
FIELD DEMONSTRATION OF ON-SITE ANALYTICAL METHODS FOR TNT AND RDX IN GROUND WATER

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ABSTRACT A field demonstration was conducted to assess the performance of eight commercially-available and emerging colorimetric, immunoassay, and biosensor on-site analytical methods for explosives 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in ground water and leachate at the Umatilla Army Depot Activity, Hermiston, Oregon and U.S. Naval Submarine Base, Bangor, Washington, Superfund sites. Ground water samples were analyzed by each of the on-site methods and results compared to laboratory analysis using high performance liquid chromatography (HPLC) with EPA SW-846 Method 8330. The commercial methods evaluated include the EnSys, Inc., TNT and RDX colorimetric test kits (EPA SW-846 Methods 8515 and 8510) with a solid phase extraction (SPE) step, the DTECH/EM Science TNT and RDX immunoassay test kits (EPA SW-846 Methods 4050 and 4051), and the Ohmicron TNT immunoassay test kit. The emerging methods tested include the antibody-based Naval Research Laboratory (NRL) Continuous Flow Immunosensor (CFI) for TNT and RDX, and the Fiber Optic Biosensor (FOB) for TNT. Accuracy of the on-site methods were evaluated using linear regression analysis and relative percent difference (RPD) comparison criteria. Over the range of conditions tested, the colorimetric methods for TNT and RDX showed the highest accuracy of the commercially-available methods, and the NRL CFI showed the highest accuracy of the emerging methods for TNT and RDX. The colorimetric method was selected for routine ground water monitoring at the Umatilla site, and further field testing on the NRL CFI and FOB biosensors will continue at both Superfund sites. The primary use for these analytical methods would be for influent and effluent monitoring for granular activated carbon (GAC) ground water and leachate treatment systems, which are projected to operate for a period of 10 to 30 years.

KEYWORDS: explosives, TNT, RDX, field analytical methods, ground water

INTRODUCTION

This paper presents a comparison of eight commercially-available and emerging on-site analytical methods used to determine 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) concentrations in ground water and leachate. Field analysis was conducted on water collected from the Explosives Washout Lagoon area at Umatilla Army Depot Activity (Umatilla),

Hermiston, Oregon, and from Site F ground water treatment system and Site A leachate treatment system at the U.S. Naval Submarine Base (SUBASE), Bangor, Washington. A description of on-site analytical methods employed and a comparison of results and method performance considerations are presented.

Field and laboratory analyses from Umatilla and SUBASE Bangor data were used to

compare the accuracy, feasibility, strengths, and weaknesses of five on-site analytical methods for TNT and three methods for RDX in ground water, and to determine the effect of ground water parameters (nitrates, humics, turbidity, etc.) on these methods. The field demonstration was conducted to provide performance data and a preliminary economic evaluation for future long-term explosives ground water remediation efforts throughout the U.S. In addition to providing field analytical data for general use, results from this project will be used to guide appropriate selection of methods for explosives ground water remediation activities at Umatilla and SUBASE Bangor. Use of field analytical methods to determine explosive concentrations in water will substantially reduce the time interval between sample collection and the availability of analytical results and reduce laboratory analytical costs.

The study design, performance parameters, and economic evaluation were developed by U.S. Environmental Protection Agency (EPA) Region 10. Field analyses were conducted by personnel from Black & Veatch Special Projects Corp. (BVSPC) under contract to U.S. EPA Region 10, the Naval Research Laboratory (NRL) Center for Bio/Molecular Science and Engineering (CBMSE), and the U.S. Army Corps of Engineers Cold Regions Research and Engineering Laboratory (CRREL). CRREL personnel also conducted laboratory analyses of ground water and leachate samples utilizing EPA SW-846 Method 8330. BVSPC conducted field analyses utilizing several commercially-available on-site analytical methods. CRREL developed the preconcentration step utilized in the colorimetric field analytical procedures performed by BVSPC and was present during field activities at Umatilla and SUBASE Bangor to provide technical

guidance. NRL CBMSE personnel developed the emerging biosensors methods for explosives analysis and were present at Umatilla and SUBASE Bangor to evaluate the field application of these methods [1].

BACKGROUND

Sites with explosives-contaminated ground water or surface water exist in a number of environmental settings. The objective of this field demonstration was to evaluate the on-site analytical methods at differing environmental conditions at Umatilla and SUBASE Bangor.

Table 1 shows a number of relevant waste disposal, chemical, geological, and hydrogeological conditions of these sites.

Umatilla Army Depot Activity

In 1941 Umatilla Army Depot Activity was established as an Army ordnance depot for the storage and handling of munitions. From the 1950s until 1965 Umatilla operated an onsite explosive washout plant that processed munitions to remove and recover explosives. Flushing and draining the explosive washout system was a standard procedure during plant operation. Waste water from this procedure was discharged through an open metal trough into two unlined infiltration basins known as the Explosive Washout Lagoons.

