antiterrorism applications. The ion mobility spectrometer is very sensitive to explosives compounds.

The company is an instrument maker and did not invest a great deal of time in developing environmental methods, particularly for water.

This is the first truly multi analyte method.

Available from:

Barringer Instruments Inc.
30 Technology Drive
Warren, NJ 07059
(phone: 908-222-9100)
(FAX: 908-222-1557)



Barringer GC-Ionscan ETV Results (soil)

	TNT	RDX
Precision (%RSD)	51%	54%
Accuracy (mean recovery)	136%	55%
False positives	25%	5%
False negatives	13%	2%
Completeness	100%	100%
Throughput	3 samples / hr	

Results of ETV demonstration.

Barringer GC-Ionscan ETV Results (water)

- Method tested: Detection limits (DL) inadequate for any normal application
- Could be combined with preconcentration using Solid Phase Extraction (SPE) to improve DL

Advantages / Disadvantages of Barringer GC-Ionscan

Advantages

- Provides on-site multianalyte results for all major target analytes
- Low false positive / false negative rates

Disadvantages

- Requires on-site chemist with experience
- Requires compressed gasses on site
- Relatively poor performance in ETV trials
- Instrument cost is high ($60,800)
- Environmental methods need further improvement

SRI / CRREL GC-TID Method

- **GC-TID Instrument manufactured by SRI (Model 8610C)**
- **Method developed by Hewitt et al. 2000 (CRREL)**
- **Allows on-site determination of important military high explosives and degradation products and some primary explosives**
    - **Nitroaromatics: TNT, 2,4-DNT**
    - **Nitramines: RDX, HMX**
    - **Nitrate esters: PETN, NG**
    - **Degradation products: TNB, 2-ADNT, 4-ADNT**
- **Instrument costs about $9000**

Very inexpensive instrument that can provide determination of all the major explosives analytes.

GC-TID = Gas Chromatography Thermionic Detector

Hewitt, A.D., T.F. Jenkins and T. Ranney (2000) On-site method for nitroaromatic and nitramine explosives in soil and groundwater using a GC-thermionic ionization detector. 2nd International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA. May 22, 2000.

Instrument available from:

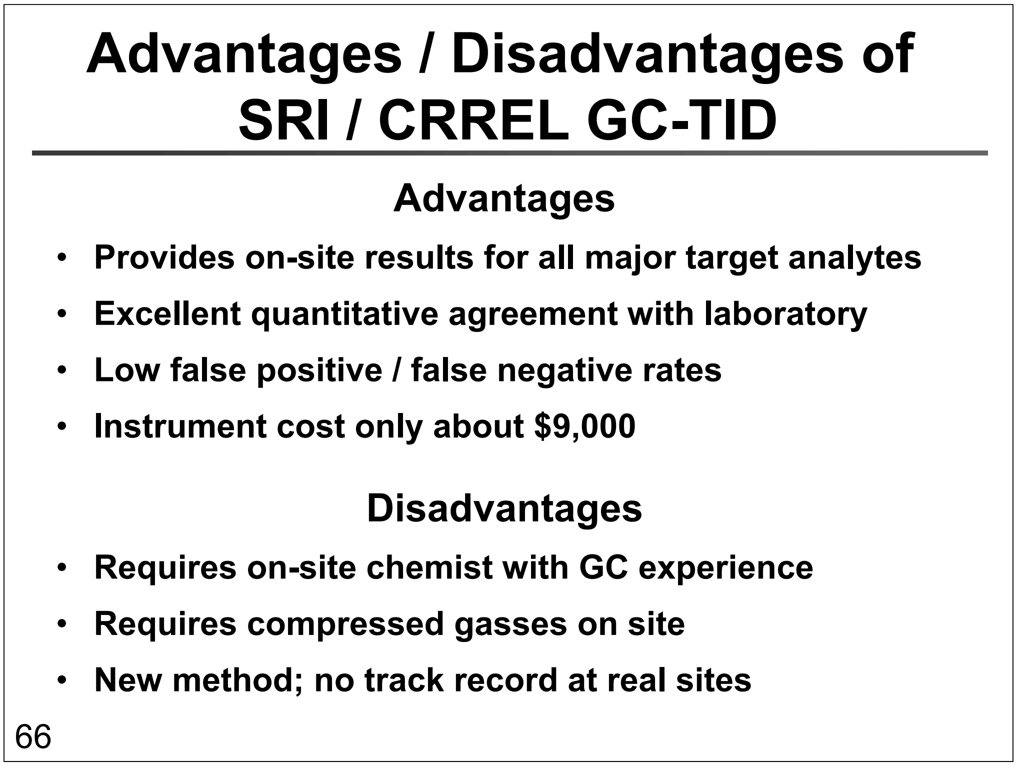
SRI Instruments
20720 Earl St.
Torrance, CA 90503
(phone: 310-214-5092)
(FAX: 310-214-5097)

