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Field-portable Gas Chromatograph Mass Spectrometer (GC-MS) Unit for Semi-volatile Compound Analysis in Groundwater

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Abstract: This effort demonstrated the use of field-portable instrumentation for the quantification of munitions constituents in groundwater, without the need to ship water samples to a fixed analytical laboratory. The results indicate that similar reporting limits can be obtained using the field-portable instrument when coupled to solid phase extraction sample preparation, yet instrument stability at the low concentration range is an issue. The instrumentation was tested on 28 groundwater samples for a variety of analytes with concentrations ranging up to 3 orders of magnitude. Detection limits for the field instrumentation are generally below regulatory thresholds. Linear regression comparison of the field results to laboratory-based analysis suggest comparability between the techniques, with the slope of the regression for all analytes being between 0.8 and 1.2, except for TNB and RDX. The RDX field results were about 70% of the laboratory results on the average. The field method consistently exhibits a significant positive bias for TNB. The field and laboratory NB results were consistent in that both the field and laboratory methods reported non-detects.

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Acronyms

ATV	All-terrain vehicle
CIT	Cylindrical ion trap
COC	Compound of concern
DoD	Department of Defense
ECB	Environmental Chemistry Branch
EPA	Environmental Protection Agency
ERDC	Engineer Research and Development Center
GC-MS	Gas chromatograph-mass spectrometer
HASP	Health and safety plan
HBV	Hepatitis B virus
HIV	Human Immunodeficiency Virus
HPLC	High Performance Liquid Chromatography
HSO	Health and Safety Officer
LAAP	Louisiana Army Ammunition Plant
LAP	Loading, assembling, and packing
LC	Laboratory control
LCC	Life cycle costs
LCS	Laboratory control sample

LIMS	Laboratory Information Management System
LOD	Limit of detection
LTM	Low thermal mass
MAAP	Milan Army Ammunition Plant
MC	Munitions constituents
MDL	Method detection limit
MSD	Mass selective detector
MSL	Mean Sea Level
NB	Nitrobenzene
NIOSH	National Institute of Occupational Safety and Health
NPV	Net present value
NS	Net savings
OSHA	Occupational Safety and Health Administration
PAH's	Polycyclic aromatic hydrocarbons
PCB's	Polychlorinated biphenyls
PI	Principal Investigator
QA/QC	Quality assurance / Quality control
QSM	Quality Systems Manual
RDX	Hexahydro-1,3,5-trinitro-1,3,5 triazine
RPD	Relative percent difference

SHSO	Site Health and Safety Officer
SIM	Single ion monitoring
SOP	Standard Operating Procedures
SPE	Solid phase extraction
SPME	Solid phase micro extraction
SUV	Sport utility vehicle
SVOCs	Semi-volatile organic compounds
TNB	1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotoluene
UV	Ultra violet
1,3-DNB	1,3- dinitrobenzene
2,4-DNT	2,4-dinitrotoluene
3,4-DNT	3,4-dinitrotoluene

Preface

This study was sponsored by the Environmental Security Technology Certification Program (ESTCP), Arlington, VA, Dr. Jeff Marqusee, Executive Director, Project Number ER-0922. The principal investigator was Dr. Anthony J. Bednar, Research Chemist, Environmental Chemistry Branch (ECB), Environmental Processes and Engineering Division (EPED), Environmental Laboratory (EL), U.S. Army Engineer Research and Development Center (ERDC).

This report was prepared by Dr. Bednar, EP-C, ERDC-EL; Amber L. Russell, Badger Technical Services (BTS), Vicksburg, MS; and Dr. Thomas Georgian, U.S. Army Corps of Engineers, CEHNC-CX, Omaha, NE. The field studies were conducted by Dr. Bednar; Ms. Russell; Charolett A. Hayes, BTS, Vicksburg, MS; William T. Jones, EP-C, ERDC-EL; Dr. Robert A. Kirgan, USAEC, Fort Sam Houston, San Antonio, TX; and Dr. Phillip Tackett, FLIR Systems Inc., West Lafayette, IN. The statistical analyses were performed by Dr. Georgian. The authors gratefully acknowledge the technical assistance provided by ARCADIS employees with groundwater sampling at the Milan, TN site. The support of Jared C. Smith, BTS, with the analysis of the groundwater samples by HPLC is also gratefully acknowledged.

The report was reviewed by Susan E. Bailey, Research Environmental Engineer, Environmental Engineering Branch (EEB), Environmental Processes and Engineering Division (EPED), ERDC-EL, and Dan Farrar, Environmental Risk Assessment Branch, EPED, ERDC-EL.

IcX Griffin (Now FLIR Systems Inc.), West Lafayette, IN, developed the Griffin 400 and 450 gas-chromatograph mass spectrometers and provided technical assistance with the implementation of the instruments in the field.

The study was conducted under the direct supervision of Warren P. Lorentz, Chief, EPED, EL; and Dr. Beth C. Fleming, Director, ERDC-EL.

COL Kevin J. Wilson was Commander of ERDC. Dr. Jeffery P. Holland was Director.

Summary

Background

Periodic groundwater sampling is often required as part of a long-term monitoring program. Traditional sampling and analytical techniques require shipping multiple liters of water to fixed laboratories that perform regulatory-approved analytical methods. The typical analysis and data reporting time at most analytical laboratories can be up to 45 days, which delays vital information on contaminant concentrations being reported to the customer. Additionally, most sample holding times have been tested for a small set of environmental matrices where it is assumed that analyte concentrations will not change significantly if analyzed within this window, typically 7 to 40 days (Jenkins et al. 1995a, 1995b; Jenkins and Grant 1987). A field-portable Gas Chromatograph-Mass Spectrometer (GC-MS) alleviates these concerns.

Objectives of the demonstration

The objective of this demonstration was to 1) demonstrate the suitability of field analysis for a suite of contaminants of concern (semi-volatile munitions constituents), and 2) demonstrate the utility, comparability, and cost savings of groundwater analysis using the Griffin 450 GC-MS.

This effort was designed to demonstrate the advantages and limitations of field-portable analytical instrumentation for the detection and quantification of munitions constituents in groundwater, which eliminates the need to ship water samples overnight, under chain of custody, to a fixed analytical laboratory. Specifically, in-field test results of the Griffin 450 GC-MS were compared to traditional MC analysis using laboratory-based High Performance Liquid Chromatography with UV Absorbance detection following USEPA method 8330.

Technology description

Mass spectrometry (MS) analysis systems can provide valuable chemical information on almost any type of sample. Traditionally, MS has been confined to fixed-site laboratory analysis due to the size and fragility of the instruments typically employed for this application. Griffin has made

efforts toward miniaturization, enabling this technology to be brought to the field to perform analysis. The Griffin instruments use a cylindrical ion trap (CIT) as the mass analyzer; this device is a simplified geometry of the classic hyperbolic ion trap and therefore more easily miniaturized. The Griffin instruments also use a low thermal mass (LTM) gas chromatograph as the GC. With a smaller ion trap, the vacuum manifold becomes smaller, and the resulting pumping and power requirements are reduced. The LTM GC column eliminates the need for a convective oven, greatly reducing the size and power consumption compared to standard GC systems. These modifications to the instrument design all serve to decrease the size and weight of the instrument. Griffin has also worked to ruggedize the instrument, enabling transport into the field for on-site analysis. The improved electronic stability and sensitivity of the Griffin 450 provide higher quality data, especially in humid environments, compared to the previous Griffin 400 model GC-MS.

Demonstration results

The instrumentation was tested on 28 groundwater samples from two distinct field sites for a variety of analytes with concentrations ranging over 3 orders of magnitude. The compounds evaluated were: NB, 1,3-DNB, 2,4-DNT, TNB, TNT and RDX. Split groundwater samples were collected and analyzed for these compounds to compare the results from a field-portable GC/MS method to the results from a conventional fixed laboratory method. Detection limits for the field-portable instrumentation are sufficient to meet regulatory threshold levels, generally around 0.002 mg/L. Linear regression comparison of the in-field results to traditional laboratory-based analysis suggest comparability between the techniques, with the slope of the regression for all analytes being between 0.8 and 1.2, except for TNB and RDX. However, the slope of the regression for RDX is between 0.8 and 1.2 for all concentrations below 10 mg/L.

As all of the paired results for NB were non-detects, only a limited evaluation was possible. However, the NB results were consistent in that both the field and laboratory methods reported non-detects for NB for all of the split sample analyses. The field method for RDX possessed a negative bias relative to the fixed laboratory method and exhibited relatively large variability across all concentration ranges evaluated. The field results were about 70% of the laboratory results on average. Therefore, it is recommended that the field method be used to obtain only screening-level data for RDX. The field and laboratory results were essentially equivalent for

concentrations less than or equal to 0.3 and 0.2 mg/L for 1,3-DNB and 2,4-DNT, respectively. The comparison was limited by the relatively small data set owing to several non-detects, and the relatively small concentration range evaluated (about 0.01 – 0.1 mg/L). Results for TNT were reliable for screening only below a concentration of 0.05 mg/L; however, between 0.05 and 10 mg/L, results from the field and laboratory were equivalent. The field method consistently exhibits a significant positive bias for TNB ($F=1.5L$). There was a very strong correlation between the laboratory and field methods for concentrations greater than about 0.05 mg/L to the highest reported concentration, but the performance of the field method was relatively poor at smaller concentrations. The TNB field results > 0.05 mg/L would need to be adjusted for bias prior to being reported.

The results indicate that similar reporting limits can be obtained using the field-portable instrument when coupled to solid phase extraction (SPE) sample preparation, although instrument stability at the low concentration range can be an issue. Furthermore, the linear dynamic range is somewhat limited, as compared to HPLC analysis, for samples with high analyte concentrations.

The cost savings of the field method were found to be \$29,620.70/year, based on 12 week-long field trips per year, with a break-even point of 3.54 years.

Implementation issues

At this point, field-portable GC-MS appears to be suitable only for screening of RDX, due to significant scatter in the comparison to laboratory results across the concentration range tested. The regression line data demonstrate that the slope is within the 0.8 to 1.2 limit except for TNB and RDX. The TNB data are skewed somewhat by two samples with high concentrations. A similar effect is observed for RDX with one high concentration sample skewing the results. These samples reflect the linear dynamic range limitations of the current instrument when large sample preconcentration factors result from the SPE procedure. Additionally, deployment of the technology requires skilled labor at this point. Deployment of the technology to field sites is feasible for any site that has sufficient space and access for deployment traditional groundwater collection activities.

1 Introduction

This document describes the field deployment and operation of the Griffin 450™ GC-MS for the detection and quantification of munitions constituents (MCs) in groundwater.

1.1 Background

The long-term monitoring requirement for facilities often involves periodic sampling of groundwater for several years, even after activities have ceased. Traditional sampling and analytical techniques require shipping multiple liters of water to fixed laboratories that perform regulatory-approved analytical methods. The typical analysis and data reporting time at most analytical laboratories can be up to 45 days, which delays vital information on contaminant concentrations being reported to the customer.

Additionally, most sample holding times have been tested for only a small set of environmental matrices, and the assumption has been made that analyte concentrations will not change significantly if analyzed within this window, typically 7 to 40 days (Jenkins et al. 1995a, 1995b; Jenkins and Grant 1987). The use of a field-portable Gas Chromatograph-Mass Spectrometer (GC-MS) alleviates these concerns. While the ability to screen groundwater by direct sampling or Solid Phase Micro Extraction (SPME) has been tested, additional sample preparation and analysis options are desirable to ensure regulatory acceptable in-field quantitation. Although field-portable instrumentation has been successfully used previously in the analysis of volatile compounds (Jenkins et al. 1995a), it has not been extended to the analysis of semi-volatile analytes, such as explosives.

Gas chromatography with a mass selective detector (MSD) is an approved method for analysis of organic contaminants (EPA Method 8270). The Griffin 450 GC-MS instrument tested and produced by Griffin is capable of air and liquid sampling, directly or via an SPME fiber. The Cylindrical Ion Trap (CIT) technology used in this system allows for miniaturization of the mass analyzer, while still maintaining the high caliber of analysis associated with traditional quadrupole mass spectrometry. In addition, a shock mount platform is used to protect the pump and electronic components, allowing for transport to remote sites. This mass spectrometer allows for analysis and follow-up investigations, including the use of tandem mass spectrometry (MS/MS) capabilities to confirm the identity of contaminants, and

unknown compounds, present in the sample matrix. Unknown compounds have the potential to produce false positives when using non-selective detectors, such as UV absorbance.

1.2 Objective of the demonstration

The objective of this ESTCP demonstration was to 1) demonstrate the suitability of field analysis for a suite of contaminants of concern (semi-volatile munitions constituents), and 2) demonstrate the utility, comparability, and cost savings of groundwater analysis using the Griffin 450 GC-MS.

The research plan for this demonstration was to collect groundwater samples at the Louisiana Army Ammunition Plant (LAAP), in Minden, Louisiana and the Milan Army Ammunition Plant (MAAP) in Milan, Tennessee, using standard well purging and sampling methods (EPA Region 1, 1996), and analyze the samples 1) in-field utilizing the Griffin 450 and 400 GC-MS instruments, and 2) in the laboratory using HPLC (EPA method 8330B). The previous generation Griffin 400 GC-MS was used as a comparison to the Griffin 450. The following analytes were included in this demonstration: nitrobenzene (NB), 1,3-dinitrobenzene (1,3-DNB), 2,4-dinitrotoluene (2,4-DNT), 1,3,5-trinitrobenzene (TNB), 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazacyclohexane (RDX).

1.3 Regulatory drivers

EPA methods 8330B and 8095 are two standard analytical methods for explosives. These methods involve collecting approximately 1 L of water, shipping the sample to a laboratory, and use of solid phase extraction and concentration for sample preparation prior to analysis. These techniques use non-specific detectors; UV absorbance in the case of 8330B, and electron capture detection in the case of 8095. Because these methods have non-specific detectors, dual chromatography column confirmation is required for absolute analyte confirmation and quantitation. The use of GC-MS, which is also an accepted methodology (EPA Methods 8270 and 529) allows for the analytes to be detected and confirmed with only a single chromatographic separation due to the selectivity of the mass spectrometer. Additionally, by using a field-portable instrument, samples can be collected and analyzed in an expedited manner, removing the cost and delay associated with sample transport to a fixed laboratory.

2 Technology

This document compares the Griffin 450 GC-MS to the more traditional HPLC-UV explosives analysis following EPA method 8330B. The Griffin 450 GC-MS was also compared to the Griffin 400 GC-MS. The improved electronic stability and sensitivity of the Griffin 450 provided higher quality data, especially in humid environments, compared to the previous Griffin 400 model GC-MS.

2.1 Technology description

2.1.1 Description of the GC-MS

Typical MS analysis systems can provide valuable chemical information on almost any type of sample. Traditionally, MS has been confined to fixed-site laboratory analysis due to the size and fragility of the instruments typically employed for this application. Efforts have been made toward miniaturization, enabling this technology to be brought to the field to perform analysis. Griffin uses a CIT as the mass analyzer; this device is a simplified geometry of the classic hyperbolic ion trap and therefore more easily miniaturized. The Griffin GC-MS also uses a low thermal mass (LTM) gas chromatograph, as does the GC. With a smaller ion trap, the vacuum manifold becomes smaller, and the resulting pumping and power requirements are reduced. With the LTM GC column, the GC oven is removed and replaced by heat tape, decreasing the power requirements further.

These modifications to the instrument design all serve to decrease the size and weight of the instrument relative to a traditional bench-top GC-MS. Griffin has also worked to ruggedize the instrument, enabling transport into the field for on-site analysis.

2.1.2 Schematic diagram of the technology

The GC-MS system consists of a heated inlet, guard columns, LTM GC, a vacuum chamber, a CIT, a turbo molecular pump, a diaphragm pump, and system electronics. The inlet, guard columns, low thermal mass (LTM) GC and the vacuum chamber are shown in Figure 2.1. Additionally, a typical field setup for both the Griffin 400 and 450 is shown in Figure 2.2. The field extraction is performed on the setup in the front left corner of the field work area shown.

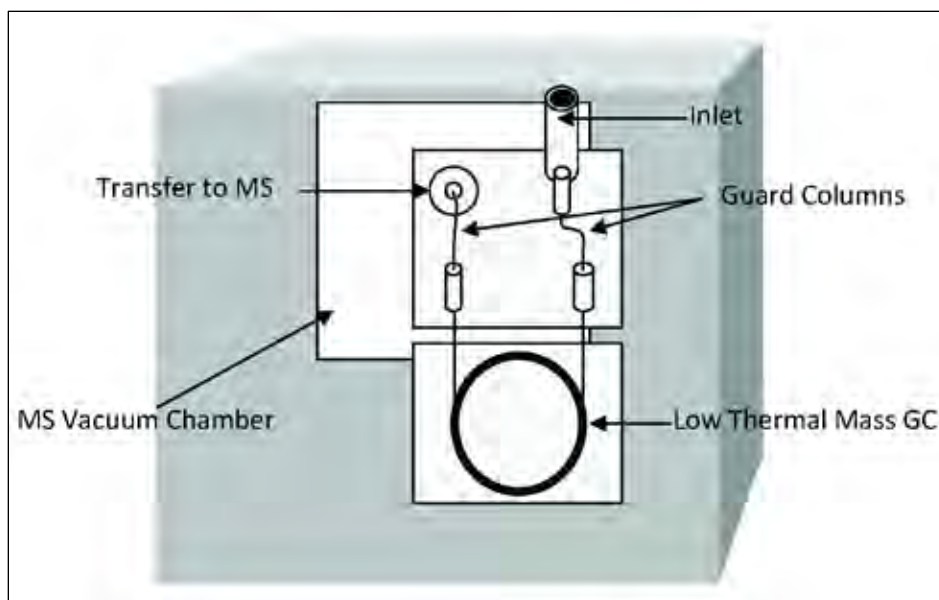


Figure 2.1. Components of the Griffin 450 GC-MS.



Figure 2.2. Field setup for the Griffin 400 (right) and 450 (left); extraction setup is shown in the front left.

2.1.3 Technology development

Existing research by the U.S. Army Engineer Research and Development Center (ERDC) has demonstrated the applicability of Griffin's 400 field-portable GC-MS to analyze munitions constituents (MC) in groundwater

(Russell et al. 2007, MacMillan and Splichal 2005, National Aeronautics and Space Administration (NASA) 2007, Bednar et al. 2009, Kirgan et al. 2008), specifically NB, 1,3-DNB, 2,4-DNT, TNB, TNT and RDX. Figure 2.3 provides structural representations of the compounds. The current demonstration leveraged this work, serving as a base for comparison.

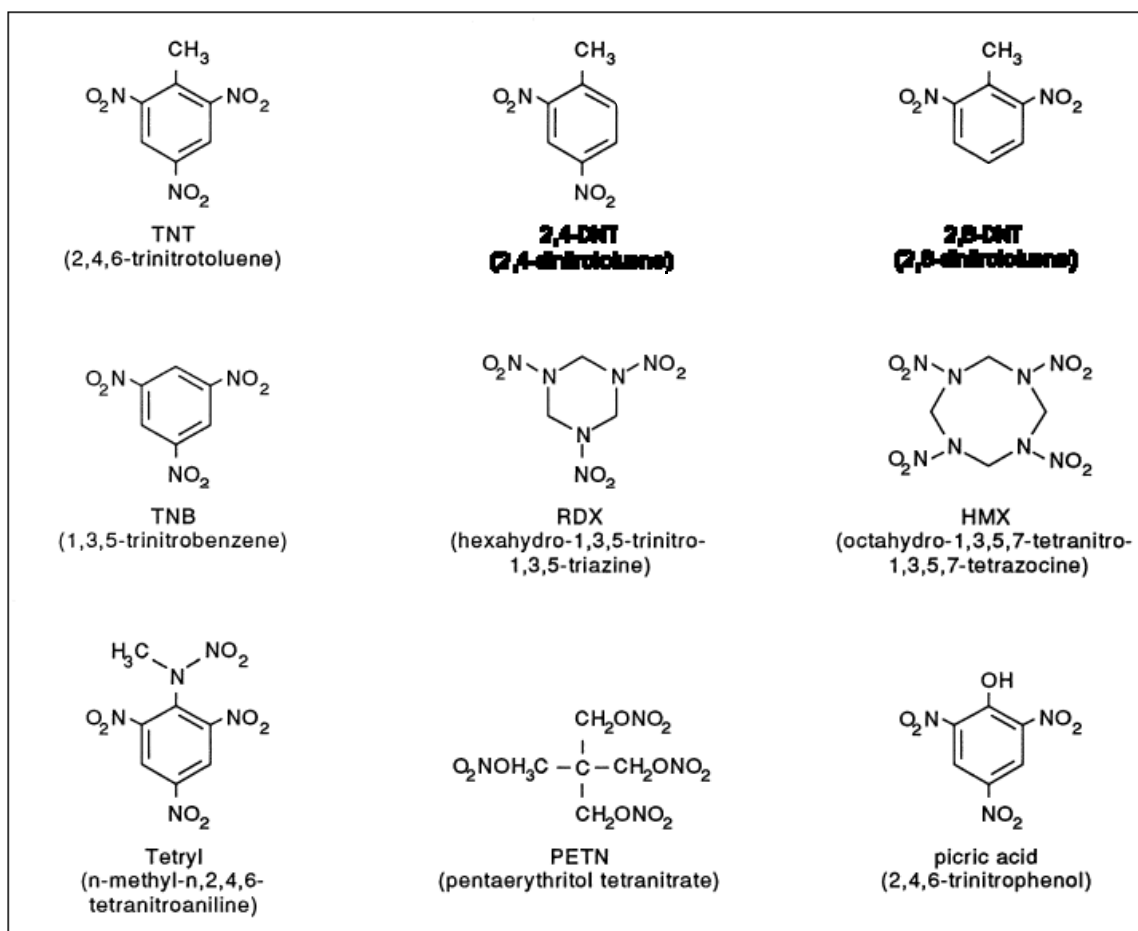
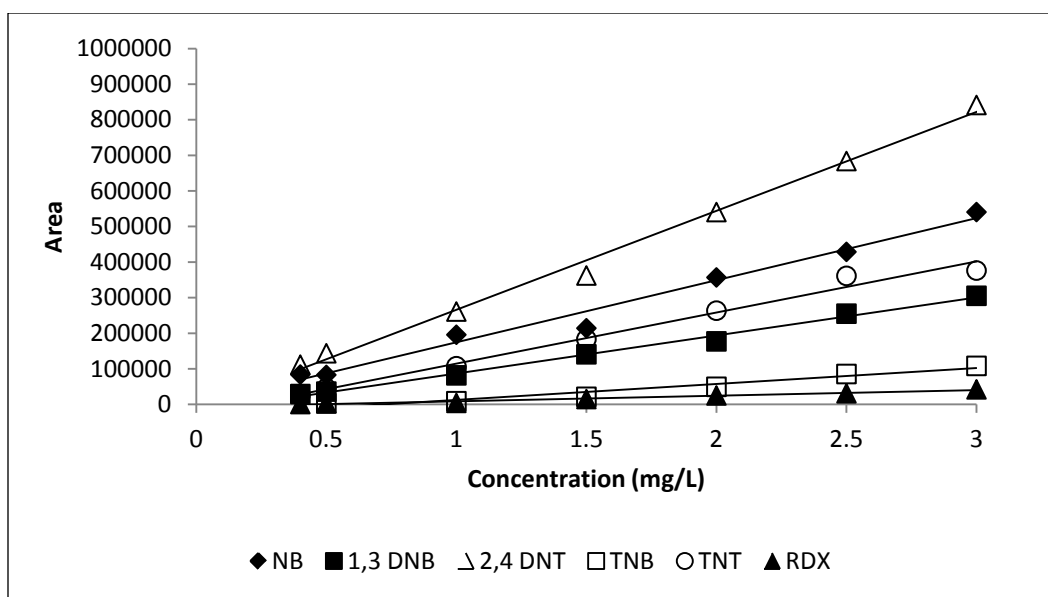


Figure 2.3. Structural representation of known MC present at LAAP.

2.2 Calibration of the Technology

The calibration for the Griffin GC-MS used mixed analyte standards with concentrations of 0.4, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 mg/L, each containing 5 mg/L of 3,4-DNT as an internal standard to correct for instrumental drift. Linear response functions were obtained for each analyte (Figure 2.4), and typically had correlation coefficients greater than 0.95. Solid phase extraction of groundwater samples between 1.56 and 10.9 µg/L fall within the GC-MS calibration range when a concentration factor of 320 is used.



*Calibration curve data were collected in the field at MAAP.

Figure 2.4. Calibration curves for NB, 1,3-DNB, 2,4-DNT, TNB, TNT and RDX.

Table 2.1. Calibration curve data parameters.

Analyte	Quantitation Mass Monitored (m/z)	Retention Time (minutes)	Calibration Curve*	R ²
NB	<u>123</u>	<u>1.43</u>	$C=(A-90.48)/174516.95$	<u>0.98</u>
1,3-DNB	<u>167</u>	<u>3.65</u>	$C=(A+19849.76)/106797.08$	<u>0.99</u>
2,4-DNT	<u>165</u>	<u>4.03</u>	$C=(A+12325.51)/278102.7$	<u>0.99</u>
TNB	<u>213</u>	<u>4.55</u>	$C=(A+32385.71)/44806.29$	<u>0.95</u>
TNT	<u>210</u>	<u>4.59</u>	$C=(A+29116.76)/143635.9$	<u>0.99</u>
RDX	<u>128</u>	<u>5.00</u>	$C=(A+7259.44)/15834.53$	<u>0.98</u>

*C is the concentration of the analyte and A is the area of the quantitation masses monitored.

2.3 Previous testing of the technology

Proof of Concept – Laboratory Tests

Results from several studies conducted under the sponsorship of the Long-Term Monitoring Program were reported in the proposal (Bednar 2008). These studies showed analyte degradation or loss during storage and shipment to fixed laboratories (Jenkins et al. 1995a, Kirgan et al. 2008, U.S. Environmental Protection Agency (USEPA) 1998) and identification of unknown contaminants utilizing the Griffin 400.

The new Griffin 450 instrument has also undergone extensive laboratory testing, including method development, and detection limit determination, as shown in Table 2.2. The verification standard was analyzed after the detection limit study. The detection limit study demonstrated that the instrument can, for most analytes, reach detection limits of less than 0.001 mg/L. The regulatory limits for most of the analytes are 0.001 mg/L or higher (e.g. 0.002 mg/L for TNT and RDX). These values are also in the range for HPLC method detection limits (MDLs), which are generally on the order of 0.0005 mg/L. The values reported for the 0.001 mg/L low-level laboratory control sample are the results of triplicate analyses collected on non-consecutive days. This low-level laboratory control sample is below the calculated MDL for NB and RDX yet used a larger SPE concentration factor to achieve acceptable recovery. The DoD Quality Systems Manual (QSM) limits for a mid-range Laboratory Control Sample are used to show acceptable recovery, with all analytes meeting these limits except TNB, which is slightly lower (as described in Chapter 3). However, application of these mid-calibration range recovery limits to the lower end of an instrument's detection range represents an extremely conservative situation, and therefore the TNB recovery is deemed acceptable.

Table 2.2. Detection limits for munitions constituents using SPE extraction and detection on the Griffin 450 GC-MS.

Analyte	Regulatory/ Decision Levels (mg/L)	MDL (mg/L)*	0.001 mg/L low- level laboratory control sample*	% REC
<u>NB</u>	0.005**	<u>0.0014</u>	<u>0.0012</u>	<u>120</u>
<u>1,3-DNB</u>	0.001	<u>0.0005</u>	<u>0.0011</u>	<u>110.9</u>
<u>2,4-DNT</u>	0.005	<u>0.0006</u>	<u>0.0008</u>	<u>75.8</u>
<u>TNB</u>	0.01***	<u>0.0002</u>	<u>0.0005</u>	<u>52.2</u>
<u>TNT</u>	0.002	<u>0.0003</u>	<u>0.0013</u>	<u>133.2</u>
<u>RDX</u>	0.002	<u>0.0005</u>	<u>0.0012</u>	<u>117.0</u>

*mean recoveries

**KS regulatory limit, EPA limit 17 mg/L

***Chronic water quality criteria

2.4 Previous field tests

2.4.1 Polyaromatic hydrocarbons (PAHs)

Field trials have included two classes of analytes, munitions constituents and polyaromatic hydrocarbons (PAHs). Results for PAHs were reported by Bednar et al. (2009). The PAH study indicated favorable comparisons between the Griffin 400 GC-MS field analysis and traditional laboratory GC-MS analysis following EPA Method 8270C.

2.4.2 Munitions constituents

Previous field studies utilizing the field GC-MS instruments at LAAP have shown agreement between field data and HPLC data for TNT and 1,3-DNB (Kirgan et al. 2009). Figure 2.5 shows the chromatogram obtained in the field from the Griffin 400 GC-MS for well 104. Figure 2.5 also shows the comparability to laboratory-determined numbers for TNT. Agreement between the sets of data is acceptable with a bias of less than 20%. An additional contaminant was detected in many of the field samples at LAAP; it was identified as the plasticizer N-(n-butyl) benzene sulfonamide using the capabilities of the Griffin 400 GC-MS.

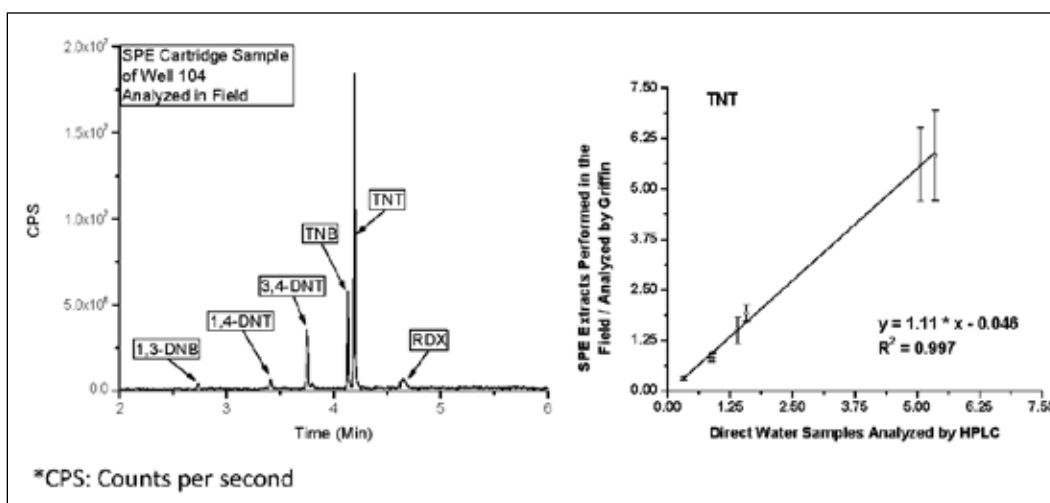


Figure 2.5. Typical chromatogram obtained by the Griffin 400 GC-MS (*left*) and a comparison between the Griffin 400 GC-MS results from the field work and the HPLC Laboratory results for TNT (*right*).

2.4.3 Expected applications of the technology

GC-MS is an accepted analytical methodology for a wide range of organic compounds (EPA Methods 8270 and 529), with MCs being one such class of analytes. This technology has been tested by the ERDC Long-Term

Monitoring Research Program for detection and quantitation of MCs in groundwater. Furthermore, it has been used for near-real-time quantitation of PAHs in dredged material during active dredging operations on the lower Mississippi River (Bednar et al. 2009). Finally, the technology is currently under evaluation for use at an Alabama Superfund site for field detection and quantitation of polychlorinated biphenyls (PCBs) in support of a site contamination delineation investigation. The utility of this technology is outlined by the wide range of potential applications for field-portable GC-MS instrumentation.

2.5 Advantages and limitations of the technology

The instrumentation provides in-field, near-real-time, confirmatory GC-MS analysis of MCs in groundwater. These data improve the quantitation of contamination found in the field and avoid errors due to potential degradation processes occurring during transport to a fixed laboratory.

The cost savings for analyzing samples in the field versus shipping to a fixed-site laboratory are based on the shipping costs as well as fiscally intangible cost related to delays in data reporting from fixed-site laboratories. Shipping costs can be over \$40/sample, depending on distance transported and the amount of ice required to maintain regulatory temperatures, whereas field analysis has no such cost.

Operating costs for the field instrumentation are lower due to less solvent and helium gas usage, and single chromatographic analysis versus the laboratory techniques that require dual column confirmation for both HPLC and GC-ECD analyses. Both field analysis and traditional analysis incur charges for field mobilization to collect samples. The field analysis has the added benefit of near-real-time data reporting, rather than traditional laboratory turnaround times of 30 days or more. Additionally, the mass spectrometer allows for analysis and confirmation of analytes in one chromatographic analysis, rather than two when using non-selective detectors, such as UV absorbance.