The Explosive Washout Lagoons were characterized as a potentially hazardous site in the initial installation assessment. In 1981 an approximate 45-acre plume of RDX was identified in the shallow ground water aquifer, apparently resulting from discharges to the lagoons. Subsequent investigations confirmed the presence of explosives in the soil and ground water. In the summer of 1994, TNT and RDX contaminated soil was excavated from the lagoon area and is

currently undergoing bioremediation treatment via composting. Ground water remediation will be conducted through an extraction and treatment system using a granular activated carbon (GAC) treatment unit. Treated ground water will then be re-infiltrated back into the shallow aquifer. A portion of the re-infiltration will occur through subsurface soils at the original Explosives Washout Lagoons to flush residual explosives from the vadose zone between the bottom of the excavated lagoon and the top of the shallow aquifer. Additional infiltration galleries on the perimeter of the contamination plume will also be used to enhance remediation during the expected 27-year operation of the treatment system.

TNT is relatively immobile when compared to RDX. TNT concentrations in ground water were highest (3,000 µg/l) near the lagoons and rapidly decreased a short distance from the lagoons. Therefore, based on relative mobility and monitoring well placement, there was no opportunity to collect samples which contained mid-range TNT concentrations (50 to 500 µg/l).

Consequently, one-half order of magnitude serial dilutions were prepared for samples from two monitoring wells which contained high TNT concentrations. Conversely, RDX is more mobile than TNT in ground water. Near the lagoons TNT and RDX concentrations are comparable. RDX concentrations further from the lagoons are higher than TNT concentrations. Consequently, the RDX contaminant plume is relatively large in areal extent.

Umatilla ground water also contains relatively high levels (8,000 to 40,000 µg/l) of nitrates. One of the objectives of the field analytical study was to determine the effect, if any, of nitrate concentrations on the methods tested. Serial dilutions were prepared with water collected from a Umatilla background well to avoid diluting the concentration of nitrates in the ground water samples. Analyses indicated that nitrate levels in the background well were comparable to nitrate levels in ground water sampling wells. By using background well water for dilutions, the validity of the analysis to determine the effect of nitrates on the field screening results was not

TABLE 1. SITE CONDITIONS FOR ON-SITE ANALYTICAL METHODS.

Parameter	Umatilla	Bangor
Waste disposal	Lagoon	Lagoon, OB/OD ^a
Primary analytes	TNT, RDX	TNT, RDX
Interfere/cross react	TNB ^b , HMX ^c	TNB ^b , HMX ^c , AmDNTs ^d
Nitrates	High	Low - Mod
Turbidity	Low	Mod - High
Humics	Low	High
Surface geology	Sandy	Loam
Hydro-geology	Fluvial/alluvial	Glacial till
Climate	Semi-arid, extreme temps	Wet, moderate temps

^aopen burn/open detonation (OB/OD)

^b1,3,5-trinitrobenzene (TNB)

^coctahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)

^d2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene (AmDNTs)

compromised.

Naval Submarine Base Bangor

SUBASE Bangor is currently an active military installation serving the Pacific Naval Submarine Fleet and associated Navy ships. Site F and Site A are inactive former military munitions sites currently undergoing remediation. Site F is a waste water lagoon and overflow area formerly used for the disposal of waste water generated during ordnance demilitarization at a neighboring munitions processing facility. The site was actively used between 1957 and 1973, during which time waste water was discharged from the segregation facility directly into the disposal area through a drain line. After 1973, waste water was collected in 55-gallon drums and delivered to the SUBASE Bangor liquid waste incinerator plant. TNT and RDX have been detected at concentrations above risk-based ground water cleanup levels in samples collected at the site. Six extraction wells were installed downgradient of the lagoons to pump contaminated ground water into a treatment system. Ground water is treated by filtration through a GAC unit. Treated water is reinjected into the aquifer.

During past operations, explosive-contaminated sediments that accumulated in the waste water lagoon at Site F were removed and transported to Site A for burning and disposal. Existing soil at Site A contains levels of TNT and RDX above risk-based cleanup criteria. The contaminated soil has been contained in a lined basin and is currently undergoing water flushing to remove TNT and RDX. Leachate from the contaminated soil flushing is collected and treated in a GAC unit. At the SUBASE Bangor site, individual ground water samples were collected directly from all six of the extraction wells at Site F. Ground water

samples were also collected from the combined flow of all six extraction wells. All combined flow samples were collected from sampling ports before and after initial particulate filters, upstream of the GAC treatment unit. Two leachate samples were collected at Site A. The first sample was collected from the primary sump area and the second sample from within the treatment plant, after the initial particulate filter, upstream of the GAC treatment unit. One-half order of magnitude serial dilutions were prepared for both leachate samples to obtain low, high, and mid-range contaminant concentrations. The leachate sample collected from the sump area contained lower TNT and RDX concentrations than anticipated which may have been due to recent rainfall. Serial dilutions utilized untreated leachate from Site A.