Methods available from:

Alan Hewitt
USA ERDC-CRREL-RG
Hanover, NH 03755
(phone: 603-646-4388)

SRI / CRREL GC-TID ETV Results (soil)

	TNT	RDX
Precision (%RSD)	17%	13%
Accuracy (mean recovery)	97%	91%
False positives	1%	0%
False negatives	3%	1%
Completeness	100%	100%
Throughput	3 samples / hr	



Advantages / Disadvantages of SRI / CRREL GC-TID

Advantages

- **Provides on-site results for all major target analytes**
- **Excellent quantitative agreement with laboratory**
- **Low false positive / false negative rates**
- **Instrument cost only about $9,000**

Disadvantages

- **Requires on-site chemist with GC experience**
- **Requires compressed gasses on site**
- **New method; no track record at real sites**

This method can provide high quality data on site but it requires a chemist familiar with gas chromatography.

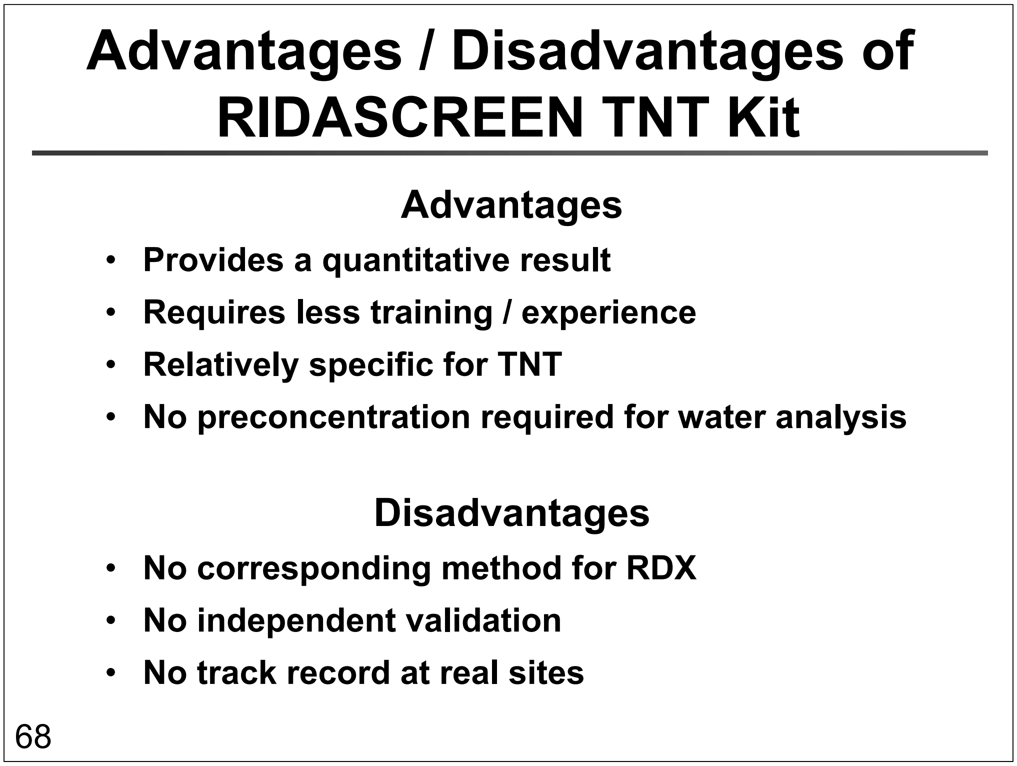
RIDASCREEN TNT Kit (Accurate Chemical & Scientific)

- Classical competitive immunoassay
- Uses 96 well plate
- Antigen-antibody reaction
- Photometric measurement at 450 nm
- Requires microtiter plate spectrophotometer
- Detection limits: 30 ppt for water, 3 ppb for soil
- Crossreactive to TNB, tetryl
- Cost $775 for 96 test well plate

Kit is manufactured in Germany and distributed in the U.S.