The limitations with this technology are environmental concerns, such as heat and humidity, which have been previously shown to be detrimental to the quality of data obtained from the Griffin 400 (Russell et al. 2007, Kirgan et al. 2008). High humidity has been shown to cause the baseline to drift (increase noise in the baseline), thereby increasing the limit of detection (Figure 2.6). The temperature and humidity ranged from 10-35 °C and

25-90% relative humidity during the course of the current demonstrations. No dependence on temperature or humidity was observed for the Griffin 450 GC-MS during this study. The Griffin 450 has updated system electronics and the addition of the inlet control board, which may explain the improved stability.

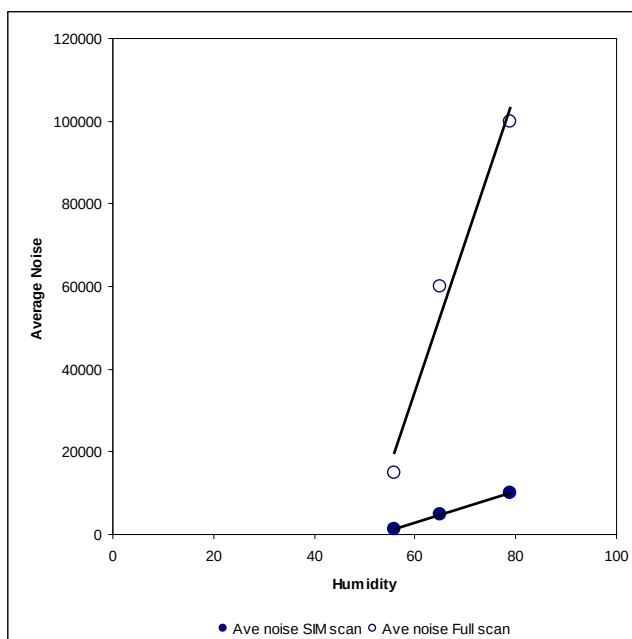


Figure 2.6. Average baseline noise observed on the Griffin 400 for both selected ion monitoring (SIM) and full scan monitoring with varying humidity conditions. Below 55% humidity the average baseline noise is constant.

Differences between the Griffin 400 GC-MS and the Griffin 450 GC-MS which result in improved field operation include:

- Updated vacuum system (including a new turbomolecular pump) provides lower trap pressures, thus better sensitivity
- New detector with onboard preamp board, also increases sensitivity by reducing noise
- More robust injector assembly
- New inlet control board on the Griffin 450 GC-MS provides software control of heated zones

Additionally, the current field instrumentation, Griffin 400 and 450, required highly trained and experienced analysts, which limits the deployment by field personnel.

3 Performance Objectives

Both qualitative and quantitative performance objectives have been identified for the GC-MS technology. Qualitative measures include day-to-day operational performance parameters, i.e. operation by portable generator-produced electricity and response to humidity. The quantitative measures will include a statistical comparison of field-generated data to the laboratory-based data produced by the benchmark method, EPA method 8330B.

The primary objective was to obtain quantitative results for MCs in groundwater that are statistically comparable to traditional techniques by the benchmark laboratory method, EPA method 8330B. Method 8330B sets the criteria for sample duplicates to $\pm 20\%$; this was the success metric utilized for the field instrument.

In particular, acceptance criteria (Table 3.1) are presented for laboratory control samples (LCSs), which are prepared by spiking reagent water and processed on a batch basis (at a frequency of at least 5%). One-liter samples were used for the LCS analysis. A blank and a laboratory control spike (LC-S) were analyzed daily, as each day is considered an analytical batch, which resulted in these quality control samples being analyzed at a rate higher than 5%.

Table 3.1. DoD QSM % LCS recovery limits and regulatory/ decision levels.

Analyte	DoD QSM % Recovery Limits	Regulatory/ Decision Levels (mg/L)
Nitrobenzene	50-140	0.005*
1,3-Dinitrobenzene	45-160	0.001
2,4-Dinitrotoluene	60-135	0.005
1,3,5-Trinitrobenzene	65-140	0.01**
2,4,6-Trinitrotoluene	50-145	0.002
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	50-160	0.002

*KS regulatory limit, EPA limit 17 mg/L

**Chronic water quality criteria

Paired groundwater samples (at least $n = 20$) were used to compare the field method to the lab method. The number of data points was adequate to do linear regressions and Kendall Thiel line analysis (e.g., plots of the lab results versus the field results). The slope and intercept provided information about bias, as the slope should be 1 and the intercept 0 when there is no bias.

The lab and the field method data sets were evaluated using linear regression fits and tests for paired data sets. Additionally the sign test, t-test, Wilcoxon or one-sample test for proportions were performed to determine using the paired data sets to determine if there is significant bias.

The performance objectives are outlined in Table 3.2.

3.1 Performance objective: Agreement between analytical methods for analytes of interest. Lack of bias with GC-MS method

The technology's effectiveness for in-field quantitation of contaminants was determined by statistical comparison of the field results to the benchmark laboratory method, EPA method 8330B.

3.1.1 Data requirements

The effectiveness of the Griffin 400 and 450 GC-MS for in-field analysis of munitions constituents was evaluated on the basis of comparison with results from the Griffin instruments to EPA method 8330B conducted at the ERDC-ECB. Data required for the statistical comparisons include field and laboratory-based HPLC data. For this comparison, the GC-MS was used to detect and quantify all munitions constituents listed. Data sets each consisting of at least 20 total paired points were used to make the comparisons.

3.1.2 Success criteria

The objective was considered met if a plot of the field data versus the HPLC data resulted in a linear regression line passing near the origin with a slope of 0.80 to 1.20. This was operationally defined as agreement between the two methods.

Table 3.2. Performance objectives.

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
Agreement between analytical methods for analytes of interest. A lack of bias with GC-MS method	Data sets each consisting of at least 20 total paired points (measurements from split samples).	Lack of statistically significant differences at the 95% level of confidence using statistical tests for paired data sets or a bias that is less than 20%. A linear relationship through the origin with a slope of nearly one (0.80 - 1.20).	Yes for 1,3-DNB, 2,4-DNT and TNT, for no RDX and TNB.
The ability to provide accurate results in clean matrices.	LCS recoveries from in-field analyses.	LCS recoveries that all fall within the acceptance ranges in the DoD Quality Systems Manual (QSM).	Yes for NB, 1,3-DNB, 2,4-DNT and TNT Limitations with RDX and TNB.
Ability to quantify analyte concentrations at the levels of interest in aqueous matrices.	Detection limits that meet commonly used decision limits for explosives in groundwater (regulatory or risk-based thresholds).	Detection limits less than the decision limits (e.g. $RDX < 0.002$ mg/L).	Yes for all compounds at the 0.001-mg/L spike level. Agreement between field and laboratory methods was only obtained for concentrations > 0.05 mg/L for TNT and TNB.
Ability to recover analytes in environmental matrices.	Matrix spike and matrix spike duplicate recoveries consistent with fixed laboratory analyses.	Matrix spike and matrix spike duplicate recoveries that fall within the acceptance ranges in the DoD QSM for spike recoveries and 20% for the relative percent differences (RPDs).	Yes for NB, 1,3-DNB, 2,4-DNT and TNT limitations with TNB no for RDX.
Qualitative Performance Objectives			
Ease of use and GC-MS operates as expected.	Feedback from field technician on usability of technology and time required	A single field technician able to take measurements and troubleshoot any problems that arise.	Problems encountered were solved with replacement of consumables.
Ease of deployment.	Deployment with standard equipment, e.g 5kW generator, single trailer needed to transport equipment.	Standard field deployment.	No problems encountered with deployment.
Technology robustness	Signal-to-noise ratio does not change relative to humidity; different matrices do not adversely affect data quality.	Data quality not affected by humidity or sample matrix composition (e.g. RPD $< 20\%$).	Data quality was not affected by humidity.

3.1.3 Results

The objective was met for 1,3-DNB, 2,4-DNT and TNT. The slopes for both RDX and TNB fell outside of the 0.80-1.20 range. RDX showed bias > 20% when all data were considered. Removal of the 1 RDX sample containing more than 10 mg/L of RDX resulted in having a regression slope within the desired range. TNB showed significant differences at the 95% level of confidence below a concentration of 0.05 mg/L. All of the linear fits possessed intercepts that were nearly equal to zero.

3.2 Performance objective: The ability to provide accurate results in clean matrices

The effectiveness of the technology for in-field quantitation of an LCS standard in a clean matrix was measured by statistically comparing the field results to the benchmark laboratory method, EPA method 8330B.

3.2.1 Data requirements

Recoveries for analytes in the LCS were used to evaluate the effectiveness of the Griffin GC-MS.

3.2.2 Success criteria

The objective was considered met if the LCS recoveries fell within the acceptance ranges in the DoD QSM outlined in Table 3.3.

Table 3.3. DoD QSM analyte recovery ranges.

Analyte	Lower Control Limit	Upper Control Limit
Nitrobenzene	50	140
1,3-Dinitrobenzene	45	160
2,4-Dinitrotoluene	60	135
1,3,5-Trinitrobenzene	65	140
2,4,6-Trinitrotoluene	50	145
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	50	160

3.2.3 Results

The blank spike (LCS and LCSD) recoveries fell within the limits of the DoD QSM for NB, 1,3-DNB, 2,4-DNT and TNT. Mixed results were seen

for TNB and RDX, where 71% and 50% of blank spike recoveries, respectively, were within the DoD QSM limits.

3.3 Performance objective: Ability to quantitate analyte concentrations at the levels of interest in aqueous matrices

The method detection limit achieved for the samples to be tested is highly dependent upon the sample preparation procedures, for example, the concentration factor achieved with the volume of water used to prepare the sample for analysis. The objective is to establish operating levels of known bias and precision (e.g., recovery ranges outlined in Table 3.3) and to demonstrate reporting of non-detects that minimize false negatives. A sample was prepared at the recovery levels and processed through the entire analytical method to demonstrate that the MC can be detected. A non-detected analyte is then reported to have a concentration as a value that is less than the recovery limits.

3.3.1 Data requirements

Recoveries that meet the decision limits, outlined in Table 3.1, were used to evaluate the effectiveness of this technology.

3.3.2 Success criteria

The objective was considered met if no false negatives were observed above the calculated method detection limit (MDL) and recoveries for the Limit of Quantitation test sample at the decision limits met the DoD QSM limits outlined in Table 3.3.

3.3.3 Results

The reporting limit study showed that all compounds of interest were recovered at the 0.001-mg/L level in clean water (Table 3.1).

3.4 Performance objective: Ability to recover analytes in environmental matrices

All demonstration QA/QC analyses were used to assess instrument operation and demonstration success. Specifically, matrix spike recoveries and comparison to laboratory-generated HPLC data were used to judge demonstration success.

3.4.1 Data requirements

The matrix-specific spike recoveries were used to evaluate the operation of the Griffin 450 and collected for at least 5% of the field samples analyzed.

3.4.2 Success criteria

The metric was deemed met if the matrix spike recoveries are within the limits of the DoD QSM outlined in Table 3.3 and duplicate RPD's are less than 20%.

3.4.3 Results

The matrix spike recoveries fell within the limits of the DoD QSM for NB, 1,3-DNB, 2,4-DNT and TNT. The matrix spike recoveries for RDX were consistently low, never falling within the DoD QSM limits. Mixed results were seen for TNB, where 71% of matrix spike recoveries were within the DoD QSM limits.

3.5 Qualitative objectives

The qualitative objectives were designed to assess the overall instrument performance in the field. Serious degradation in the signal-to-noise level has been observed during operation of the Griffin 400 in high humidity conditions. This results in unusable data and in extreme cases the noise level is so high that data are unobtainable, as the baseline noise overwhelms the detector. Additionally, the ease of deployment and operation of the instrument in the field were subjective measures of demonstration success. Demonstration operations were carried out from a central location, using a portable generator, with no uncorrectable instrument failures encountered, such as pump or electronic failure. However, the older Griffin 400 instrument has reached the end of its expected lifetime, and produced results that were not quantitatively comparable to either the laboratory analysis or the newer Griffin 450 instrument.

4 Site Descriptions

The Louisiana Army Ammunition Plant (LAAP) and the Milan Army Ammunition Plant (MAAP) were chosen as test sites for the Griffin field portable GC-MS. These sites were chosen based on having several munitions constituents present at various concentrations over several orders of magnitude to test the versatility of the instrument. Both sites have a humid climate, which allowed for the observation of instrument behavior and response as a function of humidity. Groundwater wells less than 30 m deep are located on both sites, which aided in sample collection, as deeper wells require more tubing and different sampling pumps than were available to this research project.

4.1 Site location and history

4.1.1 LAAP

The following description of the LAAP was taken from Pennington et al. (1999).

LAAP is a government-owned contractor-operated facility located 35.4 km (22 miles) east of Shreveport, LA. The primary mission of the 6,062-ha (14,974-acre) plant was to load, assemble, and package ammunition items, manufacture ammunition metal parts, and provide associated support functions for ammunition production. Eight ammunition lines and one ammunition nitrate graining plant were constructed by the Silas Mason Company between July 1941 and May 1942. Production ceased in August 1945 at the conclusion of World War II. The plant was then placed on standby status in September 1945, and in November of 1945 the Federal Government relieved Silas Mason Company of responsibilities for the plant operations.

In February 1951 with the outbreak of the Korean Conflict, Remington Rand Corporation reactivated LAAP under contractual agreement with the Federal Government. Ammunition production was suspended in October 1957, and again the facility was placed on standby status. The Federal Government again reactivated the facility in September 1962 and contracted with Sperry Rand

Corporation to operate munitions production in support of the Vietnam Conflict. In 1974 Thiokol Corporation took over the facility operations when Sperry Rand Corporation relinquished its contract. Thiokol Corporation maintained the facility until the summer of 1996 when most operations at the plant ceased. As of August 1997, five contractors were bidding to resume very limited production of black powder products at a single load line (Y line).

LAAP was placed on the National Priorities List in March 1989 due to contamination caused by past disposal of explosives-laden wastewater in 16 unlined surface impoundments located in Area P. An interim remedial action was initiated in 1988 because investigations indicated that the lagoons were a source of contamination and were contributing explosives to the groundwater system. The lagoons were remediated by draining and treating wastewater and incinerating soils. The lagoons were excavated until a total field-determined explosive concentration of less than 100 parts per million was reached. The incineration of 101,929 tons of soil and the treatment of 53,604,490 gal of wastewater and rainwater collected within the 16 lagoons was completed in 1990. The area was then backfilled with the incinerated soil, capped, and vegetated. The lagoons were covered with a minimum 0.6-m- (2-ft) -thick compacted cap of uncontaminated clay soil from Area P and a nearby borrow pit located north of the lagoons. This clay cap covers all of the original Area P including the former lagoons and is compacted to at least 90% of the standard proctor density for the clay used. The cap is covered with 10 cm (4 in.) of topsoil and has a slope of at least 1% to facilitate drainage. In 1989 Science Applications International Corporation (SAIC) under contract to the Army Environmental Center (USAEC) began a 5-year review to assess the effectiveness of the interim remedial action at Area P. The review was conducted in accordance with the Comprehensive Environmental Response, Compensation, and Liability Act of 1980. The final report was submitted to USAEC in August of 1994 (SAIC 1994). In this final report, a statistical regression analysis approach was used to identify the groundwater trends at Area P. Groundwater sampling data from 1980 through 1994 were evaluated. Quadratic and linear analyses were conducted for 108 sampling data sets. Trend categories were assigned to each of the data sets based on improving deteriorating and stable groundwater quality with regards to explosives. In these

data sets, no specific trends were identified, but in general, the overall quality of water in the Upper and Lower Terrace aquifers at Area P was improving (SAIC 1994).

4.1.2 MAAP

Milan Army Ammunition Plant (MAAP) is a government-owned contractor-operated facility located 161 km (100 miles) east/northeast of Memphis in the central section of west Tennessee, east of Milan, TN. Constructed in 1941, the primary mission of the 9122-ha (22,540-acre) facility was to produce and store fuzes, boosters and small- and large-caliber ammunition.

The O-line at the MAAP is a conventional munitions demobilization facility. Effluent from the removal of munitions was discharged into 11 unlined settling ponds with an estimated capacity of 5.5 million gallons. Sediments were routinely dredged from the ponds and stored on the ground. The ponds were lined in 1981 and the accumulated sediments placed into the ponds.

Currently, the MAAP does Loading Assembling and Packing (LAP) for fuzes and other ammunition items, such as demolition charges, mortar rounds, and 155-mm projectiles. The MAAP also stores and tests ammunition (USEPA 1998).

4.2 Site geology/hydrogeology

4.2.1 LAAP

4.2.1.1 Geology

Area P of the LAAP consists of an upper and lower terrace separated by intermittent clay. The upper terrace consists of very fine silt, clays and silty clays, while the lower terrace consists of fine sands and a trace of gravel. The terrace deposits date from the Pleistocene Age and overlay the Eocene Age Cane River Formation.

4.2.1.2 Hydrogeology

There are only slight seasonal variations in the groundwater level at the LAAP. The low permeability of the soil precludes rapid movement and recharge. The groundwater levels reach their highest levels in winter and

lowest in the fall. The movement of groundwater in the lower terrace is to the southeast, while in the upper terrace, the movement is to the east.

4.2.1.3 Geomorphology

The LAAP is located within the Western Gulf Coastal Plain physiographic province. Two major landforms are found within the LAAP, dissected uplands and rolling prairie. Regionally, the LAAP lies within the North Louisiana Syncline, a subsurface structural feature located east of the Sabine Uplift and west of the Monroe-Sharkey Platform. The groundwater flow regime is significantly modified by small uplifts in the area, which modify the local structural geology. Ground surface elevations range from about 40 m (130 ft) above mean sea level (MSL) to the east near Dorcheat Bayou and 24 m (80 ft) above MSL to the west near Clarke Bayou.

4.2.2 MAAP

4.2.2.1 Geology

The MAAP lies on the eastern flank of the Upper Mississippi River Embayment. Sediments consisting of gravel, sand, clay, lignite chalk, and limestone have been deposited in the embayment. The fluvial deposits date from the Tertiary and Quaternary age.

4.2.2.2 Hydrogeology

The principal sources of groundwater in western Tennessee are the Claiborne and Wilcox sands. This unconfined aquifer yields groundwater to private, municipal, and industrial wells in the area. Groundwater flow in this aquifer generally is about 20 feet per mile (ft/mi) to the northwest, following the direction of the regional dip of this sand. The Memphis Sand aquifer is thick, laterally continuous, and highly transmissive.

4.2.2.3 Geomorphology

The MAAP is located on the Memphis Sand of the Claiborne Group of Tertiary age in the Gulf Coastal Plain of western Tennessee. Regionally, the MAAP lies within the Upper Mississippi River Embayment. The Memphis Sand ranges to 900 ft thick and is covered in most places by Tertiary and Quaternary age fluvial deposits and Quaternary age loess and alluvium deposits.

4.3 Contaminant distribution

4.3.1 LAAP contaminant distribution

The contamination at the LAAP lies in the area surrounding the former wastewater lagoons at Area P. Monitoring wells were installed during the remediation of Area P, which included the incineration of soil and the treatment of wastewater and rainwater collected within the 16 lagoons. The monitoring well locations are shown in Figure 4.1. The overall water quality of Area P was shown to be improving in 1994 (Pennington et al. 1999), however RDX concentrations of 16 mg/L have been detected in Well 104 as recently as 2008.

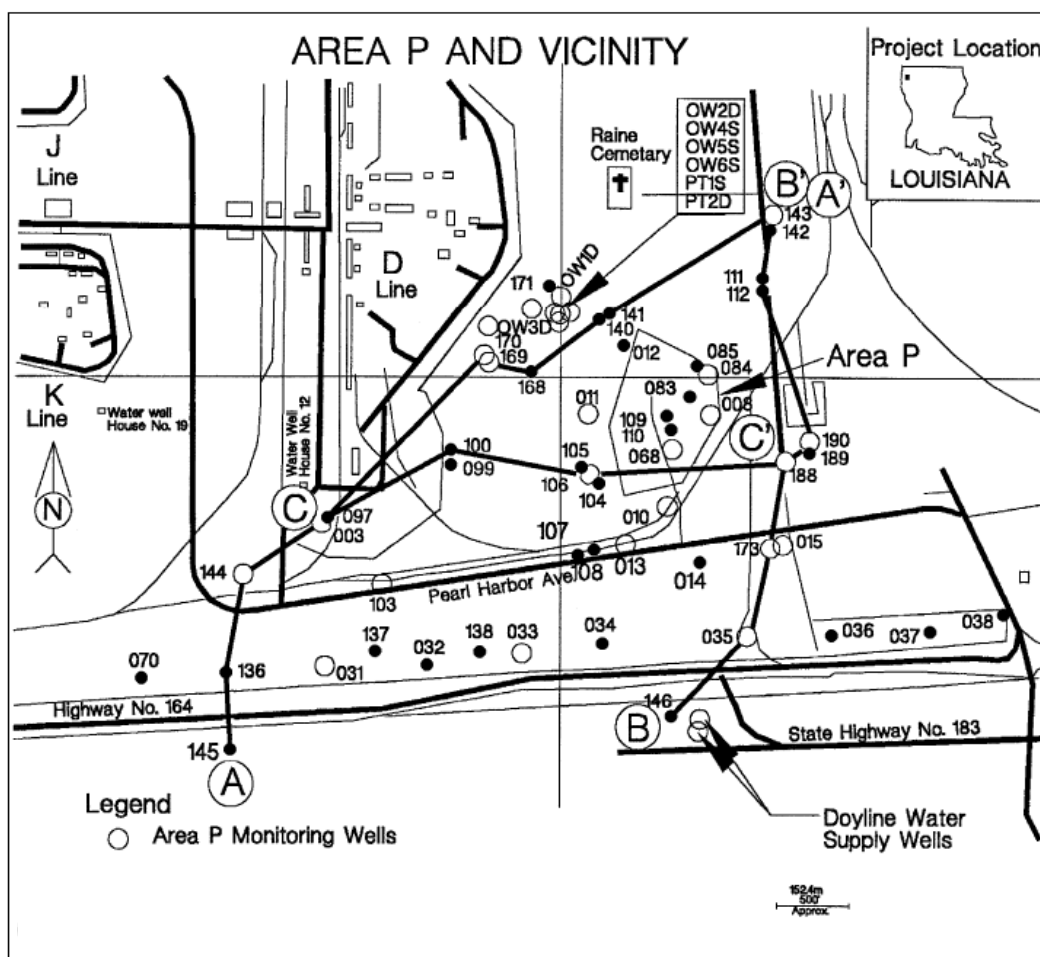


Figure 4.1. Louisiana Army Ammunition Plant – Area P and vicinity (taken from Pennington et al. (1999)).

4.3.2 MAAP contaminant distribution

The contamination at the MAAP lies in the area surrounding the former settling ponds. Monitoring wells were installed in 1979 and indicated the presence of explosives and heavy metals. The MAAP is shown in Figure 4.2. The monitoring well locations for the M-Line are located in the northwest quadrant of the MAAP between Highway 79 and state road 104.

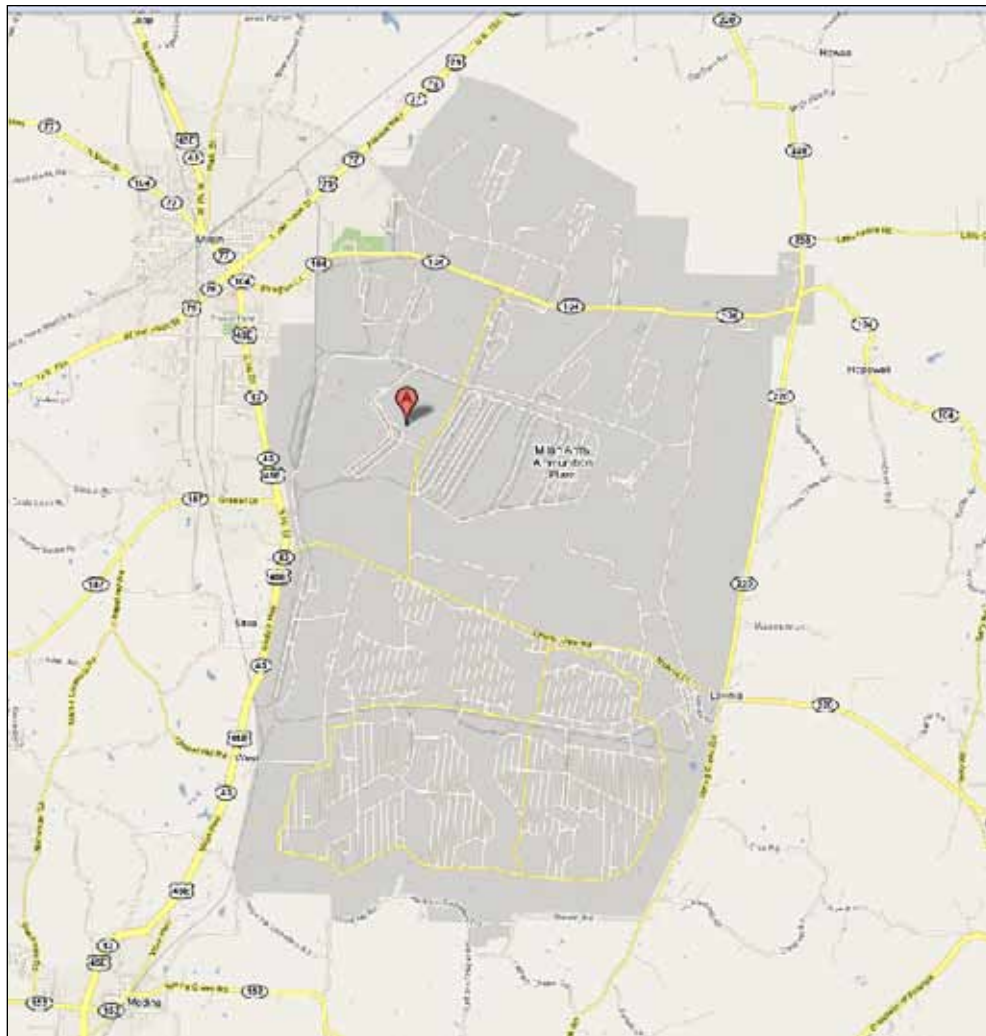


Figure 4.2. Milan Army Ammunition Plant.

5 Test Design

Munitions constituents that have been found on the sites include: NB, 1,3-DNB, 2,4-DNT, TNB, TNT, and RDX. Samples were collected in 4-L amber bottles after purging of the wells. The Griffin 400 GC-MS and the Griffin 450 GC-MS were used to analyze semi-volatile MCs in the field. Analyte concentrations in these samples were compared between the Griffin 450 and HPLC analyses. HPLC analyses were conducted at the ERDC-ECB by EPA Method 8330B. Analyte concentrations determined by the Griffin 400 and 450 GC-MS were compared.

The initial hypothesis was that there are no statistical differences between the analysis conducted in the field on the Griffin instruments and the analysis conducted at the ERDC-ECB. That is, concentrations of the analytes in samples analyzed by GC-MS in the field are comparable to those analyzed in the laboratory by HPLC, EPA method 8330B. Analyte degradation due to transportation of the water samples back to the laboratory is possible, which would result in a higher concentration determined with the field method. However, all analyses were conducted within traditional analyte holding times, and the samples were stored at 4 °C and shielded from light.

Data analyses were on an analyte-by-analyte basis. All data sets were first analyzed to determine if the data are normally distributed and if the variances are homogenous. Concentrations, for each analyte, were compared using standard statistical analyses to determine if significant differences exist between the treatments (i.e., The Griffin analysis and the HPLC analysis). Wells with analyte concentrations above and at the detection limit (0.0016 mg/L for a concentration factor of 320) were targeted for this study. However, there were analytes where many of the wells have concentrations that are below the detection limit. In those cases, comparisons were made for analytes that have detectable concentrations.

5.1 Conceptual experimental design

The field demonstration was a comparison of the field-deployable GC-MS and traditional laboratory HPLC analysis, based on EPA Method 8330B. Specifically, 4-L groundwater samples were collected using traditional sampling methodology. The 4-L water sample was split, one portion was

analyzed in the field, and the second was shipped back to the ERDC-ECB for HPLC analysis. Standard method QC sample analyses were employed, including sample duplicates, matrix spikes and matrix spike duplicates, and laboratory control samples. These analyses were used to confirm the quality of the field and laboratory data, and verify that analyte recoveries were within DoD QSM limits.

5.2 Baseline characterization

5.2.1 Water sampling

Water samples were collected from 10 monitoring wells at Area P of the LAAP and from 18 monitoring wells at the MAAP for the analysis of NB, 1,3-DNB, 2,4-DNT, TNB, TNT, and RDX. The pre-demonstration sampling was also performed at LAAP utilizing nine monitoring wells. Wells at the LAAP were sounded to determine the groundwater level before the sampling pump was deployed. Samples were collected once the pH, conductivity, dissolved oxygen, temperature, and turbidity stabilized as monitored with a field meter (YSI 556 MPS Multi probe system, YSI environmental, Yellow Springs, OH). Well water samples at the MAAP were collected by Arcadis U.S., Inc. (2849 Paces Ferry Road, Suite 400 Atlanta, GA 30339) as part of normal monitoring activities at the site.

Samples for traditional laboratory analysis were collected, stored, and shipped in a manner that prevented the degradation of the munitions constituents present, including packing on ice and storage in the dark. Each sample was labeled to identify the site, well number, and time and date of collection.

5.2.2 Contaminant concentrations

Contaminant concentrations were determined in the field with the Griffin 400 and 450 GC-MS; in the laboratory they were determined by HPLC, using EPA method 8330B. The wells selected at the LAAP have a range of munitions constituents from ~0.001 to 8 mg/L. The wells selected at the MAAP have a range of munitions constituents from ~0.001 to 0.4 mg/L. Therefore, these wells represented ideal cases to test the versatility of the instrument over a range of analyte concentrations.

5.2.3 Investigative-derived waste (IDW)

The only wastes were the purge water and water from decontamination activities. The waste water from the LAAP activities were containerized and transported back to the ERDC for disposal.

Arcadis was responsible for disposal of the waste water generated from well sampling at the MAAP as the field demonstration event was conducted simultaneously with the site's scheduled long-term monitoring sampling. Wastes generated from the field extraction and analysis were containerized and transported back to the ERDC for disposal.

5.2.4 Amount/treatment rate of material to be treated

This information was not available.

5.3 Laboratory study results

The laboratory results for the groundwater samples collected at the LAAP and the MAAP are given in Table 5.1.

Table 5.1. HPLC laboratory results for wells at LAAP and MAAP. Results shown are mg/L in groundwater.

Well #	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
108	<0.0005	0.0082	0.0738	0.7259	0.6142	2.0165
111	<0.00005	<0.00005	<0.00005	<0.00005	<0.00005	<0.00005
112	<0.00004	0.0003	0.0011	0.0003	0.0004	0.0248
105	<0.0010	0.0340	0.0093	0.7398	0.2231	0.2231
104	<0.0010	0.3286	0.1901	8.2453	6.5697	13.6107
140	<0.00025	0.0834	0.0372	0.0234	0.7790	2.9515
141	<0.00025	0.0311	0.1009	1.1211	1.2344	0.7841
142	<0.00004	<0.00004	<0.00004	<0.00004	<0.00004	<0.00004
85	<0.0010	0.0029	0.0247	6.7785	1.7333	4.0635
110	<0.0005	0.0461	0.0710	0.3817	0.6814	4.2326
MI660	<0.0001	<0.0001	0.0004	0.0007	0.0398	0.0681
MI658	<0.00008	0.0001	0.0009	0.0009	0.0958	0.1426
MI653	<0.00004	<0.00004	0.0001	0.0001	0.0011	0.0045
MI645	<0.00004	<0.00004	0.0002	0.0001	0.0004	0.2103
MI531	<0.00003	<0.00003	<0.00003	0.0001	0.0009	0.0011

Well #	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
MI570	<0.0001	<0.0001	<0.0001	0.0004	0.0047	0.0076
MI533	<0.00003	0.0001	0.0003	0.0008	0.0225	0.0711
MI536	<0.00005	<0.00005	0.0002	0.0002	0.0034	0.0348
MI537	<0.00004	<0.00004	0.0001	0.0035	0.0349	0.0341
MI538	<0.00004	<0.00004	0.0001	0.0018	0.0321	0.0700
MI654	<0.00005	<0.00005	0.0004	0.0006	0.0103	0.0755
MI355	<0.00003	<0.00003	<0.00003	0.0001	<0.00003	<0.00003
MI514	<0.00005	<0.00005	0.0003	0.0068	0.0857	0.0097
MI516	<0.00005	<0.00005	0.0001	0.0004	0.0160	0.0206
MI534	<0.00003	<0.00003	<0.00003	0.0004	0.0032	0.0026
MI569	<0.00003	<0.00003	<0.00003	0.0001	0.0001	0.0003
MI571	<0.00003	<0.00003	<0.00003	<0.00003	0.0001	0.0001
MI573	<0.00003	<0.00003	0.0002	0.0003	0.0037	0.0048

5.4 Design and layout of technology components

5.4.1 LAAP design and layout of technology components

Twelve 4-in.-diam wells were selected as potential sample wells for this demonstration, of which ten wells were sampled and selected for statistical analysis. Table 5.2 includes information on the screen depth, depth of the water table, and analytes of interest for each of the wells. Figure 5.1 shows the location of the wells on the LAAP. Additionally, well 142 was sampled with no prior knowledge of screen depth, depth of the water table, and analytes of interest.