METHODS

Eight separate on-site analytical methods were used to analyze original ground water and leachate samples, serial dilutions, and standards for TNT, RDX, 1,3,5-trinitrobenzene (TNB), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). Three types of on-site analytical methods were evaluated: 1) colorimetric, 2) kit-type immunoassay, and 3) biosensors. Published or experimentally-reported detection limits for the methods are shown in Table 2. The target detection limits for on-site analytical methods are the EPA Drinking Water Lifetime Health Advisory (HA) levels of 2 µg/l for TNT and RDX [2, 3]. Laboratory analysis for comparison was conducted using reverse phase high performance liquid chromatography (HPLC).

Colorimetric methods measure colored reaction products formed when nitroaromatic and nitramine compounds are

reacted with alkali or acidic solutions. The operator can visually determine the presence of various compounds by the color development of the extract. The absorbance at a specified wavelength is measured and correlated to the compound concentration. The CRREL-EnSys methods are colorimetric methods.

Kit-type immunoassay and biosensor methods utilize the ability of antibodies to selectively bind to a primary target analyte present in low concentrations in a complex matrix. For immunoassay methods, the sample, an enzyme conjugate of TNT or RDX, and particles with antibodies specific to TNT or RDX attached are mixed. The enzyme conjugate, and any TNT or RDX in the sample, compete for antibody binding sites on the particles. The presence of the primary target analyte (TNT or RDX) is detected by adding an enzyme substrate and a chromogen. The enzyme conjugate bound to the target compound antibody catalyzes the conversion of the enzyme substrate/chromogen mixture to a colored product. Since the enzyme conjugate was in competition with the primary target analyte in the sample for the antibody sites, the color developed is inversely proportional to the concentration of the target compound in the sample. DTECH and Ohmicron are kit-type immunoassay methods.

Biosensor methods also utilize the ability of

antibodies to selectively bind to a primary target analyte present in a water sample. Biosensors consist of a biological recognition element (i.e., labeled antibodies) in contact with a physical transducer, such as a fluorimeter or a photodiode [4, 5]. The NRL Continuous Flow Immunosensor (CFI) and Fiber Optic Biosensor (FOB) are biosensor methods.

Interference/cross reactivity

One of major differences between colorimetric and immunoassay-based methods is the response of the methods to secondary target analytes. For colorimetric methods, interference is defined as the positive response of the method to secondary target analytes chemically similar to the primary target analyte. Colorimetric methods have 100% interference for compounds within the same compound class (i.e., nitroaromatics or nitramines) and remain constant throughout the concentration range of the method. For the colorimetric TNT method, the primary target analyte is TNT and the secondary target analytes are other nitroaromatics such as TNB, 1,3-dinitrobenzene (DNB), dinitrotoluenes (DNTs), methyl-2,4,6-trinitrophenylnitramine (tetryl), etc. For the RDX colorimetric method, the primary target analyte is RDX and the secondary target analytes are other nitramines such as HMX and nitrate esters such as pentaerythritol tetranitrate (PETN). For immunoassay-based methods, cross reactivity is defined as the positive response of the method to secondary target analytes chemically similar to the primary target analyte. Cross-reactivity occurs when the antibody recognizes compounds that are similar in structure to the primary target analyte. Cross reactivity for kit-type immunoassay and biosensor methods is not 100% for compounds within the same

TABLE 2. METHOD DETECTION LIMITS.

Method	Analyte Conc. (µg/l)	
	TNT	RDX
CRREL/EnSys	0.9	3.8
DTECH	5	5
Ohmicron	0.07	--
NRL CFI	20	20
NRL FOB	20	--

compound class (i.e., nitroaromatics or nitramines) and is not constant throughout the concentration range of the methods. In addition, the cross reactivities for all immunoassay-based methods are not the same and are based on the antibodies used to develop the specific method.

TNB and HMX were the most commonly occurring co-contaminants with TNT and RDX at the test sites. TNB is reported to cause 100% additive, or positive interference, for results in the TNT colorimetric on-site analytical method [6]. HMX is 100% additive to the colorimetric RDX on-site analytical method [7]. Immunoassay-based methods exhibit TNB cross-reactivity with TNT that varies with the concentration of TNT and TNB in the sample. DTECH reported a TNB cross-reactivity of 23% for the midpoint of the TNT test range. Ohmicron reported a TNB cross reactivity of 65% for the midpoint of the TNT detection range. TNB is a known interferant in both the NRL biosensor methods; however, the percent cross reactivity has not been quantified. DNB, 2,4-dinitrotoluene (2,4-DNT), 2-amino-4,6-dinitrotoluene (2AmDNT), 4-amino-2,6-dinitrotoluene (4AmDNT), tetra, and 2,4-dinitroaniline are also known to affect immunoassay TNT tests; however, both the concentrations and cross-reactivity of these compounds are relatively low, and they were not included in the cross-reactivity evaluation. DTECH reports a HMX cross reactivity of 3% at the midpoint of the RDX test range. High concentrations of HMX may cross-react with the NRL CFI RDX method; however, this cross reactivity has not yet been quantified.