Available from:

Accurate Chemical and Scientific Corp.
300 Shames Drive
Westbury, NY 11590
(phone: 516-333-2221)
(FAX: 516-997-4948)



Advantages / Disadvantages of RIDASCREEN TNT Kit

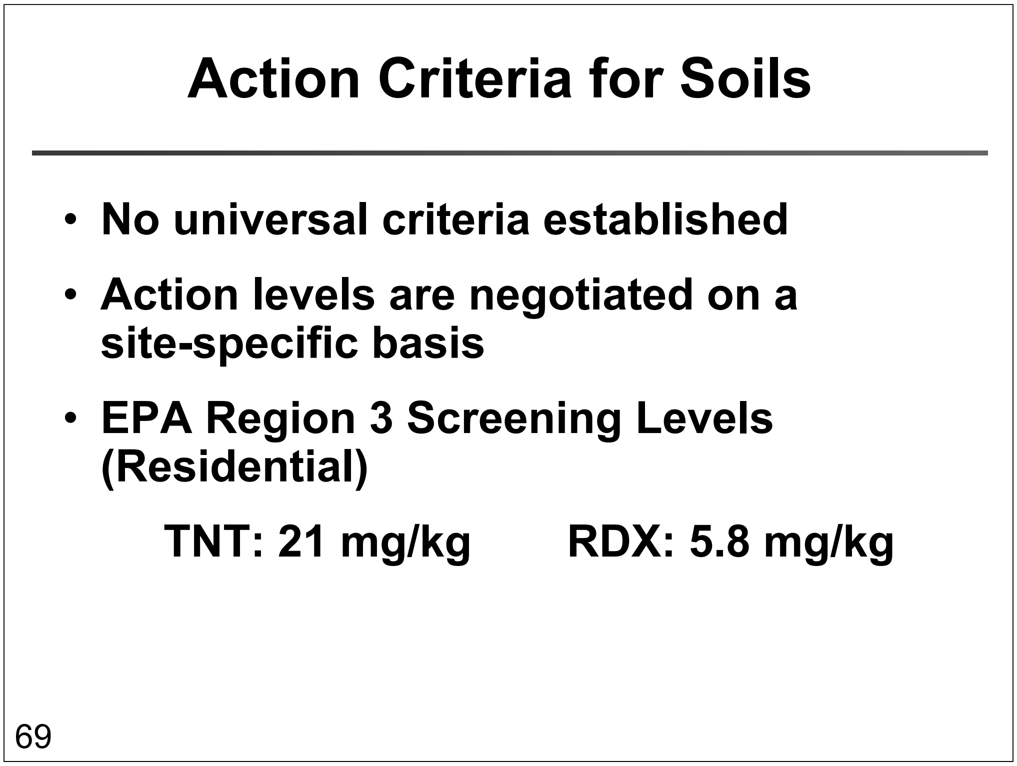
Advantages

- Provides a quantitative result
- Requires less training / experience
- Relatively specific for TNT
- No preconcentration required for water analysis

Disadvantages

- No corresponding method for RDX
- No independent validation
- No track record at real sites

The distributor could provide no performance information.