Table 5.2. Information on candidate wells at LAAP.

Well #	1,3-DNB	2,4-DNT	TNB	TNT	RDX	Terrace	Top of screen (m bgs)	Bottom of screen (m bgs)	Screen length (m)
85	X	X	X	X	X	Upper	6.86	9.91	3.05
104	X	X	X	X	X	Upper	6.86	9.91	3.05
105	X	X	X	X	X	Lower	15.09	16.61	1.52
108	X	X	X	X	X	Lower	21.95	24.38	2.44
110	X	X	X	X	X	Lower	22.86	25.91	3.05
111	n.d.	n.d.	n.d.	n.d.	X	Upper	10.06	13.11	3.05
112	X	X	X	X	X	Lower	21.28	24.32	3.05

Well #	1,3-DNB	2,4-DNT	TNB	TNT	RDX	Terrace	Top of screen (m bgs)	Bottom of screen (m bgs)	Screen length (m)
140	X	X	X	X	X	Upper	4.57	7.62	3.05
141	X	X	X	X	X	Lower	18.9	21.95	3.05
142	UNK	UNK	UNK	UNK	UNK	Upper	UNK	UNK	UNK
Alternates									
107	n.d.	X	X	X	X	Upper	13.72	15.24	1.52
109	X	X	X	X	X	Upper	6.86	9.91	3.05
83	X	X	X	X	X	Lower	5.79	8.84	3.05

n.d. = non-detect

X = analyte historically present

UNK = Unknown

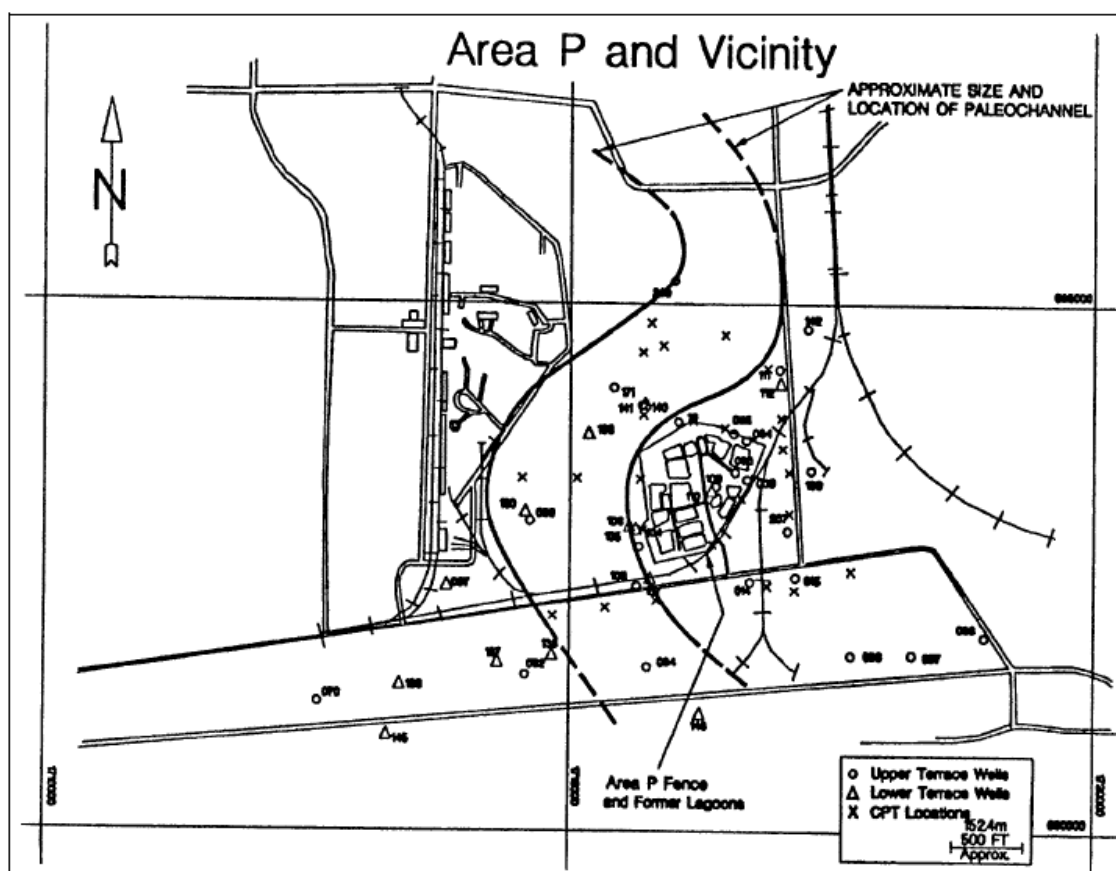


Figure 5.1. The LAAP base map showing the sites where sample wells are located (Pennington et al. 1999).

Wells were purged and then sampled once pH, conductivity, dissolved oxygen, temperature, and turbidity stabilized. These were measured in-line with an YSI unit (Yellow Springs Instruments, Yellow Springs, MO).

5.4.2 MAAP design and layout of technology components

Eighteen wells were selected as potential sample wells for this demonstration, and all 18 were sampled and selected for statistical analysis. Table 5.3 includes information on the analytes of interest for each of the wells.

Figure 5.2 shows the location of the wells on the MAAP.

Table 5.3. Information on candidate wells at MAAP.

Well #	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
M1355	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
M1514	n.d.	n.d.	X	X	X	X
M1516	n.d.	n.d.	X	X	X	X
M1531	n.d.	n.d.	n.d.	n.d.	X	X
M1533	n.d.	n.d.	X	X	X	X
M1534	n.d.	n.d.	n.d.	X	X	X
M1536	n.d.	n.d.	X	n.d.	X	X
M1537	n.d.	n.d.	X	X	X	X
M1538	n.d.	n.d.	n.d.	X	X	X
M1569	n.d.	n.d.	n.d.	n.d.	X	X
M1570	n.d.	n.d.	X	X	X	X
M1571	n.d.	n.d.	n.d.	n.d.	X	X
M1573	n.d.	n.d.	n.d.	X	X	X
M1645	n.d.	n.d.	X	n.d.	X	X
M1653	n.d.	n.d.	n.d.	n.d.	X	X
M1654	n.d.	n.d.	X	X	X	X
M1658	n.d.	n.d.	X	n.d.	X	X
M1660	n.d.	n.d.	n.d.	X	X	X

n.d. = non-detect

X = analyte historically present

Well water samples were collected by Arcadis U.S., Inc. (2849 Paces Ferry Road, Suite 400 Atlanta, GA 30339), according to standard MAAP practices following USEPA guidance.

5.5 Field testing

The field setup, for both sites, consisted of two workstations. The first workstation is used for sample extraction and preparation, and the second is used for GC-MS analysis. Electrical power was supplied by portable 5-kW generators.

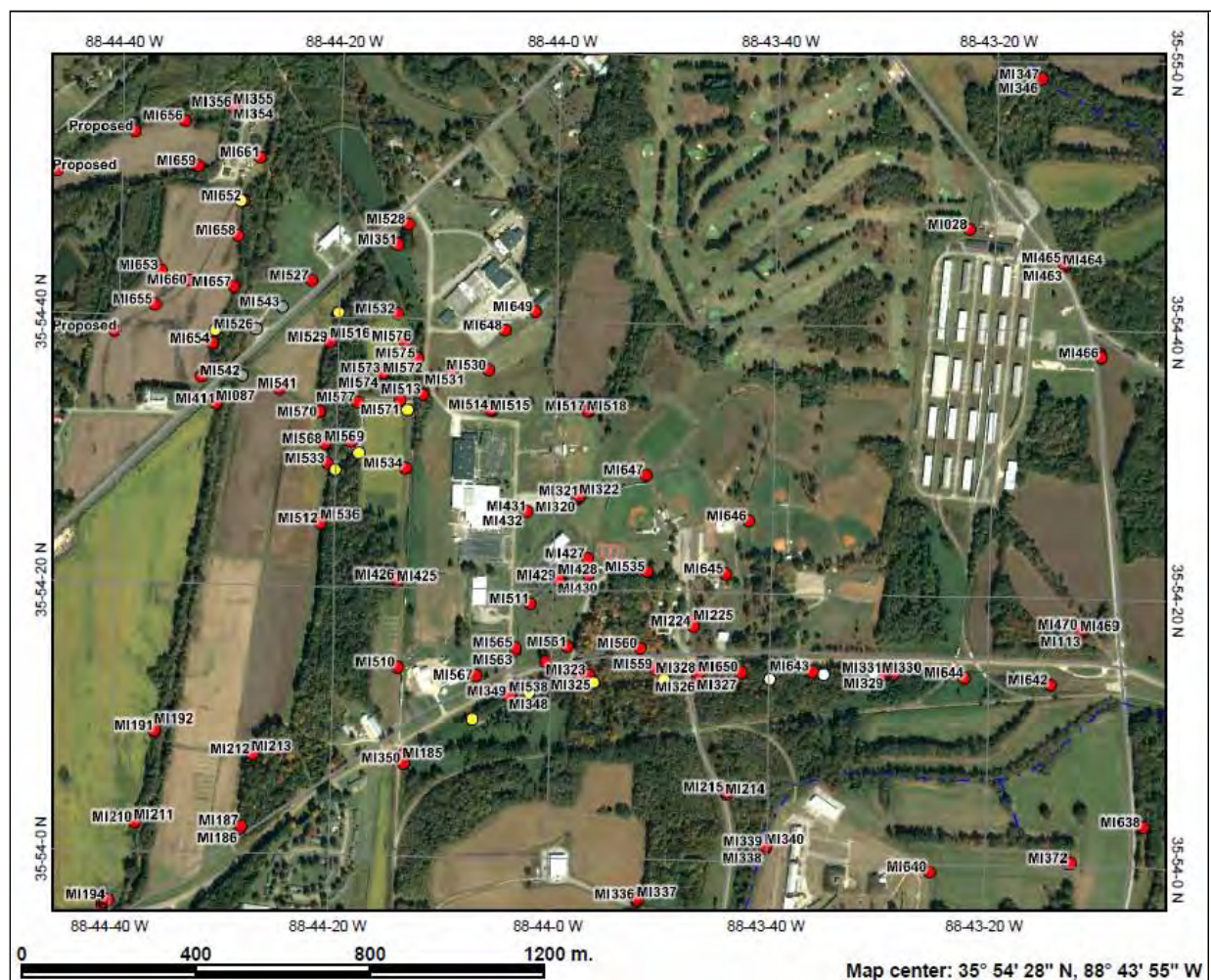


Figure 5.2. Map showing the sites where the MAAP sample wells are located.

5.5.1 Demonstration setup and start-up

All equipment was transported to the field sites in a 4-m covered trailer pulled by a Government-owned sport utility vehicle (SUV). Deployment and setup with three field personnel took approximately 2 hr, including staging of generators, setup of field supplies, accessing wells, instrumentation/computer setup, and vacuum system pump-down. The first calibration standard was analyzed within 2 hr of arrival on site. After initial unloading of trailer and vehicles, the field sampling team member(s) deployed to the first well to be sampled while the analytical team member(s) continued instrument warm-up and workstation setup.

5.5.2 Well water solid phase extraction

Three to six wells per day were evaluated. Water samples were extracted using Porapak RDX solid phase extraction (SPE) cartridges (Waters,

34 Maple Street, Milford, MA). The SPE cartridges were conditioned by eluting 15 mL of acetonitrile and then 15 mL of DI water through the cartridge in the laboratory. They were stored on ice in a sealed Ziploc bag shielded from light until needed. Water samples of 0.05 to 1.6 L were used for extraction depending on the expected concentrations of the munitions constituents, as overloading the SPE cartridge can lead to analyte breakthrough. The well water was drawn through the SPE cartridge at a rate of < 20 mL per minute. The MCs were eluted off the SPE cartridge with 5 mL of acetonitrile and collected in a 15-mL centrifuge tube. Extracts were brought to a final volume of 5 mL mixed thoroughly and then transferred to a 10-mL amber vial. A 1-mL aliquot was then transferred to a 1.5-mL amber vial, dried with sodium sulfate, and spiked with 5 µL of the internal standard, 3,4-DNT, for a final concentration of 5 mg/L.

5.5.3 Analysis by GC-MS

Extract analysis was performed during field operations. Three to six well samples along with the required spikes and duplicates were analyzed per day. The instrument calibration standards were analyzed and a calibration curve was determined concurrently with well water collection and extraction. Calibration verification standards were analyzed periodically to confirm instrument calibration.

Analysis by GC-MS of the SPE extracts commenced once the calibration curve was determined and a verification standard had been analyzed. The GC profile was ramped from 40 °C to 280 °C over approximately 10 minutes such that the contaminants of interest are chromatographically resolved. Samples were analyzed on the GC-MS by injection of 1-µL volumes onto the column, with the split flow adjusted such that there is a flow of greater than 20 mL/min out the split.

The operational conditions of the GC-MS were as follows: The injection inlet was maintained at 200 °C with a constant helium carrier gas flow of 1 mL/min. The column temperature profile started at 40°C and was held for 1.5 minutes. The column temperature was then ramped from 40 °C to 135 °C at a rate of 30 °C/min. The rate was then adjusted to 50°C/min with a final temperature of 280 °C. The final temperature was held for 2 minutes. The run time for the entire temperature program and sample data collection was approximately 9 minutes. Selected ion monitoring (SIM) mode was used to detect a standard list of ions for the munitions constituents (MCs) of interest (Table 5.4).

Table 5.4. Instrumentation and operating conditions for the field GC–MS systems.

Griffin 450™ GC-MS	Operating Conditions
LTM column	Restek TNT1
Helium carrier gas split flow rate	20 mL/min
Ionization voltage	70 eV
Injection port temperature	200 °C
Temperature ramp range	40-280 °C
Nitrobenzene (NB) SIM Quantitation mass monitored, Retention Time	123 <i>m/z</i> , 1.43 min.
1,3-dinitrobenzene (1,3-DNB) SIM Quantitation mass monitored, Retention Time	167 <i>m/z</i> , 3.65 min.
2,4-dinitrotoulene (2,4-DNT) SIM Quantitation mass monitored, Retention Time	165 <i>m/z</i> , 4.03 min.
3,4-dinitrotoluene (3,4-DNT) SIM Quantitation mass monitored, Retention Time	182 <i>m/z</i> , 4.23 min.
Trinitrobenzene (TNB) SIM Quantitation mass monitored, Retention Time	213 <i>m/z</i> , 4.55 min.
2,4,6-trinitrotolene (TNT) SIM Quantitation mass monitored, Retention Time	210 <i>m/z</i> , 4.59 min.
Hexahydro-1,3,5-trinitro-1,3,5 triazine (RDX) SIM Quantitation mass monitored, Retention Time	128 <i>m/z</i> , 5.0 min.
Typical injection volume	1 µL
Total chromatogram time	9 min

5.5.4 Demonstration shutdown and demobilization

Instrument shutdown at the end of the day consisted of performing a final check standard followed by the instrument's preprogrammed shutdown sequence. The final check standard ensured the calibration held after the last samples were analyzed. The shutdown sequence turned off all instrument electronics and shut down the vacuum system. The instrument was locked in the transport trailer overnight. At the end of the field demonstration, all sampling supplies and instruments were repacked and loaded for transport back to the ERDC-ECB for cleaning.

5.5.5 Gantt chart

Table 5.5 outlines the schedule of field activities.

Table 5.5. Gantt chart for the field activities.

Time	800	900	1000	1100	1200	1300	1400	1500	1600	1700
Setting up Field Laboratory										
Instrumentation Setup										
Sampling										
Sample Extraction										
Calibration Standards										
Sample Analyses										
Loading of Field Supplies										
Final Calibration Check										
Shut Down of Instruments										

5.6 Sampling methods

Twenty-eight wells were sampled for MCs analysis. For each well, a 4-L whole-water sample was collected. Additional water for QA/QC samples was collected as needed. The QA/QC samples were also collected in 4-L amber bottles; they were then split into four 1-L amber bottles for analysis in the field and shipment back to ERDC-ECB for laboratory analysis.

The Griffin GC-MS instruments were placed in a central location relative to the well locations (Figures 5.1 and 5.2). The necessary supplies and samples are summarized in Tables 5.6 and 5.7, respectively. One of the wells was chosen each day for QA/QC because each day is an “analytical batch.”

Table 5.6. Summary of bottles and glassware supplies needed per well.

Containers (per well)	Griffin 450	Griffin 400 ¹	ECB samples ²
4-Liter Amber Bottle	1	---	---
1-Liter Amber Bottle	2	---	3
15-mL Centrifuge vials	2	---	3
10-mL Amber vials	2	---	3
1.5-mL Amber vials	2	---	3

¹ The same SPE extracts were analyzed using the Griffin 450 GC-MS and the Griffin 400 GC-MS.

² The same 4-L sample used for the Griffin field samples was used for the laboratory analyses conducted at the ECB.

Table 5.7. Summary of samples collected for a regular sampling event.

Well	Total Number of 1 L water samples ¹	GC-MS Analyses	HPLC Analyses	QA/QC Samples
A	6	3	3	4
B	2	1	1	0
C	2	1	1	0

¹ Bottles from the GC-MS analyses were refilled and shipped to ERDC for the HPLC analyses.

5.6.1 Sample collection

The wells at the LAAP were sampled by positioning the Redi-Flo2 pump in the well at a depth of half the screened interval. The pump discharge was attached to the YSI unit and pumping commenced. The purge water was collected into a bucket while the pH, conductivity, dissolved oxygen, temperature, and turbidity were monitored. When the field parameters were stable, a 4-L amber bottle was filled. The sample was then taken to the central location for splitting and in-field extraction and analysis.

Groundwater samples at the MAAP were collected by Arcadis, according to standard MAAP practices following USEPA guidance.

5.6.2 Operating parameters for the technology

All mass spectrometers typically require equilibration time to achieve the desired vacuum pressure and temperature, requiring early deployment on any given day. The Griffin 450 GC-MS typically requires an equilibration time of 2 hr for the analytes in this study. Electrical power for all field operations was supplied by a portable generator. Tents and a trailer were supplied to shield all electrical equipment from wind and rain.

The wells were purged and then sampled once the field parameters had stabilized. A 4-L sample of the formation water was collected. The well setup, purging, and pumping allowed adequate equilibration time for the instrument. Extracts were then prepared by SPE, brought to volume and spiked with the internal standard and analyzed on the Griffin 450 GC-MS. Samples were stored on ice until they were shipped to the ERDC-ECB Laboratory for analyses.

5.6.3 Sample analysis

Samples were analyzed in the field on the Griffin 450 GC-MS by injection of 1- μ L volumes onto the column, with the split flow adjusted such that there is a flow of greater than 20 mL/min out the split. The column temperature was ramped from 40 °C to 280 °C over approximately 10 minutes. The identifiable mass for each explosive was monitored and used to quantify and identify the explosive. The peak integration areas obtained from the chromatogram were entered into a calibration curve and concentrations were determined. The same procedure was used to analyze samples on the Griffin 400 GC-MS.

All groundwater samples collected were also shipped to the laboratory and analyzed by HPLC following EPA Method 8330B with dual column confirmation using an Agilent 1200 HPLC and UV absorbance detector. These laboratory analyses were used as the baseline values for comparison to the field Griffin 450 GC-MS results. Analyses were performed within the customary holding times on samples that were maintained under chain of custody control, stored at proper temperature, and shielded from light.

The total number and types of samples collected for all sampling events are shown in Tables 5.8 and 5.9. Holding times for the groundwater samples were 7 days; however, the holding time once the water samples are extracted into acetonitrile is 30 days.

5.7 Sampling results

Split groundwater samples were collected and analyzed for the compounds NB, 1,3-DNB, 2,4-DNT, TNB, TNT and RDX to compare the results from the Griffin 450, a field-portable GC/MS, to the HPLC results from a conventional fixed laboratory.

The results from the field and laboratory analysis of groundwater samples are shown in Tables 5.10 and 5.11. Scatter plots of the results from laboratory HPLC analysis versus the field Griffin 450 analysis for 1,3-DNB, 2,4-DNT, TNB, TNT and RDX are shown in Figures 5.3-5.7. NB was not detected in any of the groundwater samples and therefore no comparison is made. Scatter plots shown below contain all data collected in the field and laboratory analyses. Truncated scatter plots are shown in Appendix B; they illustrate trends in low concentration versus higher concentrations.

Table 5.8. Total number and types of samples collected.

Component	Matrix	Number of Samples	Analyte	Location
Pre-demonstration sampling	Groundwater	9	NB, 1,3-DNB, 2,4-DNT, TNB, TNT, RDX	Monitoring Wells at LAAP
Technology performance sampling	Groundwater	10 LAAP 18 MAAP	NB, 1,3-DNB, 2,4-DNT, TNB, TNT, RDX	Monitoring Wells at LAAP and MAAP

Table 5.9. Total number and types of groundwater samples collected.

Matrix	Analyte	Method	Container	Preservative ¹	Holding Time
Groundwater	NB	EPA 8330B and modified EPA 8270 and 529	1-L amber bottle	None	7 Days
	1,3-DNB	EPA 8330B and modified EPA 8270 and 529	1-L amber bottle	None	7 Days
	2,4-DNT	EPA 8330B and modified EPA 8270 and 529	1-L amber bottle	None	7 Days
	TNB	EPA 8330B and modified EPA 8270 and 529	1-L amber bottle	None	7 Days
	TNT	EPA 8330B and modified EPA 8270 and 529	1-L amber bottle	None	7 Days
	RDX	EPA 8330B and modified EPA 8270 and 529	1-L amber bottle	None	7 Days

The groundwater samples were analyzed in the field on both the Griffin 450 GC-MS and the Griffin 400 GC-MS for comparison. However, the results from the Griffin 400 GC-MS were limited, owing to repeated and systematic instrument failures. The problems with the Griffin 400 GC-MS included maintaining vacuum, high baseline noise, and stable calibration. These issues resulted in the inability of Griffin 400 GC-MS to meet DL requirements, to pass the calibration verification check standards, and to detect RDX.

Table 5.10. Griffin 450 results for wells at LAAP and MAAP. Results shown are mg/L in groundwater.

Well #	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
108	<0.0178	0.0107	0.0643	1.1542	0.7663	3.1228
111	<0.0016	0.0009	<0.0007	0.0031	0.0015	<0.0006
112	<0.0015	0.0011	0.0007	0.0030	0.0027	0.0292
105	<0.0356	0.0407	0.0227	1.0887	0.1939	0.1939
104	<0.0356	0.2980	0.1678	12.5725	6.7263	17.9812
140	<0.0089	0.0846	0.0355	0.0283	0.8421	1.9238
141	<0.0089	0.1059	0.1002	1.5073	1.1937	0.6502
142	<0.0015	<0.0006	<0.0007	0.0033	0.0008	0.0029
85	<0.0356	<0.0133	0.0256	10.2946	2.0208	2.8327
110	<0.0178	<0.0067	<0.0080	0.0594	0.0376	0.0442
MI660	<0.0036	<0.0013	<0.0016	<0.0006	0.0289	0.0285
MI658	<0.0030	0.0025	0.0017	0.0081	0.0977	0.0890
MI653	<0.0015	0.0010	<0.0007	<0.0002	0.0018	0.0040
MI645	<0.0015	<0.0006	<0.0007	<0.0002	0.0012	0.1384
MI531	<0.0011	<0.0004	<0.0005	<0.0002	0.0010	0.0030
MI570	<0.0045	<0.0017	<0.0020	<0.0007	0.0054	0.0091
MI533	<0.0011	<0.0004	<0.0005	<0.0002	0.0188	0.0680
MI536	<0.0018	<0.0007	<0.0008	0.0042	0.0028	0.0368
MI537	<0.0015	<0.0006	<0.0007	0.0037	0.0084	0.0146
MI538	<0.0015	<0.0006	<0.0007	0.0035	0.0127	0.0155
MI654	<0.0018	<0.0007	<0.0008	0.0282	0.0181	0.0367
MI355	<0.0011	<0.0004	<0.0005	0.0019	0.0012	0.0285
MI514	<0.0018	<0.0007	<0.0008	0.0052	0.0788	0.0042
MI516	<0.0018	<0.0007	<0.0008	0.0032	0.0094	0.0016
MI534	<0.0011	<0.0004	<0.0005	0.0020	0.0021	0.0133
MI569	<0.0011	<0.0004	0.0005	0.0022	0.0008	0.0015
MI571	<0.0011	<0.0004	<0.0005	<0.0002	0.0008	0.0014
MI573	<0.0011	<0.0004	0.0006	0.0023	0.0309	0.0708

Table 5.11. HPLC results for wells at LAAP and MAAP. Results shown are mg/L in groundwater.

Well #	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
108	<0.0005	0.0082	0.0738	0.7259	0.6142	2.0165
111	<0.00005	<0.00005	<0.00005	<0.00005	<0.00005	<0.00005
112	<0.00004	0.0003	0.0011	0.0003	0.0004	0.0248
105	<0.0010	0.0340	0.0093	0.7398	0.2231	0.2231
104	<0.0010	0.3286	0.1901	8.2453	6.5697	13.6107
140	<0.00025	0.0834	0.0372	0.0234	0.7790	2.9515
141	<0.00025	0.0311	0.1009	1.1211	1.2344	0.7841
142	<0.00004	<0.00004	<0.00004	<0.00004	<0.00004	<0.00004
85	<0.0010	0.0029	0.0247	6.7785	1.7333	4.0635
110	<0.0005	0.0461	0.0710	0.3817	0.6814	4.2326
MI660	<0.0001	<0.0001	0.0004	0.0007	0.0398	0.0681
MI658	<0.00008	0.0001	0.0009	0.0009	0.0958	0.1426
MI653	<0.00004	<0.00004	0.0001	0.0001	0.0011	0.0045
MI645	<0.00004	<0.00004	0.0002	0.0001	0.0004	0.2103
MI531	<0.00003	<0.00003	<0.00003	0.0001	0.0009	0.0011
MI570	<0.0001	<0.0001	<0.0001	0.0004	0.0047	0.0076
MI533	<0.00003	0.0001	0.0003	0.0008	0.0225	0.0711
MI536	<0.00005	<0.00005	0.0002	0.0002	0.0034	0.0348
MI537	<0.00004	<0.00004	0.0001	0.0035	0.0349	0.0341
MI538	<0.00004	<0.00004	0.0001	0.0018	0.0321	0.0700
MI654	<0.00005	<0.00005	0.0004	0.0006	0.0103	0.0755
MI355	<0.00003	<0.00003	<0.00003	0.0001	<0.00003	<0.00003
MI514	<0.00005	<0.00005	0.0003	0.0068	0.0857	0.0097
MI516	<0.00005	<0.00005	0.0001	0.0004	0.0160	0.0206
MI534	<0.00003	<0.00003	<0.00003	0.0004	0.0032	0.0026
MI569	<0.00003	<0.00003	<0.00003	0.0001	0.0001	0.0003
MI571	<0.00003	<0.00003	<0.00003	<0.00003	0.0001	0.0001
MI573	<0.00003	<0.00003	0.0002	0.0003	0.0037	0.0048

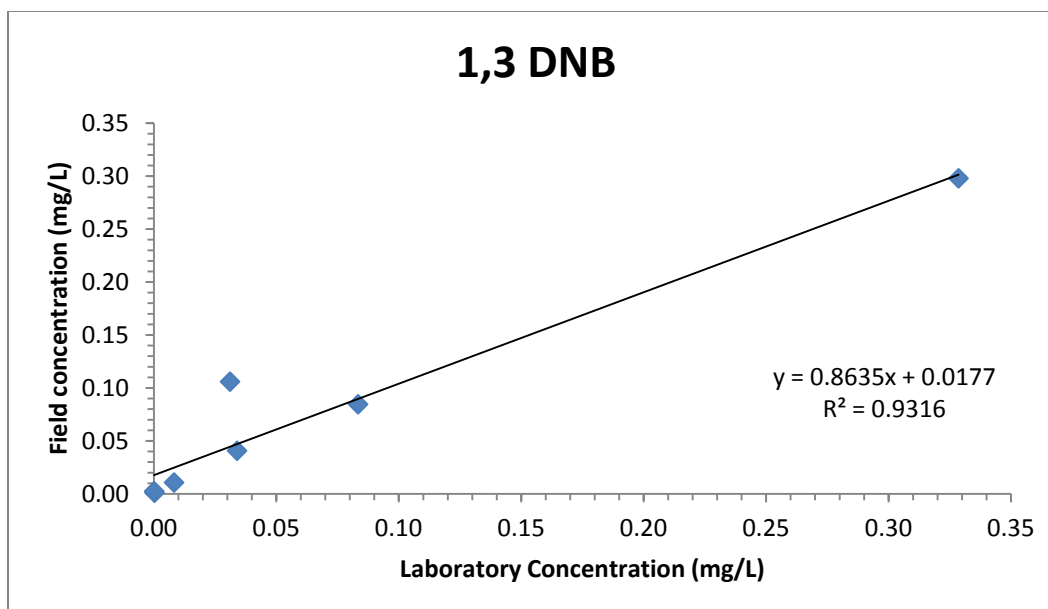


Figure 5.3. Griffin 450 field-analyzed data vs. traditional laboratory analysis by HPLC for 1,3-DNB.

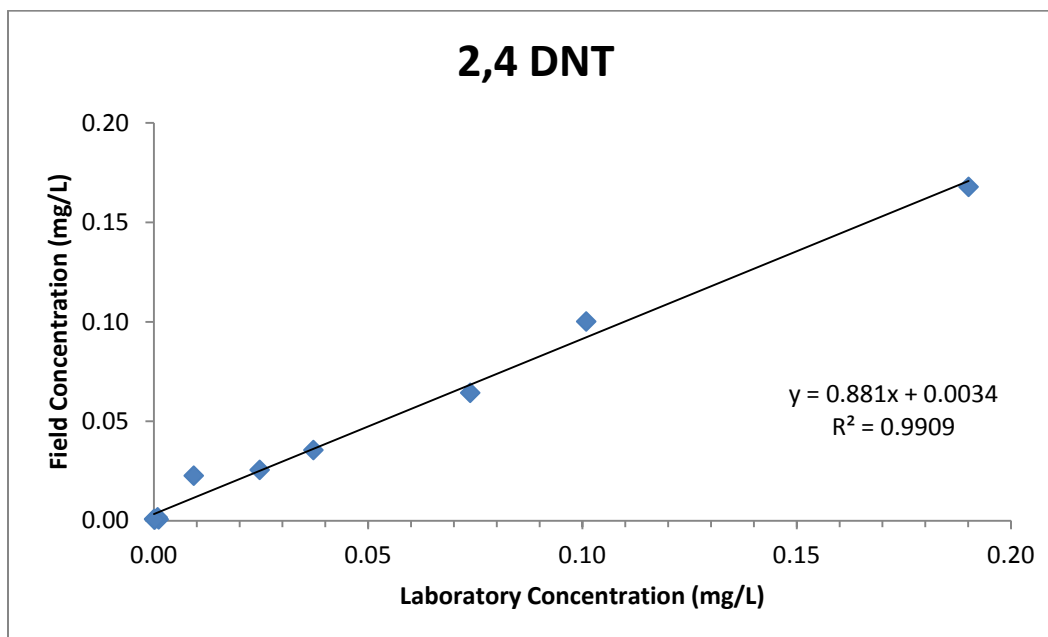


Figure 5.4. Griffin 450 field-analyzed data vs. traditional laboratory analysis by HPLC for 2,4-DNT.

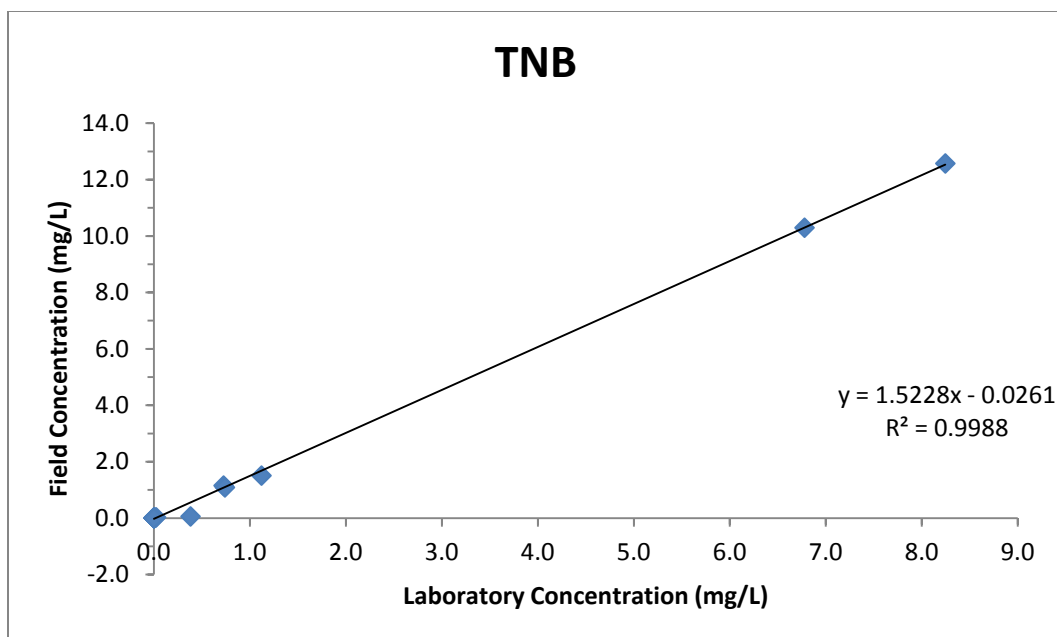


Figure 5.5. Griffin 450 field-analyzed data vs. traditional laboratory analysis by HPLC for TNB.