CRREL-EnSys methods

EnSys test kits are commercially-available colorimetric methods developed for the detection of TNT and RDX in soil [6, 7]. Additional sample preparation is required to utilize the EnSys tests for ground water samples. A TNT and RDX preconcentration step, which uses a solid phase extraction (SPE), has been developed by CRREL for this purpose [8]. The SPE preconcentration step is required for the colorimetric analysis of TNT and RDX in ground water. The use of the CRREL preconcentration step in connection with the EnSys field analytical method is referred to as the CRREL-EnSys Method.

CRREL preconcentration step

The CRREL SPE preconcentration method passes a 2 liter volume of sample through two membranes. Jenkins, *et al.*, found that any TNT in the sample will be completely retained on the top membrane [8]. After the sample passes through the membrane stack, the amount of RDX retained on the bottom membrane will be approximately equal to RDX retained on the top membrane. The acetone extract from the top membrane will contain RDX and TNT. Based on an evaluation performed by Jenkins, the presence of RDX in the sample extract does not interfere with TNT colorimetric tests [6]. The extract from the bottom membrane can be used for accurate RDX testing because all TNT has been completely retained in the top membrane.

In consultation with CRREL, modifications were made to this procedure during analysis at Umatilla and SUBASE Bangor. One deviation at both sites involved the elimination of the glass filter from the standard preconcentration apparatus. The glass filter was unnecessary for most samples due to the overall low turbidity of

the ground water samples collected from both sites. If a turbid sample was encountered, then a glass filter was placed on the preconcentration apparatus and the sample was filtered and collected in the vacuum flask. The glass filter was then removed and discarded. The filtered sample was collected in a clean glass beaker and the apparatus was reassembled with the standard membrane stack in place. The filtered sample was then processed according to the SPE preconcentration procedure. The glass filter decreased the preconcentration time for turbid samples by reducing membrane particulates clogging.

An additional change to the published procedures involved removing the buildup of nitrates from the membrane stack. High concentrations of nitrates are present in the ground water at Umatilla and nitrates interfere with EnSys RDX analysis. Nitrate interference can be minimized through the use of an ion exchange resin. The resin removes the nitrates from the extract prior to EnSys analysis. A second nitrate removal technique involves rinsing the membrane stack with deionized water after the sample has been filtered, but prior to extracting RDX with acetone. This technique removes residual nitrate containing water from the membranes. BVSPC used this second nitrate removal method. Membranes were rinsed with 10 ml of deionized water prior to elution of the RDX with acetone.

EnSys TNT test method (EPA SW-846 Method 8515)

Extract obtained from the top filter in the CRREL preconcentration step was analyzed using the EnSys TNT test method (EPA SW-846 Method 8515). EnSys TNT method is designed for soil samples; therefore, concentration calculations and detection limits were based on Jenkins, *et al.*, rather

than on the EnSys TNT soil method [8]. The initial absorbance is multiplied by two and subtracted from the final absorbance to eliminate background absorbance. EnSys recommends subtracting four times the initial absorbance to eliminate background interference. However, a factor of two was experimentally determined by Jenkins to be sufficient [6].

In some field analytical applications, it may be important to know more than just the concentration of TNT in a sample. The color development of the extract in colorimetric tests can give the operator an indication of what type of compounds are present in the media being tested. In general, TNT and TNB turn the extract red, tetryl turns the extract orange, DNB turns the extract purple, 2,4-DNT turns the extract blue, and 2,6-DNT turns the extract pink after addition of the TNT indicator solution.

EnSys RDX test method (EPA SW-846 Method 8510)

Extract obtained from the bottom filter in the CRREL preconcentration step was analyzed using the EnSys RDX test method (EPA SW-846 Method 8510). The EnSys RDX method is designed for soil samples; therefore, concentration calculations and detection limits were based on Jenkins, *et al.*, rather than on the EnSys RDX soil method [8].

DTECH TNT and RDX methods (EPA SW-846 Methods 4050 and 4051)

DTECH TNT and RDX immunoassay methods can be used for both soil and water. The water detection range without dilutions is from 5 to 45 µg/l for TNT and RDX [9, 10]. DTECH will provide dilution instructions for concentrations above this

range. DTECH results can be obtained in two ways. When a color chart is used, the reference color from the test is matched to a reference color on the chart. When the reference colors match, the sample color is then compared to the color chart to determine the concentration range. However, the colors printed on the chart tend to have a gray tint and do not effectively match the color of the test, creating a high degree of subjectivity.

The alternative method for obtaining DTECH results involves using the DTECHTOR. The DTECHTOR is a reflective photometer which can be set to read the absorbance of the reference and sample colors. When the reference absorbance reaches a range from 220 to 250 for TNT and a range from 320 to 350 for RDX, the test absorbance value is read. The DTECHTOR will display the percent difference between the reference and sample colors, which corresponds to a specific concentration range provided by DTECH. Utilizing the DTECHTOR eliminates the subjectivity of the visual test. BVSPC utilized the DTECHTOR during field analysis. In an effort to obtain an actual concentration for comparison purposes, BVSPC assumed a linear correlation between the DTECHTOR measurement and the associated concentration range. In this way, the DTECHTOR value was used to derive an estimated concentration. The estimated concentration was used to determine the accuracy of the results.