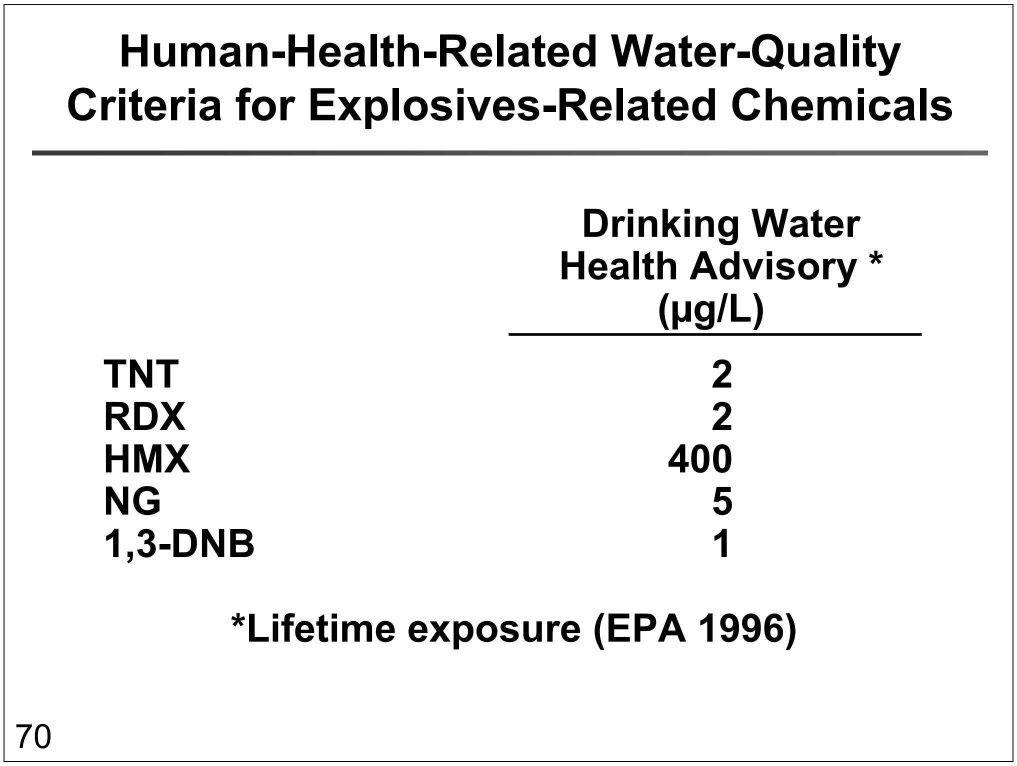


Action Criteria for Soils

- **No universal criteria established**
- **Action levels are negotiated on a site-specific basis**
- **EPA Region 3 Screening Levels (Residential)**

TNT: 21 mg/kg RDX: 5.8 mg/kg

There is no universal criteria for action levels for explosives in soils. The action level for a specific site is negotiated between the regulator and the responsible party (often the DoD).



Human-Health-Related Water-Quality Criteria for Explosives-Related Chemicals

	Drinking Water Health Advisory * (µg/L)
TNT	2
RDX	2
HMX	400
NG	5
1,3-DNB	1

*Lifetime exposure (EPA 1996)

Again, no water quality criteria has been established, but these human health advisory numbers are often used.

Detection Limits

	Soil (mg/kg)	Water (μg/L)
SDI EnSys (TNT, RDX)	1.0	1, 5
SDI DTECH (TNT, RDX)	0.5	5
RI Fast 2000 (TNT, RDX)	--	20
Barringer GC-Ionscan (TNT, RDX)	0.3	25
SRI / CRREL GC-TID (TNT, RDX)	0.005, 0.5	--
TI SPREETA (TNT)	0.3	--
RIDASCREEN (TNT)	0.003	--

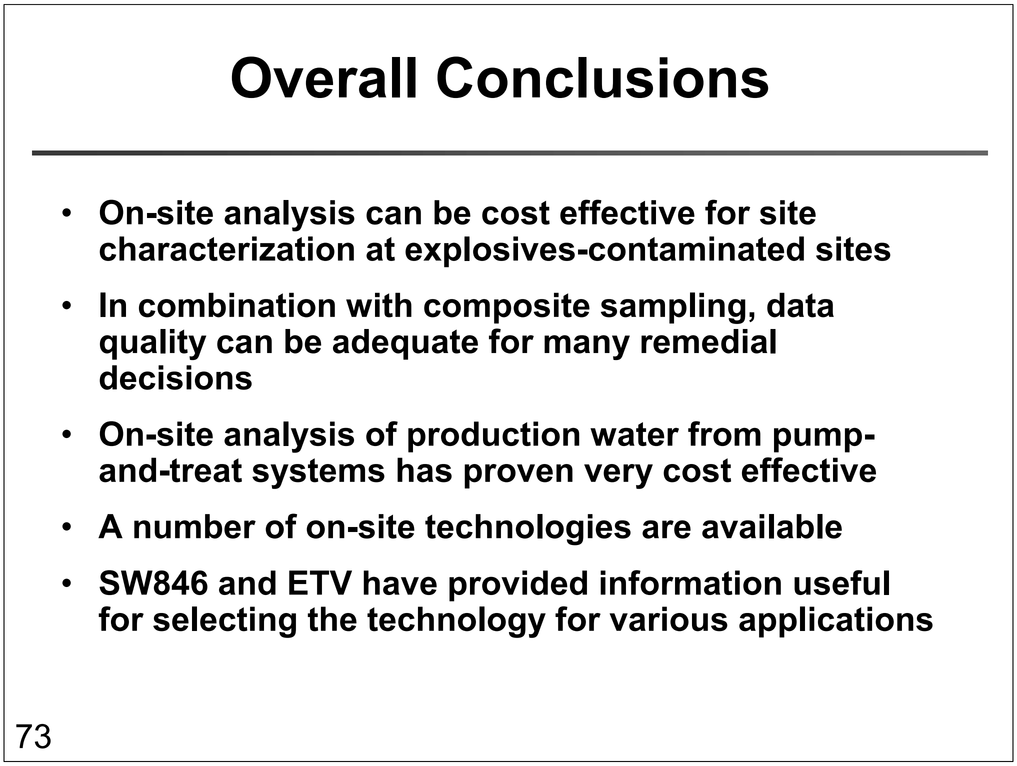
What About Other Explosives?