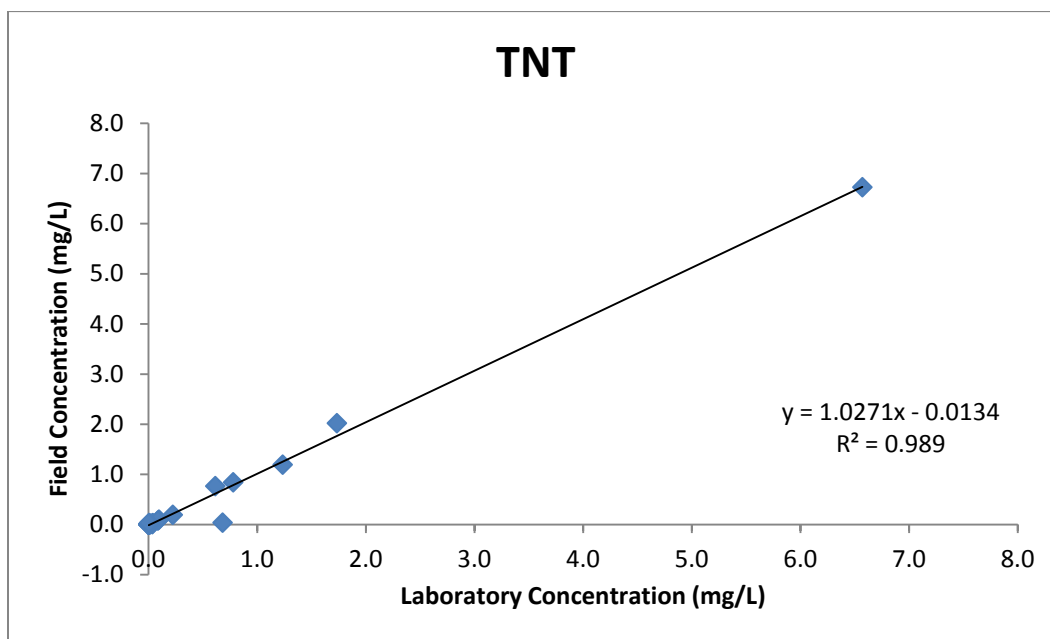


Figure 5.6. Griffin 450 field-analyzed data vs. traditional laboratory analysis by HPLC for TNT.

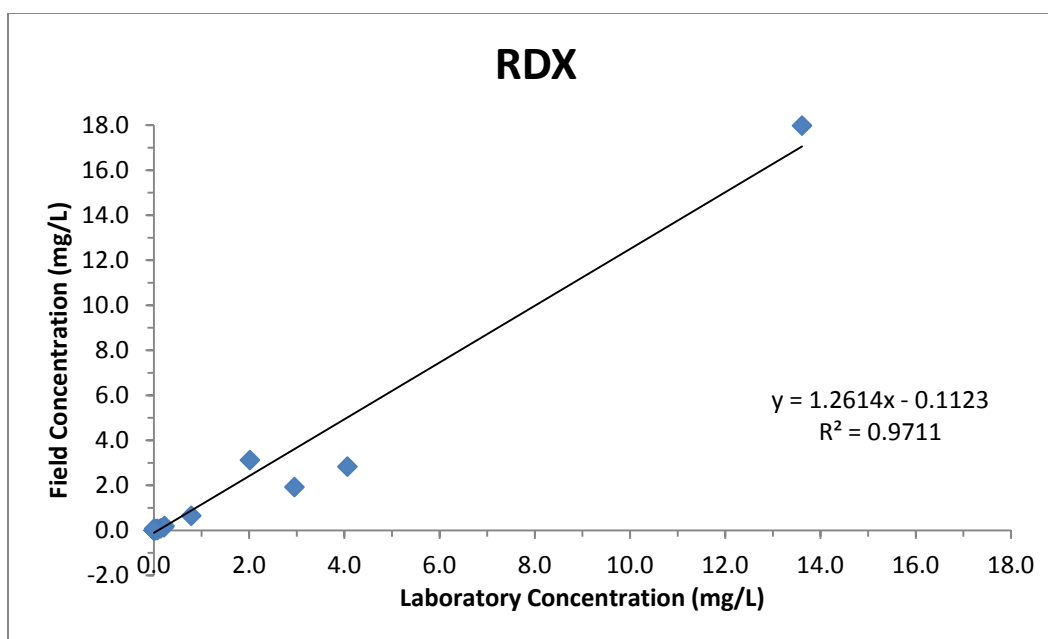


Figure 5.7. Griffin 450 field-analyzed data vs. traditional laboratory analysis by HPLC for RDX.

The regression line data in Figures 5.3 through 5.7 demonstrate that the slope is within the 0.8 to 1.2 limit, except for TNB and RDX. However, the TNB data are skewed somewhat because of two samples with high concentrations. A similar effect is observed for RDX with one sample skewing the results. These samples reflect the linear dynamic range limitations of the current instrument when large sample preconcentration factors result from the SPE procedure. The truncated data sets used in Appendix B show that there are ranges where the data are comparable to the laboratory results. See below, where F corresponds to Griffin field data and L corresponds to HPLC data from the laboratory.

Compound	Relationship	Remarks
1, 3-DNB	$F \approx L$	$F \leq 0.3 \text{ mg/L}$
2, 4-DNT	$F \approx L$	$F \leq 0.2 \text{ mg/L}$
TNT	$F = L$	$0.05 \text{ mg/L} \leq F \leq 10 \text{ mg/L}; F < 0.05 \text{ screening-level}$
RDX	$F \approx 0.7 L$	$F \leq 1 \text{ mg/L}$ Use for screening-level purposes only
TNB	$F = 1.5 L$	$0.05 \text{ mg/L} \leq F \leq 10 \text{ mg/L}; F < 0.05 \text{ screening-level}$

Additional statistical analysis can be found in Appendix B.

6 Performance Assessment

6.1 Performance objective: Agreement between analytical methods for analytes of interest. Lack of bias with GC-MS method

Graphical analysis of the plots of the Griffin field data versus the HPLC laboratory data for the MCs of interest show linear regression slope values between 0.80 and 1.20 for 1,3-DNB, 2,4-DNT and TNT. Nitrobenzene was not detected from any of the well samples, therefore only the non-detect and the control samples could be compared. The linear regression comparison of the field results to the traditional laboratory results for RDX resulted in a slope of 1.2614; however, if only concentrations below 5 mg/L are considered, the result is a slope of 0.8614. Trinitrobenzene was the only compound investigated that showed significant differences at the 95 % level of confidence.

The regression line data in Table 6.1 demonstrate that the slopes are 0.8 to 1.2, except for TNB and RDX. However, the TNB data were skewed somewhat by two samples with high concentrations. A similar effect was observed for RDX with one high concentration sample skewing the results. These samples reflect the linear dynamic range limitations of the field instrument. When large sample preconcentration factors result from the SPE procedure, the data can fall outside the linear dynamic range of the field instrument. When truncated data sets (below 5 mg/L for instance) are considered, they show that there are ranges where the field results are comparable to the laboratory results. The field method for RDX possessed a negative bias relative to the fixed laboratory method and exhibited relatively large variability across all concentration ranges evaluated. The field results were about 70% of the laboratory results on the average for concentrations below 1 mg/L. There was variable quantitative agreement for individual split samples. However, there was excellent qualitative agreement between the field and laboratory results. Therefore, it is suggested that the field method provides only screening-level data for RDX. The field method may possess positive biases for 1,3-DNB and 2,4-DNT. However, these biases are < 0.001 mg/L on the average and seem too small to be of any practical significance. The field method also consistently exhibits a significant positive bias for TNB. There was a very strong correlation between the laboratory and field methods for concentrations greater than about

Table 6.1. Slopes from linear regression analysis of Griffin 450 results vs. traditional HPLC results.

Slope	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
Slope complete data set	N.A.	.8635	0.881	1.5228	1.0271	1.2614
Slope of truncated data	N.A.	0.8635	0.881	0.9407	1.0377	0.8614

0.05 mg/L to the highest reported concentration, but the performance of the field method was relatively poor at smaller concentrations. A positive bias was identified by both the sign test and Prentice-Wilcoxon test and via visual examinations of the box plots. The bias is relatively small (about 0.002 mg/L on the average) but may be indicative of a lack of agreement between the field and laboratory method (See Appendix B).

6.2 Performance objective: The ability to provide accurate results in clean matrices

Control samples (Blank and LCS) analyzed each day as part of the analytical batch of samples generally resulted in analyte recoveries within the DoD QSM limits (Table 6.2). However, not all results are within the limits, suggesting that poor recovery can be an issue if the samples are not thoroughly dry prior to injection into the instrument inlet.

Table 6.2. Griffin 450 LCS % recoveries reported to two significant figures. Values in bold are outside DoD QSM limits.

Day	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

The objective was met for NB, 1,3-DNB, 2,4-DNT and TNT for all days except the Day 2 at the LAAP. The well sample selected on day 2 at the LAAP was highly contaminated and the spike was too low to be detected in all cases except for NB, which was not present in the matrix water. RDX recoveries were only within DoD QSM limits in 50% of the LCS control samples.

6.3 Performance objective: Ability to quantitate analyte concentrations at the levels of interest in aqueous matrices

The reporting limit study performed in the laboratory (see Section 2.3, Proof of Concept- Laboratory Tests) using a 0.001 mg/L aqueous sample and SPE sample extraction clearly demonstrates the technology's ability to quantify analytes of concern at environmentally and regulatory relevant levels (Table 2.1).

6.4 Performance objective: Ability to recover analytes in environmental matrices

Matrix spike samples (MS and MSD) were analyzed each day as part of the analytical batch of samples and generally resulted in analyte recoveries within the DoD QSM limits. However, not all results are within the acceptance limits (Table 6.3). RDX in particular shows poor recovery of matrix spikes, indicating the difficulty encountered with RDX analysis by GC methods. The laboratory HPLC analysis of the groundwater samples did not suffer from the same poor recovery of RDX in the matrix spike samples. The field extracts were also analyzed in the laboratory by HPLC resulting in matrix spike percent recovery within DoD QSM limits. Poor recovery can be an issue on the GC-MS if the samples are not thoroughly dry prior to injection into the instrument inlet or if there has been degradation to the analytical column. Methods EPA 529 and 8095 have also shown difficulties with RDX, analyte breakdown, and co-elution with PETN, respectively.

The objective was met for NB, 1,3-DNB, 2,4-DNT, and TNT for all days except the second day of sampling at the LAAP. The well sample selected on day 2 and the LAAP were highly contaminated and the spike was too low to be detected in all cases except for NB, which was not present in the matrix water. RDX consistently has low recoveries.

6.5 Qualitative objectives

One analyst was able to maintain and operate the Griffin 450 system for the duration of both demonstrations. However, there were a few instrument problems mainly resulting from transport of the instrument to the site. The most common problem encountered was insufficient vacuum. This was a result of a loose or cracked graphite ferrule. All of the issues were overcome by replacing instrument consumables. This does highlight

a limitation of the technology; currently it requires highly trained operators for successful deployment. However, similar success was not observed with the older Griffin 400 GC-MS, which has reached the end of its expected life. Quantitatively comparable data were not obtained, and therefore all results shown above were collected with the newer Griffin 450 instrument, which operated successfully during the demonstrations.

Table 6.3. Griffin 450 MS % recoveries. Values in bold are outside DoD QSM limits.

Day	Sample ID	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	111MS	96	86	91	74	63	45
	11MSD	100	74	120	100	92	38
LAAP Day 2*	104MS	92	27	84	750	490	-2200
	104MSD	99	87	111	-1000	-900	-3800
LAAP Day 3	142MS	80	72	73	75	72	54
	142MSD	96	100	93	88	81	49
MAAP Day 1	MI531MS	120	110	110	66	55	9.8
	MI531 MSD	120	77	96	79	58	26
MAAP Day 2	MI536MS	110	68	100	59	54	260
	MI536 MSD	120	99	120	89	81	200
MAAP Day 3	MI355MS	160	110	110	22	61	20
	MI355MSD	140	93	110	23	66	37
MAAP Day 4	MI569MS	70	99	94	66	86	33
	MI569MSD	98	130	100	76	96	34

* The well sample chosen was highly contaminated with the MCs of interest except for NB, therefore the spike was insignificant compared to the amount of analyte present, resulting in poor recoveries.

7 Cost Assessment

One of the objectives of this demonstration is to document the cost savings associated with this field analysis technology compared with traditional laboratory analysis. Documented costs include all equipment (capital) costs, disposal costs, shipping costs, sampling costs, labor costs, travel, and per diem. Table 7.1 documents and explains these costs. Table 7.2 documents the labor costs associated with field sampling and analysis. Table 7.3 details the cost per sample for both the traditional laboratory and field analysis. The cost for the field analysis is approximately 50% of the laboratory analyses per sample.

7.1 Cost model

7.1.1 Cost element: Field deployment

Field deployment was required to collect samples for both field and laboratory analysis. The data were tracked using an Excel spreadsheet and included the following cost parameters: labor, materials, and travel. Labor was tracked according to the type of personnel required to collect samples (field technician, engineer, program manager, etc.) and their associated labor hours. In addition, all material purchases and analytical laboratory costs were recorded in the spreadsheet.

7.1.2 Cost element: Field analysis

Field analysis was required to determine the functionality and limitations of the Griffin 450 GC-MS in field conditions. The data were tracked using an Excel spreadsheet and included the following cost parameters: labor, materials, and analysis. Labor was tracked according to the type of personnel required to conduct the field analysis (field technician, chemist, program manager, etc.) and their associated labor hours. In addition, all material purchases and analytical laboratory costs were recorded in the spreadsheet.

Table 7.1. Cost model for field analysis of groundwater.

Cost Element	Data to be Tracked	Estimated Costs	
Start-up	Instrument purchase	Griffin 450	\$105,000
Field deployment	Personnel required and associated labor Materials	Technician, 10 h	\$900
		Materials	\$100
Field analysis	Personnel required and associated labor Materials Deployment costs	Field technician, 80 h	\$7,200
		Mass spectrometrists, 40 h	\$3,600
		Materials	\$1011
		Per diem	\$1740
		Truck	\$750
Laboratory analysis	Materials Cost per sample analysis Shipping	Mileage, \$0.52 per mile	\$507
		Materials	\$ Included in cost per sample
		Analysis cost per sample	\$250
Material cost	<u>Supplies for Well Water Sampling Required for Field and Laboratory Analysis:</u> Field sampling deployment : Teflon tubing: Depth of well and location of screened interval Sample containers Amber bottles (1 L) and vials (10 mL and 1.5 mL) Extraction consumables: SPE columns Acetonitrile Centrifuge tubes (15 mL) Disposable pipets (10 mL) <u>GC-MS Consumables</u> LTM column, guard columns and inlet liners Helium <u>HPLC Consumables</u> Column Solvent Helium	Shipping per sample	\$40
		Teflon tubing, per ft	\$4.05
		Amber Bottles, per week	\$545
		SPE cartridges, per week	\$336
		Acetonitrile, 1 L	\$130
		Centrifuge tubes, per week	\$35
		Disposable pipets, per week	\$19
		LTM column	\$3000
		Consumables kit	\$570
		Helium, per bottle	\$317
		Dual confirmation columns	\$2000
		Acetonitrile, methanol	\$500
		Helium	\$ 0
Waste disposal	Purge water was brought back to the ERDC for disposal	no cost tracking	
Operation and maintenance costs	No unique requirements anticipated, but issues that arise were noted		

Table 7.2. Labor costs for field sampling and analysis.

Cost Element	Data Tracked During the Demonstration	Costs	
Mobilization Costs ¹	Instrument packing and unpacking	Lab Technician, 8 hr	\$720
	Materials for analysis	Supplies	\$1850
Cost of Analysis ²	Sample preparation	Lab Technician, 8 hr	\$720
	Sample analysis and data reporting	Lab Technician, 8 hr	\$720
Waste Disposal	Disposal costs for water collected	NA ³	NA ³

¹Cost for total trip²Cost per 10 analyses³Disposal costs and field sampling incurred for field- or laboratory-based analysis.**Table 7.3. Cost per sample.**

	Laboratory Costs	Field GC-MS Costs
Overnight Shipping + Ice	\$40/sample ¹	NA
Analysis	\$250/sample	\$60/sample ²
Field Supplies	NA ³	\$105/sample ⁴
Total	\$290/sample	\$165/sample

¹\$157.00 for overnight shipping of 30-lb cooler from Denver, CO to Vicksburg, MS, which could contain four 1-L samples with ice²Cost calculated as two field technicians for extraction and analysis at a rate of 2.5 samples/hour and includes instrument mobilization³Costs included in the analysis⁴Costs include ~120 analyses per chromatography column, He, and other consumables

7.1.3 Cost element: Laboratory analysis

Laboratory analysis was required in order to compare the field method with EPA method 8330B. The data were tracked using an Excel spreadsheet and included the following cost parameters: labor, materials, and analysis.

Labor was tracked based on the type of personnel required to conduct the laboratory analysis (technician, engineer, program manager, etc.) and their associated labor hours. In addition, all material purchases and analytical laboratory costs were recorded in the spreadsheet.

7.1.4 Cost element: Material cost

Materials were required for both the field and laboratory analyses. Materials data were tracked using an Excel spreadsheet and included the following cost parameters: Teflon tubing and consumables for extraction and GC-MS and HPLC operation. Capital costs associated with the acquisition of the field and laboratory-based analytical instrumentation

are also included. The Griffin 450 GC-MS had an initial cost of \$105K, compared to a typical laboratory HPLC system that has an initial cost of approximately \$80K, depending on instrument manufacturer and specifications.

7.1.5 Cost element: Waste disposal

Purge water was brought back to the ERDC for disposal, without cost tracking, as costs for disposal were identical for laboratory and field analysis.

7.2 Cost drivers

Traditional fixed laboratory analytical cost will not decrease substantially with time; rather, costs have remained relatively stable over the past 10 years for method 8330 analysis. Furthermore, shipping costs will continue to increase with increasing fuel costs and transportation costs. Labor costs for field deployment will also increase; however, this increased expense is incurred for sampling regardless of field or laboratory analysis. The increased labor costs will, however, increase the field analysis cost. There are several intangible benefits to the field-portable instrumentation, which include near-real-time availability of the data and the identification of unknown compounds or new contaminants. The potential benefits of near-real-time analysis are more pronounced during a site investigation phase, where analyte concentrations could impact well installation locations. In such a scenario, groundwater monitoring wells could be installed, since field instrumentation provided data on analyte concentration, effectively 'plume mapping' the site in near real time. Additionally, the selectivity of the GC-MS for analyte confirmation allows the technology to be applied to other classes of contaminants, such as polycyclic aromatic hydrocarbons and polychlorinated biphenyls, among others.

7.3 Cost analysis

7.3.1 Background

The MAAP site was selected as a representative site for the cost analysis. The site at the MAAP was actively sampled and therefore more accurately represented adding the field analysis to a preexisting sampling regime. The life cycle analysis comparing standard laboratory analysis and the Griffin 450 GC-MS field analysis is shown in Table 7.4. Total costs incurred for field

Table 7.4. Life cycle cost.

Year	Field Analysis Total Costs	Laboratory Analysis Total Costs	Laboratory - Field Analysis Costs
1	\$352,7391	\$277,360	\$-75,379
2	\$600,478	\$554,719	\$-45,759
3	\$848,217	\$832,079	\$-16,138
4	\$1,095,956	\$1,109,438	\$13,483
5	\$1,343,695	\$1,386,798	\$43,103
6	\$1,591,433	\$1,664,158	\$72,724
7	\$1,839,172	\$1,941,517	\$102,345
8	\$2,086,911	\$2,218,877	\$131,966
9	\$2,334,650	\$2,496,236	\$161,586
10	\$2,582,389	\$2,773,596	\$191,207

¹Includes purchase of Griffin 450 at \$105,000. Yearly field analysis costs are \$247,739.

and laboratory analysis through ten years are shown; however, the field instrument has a life expectancy of approximately seven years (as demonstrated by the current Griffin 400 instrument), compared to a laboratory instrument which might be expected to last ten years. Figure 7.1 compares the total costs for the standard laboratory analysis and the Griffin 450 GC-MS field analysis. The field analysis total costs assume 12 five-day sampling events yearly and 25 samples analyzed per sampling event for a total of 300 samples analyzed per year (\$247,739/year). The total cost for year one of the field analysis includes the purchase of the Griffin 450 GC-MS (\$105,000). The laboratory analysis total cost assumes 300 samples are analyzed yearly (equivalent to 25 samples analyzed 12 times a year) for a yearly cost of \$277,360. This cost also includes shipping at approximately \$40/sample. It should be noted that this shipping cost is highly conservative, where it estimates that four 1-L samples could be shipped for \$160.00 over a given distance (e.g. Denver, CO to Vicksburg, MS). Due to the need to ship additional waters (e.g. for QC purposes), and the fact that distances could be greater, this shipping estimate should be considered a lower rather than upper bound.

The cost difference between the field and laboratory analysis is also shown in column 4 of Table 7.4. Figure 7.2 shows the cost difference between the field and laboratory analysis as a function of time. The break-even point between the two analyses occurs in year 3. The laboratory analysis costs assume that no startup costs were incurred. However, new HPLC instrumentation would more than likely need to be purchased during a 10-year

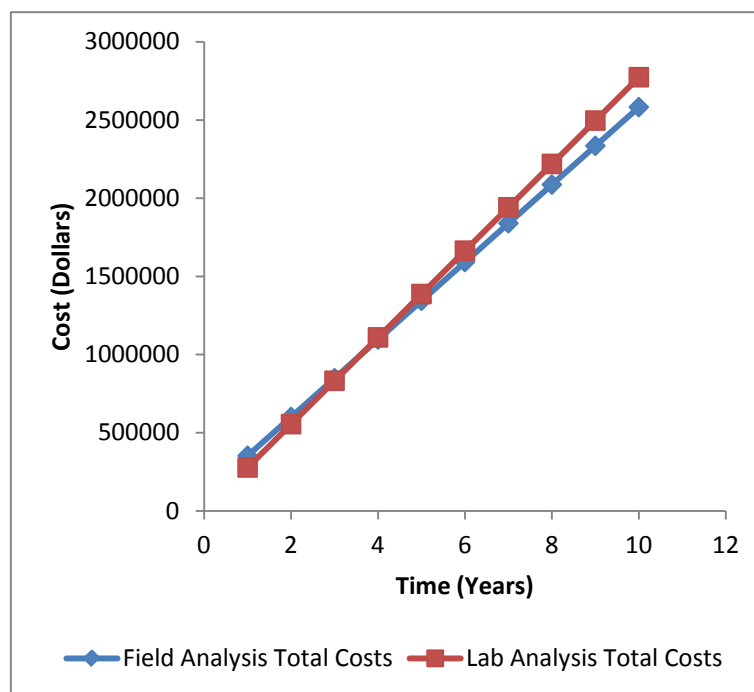


Figure 7.1. Total cost for traditional laboratory (\$277,360/year) and field analysis \$247,739/year).

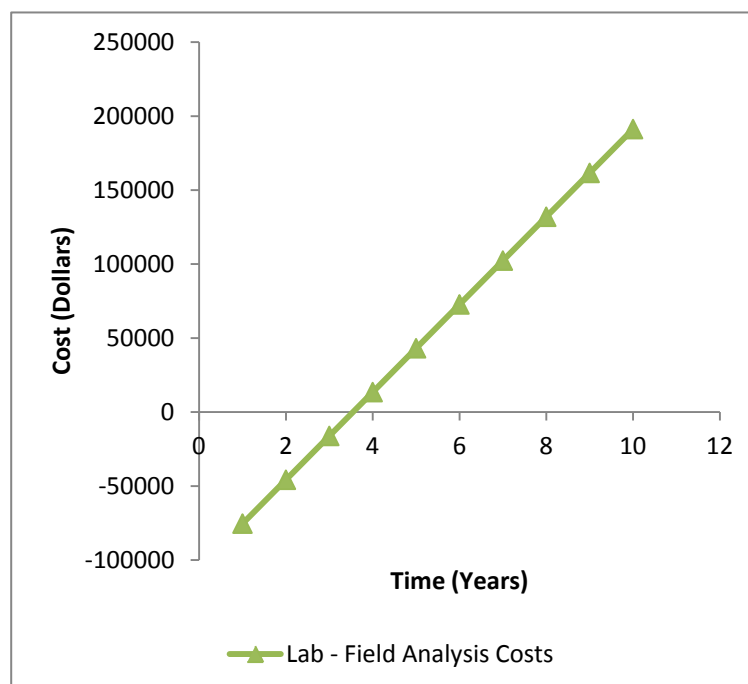


Figure 7.2. Difference in cost between the traditional laboratory analysis and the field analysis. Break-even point occurs at 3.54 years.

cycle. The break-even point occurs in year 1 when the cost of a new HPLC (\$80,000) is taken into account. There are, however, intangible benefits of the field instrumentation, including near-real-time availability of data, which may be important during well installation or plume delineation, as well as ability to identify unknown compounds with the mass spectrometer. While these capabilities may not be directly applicable to long-term monitoring activities (e.g. a set number of wells will already be installed), they are 'value added.'

7.3.2 Net Present Value (NPV) analysis

The life cycle costs (LCC) of both the field and traditional laboratory analysis were calculated (Fuller and Peterson 1996) for 7- and 10-year study periods. These study periods were selected based on life expectancy of the field and laboratory instruments. Future costs were discounted to net present values using rates from Energy Price Indices and Discount Factors for Life-Cycle Cost Analysis (Rushing et al. 2010). The 7-year LCC for the field and laboratory analysis were found to be \$1,745,032 and 1,836,123 respectively (Table 7.5).

Table 7.5. NPV life cycle cost.

Study period	LCC Field Analysis	LCC Laboratory Analysis	Net Savings (Laboratory - Field)
7	\$1,745,032	\$1,836,123	\$91,091.02
10	\$2,384,199	\$2,551,712	\$167,513.2

Benefits of the field analysis are primarily in the form of future operational savings; therefore the net savings (NS) of the field analysis relative to the traditional laboratory analysis was calculated. The net savings of the field analysis to the traditional laboratory analysis over 7 years is \$91,091.02 in present-value dollars. The field analysis becomes cost-effective at approximately 3.7 years when corrected for present value.

8 Implementation Issues

A technical report is currently being drafted which will be useful for other organizations to lessen the learning curve required to successfully bring the demonstrated technology on-line. Furthermore, through discussions with researchers and innovative technology advocates at the US EPA, regulatory acceptance of the technology for quantitation of munitions constituents in groundwater is being pursued. Due to the fact that GC-MS is already a regulatory approved analytical methodology, acceptance of the current field application is based solely on the ability to generate laboratory-quality data with similar reporting limits and costs. Currently, a significant drawback to implementation of the technology is the requirement to have a trained and experienced analytical chemist on staff to operate the instrument, properly maintain it, and troubleshoot as needed. The instrument has been shown to have limitations in detection limits, stability, and linear dynamic range, when compared to traditional laboratory-based analytical equipment. The field-portable Griffin GC-MS appears to have quantitative capabilities for 1,3-DNB, 2,4-DNT and TNT. However, at this point it appears to only be suitable for screening of TNB and RDX. The regression line data demonstrate that the slope is within the 0.8 to 1.2 limit except for TNB and RDX. The TNB data are skewed somewhat by two samples with high concentrations. A similar effect is observed for RDX with one sample skewing the results. These samples reflect the linear dynamic range limitations of the current instrument when large sample preconcentration factors result from the SPE procedure. Further testing would be required to make stronger conclusions, owing to gaps between the high and low concentrations and to relatively few data points in some data sets. The initial cost of the instrument, at approximately \$100K, also represents a formidable obstacle, which causes the break-even cost point to be several years in the future, depending on the analytical workload of the user. However, the technology has applications far beyond MCs in groundwater, and therefore may be applicable to other environmental investigations, which will add to the return on investment.

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Appendix A: Points of Contact

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Appendix B: Statistical Comparison of the Field and Laboratory Results

Summary: Evaluation of field GC/MS results

The compounds NB, 1, 3-DNB, 2, 4-DNT, TNB, TNT and RDX were evaluated. Split groundwater samples were collected and analyzed for these compounds to compare the results from a field-portable (gas chromatograph/mass spectrometer (GC/MS) method (denoted by the variables y or F in this document) to the results from a conventional fixed laboratory method (denoted by the variables x or L). Parametric and non-parametric linear fits were performed for the remaining five compounds.

As all of the paired results for NB were non-detects, only a limited evaluation was possible as discussed in Chapter 1. The field and laboratory NB results were consistent in that both the field and laboratory methods reported non-detects for NB for all of the split sample analyses.

The results for the evaluations of the remaining compounds are summarized as follows:

Compound	Relationship	Remarks
1, 3-DNB	$F \approx L$	$F \leq 0.3 \text{ mg/L}$
2, 4-DNT	$F \approx L$	$F \leq 0.2 \text{ mg/L}$
TNT	$F = L$	$0.05 \text{ mg/L} \leq F \leq 10 \text{ mg/L}; F < 0.05 \text{ screening-level}$
RDX	$F \approx 0.7 L$	<i>Use for screening-level purposes only</i>
TNB	$F = 1.5 L$	$0.05 \text{ mg/L} \leq F \leq 10 \text{ mg/L}; F < 0.05 \text{ screening-level}$

The field method for RDX possessed a negative bias relative to the fixed laboratory method and exhibited relatively large variability across all concentration ranges evaluated. The field results were about 70% of the laboratory results on the average. There was variable quantitative

agreement for individual split samples. However, there was excellent qualitative agreement between the field and laboratory results. Therefore, it is recommended that the field method be used to obtain only screening-level data for RDX.

The field method consistently exhibits a significant positive bias for TNB. There was a very strong correlation between the laboratory and field methods for concentrations greater than about 0.05 mg/L to the highest reported concentration but the performance of the field method was relatively poor at smaller concentrations. The TNB field results > 0.05 mg/L would need to be adjusted for bias prior to being reported.

The field method produced results comparable to the laboratory method for TNT for concentrations greater than 0.05 mg/L to the highest concentration reported (about 10 mg/L). The field TNT results were not quantitatively reliable at smaller concentrations (e.g., exhibited large variability).

The field method seemed to produce comparable results to the laboratory method for 1, 3-DNB and 2, 4-DNT for the range of concentrations reported. However, the following limitations should be noted: The data sets were heavily censored (non-detects were removed); the sample sizes for the uncensored pairs were relatively small; and a relatively small concentration range was evaluated (about 0.01 – 0.1 mg/L), where most of the concentrations were less than 0.05 mg/L. The data were inadequate to evaluate the performance of the method at larger concentrations (e.g., > 0.5 mg/L). Somewhat conflicting results were also obtained regarding the absence bias (e.g., refer to Table 2.5). However, if bias exists, it appears to be no more than about 10%.

B.1 Comparison of Field and Laboratory Performance for NB

Non-detections were reported for both the field and corresponding laboratory analyses for $n = 36$ groundwater split samples (pairs). The proportion of times the field and laboratory methods were observed to agree $p = 1$. This measured proportion p is considered an estimate of the population (“true”) proportion P . A $(1 - \alpha)100\%$ confidence interval for P is calculated using the formula:

$$\left[\left(1 + \frac{(n-c+1)F_{1-\frac{\alpha}{2}, 2n-2c+2, 2c}}{c} \right)^{-1}, \left(1 + \frac{(n-c)}{(c+1)F_{1-\frac{\alpha}{2}, 2c+2, 2n-2c}} \right)^{-1} \right] \quad (1)$$

$p = c / n$ = Sample (measured) proportion

n = Total number of pairs (i.e., splits of groundwater samples analyzed by the laboratory and field method)

c = Number of “concordant” pairs; that is pairs that agree

F_{γ, v_1, v_2} = γ 100th percentile of F distribution with v_1 and v_2 degrees of freedom

As all of the pairs agree, $c = n$ and $p = 1$. The upper bound of the confidence interval for P is 1, and $F = F_{1-\alpha}$ for the lower bound of the confidence interval. The 95% interval for P is calculated from the above equation using the commercial statistical software package Minitab:

Test of $p = 0.9$ vs $p \text{ not} = 0.9$

Exact

Sample X N Sample p 95% CI P-Value

1 36 36 1.000000 (0.920153, 1.000000) 0.025

The output from Minitab indicates that the “true” portion of agreements between the laboratory and field method pairs P is between 0.92 and 1 with 95% confidence; there was over 95% confidence that P is at least 0.9. A comparable result can be obtained using the binomial distribution:

$$Pr(X = c) = \frac{n!}{(n-c)!c!} \times P^c (1-P)^{n-c} \quad (2)$$

$Pr(X = c)$ = Probability c of the n pairs (splits) agree

P = “True” proportion of splits that agree

As $c = n$, to achieve 95% confidence,

However, it should be noted that this evaluation only demonstrates that the field and laboratory results are consistent when NB is not present at detectable levels; it does not demonstrate that field and laboratory method will produce comparable results when NB is present at detectable levels.