Ohmicron TNT method

Ohmicron's TNT RaPID Assay can be used for the determination of TNT in water and soil [11]. Ohmicron does not currently produce an RDX field analytical method. The method detection limit for TNT in water is 0.07 $\mu\text{g/l}$. A control solution of 2.0 $\mu\text{g/l}$

TNT is included in the Ohmicron kit and should be analyzed with every test batch. Four standards at 0.0 $\mu\text{g/l}$, 0.25 $\mu\text{g/l}$, 1.0 $\mu\text{g/l}$, and 5.0 $\mu\text{g/l}$ concentrations should be analyzed. A replicate analysis should be conducted for all samples, standards, and the control. The relationship between RaPID Analyzer (analyzer) absorbance values and the concentration of TNT in samples can be calculated manually or determined automatically by inputting specific parameters in to the analyzer. To construct the calibration curve manually, the mean absorbance value for each of the standards (%B) must be calculated and divided by the mean absorbance value for the zero standard (B0). The resulting value (%B/B0) should be plotted on the vertical axis of logarithmic graph paper versus TNT concentration ($\mu\text{g/l}$) on the horizontal axis. Calculated values of %B/B0 for the samples will yield TNT concentrations ($\mu\text{g/l}$) by using the standards calibration curve.

The analyzer operating manual provides detailed instructions for inputting parameters into the instrument such that a calibration curve, based on the standard concentrations, can be automatically calculated and stored. Once the curve is stored in the analyzer, all readings taken from the analyzer will be concentrations based on interpolation from the curve, displayed in $\mu\text{g/l}$. The upper concentration limit of the TNT water test range is 5.0 $\mu\text{g/l}$. Sample concentrations above this limit must be diluted. Analyzer results for diluted samples must be multiplied by the dilution factor. Calibration curves were calculated automatically by the analyzer for all Umatilla and SUBASE Bangor samples.

NRL TNT and RDX Continuous-Flow Immunosensor

The NRL Continuous Flow Immunosensor (CFI) is an antibody-based biosensor capable of detecting low molecular weight molecules in aqueous solutions [12]. TNT or RDX antibodies are immobilized onto a solid support matrix that is saturated with a fluorescent labeled antigen. The support matrix is then placed in a disposable laboratory column. A peristaltic pump is used to pump an aqueous buffer solution through the column. Sample injection is facilitated by a sample injector line located upstream of the column. Samples are prepared with a buffer solution prior to injection into the system. A fluorimeter is located downstream of the column. When a sample containing TNT or RDX is introduced, the TNT or RDX in the sample binds to the immobilized antibody, causing some of the labeled antigen to be displaced. The labeled antigen is detected downstream in the fluorimeter, resulting in a positive signal. The intensity of the fluorimeter signal is proportional to the concentration of TNT or RDX in the sample. The fluorimeter signal is recorded and analyzed by a signal integrator/laptop computer. All of the solutions tested by the NRL CFI contained either the sample or the control water. The fluorimeter readings recorded four minutes after injection are compared for all samples.

NRL TNT Fiber-Optic Biosensor

The Fiber-Optic Biosensor (FOB) method for the detection of TNT is based upon a competitive immunoassay using a fluorescent dye as the reporter molecule [13, 14]. Fluorescently labeled TNB is used as the competitor for the competitive immunoassay on the surface of an optical probe. The labeled TNB is exposed to an antibody-coated optical fiber for four minutes, generating a specific signal that

corresponds to the 100% or reference signal. The 100% or reference signal is defined as the signal change associated with the labeled TNB alone. Inhibition of this signal is observed when TNT is present in a sample. The percent inhibition observed is proportional to the TNT concentration in the sample. A 100% signal value is determined both before and after running the sample in order to normalize for the gradual decrease in antibody activity.

For the Umatilla and SUBASE Bangor project, the NRL FOB was analyzed using two different test solution concentrations to determine which concentration would yield optimal results. The first test solutions contained 20% sample and 80% water and buffer solution and is referred to as fiber optic (20%). Test solutions containing 85% sample and 15% buffer solution were also analyzed and referred to as fiber optic (85%). A standard curve was constructed based on the TNT standards. Using this standards curve, sample results reported as percent inhibition were converted to ng/ml ($\mu\text{g/l}$). Accuracy for the 85% sample was higher and is reported in this paper.

Laboratory analysis (EPA SW-846 Method 8330)

Splits of all samples were shipped to the CRREL laboratory for EPA SW-846 Method 8330 high performance liquid chromatography (HPLC) explosives analysis utilizing the direct inject method for samples above 20 $\mu\text{g/l}$ [15, 16]. NRL CBMSE also performed Method 8330 analysis on splits from the standards and some of the samples. TNT, RDX, TNB, and HMX results were determined by CRREL and by NRL for a portion of the data set. Standard analytical reference materials (SARMs) of TNT, RDX, TNB, and HMX were obtained from the U.S. Army Environmental Center. Standards

contained various predetermined concentrations of TNT, RDX, TNB, and HMX. Standards were used to calculate a response factor for the CRREL-EnSys method, to determine if TNB and HMX act as positive interference/cross reactivity for TNT and RDX, respectively, and to provide laboratory and on-site method analyses checks. All environmental samples were also analyzed by a commercial laboratory for nitrate/nitrite using EPA Method 353.2 [17].