- **Ammonium picrate / picric acid**
  - **Thorne and Jenkins 1997**
- **NG and PETN**
  - **EnSys (SDI) RDX test works for these too**
  - **Barringer GC-Ionscan**
  - **SRI / CRREL GC-TID**

There is a colorimetric method for ammonium picrate/picric acid that is available from CRREL.

There are several methods that can determine nitroglycerine and PETN. The Barringer and SRI methods are multi-analyte methods and the SDI EnSys method can provide estimates for these compounds in the absence of RDX and HMX.

Thorne, P.G., and T.F. Jenkins (1997) Development of a Field Method for Quantifying Ammonium Picrate and Picric Acid in Soil. Field *Analytical Chemistry and Technology*, 1:165-170.



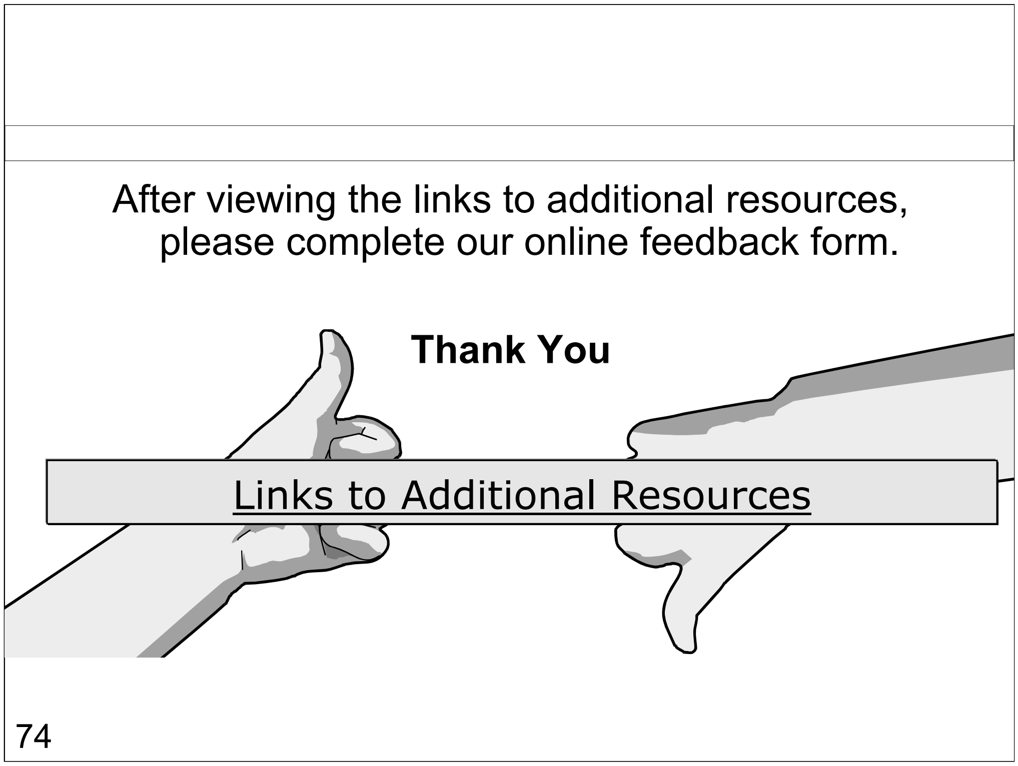
Overall Conclusions

- On-site analysis can be cost effective for site characterization at explosives-contaminated sites
- In combination with composite sampling, data quality can be adequate for many remedial decisions
- On-site analysis of production water from pump-and-treat systems has proven very cost effective
- A number of on-site technologies are available
- SW846 and ETV have provided information useful for selecting the technology for various applications

In conclusion, there are a number of technologies available for on-site determination of explosives in soil and water.

Because of the nature of the distribution of explosives (spatially very heterogeneous), these methods combined with composite sampling provide a very cost effective means of conducting site characterization.

These methods have undergone third party evaluations and several have demonstrated good performance at explosives-contaminated sites.



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