B.2 Comparison of field and laboratory performance for other explosives

This section addresses preliminary statistical evaluations that were performed for the five remaining explosives evaluated: 1, 3-DNB, 2, 4-DNT, TNB, TNT and RDX. It presents some descriptive statistics and summarizes the results of various statistical tests using Minitab and Minitab macros that can be downloaded from the website:

www.practicalstats.com/nada

Table B1 indicates that all of the data sets are censored to some degree (i.e., contain non-detects). A pair is censored if

$$(< RL_x, y) \quad (3)$$

$$(x, < RL_y) \quad (4)$$

$$(< RL_x, < RL_y) \quad (5)$$

where x denotes a result from the laboratory method; y a result from the field method; and RL is the Reporting Limit for a non-detect (for either the laboratory or field method). The degree of censoring ranges from about 30% to 80% for 1, 3-DNB, 2, 4-DNT, and TNB. Therefore, the non-parametric methods were considered the most appropriate for these data sets. Parametric methods were also subsequently used to evaluate the paired data sets. The censored pairs were removed from the data sets when parametric methods were used (rather than substituting surrogate values for the non-detects).

Table B2 presents some descriptive statistics for the field and laboratory results.

Table B1. Number of pairs and proportion of detected results.

Variable	<i>n</i>	D	ND	%ND	Uncensored Pairs
13DNB_F	36	10	26	72.2	7
13DNB_L	36	14	22	61.1	
24DNT_F	36	12	24	66.7	10
24DNT_L	36	28	8	22.2	
TNB_F	36	28	8	22.2	26
TNB_L	36	33	3	8.3	
TNT_F	36	35	1	2.8	32
TNT_L	36	33	3	8.3	
RDX_F	34	33	2	5.9	32
RDX_L	34	33	1	2.9	

Key

n = number of pairs

F = Field method (Griffin 450)

L = Laboratory method (ECB LC)

D = Number of detections

ND = Number of non-detections

Table B2. Range of concentrations.

Variable	Group ID	N	Minimum	Maximum	(mg/L)
13DNB All	Field	36	0.000781	0.29796	
	Lab	36	0.00000574	0.32856	
24DNT All	Field	36	0.000497	0.16783	
	Lab	36	0.00000600	0.19009	
24DNT_F	Field	36	0.000781	12.573	
	Lab	36	0.0000205	8.245	
24DNT_L	Field	36	0.000780	6.726	
	Lab	36	0.000125	6.570	
TNB_F	Field	34	0.000781	17.981	
	Lab	34	0.0000719	13.611	

The differences between the field and laboratory method were initially calculated to determine if the field method is biased relative to the laboratory method. The results are presented in Appendices B.8, B.9, and B.10. However, this approach assumes bias is not a function of concentration and constitutes only a “first-tier” or screening-level evaluation to determine if there are large average biases between the field and laboratory

methods. These evaluations were not considered as useful as the linear fits in Sections B.11 and B.12.

Appendix B.8 shows box plots for the above data sets. They were generated by segregating the detections (group identifier = 0) and the non-detections (group identifier = 1). The box plots for the non-detects, which are plots of the reporting limits (RLs) for the non-detects, were not used. The box plots for 1, 3-DNB and 2, 4-DNT suggest that the field method may possess a small positive bias relative to the laboratory method.

The sign test and Prentice-Wilcoxon tests for paired data were performed to determine if the field method exhibits a bias overall relative to the laboratory method. The sign test compares paired observations (x , y) where x denotes a sample result from the laboratory method and y the corresponding sample result from the field method. If the field method is not biased relative to the laboratory method, the number of positive and negative differences should be roughly equal to $y - x$. However, the sign test does not take into account the magnitude of the differences $y - x$. The Minitab macro "csign" (v. 1.6) was used to compute the sign test for the left-censored paired data sets for five explosives. This macro uses the "Modified Sign Test" of Fong et al. (2003) to calculate tie-corrected p-values.

The results of the sign tests are summarized in Appendix B.9. Statistically significant differences at the 95% level of confidence were identified for the first three explosives; that is, the field method tended to produce larger results than the laboratory method for 1, 3-DNB, 2, 4-DNT, and TNB.

The Prentice-Wilcoxon test was also performed to compare the field and fix-laboratory split analyses. The test entails comparisons between observations using the differences between ranks. Unlike the sign test, the Prentice Wilcoxon test takes into account the magnitude of differences between x and y . A description of the test can be found in the reference. This Minitab macro "PPW" (v. 2.7) was used to do the Prentice-Wilcoxon tests. The results are summarized in Appendix B.10. A significant difference between the laboratory and field results at the 95% confidence level occurred for only TNB. The TNB field results tended to be larger on the average than the corresponding laboratory results. Appendix B.10 presents box plots for the differences between the field and laboratory results ($F - L$). These box plots suggest that the field method test may

possess a positive bias relative to the laboratory method for the explosives 1, 3-DNB, 2, 4-DNT, and TNB.

A summary of the results in Appendix B.8, B and C is presented below in Table B3. The field method does not exhibit any significant bias for RDX. The field method may possess positive biases for 1, 3 – DNB and 2, 4-DNT. However, these biases are < 1 ppb on the average and seem too small to be of any practical significance. The largest bias was observed for TNB, and is the only contaminant that consistently exhibits a bias. A positive bias was identified by both the sign test and Prentice-Wilcoxon test and via visual examinations of the box plots. The bias is relatively small (about 2 ppb on the average) but may be indicative of a lack of agreement between the field and laboratory methods.

Table B3. Summary of results for Appendices B.8, B.9, and B.10.

Analyte	Box plots of Detects ^{1,2} (Appendix B.8)	Sign Test ² (Appendix B.9) p-value δ (ppb) ³	Prentice-Wilcoxon Test (Appendix B.10) p-value δ (ppb) ³	Box plots of F-L (Appendix B.10) ¹	Conclusion
1,3-DNB	F > L	F > L p = 0.00 δ = 0.8	F = L p = 0.11 δ = 0.9	F > L	F = L
2,4-DNT	F > L	F > L p = 0.00 δ = 0.5	F = L p = 0.053 δ = 0.9	F > L	F > L?
TNB	F = L	F > L p = 0.00 δ = 2.4	F > L p = 0.00 δ = 2.5	F > L	F > L
TNT	F = L	F = L p = 0.24 δ = 0.5	F > L p = 0.033 δ = 0.6	F = L	F = L
RDX	F = L	F = L p = 0.86 δ = -0.5	F = L p = 0.73 δ = -0.3	F = L	F = L

¹ Determined based on qualitative visual evaluations.

² F = Field results, L = Laboratory results

³ δ = Median difference between the field and laboratory results (F – L).

Non-parametric linear fits were performed using the Akritas-Theil-Sen slope estimator and the Minitab macro “ATS” (v. 2.4). The approach is described in Helsel (2005) and Akritas et al. (1995).

The approach is used to perform linear fits ($y = m x + b$) for doubly censored paired data sets (i.e., censoring occurs for the x - and y -variables). The procedure calculates a slope that results in a value of the correlation coefficient for Kendall's tau that is approximately zero for the correlation between the x -variable and the y -variable residuals. The plots and equations of the linear fits are shown in Section B.11.

The ATS macro was used to generate plots of the field results versus the laboratory results and, as a "cross check," plots of the laboratory results versus the field results. All of the absolute values of the intercepts for the linear fits were all less than 2 ppb; most were less than 1 ppb. As 1 ppb is equal to the reporting limit for the field method, the intercepts do not seem to be different from zero. The field TNB results exhibit a significant positive bias: $F \approx 1.5 L$. The field RDX results exhibit a significant negative bias: $F \approx 0.70 L$. The plot for RDX also exhibits the most scatter about the line. The calculated values of Kendall tau are presented below. Despite the small values for Kendall's tau for 1, 3-DNB and 2, 4-DNT, there is a relative good fit; the values for Kendall's tau are likely owing to the large proportion of censored results (censored values are interpreted as ties, decreasing the value of Kendall's tau).

Table B4. Kendall's tau of field vs. laboratory results.

Analyte	τ
1, 3-DNB	0.3
2, 4-DNT	0.3
TNB	0.6
TNT	0.8
RDX	0.8

Only slopes with uncensored x -values are used to compute the Akritas Theil Sen slope estimators outputted by the ATS macro. The "CKend" macro uses slopes with both censored and uncensored x -values to compute the Turnbull estimate of the median slope. Plots of the field results versus the laboratory results created using the CKend macro are presented in Appendix E and are similar to those shown in Appendix D. The absolute values of the intercepts were less than 1 or 2 ppb. They also indicate that the field method exhibits a positive bias for TNB ($F \approx 1.3 L$) and a negative bias for RDX ($F \approx 0.7 L$).

The slopes calculated for the field-versus-laboratory fits computed using “ATS” and “CKend” are summarized in Table B5 below. (This table also summarizes the results of parametric regression fits discussed in Sections B3 -B7.) The slopes for TNB and RDX consistently indicate there is a positive bias for the field method for TNB and a negative bias for RDX. The slopes for 1, 3-DNB, 2, 4-DNT, and TNT are generally near 1 but exhibit some variation depending on the method of calculation.

It is believed that the smaller slope for TNT (0.9) from the non-parametric fits is owing to different behavior of the field method at low concentrations. Section B4 suggests the field method behaves differently at low concentrations. A slope of 1.0 is obtained for TNT at concentrations larger than 0.05 mg/L. Therefore, the non-parametric linear fits that were performed using all of the paired results (censored and uncensored) were not considered as reliable as the parametric linear fit presented in Section B4.

Table B5. Slope estimates of field versus laboratory linear fits.

Analyte	$F \approx m L$ $L \approx m' F$ ($m \neq 1/m'$) Appendix D	$F \approx m L$ $L \approx m' F$ ($m = 1/m'$) Appendix E	Regression Analyses of Uncensored Pairs $F \approx m L$ (Sections 3 -7)
1, 3-DNB	1.2 (1.0)	1.0 (1.0)	0.9
2, 4-DNT	1.0 (1.0)	0.9 (1.1)	0.9
TNB	1.5 (0.7)	1.3 (0.8)	1.5
TNT	0.9 (1.0)	0.9 (1.1)	1.0
RDX	0.7 (1.2)	0.7 (1.4)	Not calculated

B.3 Evaluation of detected RDX results

As only a small portion of the paired RDX data consist of censored values (two points), these values were removed from the data set to use parametric methods. Also, as shown in Figure B1(a) (scatter plot for the uncensored RDX pairs), there is large scatter and poor agreement between the laboratory and field results at concentrations greater than about 1 mg/L. Figure B1(b) was created by expanding the lower portion of the x- and y-axis of the scatter plot in Figure B1(a). Figure B2(b) shows that there is an

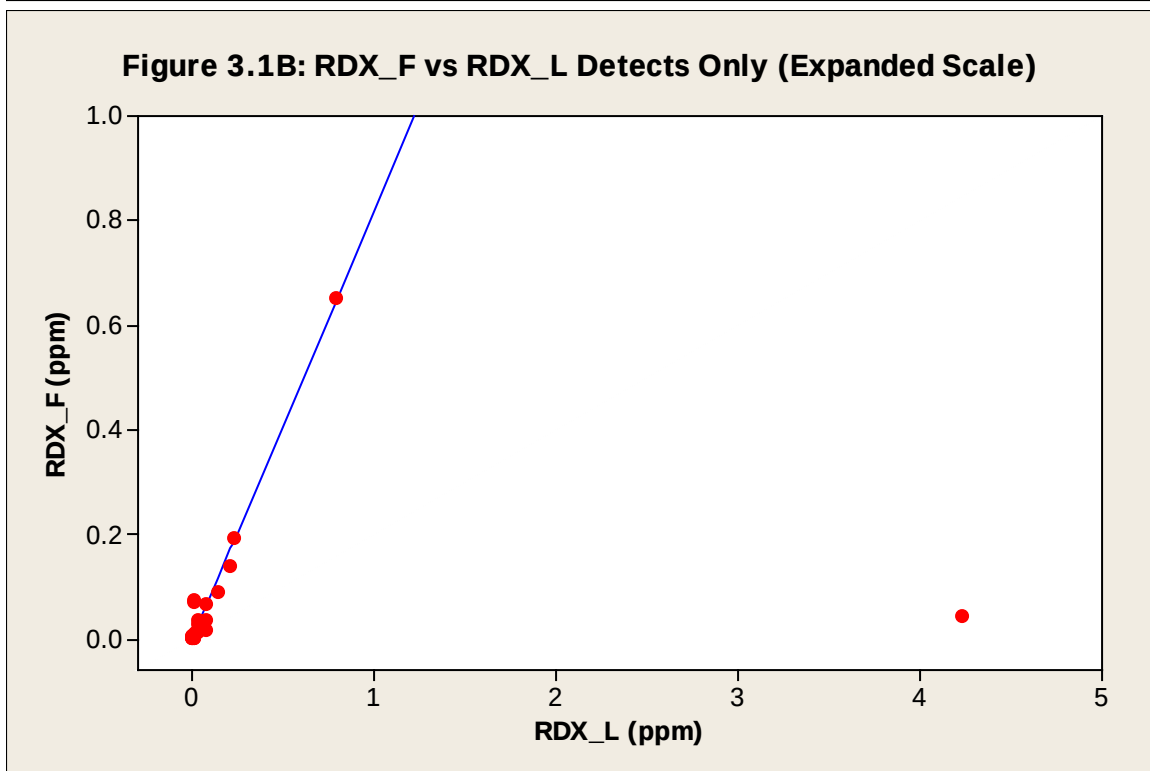
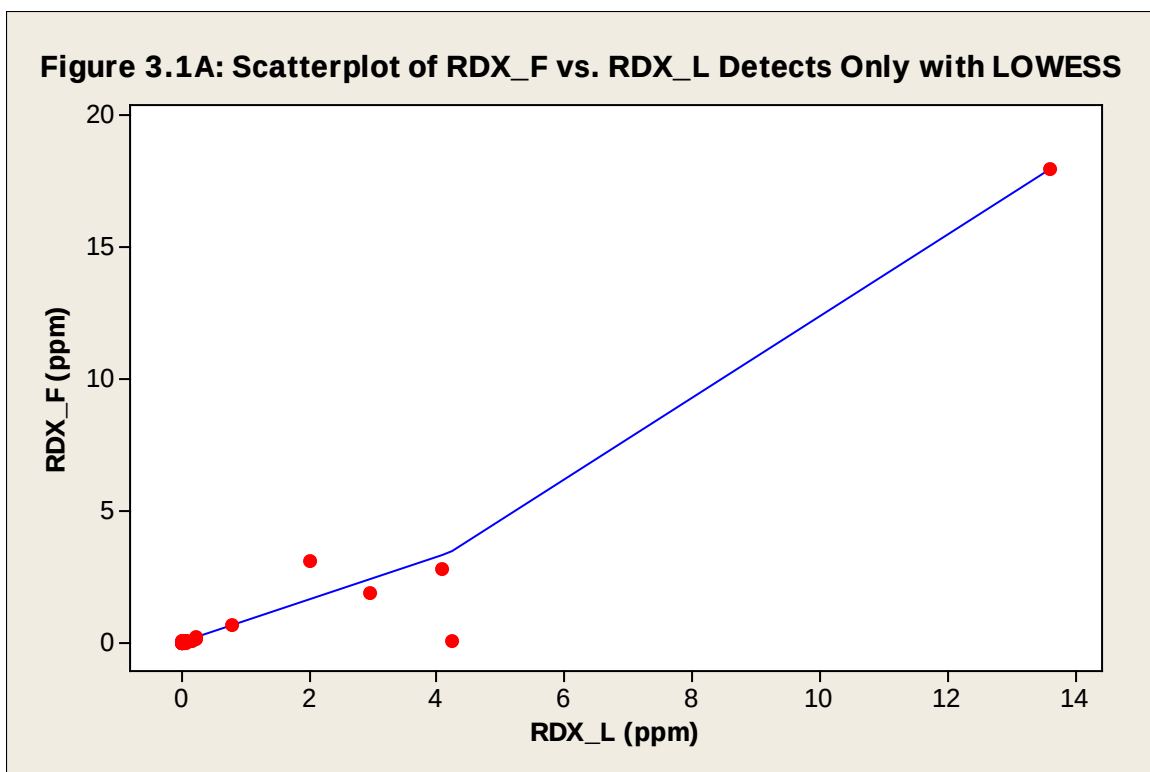


Figure B1. Scatter plots for the uncensored pairs.

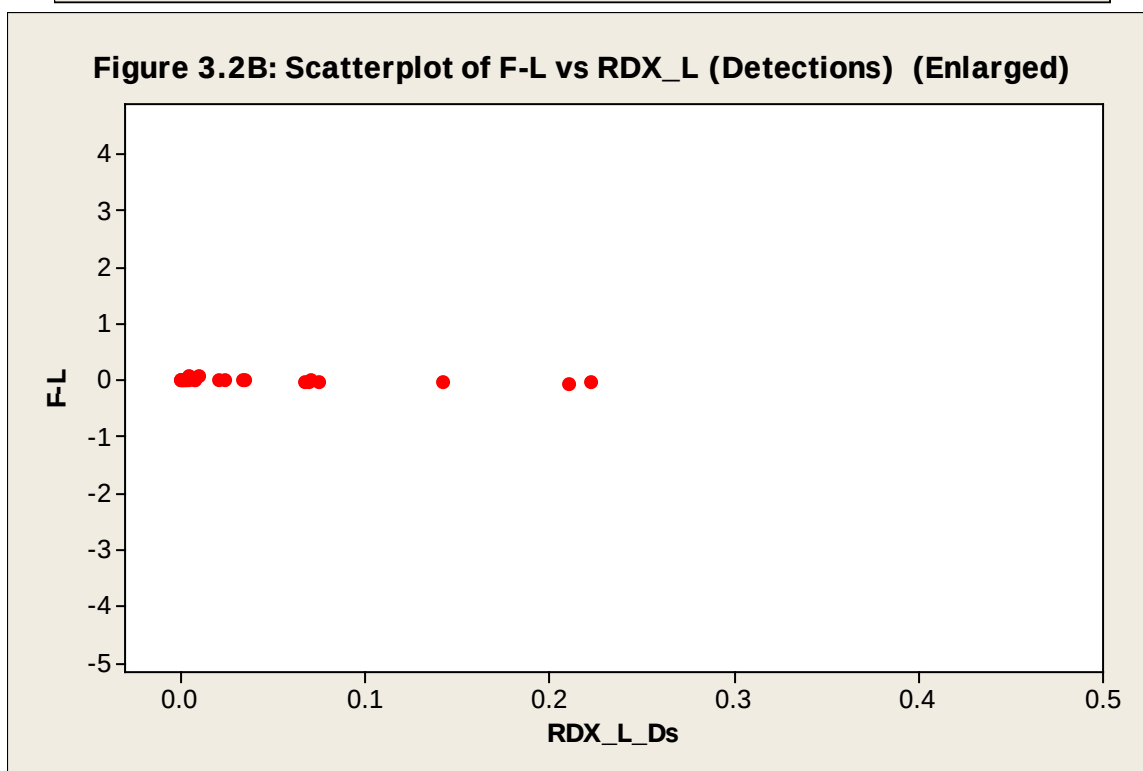
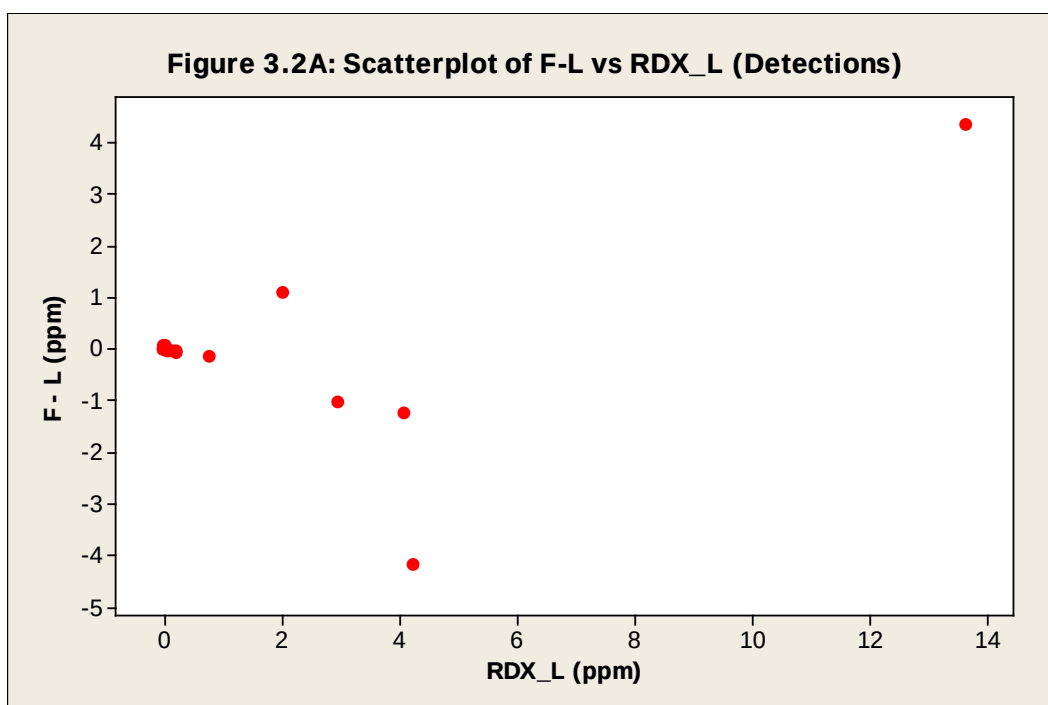


Figure B2. RDX scatter plots showing outlier.

outlier at (L= 4.2, F= 0.044) and most of the points are clustered at concentrations less than 0.5 mg/L. Figures B2(a) and B2(b) also indicate that the differences between the field and laboratory results are highly variable for concentrations greater than 0.5 mg/L.

The outlier ($L = 4.2$, $F = 0.044$) was removed from the data set and only paired results less than 0.5 mg/L were evaluated. The resulting set of $n = 26$ paired points will be referred to as the “trimmed RDX data.” Figure B3 is a scatter plot of the “trimmed” RDX data set.

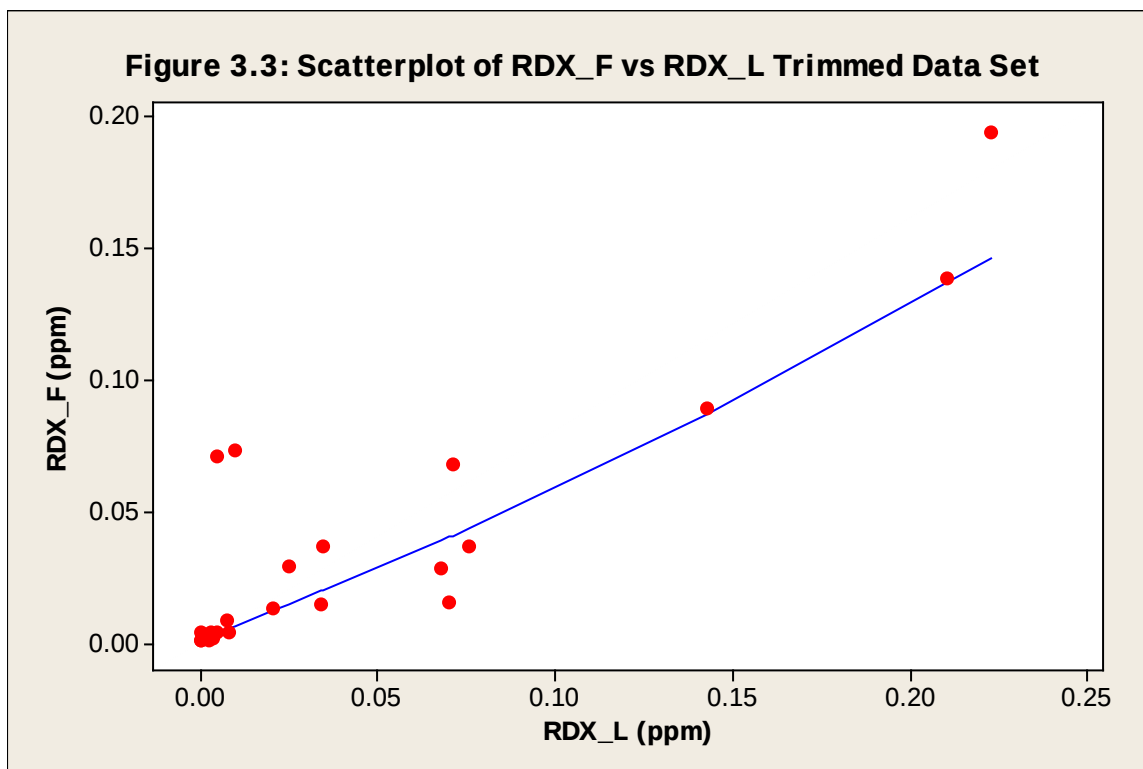


Figure B3. Scatter plot of “trimmed” RDX data set.

As shown in Figure B3, there is still large scatter for the “trimmed data set” even over this smaller concentration range about the nearly linear LOWESS curve. A linear regression fit was done after a log transform was performed for both the field and laboratory results. A log transform for the laboratory and field results was needed to normalize the residuals for an ordinary least squares linear regression fit. The normal probability plots shown in the upper left-hand corner of Figure B5 and Figure B6 indicate that the residuals are approximately normally distributed (in indicated linearity of the plotted residuals and the p -value > 0.1). Figure B4 shows the scatter plot and calculated regression line after the log transformation is performed.

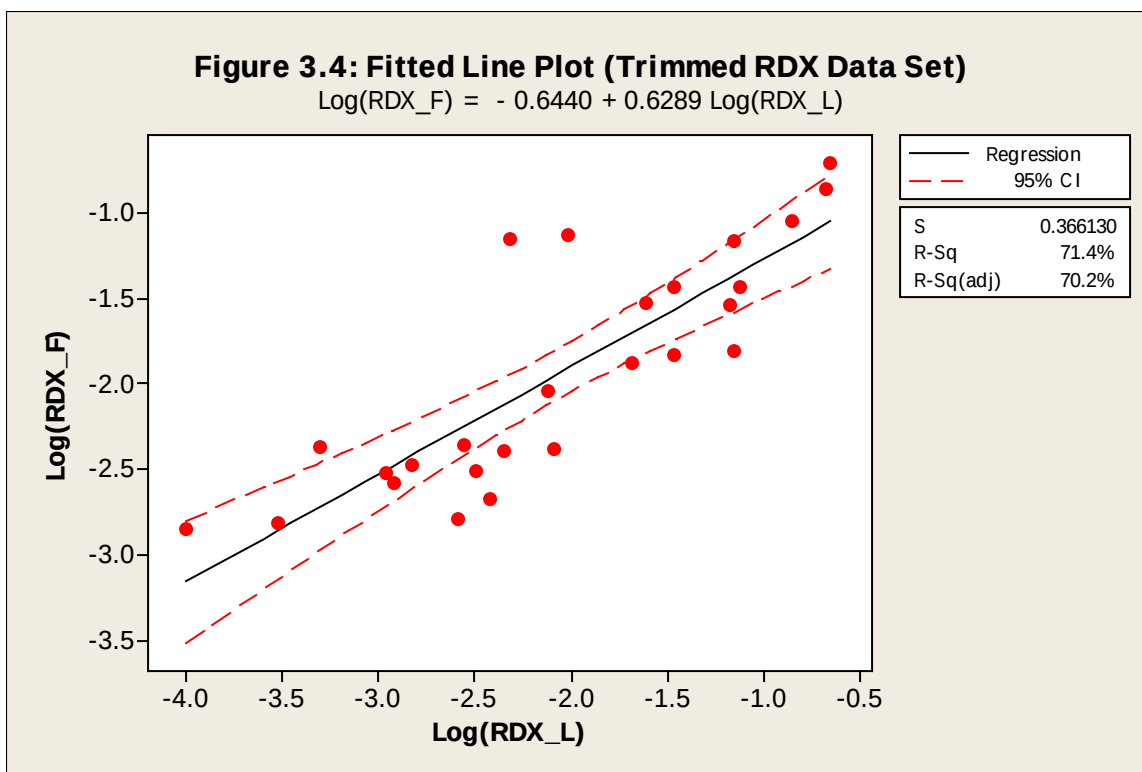


Figure B4. Fitted line plot for trimmed RDX data set.

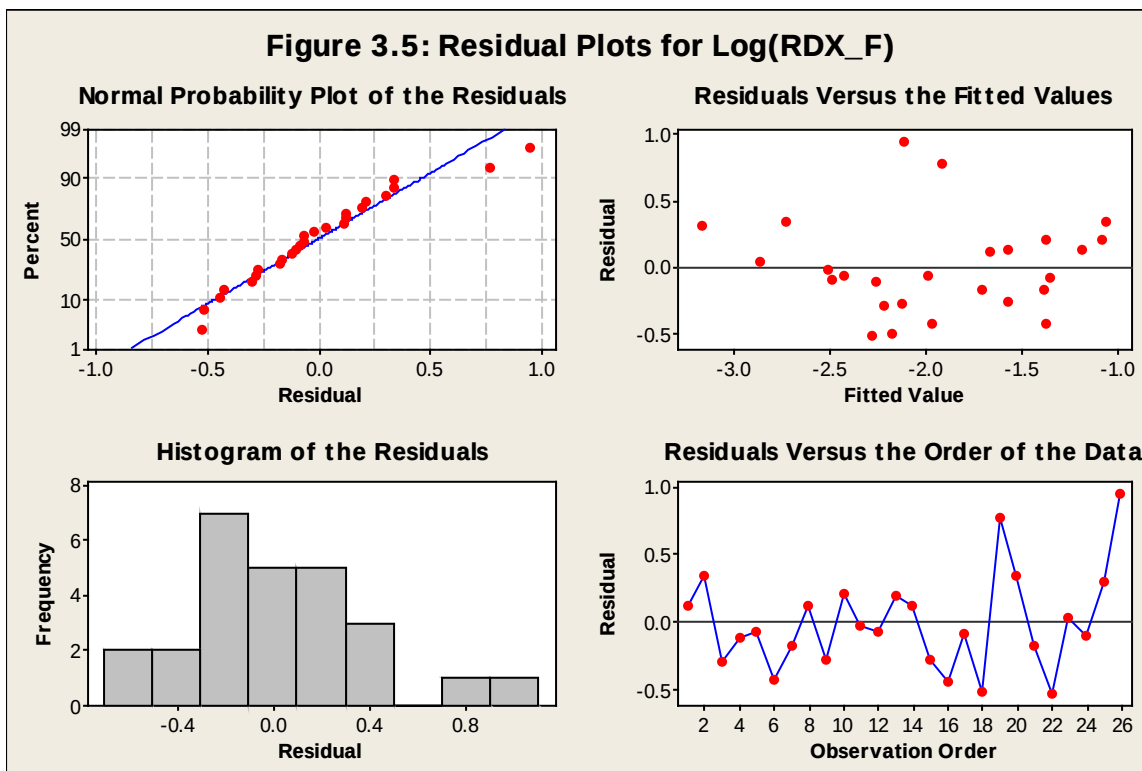


Figure B5. Residual plots for RDX data sets.