RESULTS

The CRREL SW-846 Method 8330 results were used as a baseline to evaluate the accuracy of the TNT and RDX on-site analytical methods. The results from the two sites are evaluated separately because of the different environmental settings at each site. Umatilla is in a relatively arid setting with minimal soil development in granular strata, while SUBASE Bangor is in a relatively wet climate with soils containing a high organic content. The aquifer sampled at Umatilla consists primarily of flood plain gravels. Ground water at the explosives washout lagoons have high nitrate concentrations and low turbidity. SUBASE Bangor hydrogeology consists of fluvial/glacial deposition. Ground water and leachate from SUBASE Bangor tend to have relatively high organic content and higher turbidity.

Accuracy

Accuracy is a measure of bias in the testing and analyses procedures. The closer a measured value is to the true value, the more accurate the measurement. For comparison of on-site analytical results, Method 8330 concentrations were considered to be the “true value” or baseline concentration. The accuracy of on-site analytical results was

estimated using two separate methods, linear regression analysis and relative percent difference (RPD). The DTECH method provides a concentration range. To obtain an actual DTECH concentration, a linear correlation between the DTECHTOR measurement and the concentration range was assumed. The DTECHTOR measured value was used to generate an estimated concentration. The derived estimated concentration was used in linear regression and RPD calculations.

Linear regression analysis

The first method used linear regression analysis of the on-site method concentration versus the Method 8330 concentrations. Overall quality of the data can be evaluated using linear regression. Under ideal conditions, true accuracy would have a slope of 1.0 and a correlation coefficient (R) of 1.0. A slope less than 1.0 indicates that on-site method results are less than Method 8330 concentrations. A slope greater than 1.0 indicates that on-site method results are greater than Method 8330 concentrations. The closer the R value is to 1.0, the better the correlation is to the best fit line, indicating less scatter in the data. Linear regression parameters of slope, correlation coefficient (R), and number of samples (N) for a zero intercept line are shown in Table 3.

Relative percent difference

The second method compared the relative percent difference (RPD) between Method 8330 concentrations and the results of each on-site analytical method. The RPD between Method 8330 concentrations and on-site analytical concentrations was calculated with the following equation:

Relative Percent Difference (RPD)

$$RPD = \frac{(DF - DL)}{\frac{DF + DL}{2}} \times 100,$$

where DF = field method concentration and DL = lab method concentration.

Based on this equation, the smaller the absolute RPD, the closer the on-site analytical result and Method 8330 concentration, the more accurate the on-site analytical method. RPD mean and median results and number of samples (N) are shown in Table 4.

CONCLUSIONS

The accuracy of the methods varied depending on the site-specific ground water

water quality parameters. No single field analytical method outperformed the other methods in all of the comparisons. Ground water at Umatilla tends to have high nitrate concentrations and low turbidity. Ground water and leachate at SUBASE Bangor tends to have relatively high organic content and higher turbidity.

Colorimetric TNT accuracies were similar at both sites. Colorimetric RDX results were slightly more accurate at SUBASE Bangor than at Umatilla. Nitrates are known to affect the CRREL-EnSys RDX analysis. A nitrate removal step was implemented at both sites. However, residual nitrates may have remained on the membranes after the nitrate removal step for Umatilla samples. Residual nitrates which remain on the

TABLE 3. LINEAR REGRESSION ANALYSIS.

Umatilla Army Depot Activity, Oregon TNT—Regression Parameters			
Method	Slope	R	N
CRREL/EnSys	1.5	0.97	15
DTECH	2.0	0.88	15
NRL CFI	1.4	0.69	11
NRL FOB	1.6	0.91	12
RDX—Regression Parameters			
Method	Slope	R	N
CRREL/EnSys	0.86	0.86	23
DTECH	1.2	0.96	23
NRL CFI	0.98	0.71	20
Naval Subase Bangor, Washington TNT—Regression Parameters			
Method	Slope	R	N
CRREL/EnSys	1.1	0.994	9
DTECH	11.0	0.994	7
Ohmicron	1.1	0.98	7
NRL CFI	1.4	0.82	7
NRL FOB	0.89	0.64	8
RDX—Regression Parameters			
Method	Slope	R	N
CRREL/EnSys	0.97	0.92	12
DTECH	2.0	0.60	12
NRL CFI	0.72	0.64	12

TABLE 4. RELATIVE PERCENT DIFFERENCE RESULTS.