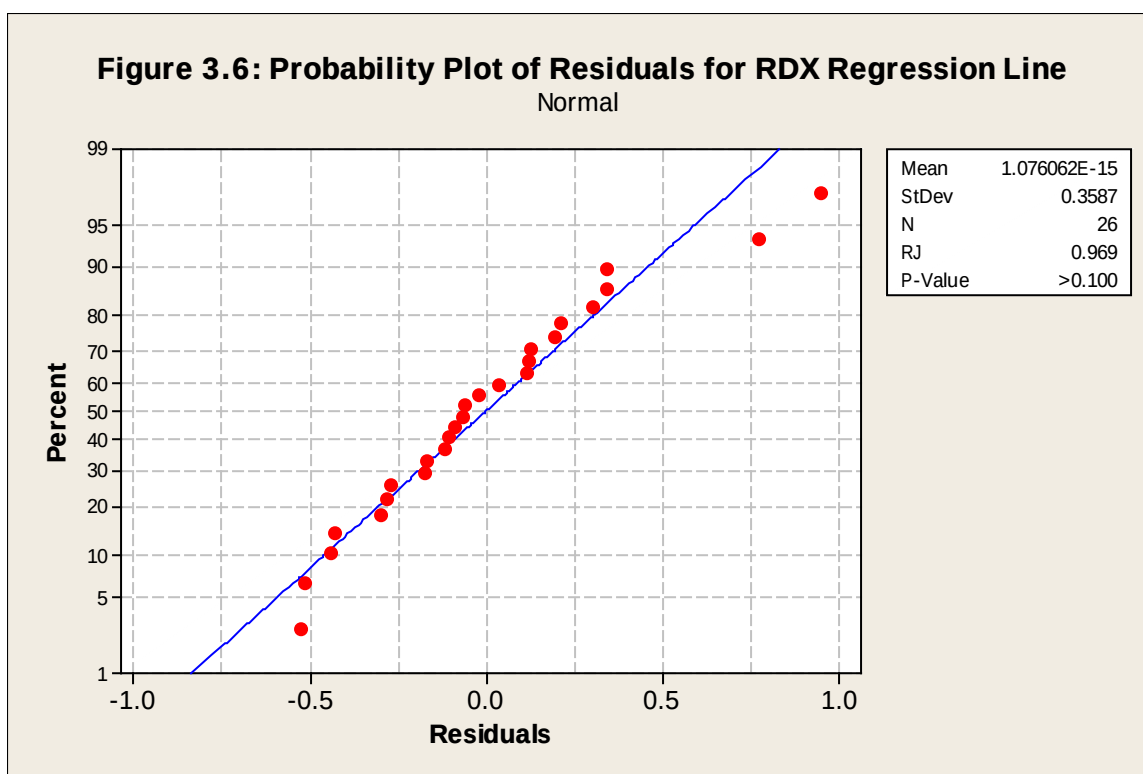


Figure B6. Probability plot of residuals for RDX regression line.

However, the trimmed data set still exhibits moderate scatter; Pearson's $r^2 \approx 0.7$. The regression equation is expressed in terms of the untransformed coordinates is as follows:

$$F = 10^{-0.64} L^{0.63} \approx 0.23 L^{0.63} \quad (6)$$

The equation is non-linear and indicates the field method produces smaller RDX concentrations than the laboratory method (e.g., when $L = 1$ mg/L, $F = 0.23$ mg/L). Plots of the observed field results (red dots) and corresponding results calculated using the above regression equation (black curve) are shown in Figure B7. The regression curve that models the field results is negatively biased for concentrations greater than about 0.1 mg/L. There is also large scatter about the regression curve at concentrations less than 0.1 mg/L.

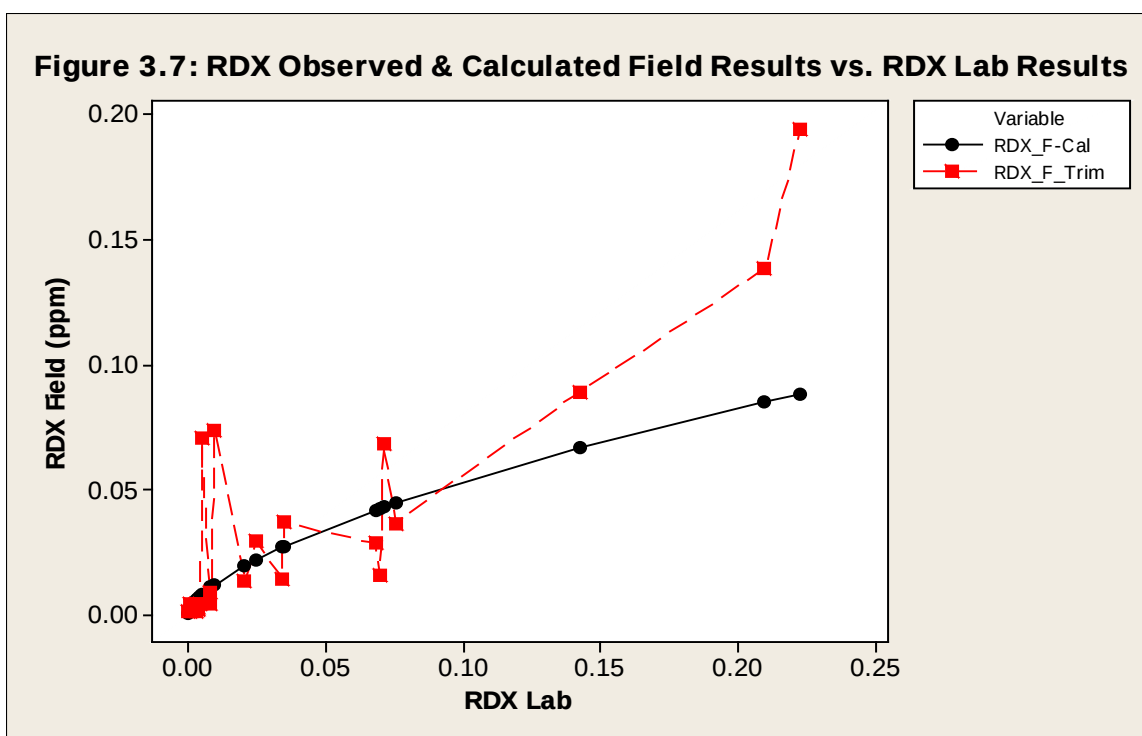


Figure B7. Field results versus lab results for RDX.

Paired uncensored results for which the field method produced detected concentrations $> 0.05 - 5$ mg/L were subsequently evaluated. This resulted in the following set of $n = 9$ uncensored paired measurements:

Table B1. Pairs where field results are 0.05 – 5 mg/L.

RDX_F	RDX_L
0.1939	0.2231
1.9238	2.9515
0.6502	0.7841
2.8327	4.0635
0.0890	0.1426
0.1939	0.2231
0.1384	0.2103
0.0680	0.0711
0.0734	0.0097
0.0708	0.0048

A scatter plot and the regression line calculated are shown in Figure B8. Residual plots for RDX are shown in Figure B9.

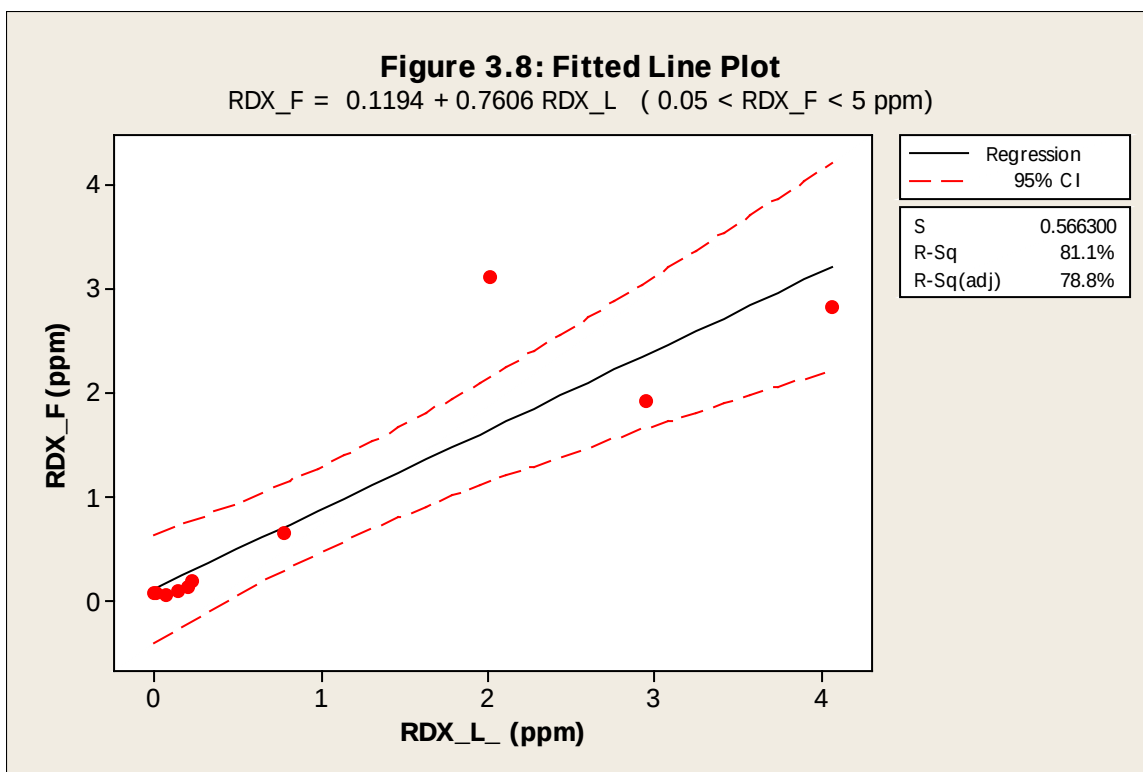


Figure B8. Scatter plot and regression line for RDX.

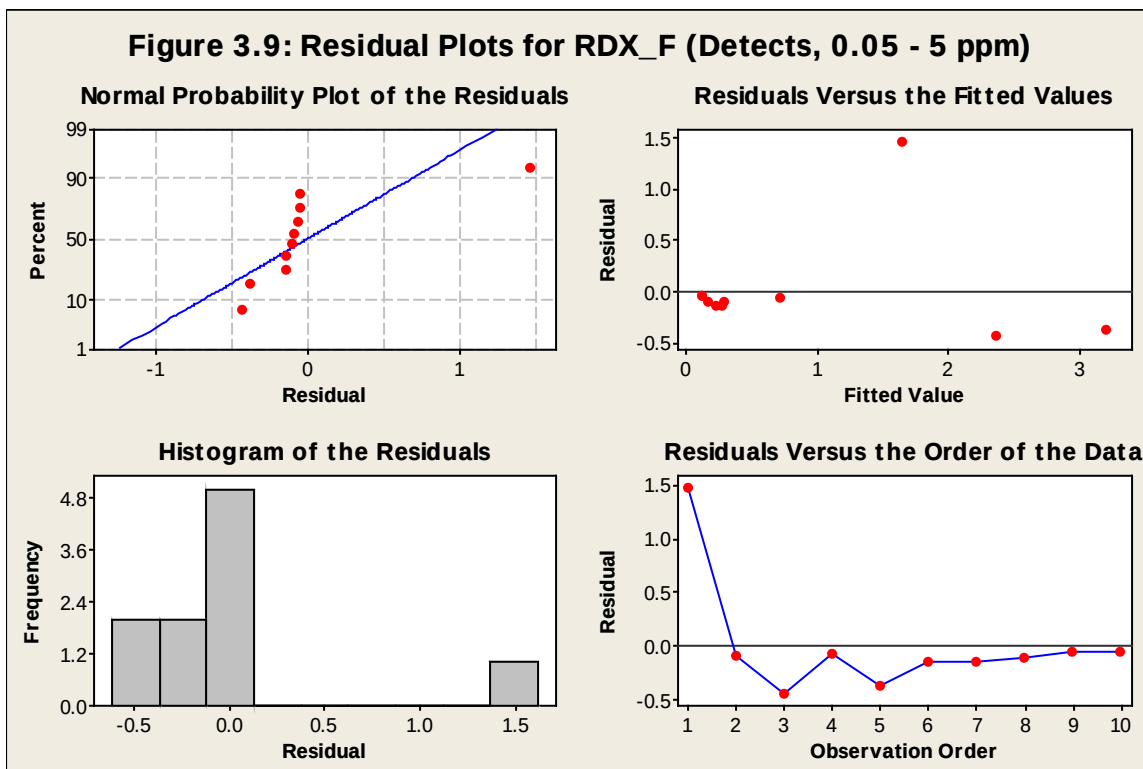


Figure B9. Residual plots for RDX.

The linear fit is relatively poor. The residuals are not normal; the degree of scatter increases with concentration. The slope is about 0.8; the intercept is somewhat larger than zero; $r^2 \approx 0.8$. A log transform would not appreciably improve the fit.

The field method would be appropriate as a screening method for qualitative determination of presence/absence. All of the $n = 34$ pairs produces consistent results for presence/absence. A pair (x, y) is considered to be in agreement or “concordant” if one of the following conditions is satisfied:

$$x < RL_x \text{ and } y < RL_y,$$

$$x \text{ is a detected value, } y < RL_y \text{ and } x < RL_x$$

RL_x is the reporting limit for the laboratory method; RL_y is the reporting limit for the field method; x denotes a laboratory result; y denotes a field result; and $RL_x < RL_y$. All of the RDX pairs were concordant. Using the approach in Section B2, it can be concluded with 95% confidence that the “true” portion P of concordant pairs is:

$$P = \exp\{\ln(0.05) / 34\} = 0.92 \quad (7)$$

In other words, there is 95% confidence the field and laboratory methods will be consistent with respect to reporting the non-detects and detects of RDX at least 90% of the time.

Conclusion: The field method does not produce comparable results to the laboratory method for RDX. The field method produces variable results across all concentration ranges evaluated. Kendall’s tau was only 0.8 for all the censored and uncensored pairs (even though only a small portion of the paired data set was censored). The square of Pearson’s r was also about 0.8 for uncensored pairs for which the field results range from about 0.05 – 5 mg/L. Both non-parametric and parametric methods used to fit the field-versus-laboratory plots suggested that the field method possesses a negative bias of about 20% - 30% relative to the laboratory method. However, the qualitative agreement between the laboratory and field results suggests that the field method can be used for screening purposes.

B.4 Evaluation of detected TNT results.

As only a small portion of the paired TNT data consist of censored values (4 of the 36 pairs), these values were removed from the data set to use parametric methods. A scatter plot of all the detected results is presented in Figure B10.

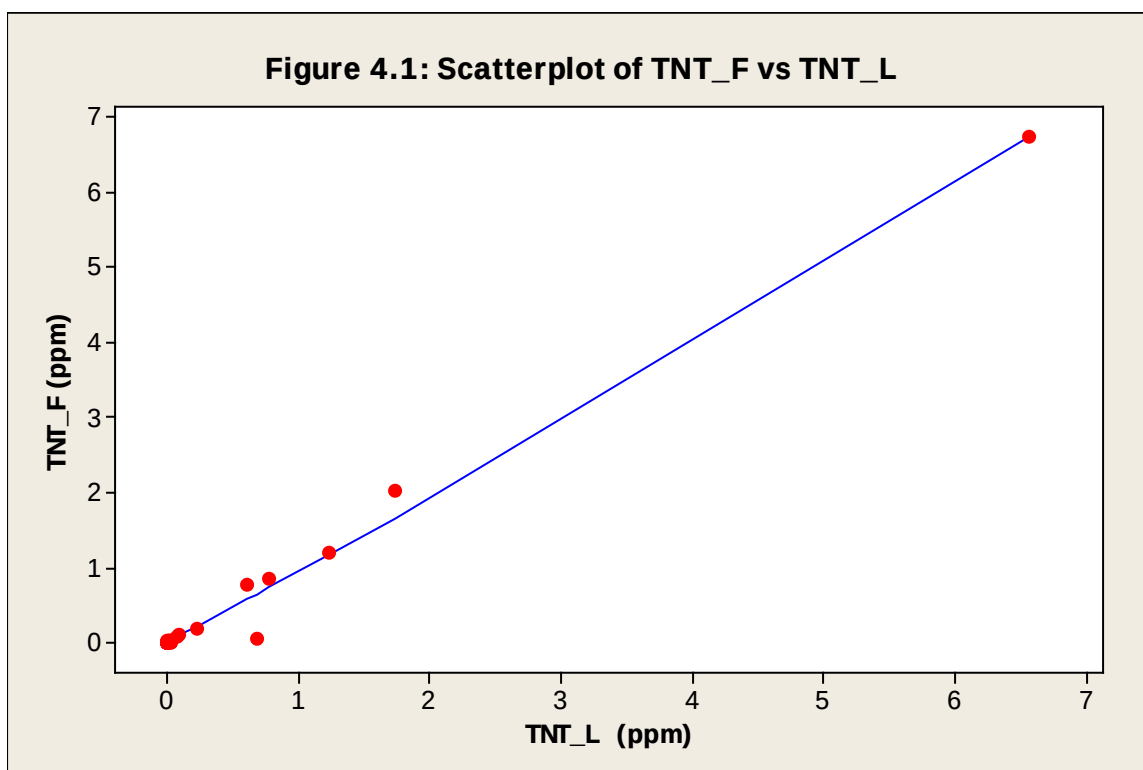


Figure B10. Scatter plot of all detected results for TNT.

An ordinary least squares regression fit is shown in Figure B11. The slope is near one and the line nearly passes through the origin; the square of the correlation coefficient, $r^2 \approx 0.99$. However, the large correlation coefficient is predominately owing to a few large paired values; the largest is ($L = 6.6$, $F = 6.7$). Also, the residuals are not normal but are lognormal as shown in Figure B12. Performing a log transform to normalize the residuals for a linear regression fit (Figure B13) also results in a relatively poor fit, as shown in Figures B14 and B15. The resulting equation (Figure B15) is not linear in the untransformed coordinates (as shown below):

$$F \approx 10 - 0.29 L^{0.82} \approx 0.51 L^{0.82} \quad (8)$$

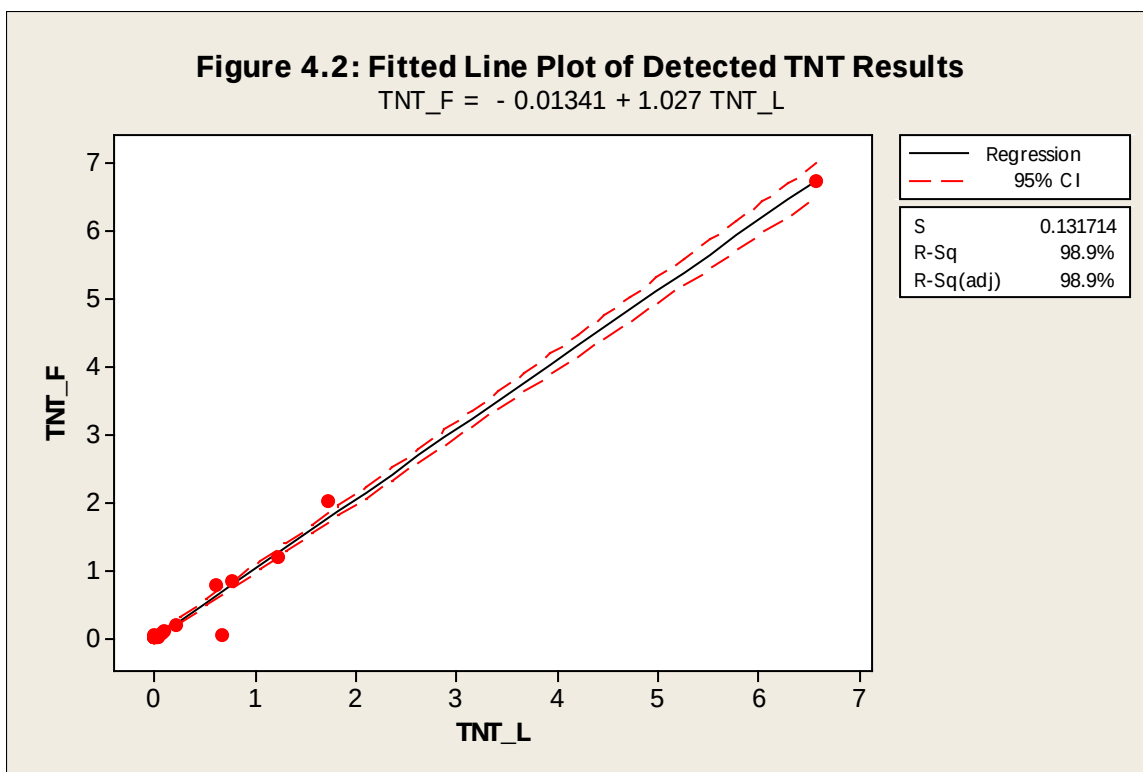


Figure B11. Fitted line plot of detected results.

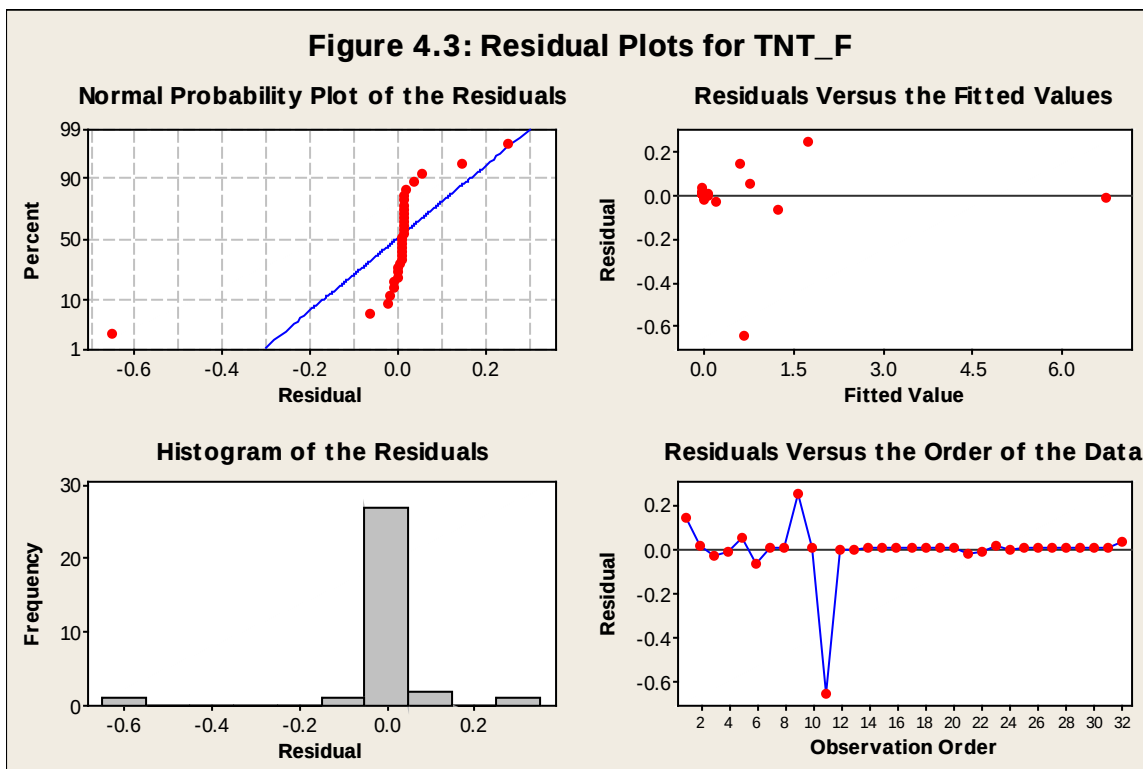


Figure B12. TNT residual plots.

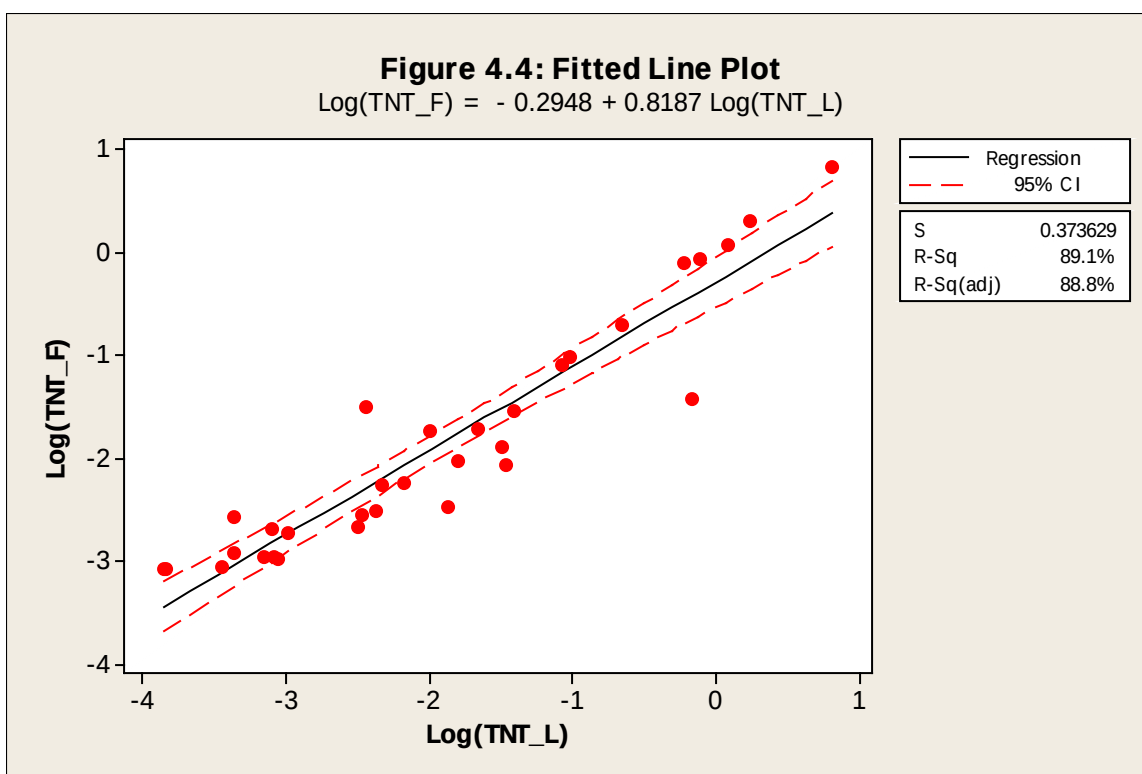


Figure B13. Log transformed residuals for linear regression fit.

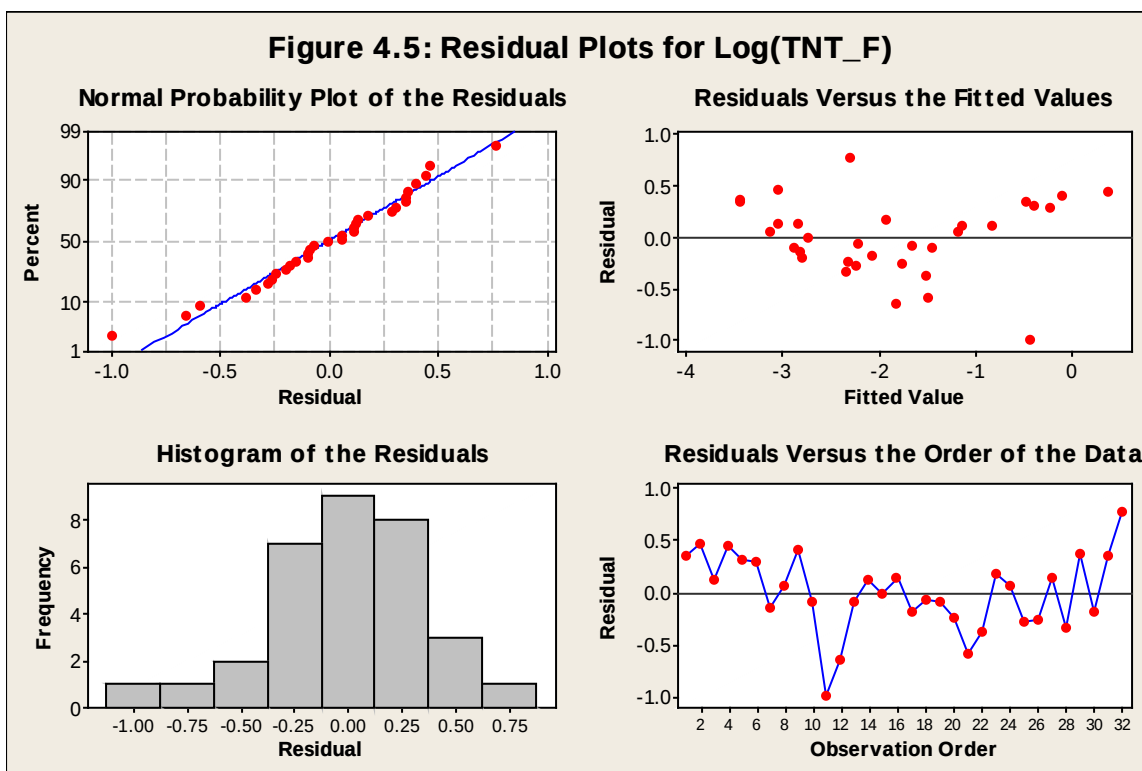


Figure B14. Residual plots for TNT showing relatively poor fit.

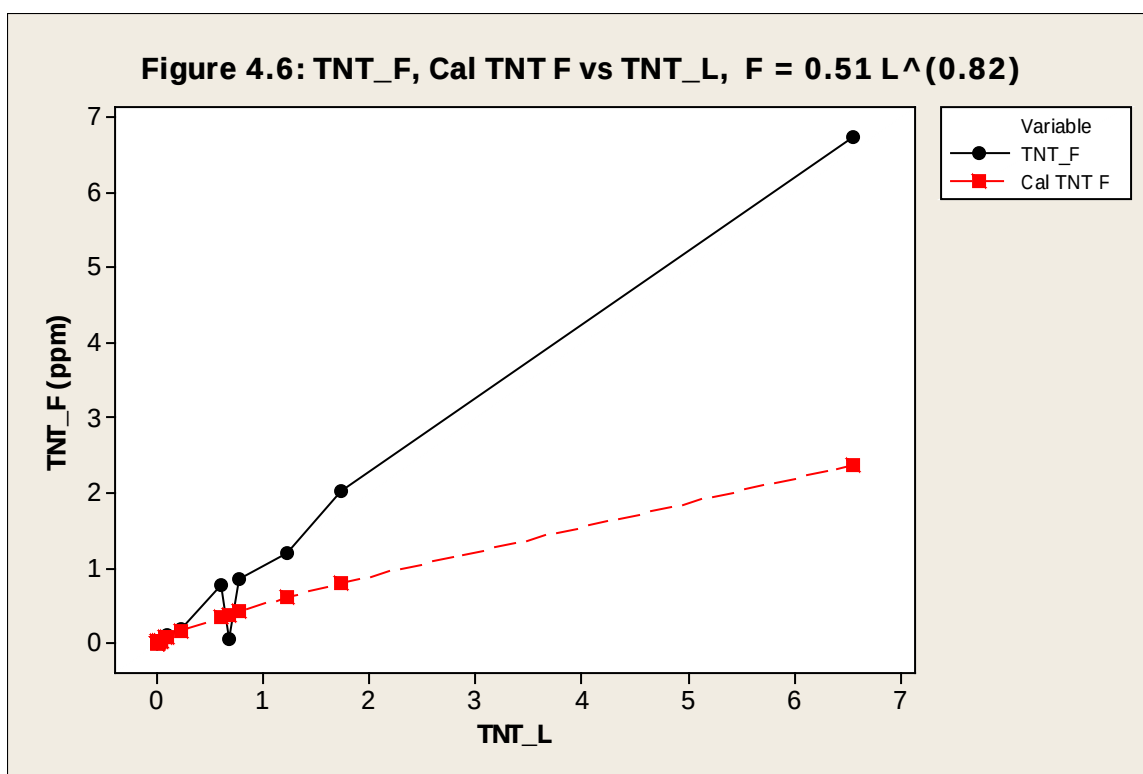


Figure B15. Normalized residuals for a linear regression fit.

The high-concentration pair ($L = 6.6$, $F = 6.7$) was removed from the data set to generate the regression line shown in Figure B16; note that r^2 decreases to ≈ 0.91 . The slope is near one and the intercept is near zero, but the residuals are still not normally distributed. There is also large scatter for concentrations > 0.5 mg/L as shown in the $F - L$ versus L scatter plots in Figure B17.

The scatter plots above suggest larger variability between the field and laboratory results for concentrations greater than 0.5 mg/L. Therefore, only pairs for which the field result is < 0.5 mg/L were retained.

Unfortunately, this results in a rather prominent outlier, ($F = 0.037588$, $L = 0.681405$), as shown in Figure B18. This outlier was also eliminated to determine “best case” correlation between the TNT lab and field results. The resulting data set ($n = 26$) will be referred to as the “trimmed TNT pair data set.” A scatter plot of these pairs is shown in Figure B19.

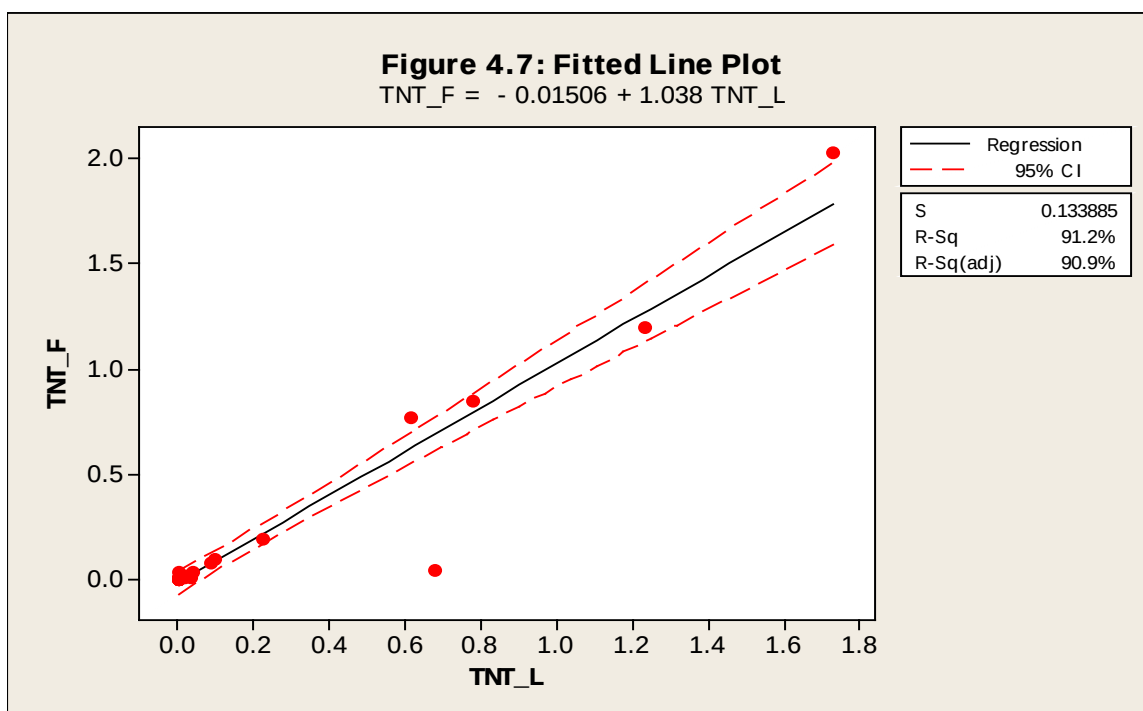


Figure B16. Regression line for TNT.

The regression line for the trimmed data set (Figure B20) passes nearly through the origin but the slope is only 0.9. The square of the correlation coefficient $r^2 = 0.96$, but this statistic is heavily influenced by a few large pairs. The residuals are not normal, but are log normal (Figure B22). However, a log normal transformation gives a poor fit (Figures B21 and B22). This results in a non-linear equation:

$$F \approx 10^{-0.78} L^{0.64} \approx 0.17 L^{0.63} \quad (9)$$

Refer to Figure B23 for a plot of the observed and calculated values of the field concentrations using Equation 9.

The correlation between the field and laboratory results is relatively poor in the concentration range 0 – 0.05 mg/L. Some correlation coefficients between the field and laboratory results for concentrations in this range are presented below. Figure B24 presents a linear regression fit for detected TNT concentration < 0.05 mg/L.

CORRTYPE	CORR_VAL	P_VALUE
PEARSON'S R	0.607575	0.0021050
SPEARMAN'S RHO	0.880435	0.0000000
KENDALL'S TAU_A	0.731225	0.0000012
KENDALL'S TAU_B	0.731225	0.0000012

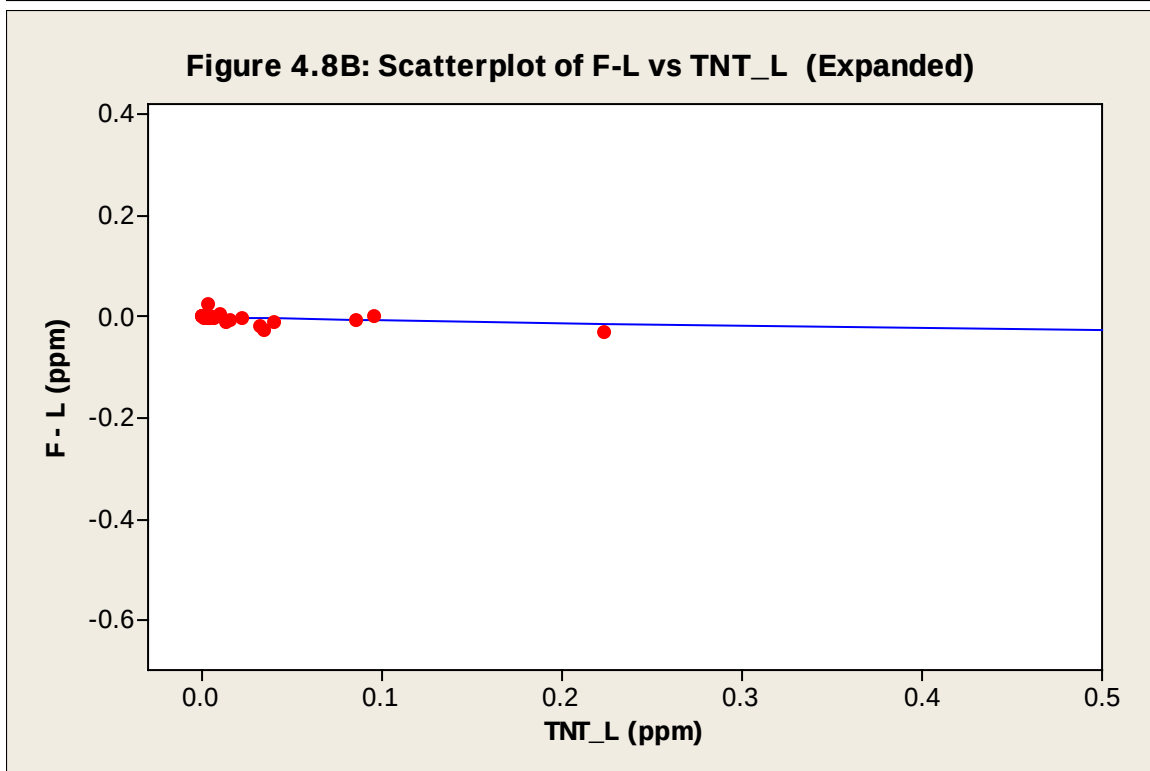
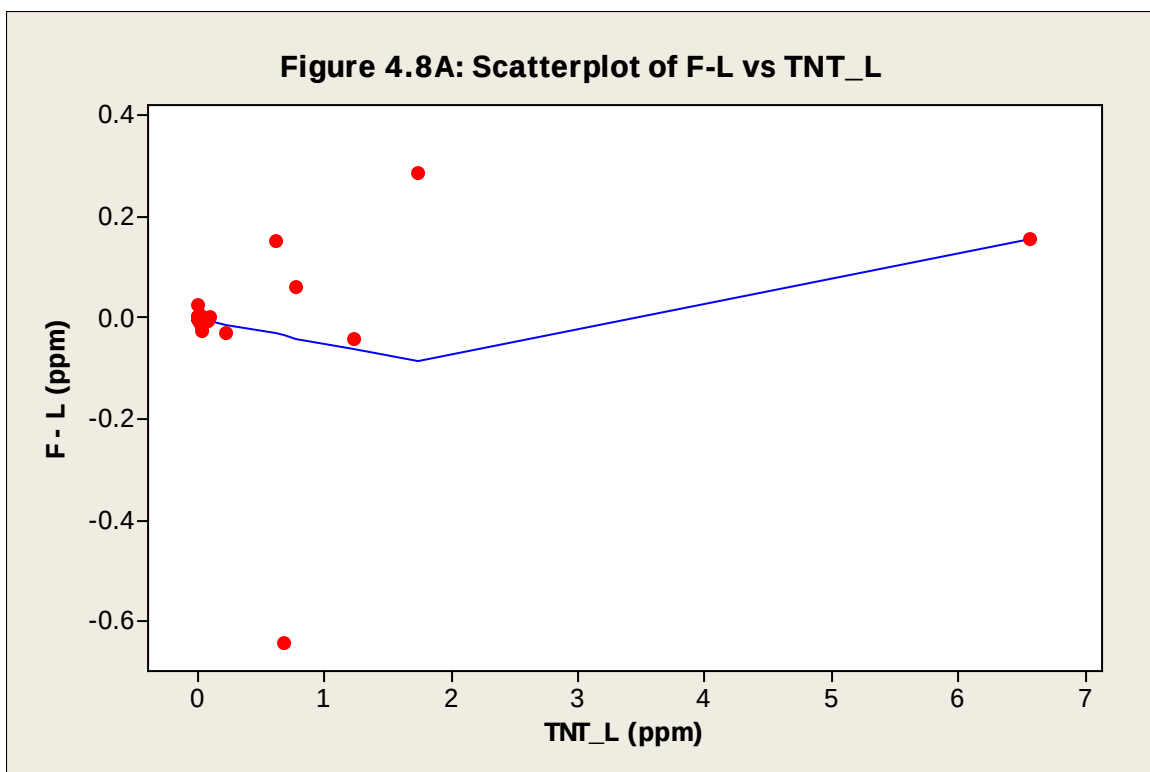


Figure B17. Scatter plots for F-L versus L.

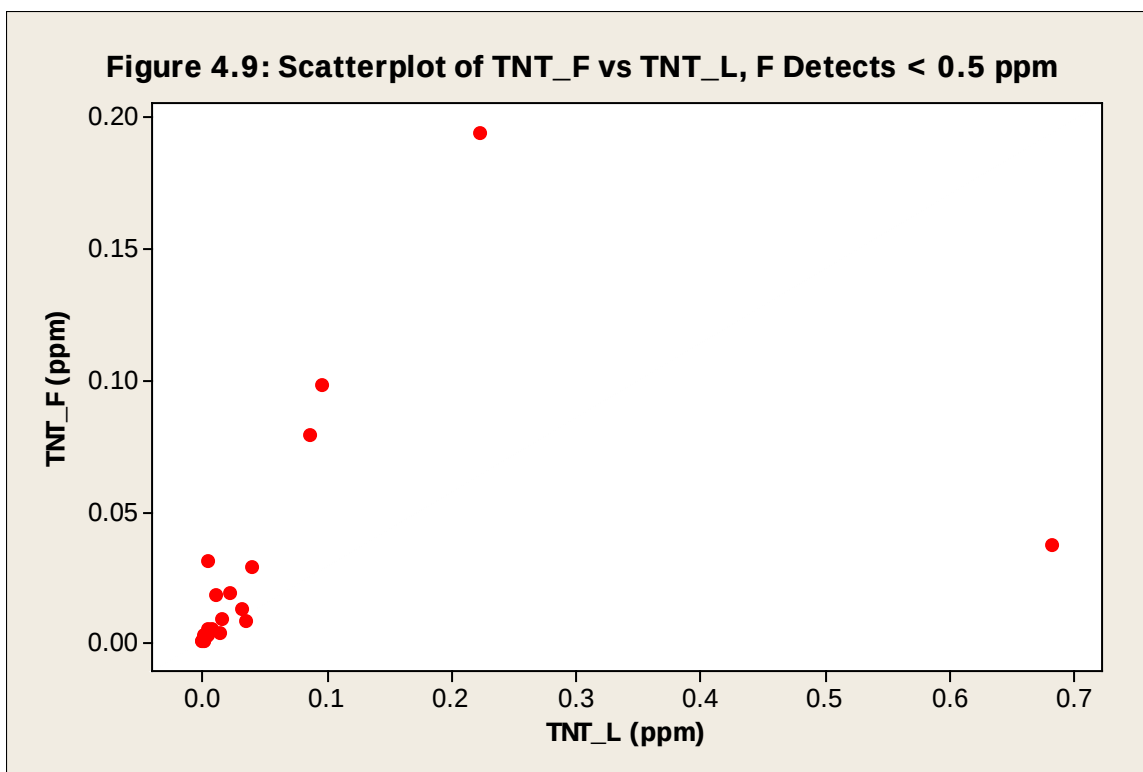


Figure B18. TNT scatter plot showing outlier.

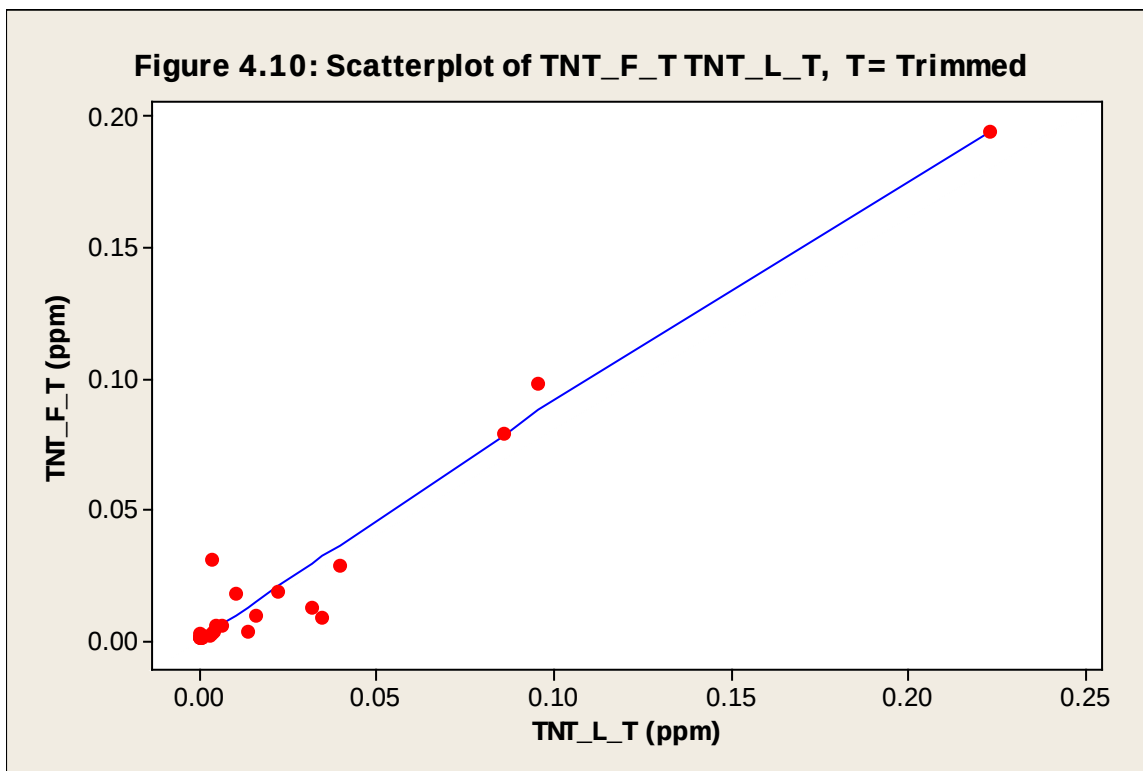


Figure B19. Scatter plot of “trimmed” TNT pair data set.

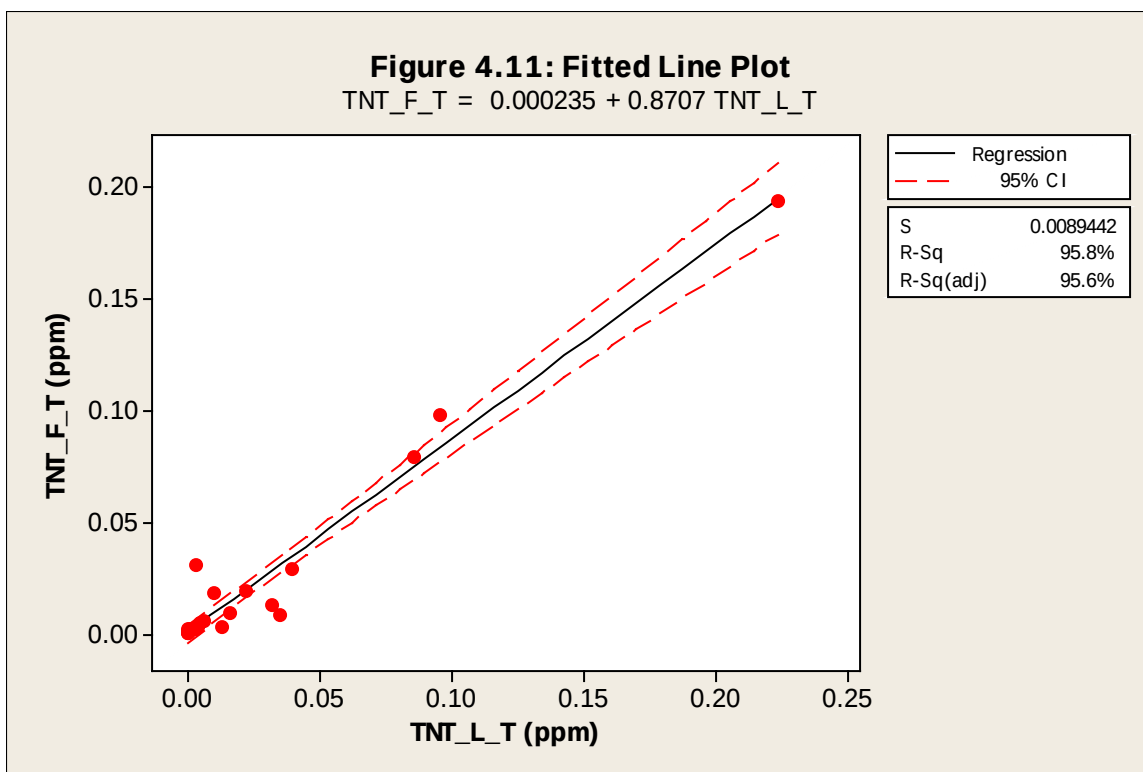


Figure B20. Regression line for trimmed data set.

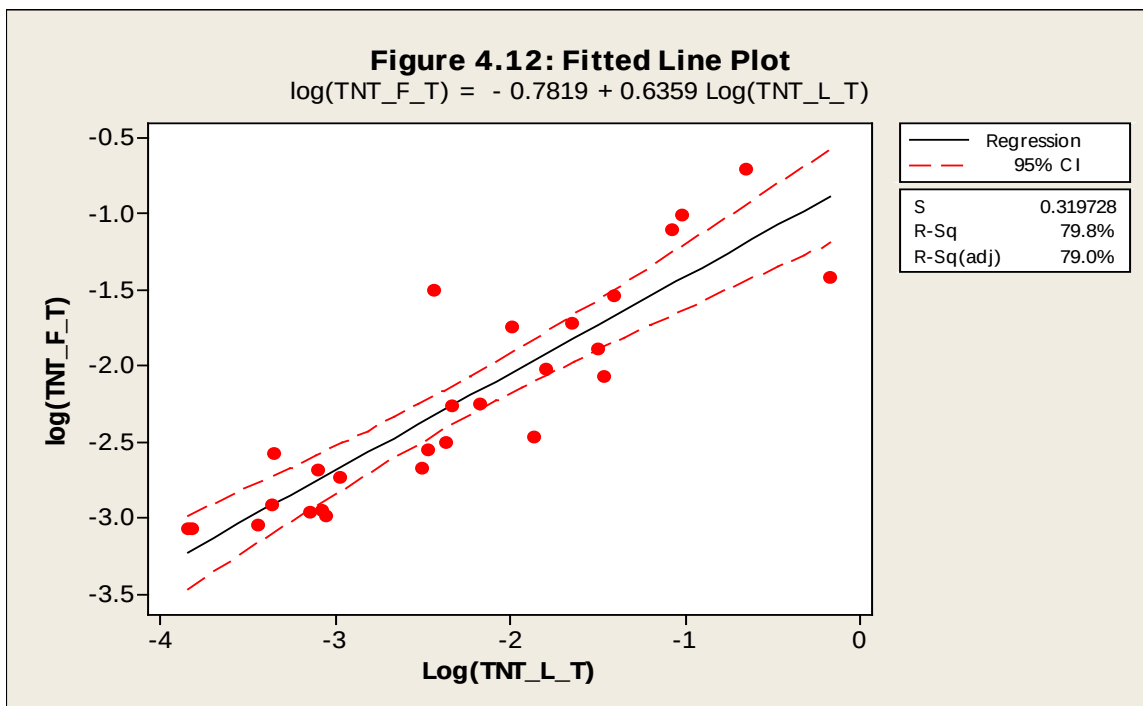


Figure B21. Fitted line plot for TNT.

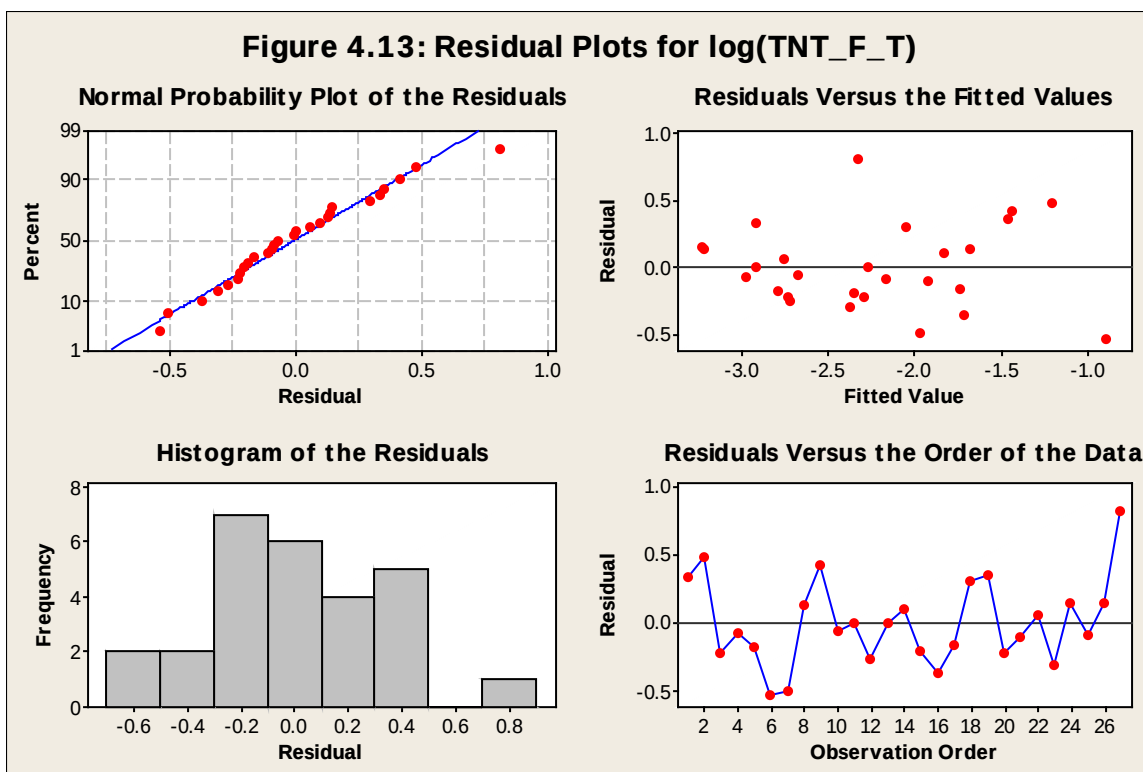


Figure B22. Log normal residual plots for TNT.

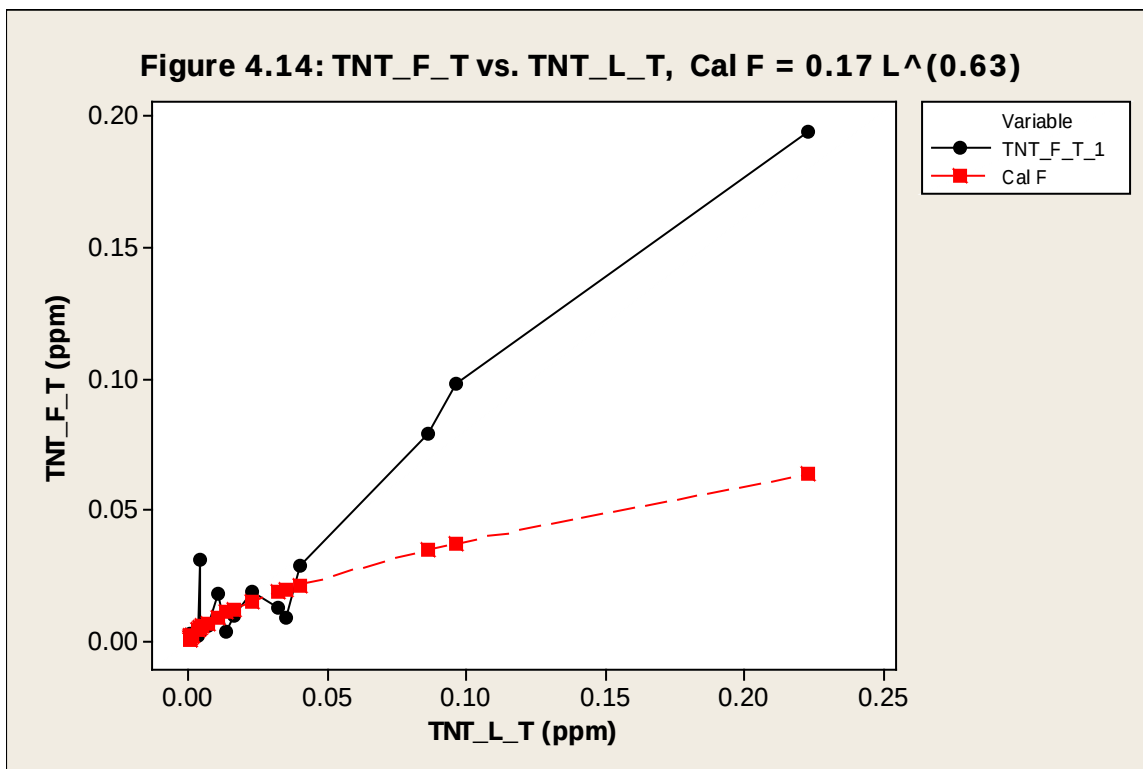


Figure B23. Observed and calculated values of field concentrations for TNT.

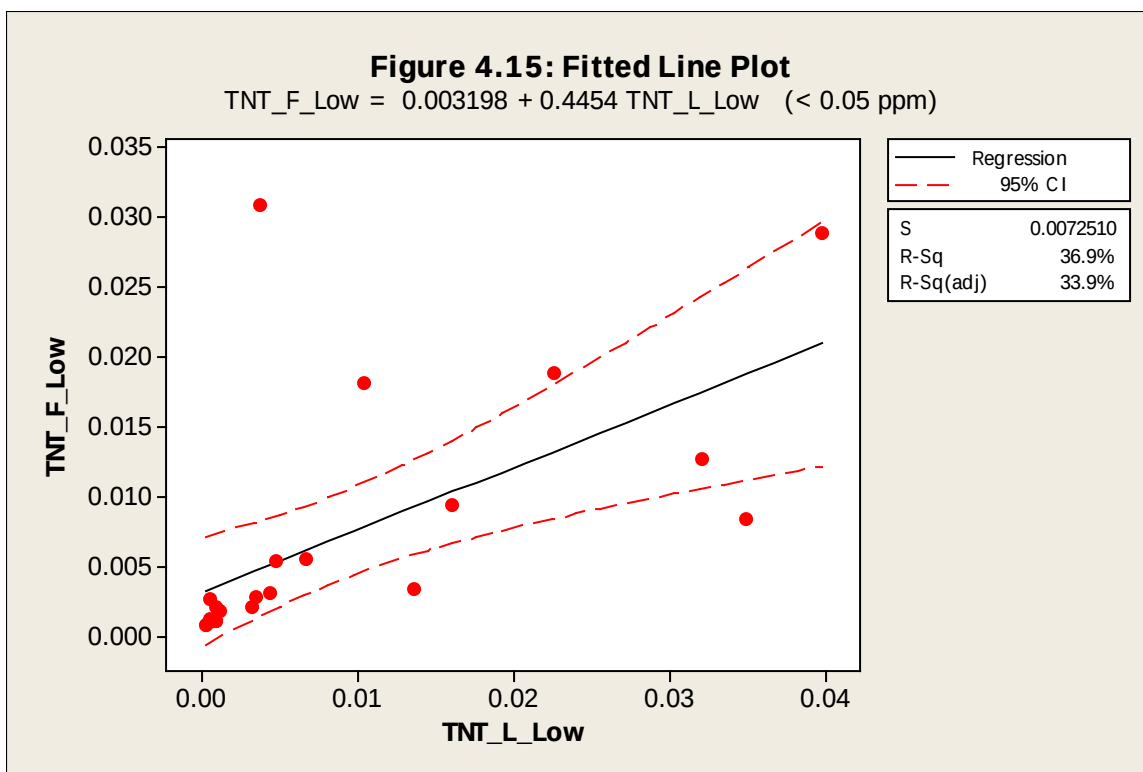


Figure B24. Linear regression fit for detected TNT concentration <0.05 mg/L.

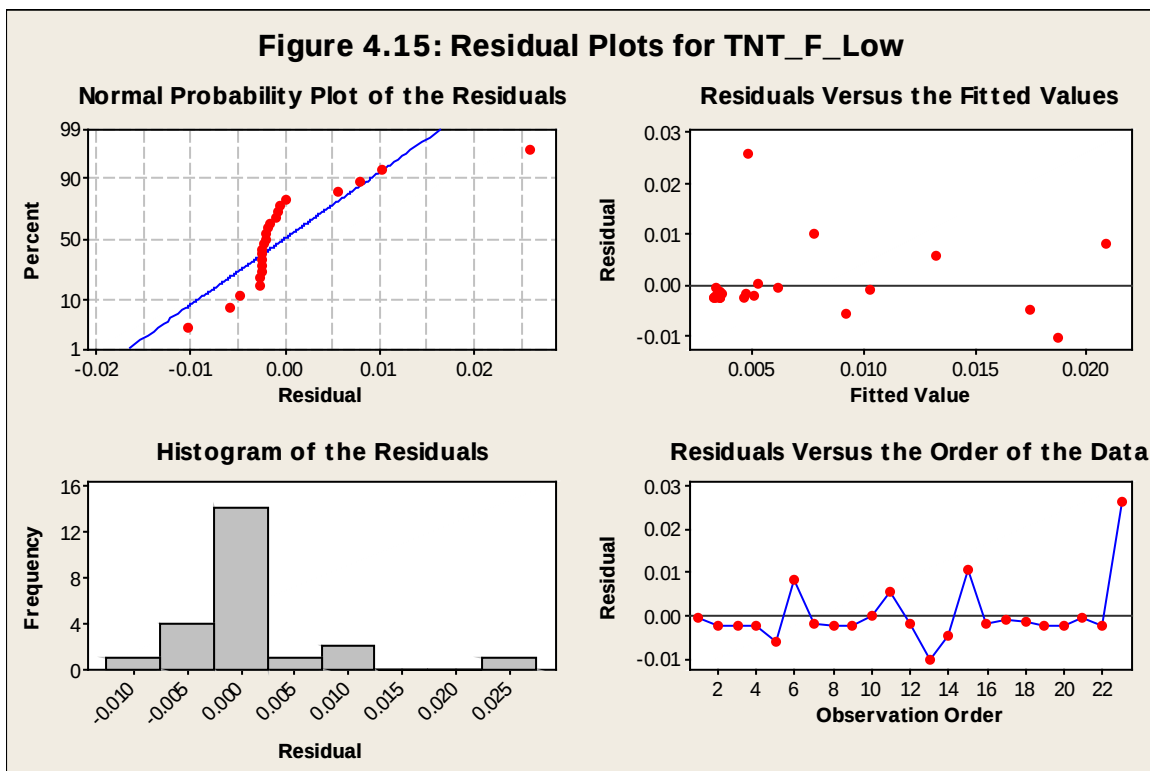


Figure B25. Residual plots for TNT "low" values.

Figure B25 indicates the residuals are not normal. The square of the correlation coefficient is only 0.3 – 0.4 (Figure B25). The slope is not near one and there is large scatter.

Pairs with field results < 0.05 mg/L were omitted from the original data set of $n = 32$ detected concentrations. This produced a “high-level” paired data set for TNT consisting of only $n = 8$ points. The results are listed below.

Table B2. Uncensored TNT pairs where field results > 0.05 mg/L.

TNT_L	TNT_F
0.614	0.766
0.223	0.194
6.57	6.73
0.779	0.842
1.23	1.19
1.73	2.02
0.0958	0.0977
0.0857	0.0788

A regression line using these values is shown in Figure B26.

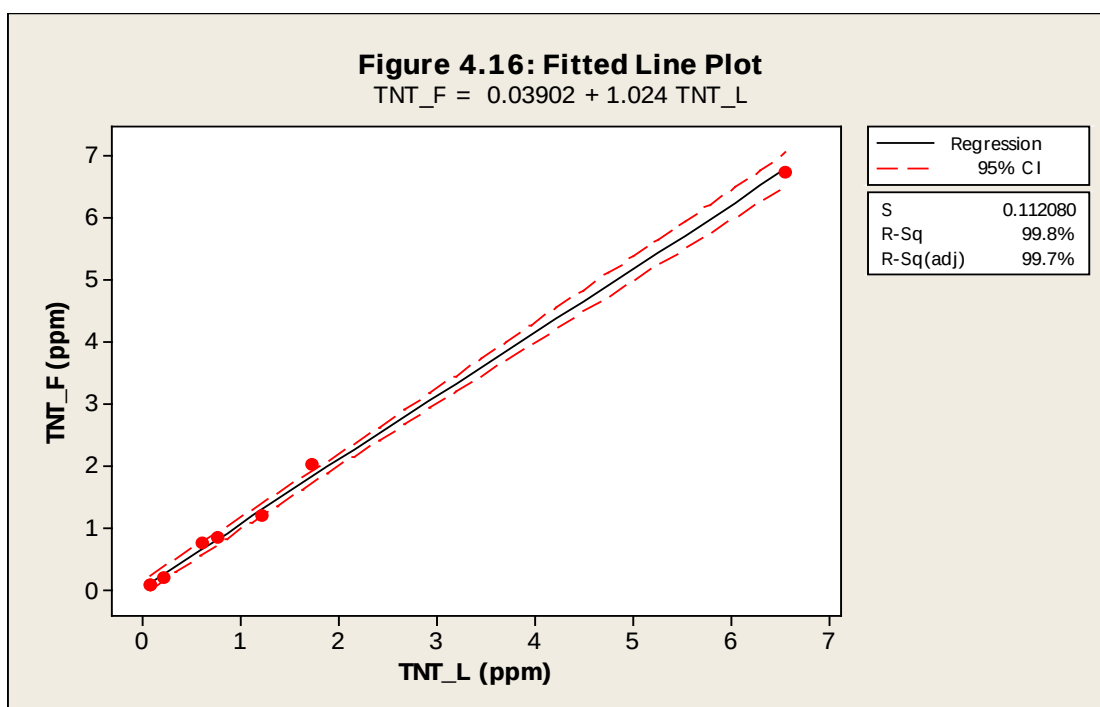


Figure B26. Regression line for “high-level” paired TNT data set.