Umatilla Army Depot Activity, Oregon TNT—Relative Percent Difference			
Method	Mean RPD	Median RPD	N
CRREL/EnSys	66.0	44.9	15
DTECH	63.9	47.8	15
NRL CFI	74.2	29.6	11
NRL FOB	33.0	25.1	12
RDX—Relative Percent Difference.			
Method	Mean RPD	Median RPD	N
CRREL/EnSys	32.8	27.4	23
DTECH	53.1	32.2	23
NRL CFI	26.2	18.7	20
Naval Subase Bangor, Washington TNT—Relative Percent Difference			
Method	Mean RPD	Median RPD	N
CRREL/EnSys	58.3	63.3	9
DTECH	143.0	152.5	7
Ohmicron	80.4	92.4	7
NRL CFI	52.3	38.3	7
NRL FOB	106.6	115.6	8
RDX—Relative Percent Difference			
Method	Mean RPD	Median RPD	N
CRREL/EnSys	21.0	21.4	12
DTECH	67.0	56.3	12
NRL CFI	30.6	22.9	12

membrane would be extracted with the RDX and consequently would affect the accuracy of the RDX analysis. The overall accuracy of the CRREL-EnSys RDX results was acceptable, as indicated by linear regression analyses and RPDs. Based on these results, the nitrate removal step is recommended, particularly for use at sites which contain high nitrate concentrations.

Generally, immunoassay-based field analytical methods for TNT and RDX were more accurate at Umatilla than at SUBASE Bangor. Due to the nature of the immunoassay and biosensor methods, there is a potential for interference from organic material and suspended particulates. These materials may compete with explosives compounds for binding sites. The binding of organics and suspended particulates would generally lead to biased high TNT or RDX results for reverse coloration methods.

The majority of the TNT RPD values for both sites were positive and the linear regression slopes were greater than 1.0, indicating that TNT on-site analytical results tended to be higher than the Method 8330 TNT results. This positive bias could be due to TNB interference/cross reactivity. In the combined TNT data set, the CRREL-EnSys method and NRL CFI had similar accuracy, followed by the NRL FOB, Ohmicron, and DTECH methods.

For both Umatilla and SUBASE Bangor, there was a relatively even distribution between positive and negative RDX RPDs for the CRREL-EnSys and DTECH methods, indicating no discernible tendency for the on-site analytical method to be higher or lower than the Method 8330 RDX results. The NRL RDX CFI biosensor results tended to be lower than Method 8330 RDX results. For the combined RDX data set, the CRREL-EnSys method and NRL CFI

methods showed similar accuracy, followed by DTECH.

In general, all the on-site analytical methods performed better on RDX than TNT. This could be due, at least in part, to the concentrations of each compound encountered. RDX concentrations tended to be higher than TNT concentrations. Higher concentrations required dilutions to get results into the working range of the method. The results may be subsequently less affected by matrix interference.

PRELIMINARY ECONOMIC EVALUATION

A preliminary economic evaluation for a long-term ground water remediation program was based on a typical “pump and treat” system with a number of components [18, 19]. These include extraction wells piped into two 10,000- to 20,000-pound GAC units in series, and that treated ground water would be reinjected into the aquifer. Design flow rates for the systems are estimated between 500 and 1,500 gallons per minute. Sampling would be conducted weekly to bi-weekly at two or three locations (influent, between GAC units, and effluent) in the treatment system. This results in an estimated 50 to 150 samples per year, excluding individual extraction well samples and quality assurance samples. The treatment system would be expected to operate for 10 to 30 years at an estimated total remediation cost of \$5 to \$6 million.

Field analytical methods have three cost components including per sample consumables, initial equipment costs, and instrument costs. Table 5 shows these components for the eight methods evaluated. Figures 1 and 2 show the costs for conducting on-site analytical monitoring for TNT and RDX, and for TNT only,

excluding labor, for a two to ten year time period, based on a 100 sample per year average. For comparison, typical cost for EPA Method 8330 with 30 day turn around time is from \$250 to \$350 per sample.

RECOMMENDATIONS

Based on the results of this study, the CRREL-EnSys colorimetric TNT and RDX methods were selected for routine ground water monitoring at the Umatilla site based on several considerations. These include accuracy, precision, detection limits, ability to detect total explosives (i.e., nitroaromatics plus nitramines), ease of use, and the cost per sample. In addition, the NRL biosensor methods show considerable promise for continued development based on a number of factors. These include accuracy, analysis time, ease of use, lifecycle costs, substantial reduction in solvent, solid, and chemical wastes generated during analysis, and data integration capabilities. Further testing of the NRL biosensors will be conducted at both Umatilla and SUBASE Bangor in the future.

The primary use for these methods would be for influent and effluent monitoring for ground water and leachate treatment systems, which are projected to operate for a period of 10 to 30 years.

Site conditions are important when choosing a on-site analytical method. Site geology and ground water quality also affects which methods should be chosen. The immunoassay-based methods generally performed better at Umatilla than at SUBASE Bangor. SUBASE Bangor ground water has a higher organic content than Umatilla ground water. Organic material may cause non-specific binding during analyses which could decrease the accuracy of the immunoassay-based methods. The colorimetric method had similar results at both sites, indicating minimal affect of ground water quality on accuracy. However, a nitrate removal step was implemented for the colorimetric analyses. Factors such as the field location, access to electricity, and whether the instrument station will remain in a given area or be moved to various

TABLE 5. PRELIMINARY ECONOMIC EVALUATION.

Cost Items (\$)—TNT and RDX			
Method	Consume/Sample	Initial Equip.	Instrument
CRREL/EnSys	76.60	550	1600 ^a
DTECH	51.50	0	300 ^b
NRL CFI	8.00	800	20 K ^d
Cost Items (\$)—TNT Only			
Method	Consume/Sample	Initial Equip.	Instrument
CRREL/EnSys	37.10	550	1600 ^a
DTECH	25.75	0	300 ^b
Ohmicron	5.80	1,305	3985 ^c
NRL CFI	4.00	800	20 K ^d
NRL FOB	2.00	800	18 K ^e

^aHach DR2000 Spectrophotometer

^bEM Science Detector

^cOhmicron RPA-1 RaPID Analyzer

^dResearch International CFI Prototype

^eResearch International Analyte 2000 FOB

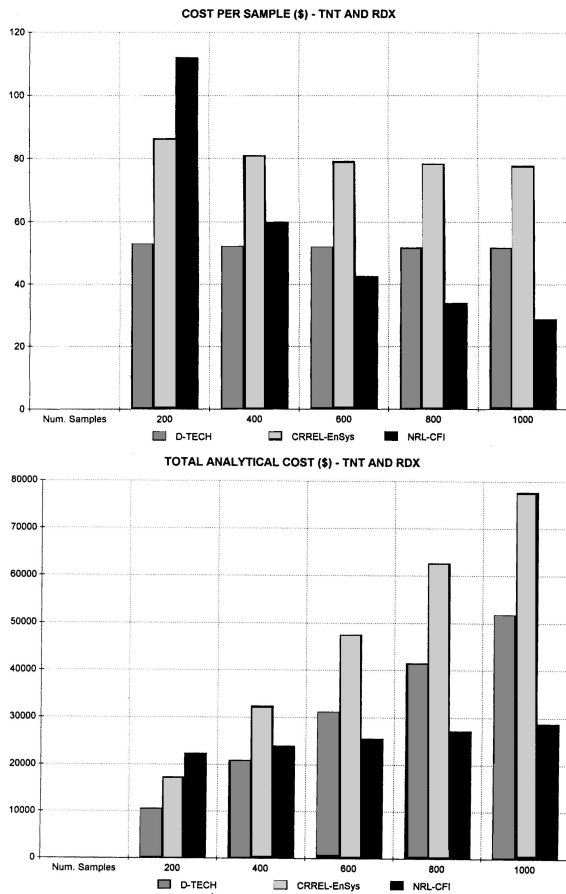


FIGURE 1. COST PER SAMPLE AND TOTAL ANALYTICAL COST(\$)—TNT AND RDX.

field location, access to electricity, and whether the instrument station will remain in a given area or be moved to various locations should also be considered.

The user must also determine which compounds are of concern at the site and for the project. Different on-site analytical methods have different levels of interference/cross-reactivity with other compounds. The data user must determine if there is a need to minimize (using immunoassay methods) or maximize (using colorimetric methods) the detection of other explosives-related compounds. If the project requires RDX analysis in addition to TNT analysis, then an on-site analytical method

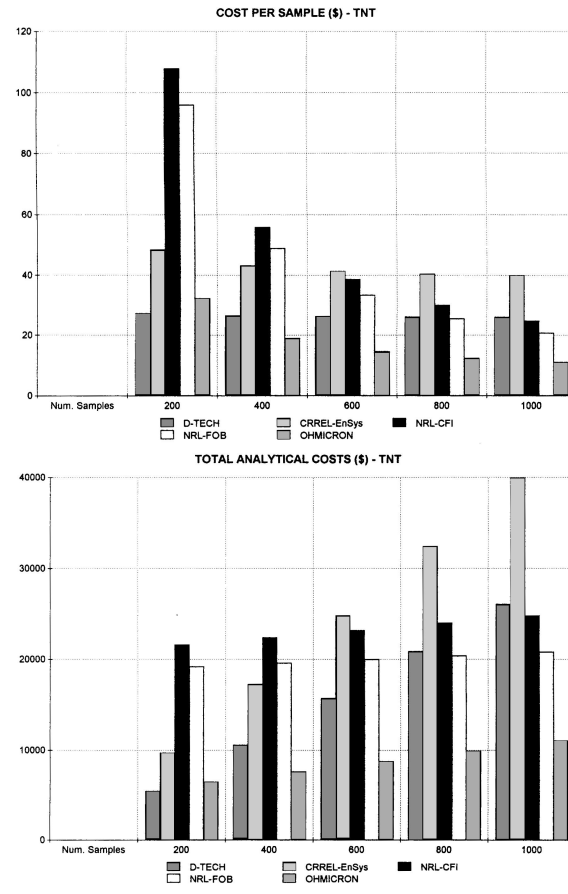


FIGURE 2. COST PER SAMPLE AND TOTAL ANALYTICAL COST(\$)—TNT ONLY.

that can analyze for both compounds should be used. The ultimate use of the data must be known when choosing an on-site analytical method.

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