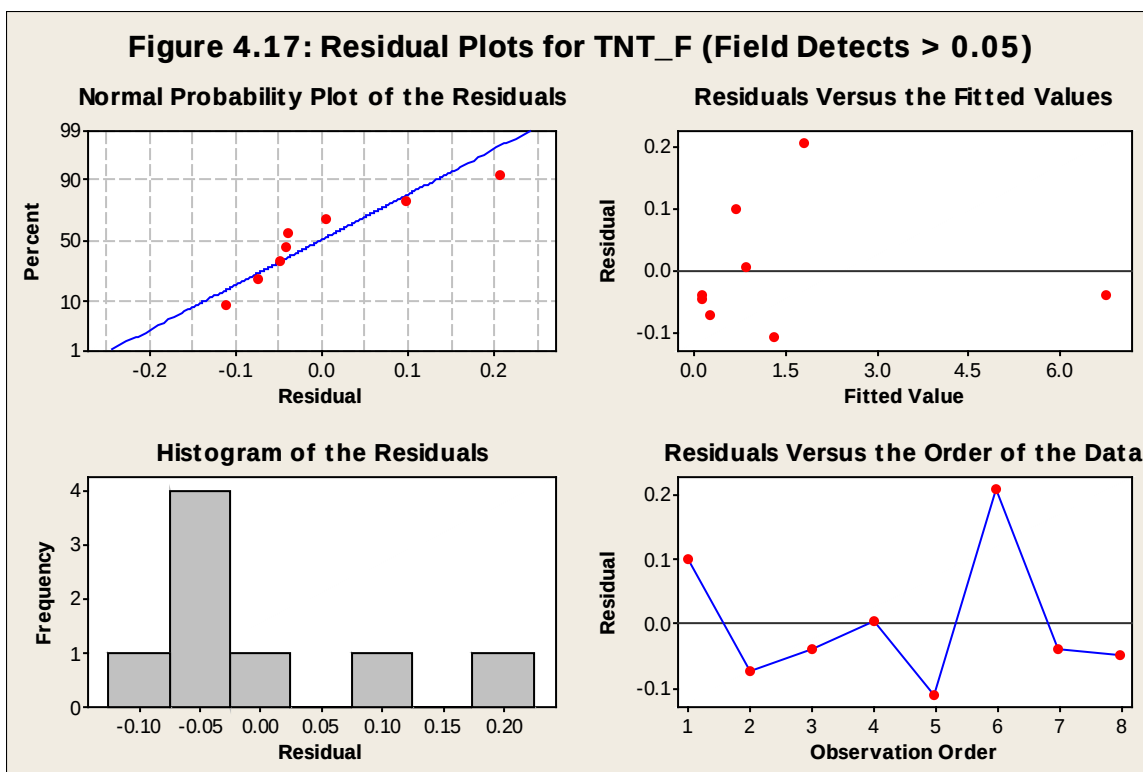


Figure B27. Residual plots for TNT field detects >0.05.

As shown above, this produced a good linear regression fit. The square of the regression coefficient is nearly 1 ($r^2 = 0.997$). The residuals are also approximately normal. The slope is nearly equal to 1 and the line passes nearly the origin. The y-intercept is not statistically different from zero. The output from Minitab is presented below.

The regression equation is

$$\text{TNT_F} = 0.0390 + 1.02 \text{ TNT_L}$$

Predictor	Coef	SE	Coef	T	P
-----------	------	----	------	---	---

Constant	0.03902	0.04839	0.81	0.451	
----------	---------	---------	------	-------	--

TNT_L_H	1.02402	0.01961	52.23	0.000	
---------	---------	---------	-------	-------	--

S = 0.112080 R-Sq = 99.8% R-Sq(adj) = 99.7%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	34.267	34.267	2727.83	0.000
Residual Error	6	0.075	0.013		
Total	7	34.342			

Unusual Observations

Obs	TNT_L	TNT_F	Fit	SE Fit	Residual	St Resid
3	6.57	6.7263	6.7665	0.1085	-0.0402	-1.43 X

X denotes an observation whose X value gives it large influence.

As the y-intercept is not statistically different from zero, a second fit was done forcing the line through the origin. The output from Minitab is presented below.

The regression equation is

$$\text{TNT_F} = 1.03 \text{ TNT_L}$$

Predictor	Coef	SE Coef	T	P
-----------	------	---------	---	---

Noconstant

TNT_L_H	1.03309	0.01565	66.02	0.000
---------	---------	---------	-------	-------

S = 0.109242

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	52.018	52.018	4358.89	0.000
Residual Error	7	0.084	0.012		

Total 8 52.102

Unusual Observations

Obs	TNT_L_H	TNT_F_H	Fit	SE	Fit	Residual	St	Resid
3	6.57	6.7263	6.7871	0.1028	-0.0608	-1.64	X	
6	1.73	2.0208	1.7907	0.0271	0.2302	2.18	R	

R denotes an observation with a large standardized residual.

X denotes an observation whose X value gives it large influence.

Therefore, for concentrations > 0.05 mg/L, as measured by the field method, $TNT_F_H = 1.03 \text{ } TNT_L_H$

As the standard error for the slope is 0.016, the 95% confidence interval for the slope is:

$$1.03 \pm t_{97.5, 7} (0.0156) = 1.03 \pm 2.36 (0.0156) = 1.03 \pm 0.04 = [0.99 - 1.07].$$

Slope of one falls within this interval; that is, the slope of the regression line is not statistically different from one at the 95% level of confidence.

Conclusion: The field method gives comparable results to the laboratory method for field concentrations approximately within the range 0.05 mg/L – 10 mg/L. The slope of the regression line for the uncensored pairs for field results in this concentration range is nearly equal to 1 and the line passes through the origin, with a correlation coefficient of nearly one. The non-parametric fits produce slopes of 0.9 – 1. The slightly smaller slopes are probably owing to the poor fit at low concentrations (e.g., see Figure B25). The field method is not recommended for “definitive” TNT data for concentrations less than about 0.05 mg/L.

B.5 Evaluation of detected TNB results

The censored TNB pairs were removed from the data set; the sample size of the resulting uncensored data set $n = 26$. A scatter plot of the data set is shown in Figure B28 below.

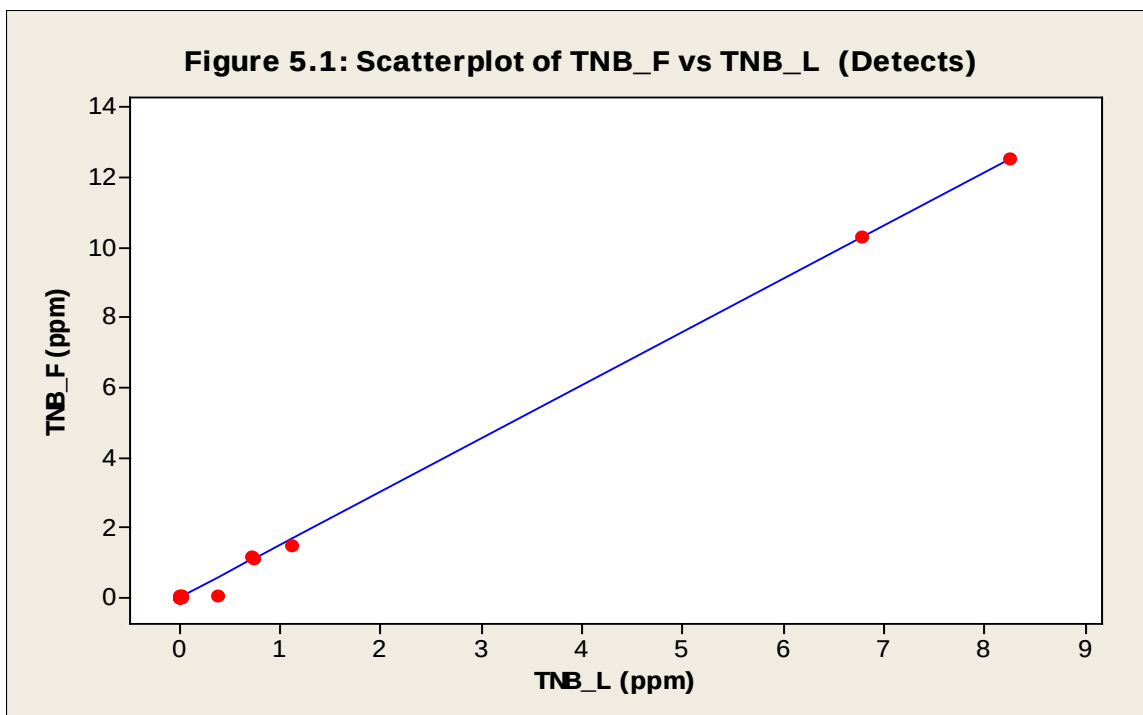


Figure B28. Scatter plot of TNB data set.

There appears to be good agreement between the field and laboratory concentrations for field concentrations greater than about 1 mg/L. The detects were stratified into two smaller data sets: a low concentration data set, with field readings < 0.05 mg/L and a high concentration data set, with field readings > 0.05 mg/L (Table B3).

Table B3. Uncensored TNB pairs where the field concentrations > 0.05 mg/L.

TNB_F	TNB_L
1.15	0.726
1.09	0.740
12.6	8.25
1.51	1.12
10.3	6.78
0.0594	0.382

Regression plots for the two data sets are presented below.

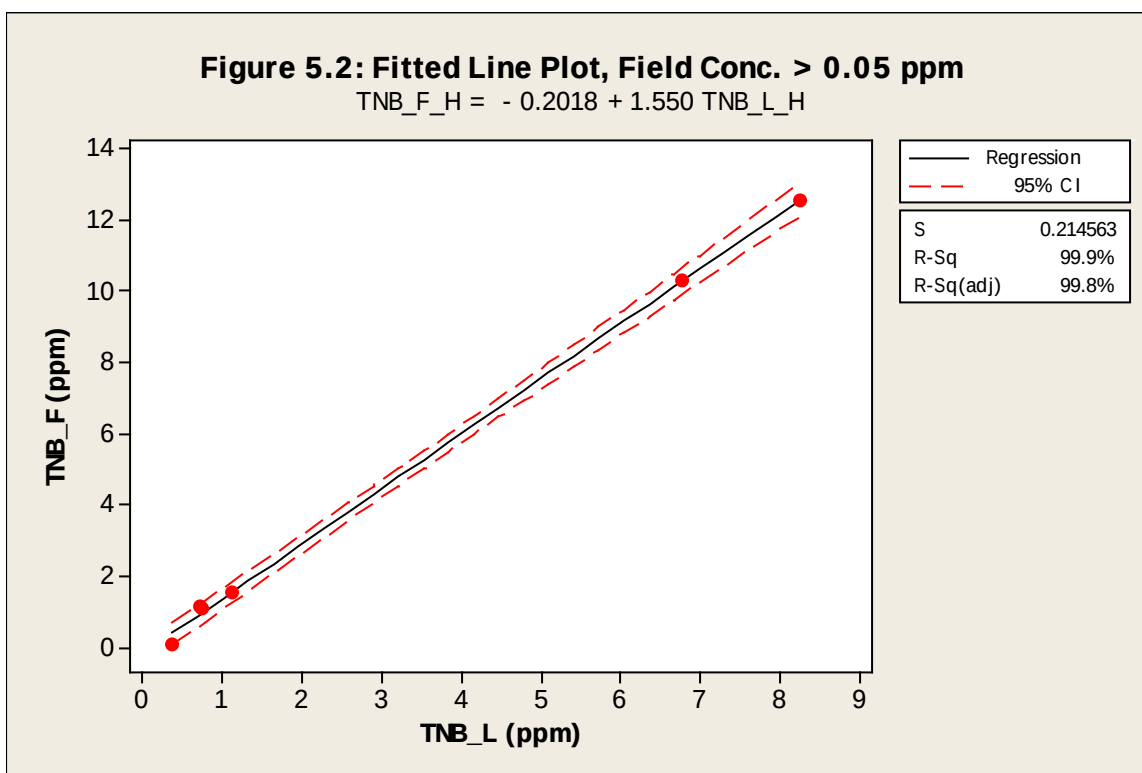


Figure B29. Regression plot for TNB low concentration data set.

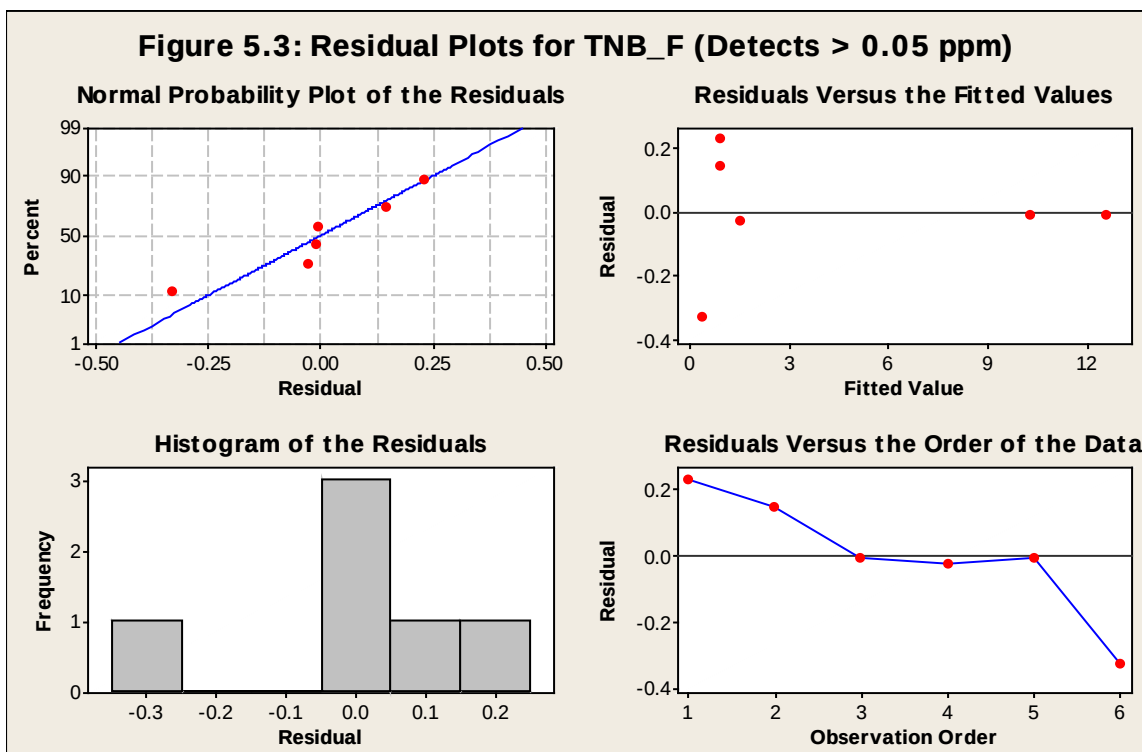


Figure B30. Regression plot for TNB high concentration data set.

This results in normal residuals and a correlation coefficient near one. However, the line passes near the origin with a slope of about 1.6. The Minitab output is presented below.

The regression equation is

$$\text{TNB_F} = -0.202 + 1.55 \text{ TNB_L}$$

Predictor	Coef	SE Coef	T	P
Constant	-0.2018	0.1196	-1.69	0.167
TNB_L_H	1.54998	0.02715	57.09	0.000

S = 0.214563 R-Sq = 99.9% R-Sq(adj) = 99.8%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	150.05	150.05	3259.28	0.000
Residual Error	4	0.18	0.05		
Total	5	150.23			

As the p-value for the intercept is greater than 0.05, the intercept is not significantly different from zero. Therefore, the regression line was subsequently forced through the origin. The Minitab output is presented below.

The regression equation is

$$\text{TNB_F} = 1.52 \text{ TNB_L}$$

Predictor	Coef	SE Coef	T	P
Noconstant				
TNB_L	1.51879	0.02327	65.26	0.000

S = 0.251101

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	268.53	268.53	4258.81	0.000
Residual Error	5	0.32	0.06		
Total	6	268.84			

Unusual Observations

Obs	TNB_L_H	TNB_F_H	Fit	SE Fit	Residual	St Resid
3	8.25	12.573	12.523	0.192	0.050	0.31 X
6	0.38	0.059	0.580	0.009	-0.520	-2.07R

R denotes an observation with a large standardized residual.

X denotes an observation whose X value gives it large influence.

The line passes through the origin with a slope of about 1.5; the correlation coefficient is nearly one.

The regression fit is very poor at low concentrations, as shown in Figure B31. This figure shows the regression line for detected TNB concentrations where the field concentrations are less than 0.05 mg/L. The residuals are not normal. The correlation coefficient is relatively small owing to the large scatter; $r^2 \approx 0.4$ (though the slope is closer to 1). These results suggest that the field method exhibits a different response for concentrations < 0.05 mg/L.

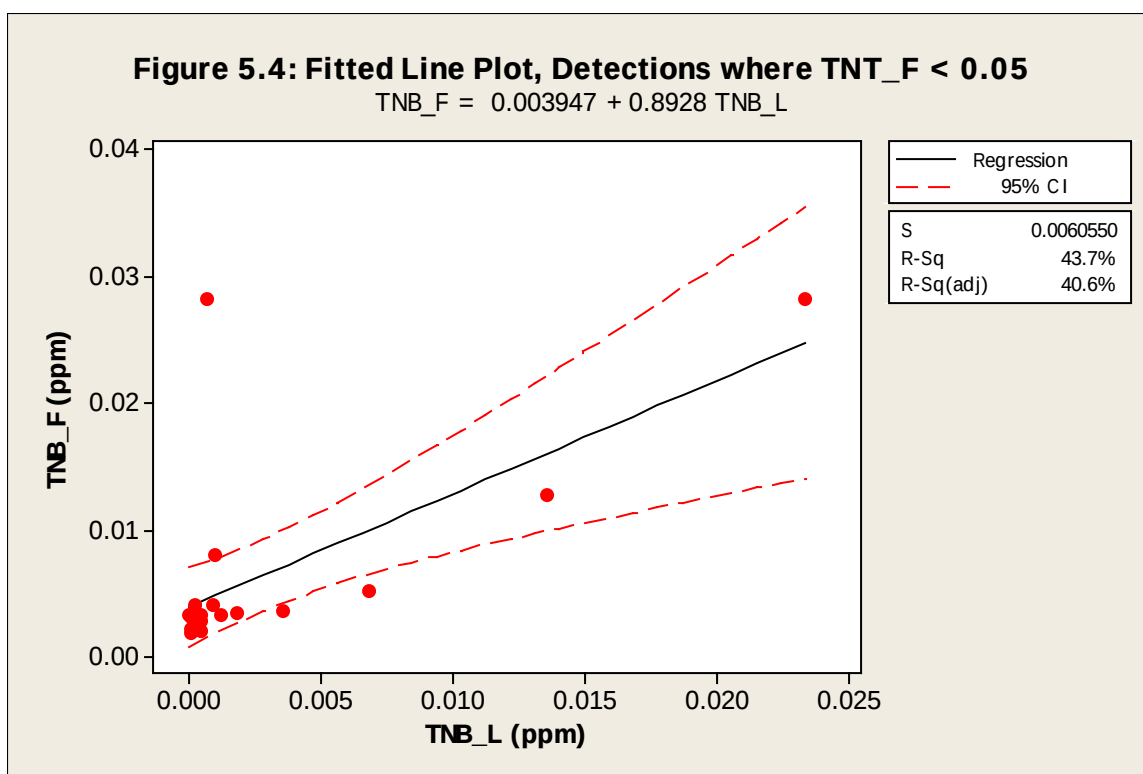


Figure B31. Fitted line plot for TNB low concentrations.

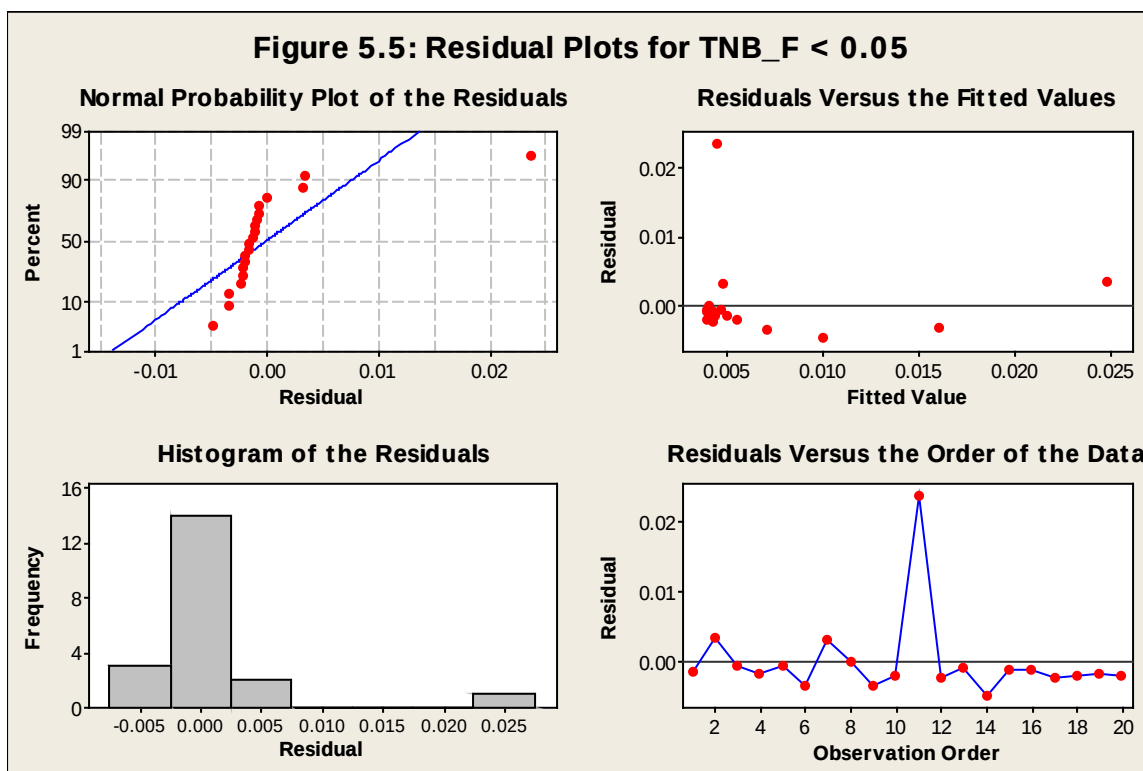


Figure B32. Residual plots for TNB low concentrations.

Conclusions: Overall, the field method possesses a positive bias for TNB relative to the laboratory method. For the uncensored TNB results for which the field concentration is > 0.05 mg/L, the regression line passes through the origin and possesses a slope of about 1.5. This is similar to the lines calculated using the non-parametric fits (for the entire concentration range); slopes of 1.3 - 1.5 were calculated. The parametric regression fit from 0.05 to about 10 mg/L is considered the most reliable as the field method exhibits different performance at lower concentrations. This is also consistent with the two-sample tests done in Section B2; the largest positive bias for the field method was identified for TNB. The TNB field method results for concentrations > 0.05 mg/L were very consistent with the laboratory method but possess a positive bias; the field results would need to be multiplied by a correction factor of about 0.7 to obtain the corresponding laboratory results.

B.6 Evaluation of detected 2, 4-DNT results.

The set of uncensored 2, 4-DNT pairs consists of only 10 results. A scatter plot is shown below in Figure B33.

The LOWESS exhibits some curvature, but the degree of scatter seems small even at relatively low concentrations (< 0.05 mg/L), as shown in Figure B34. Therefore, the entire uncensored data set was used to perform a regression fit.

The residuals are not normal (Figure B35) but a log transform would not improve the fit. The lack of normality is primarily owing to the outlier evident in Figure B34. To illustrate, the regression fit (Figure B36) was done by removing the outlier. As shown in Figure 37, removing the outlier tends to normalize the residuals. Also, the outlier does not substantively affect the linear fit.

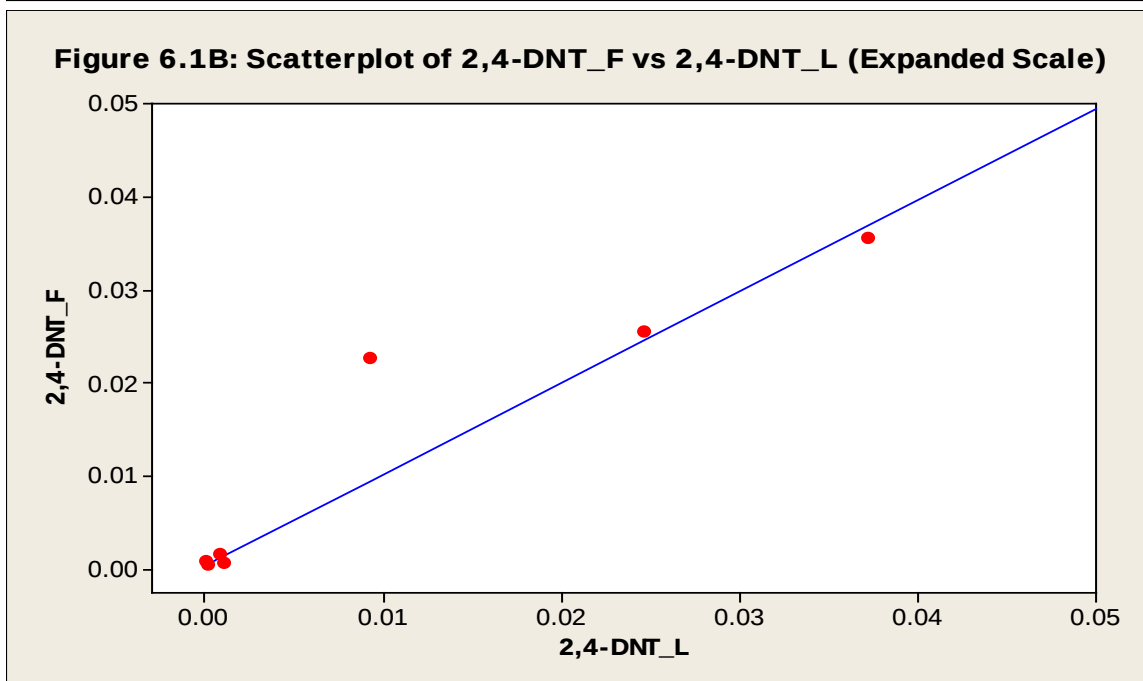
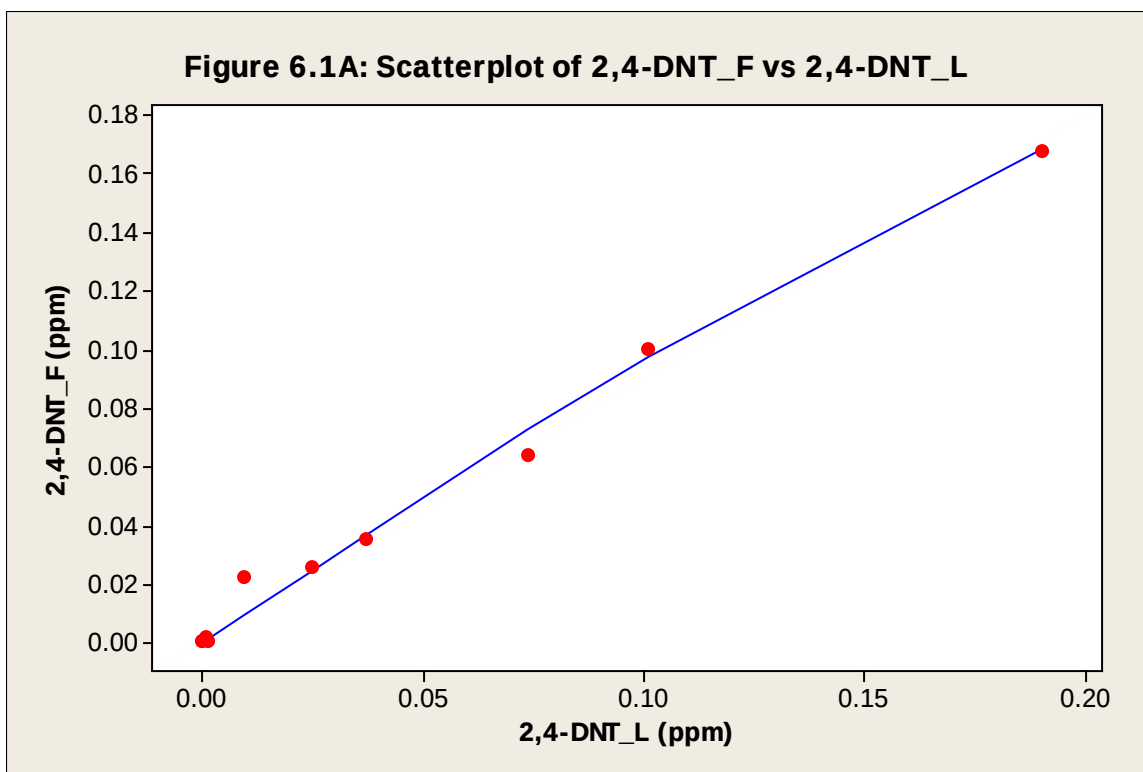


Figure B33. Scatter plots for detected 2,4-DNT results.

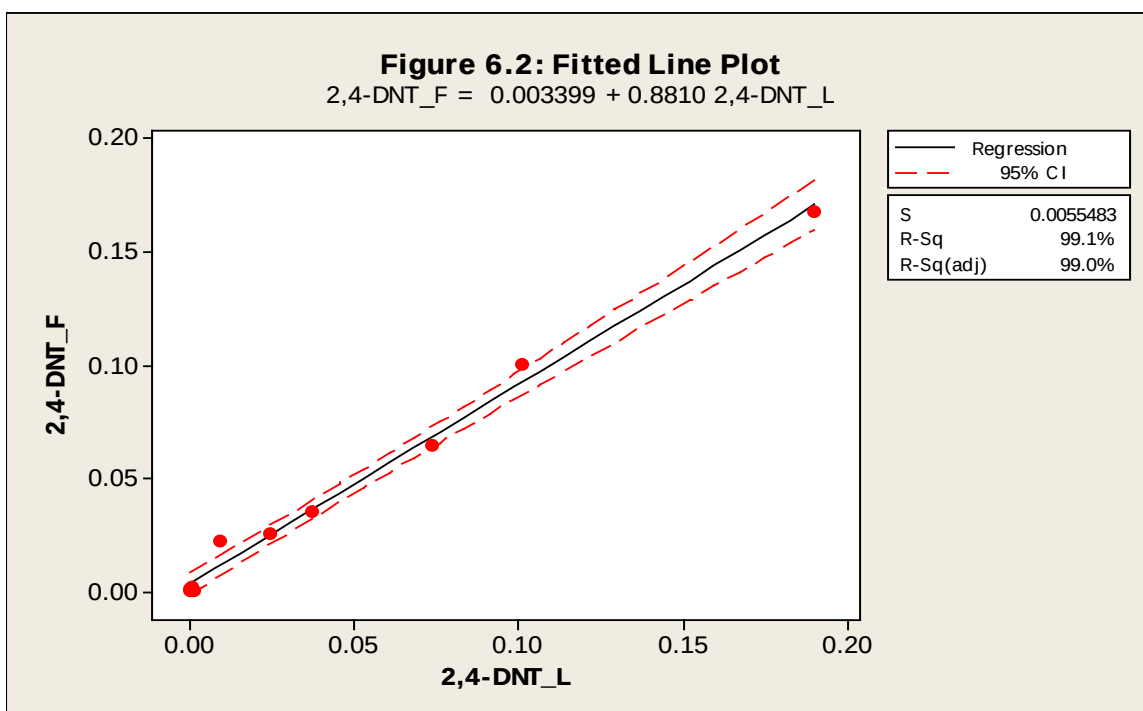


Figure B34. Fitted line plot for 2,4-DNT.

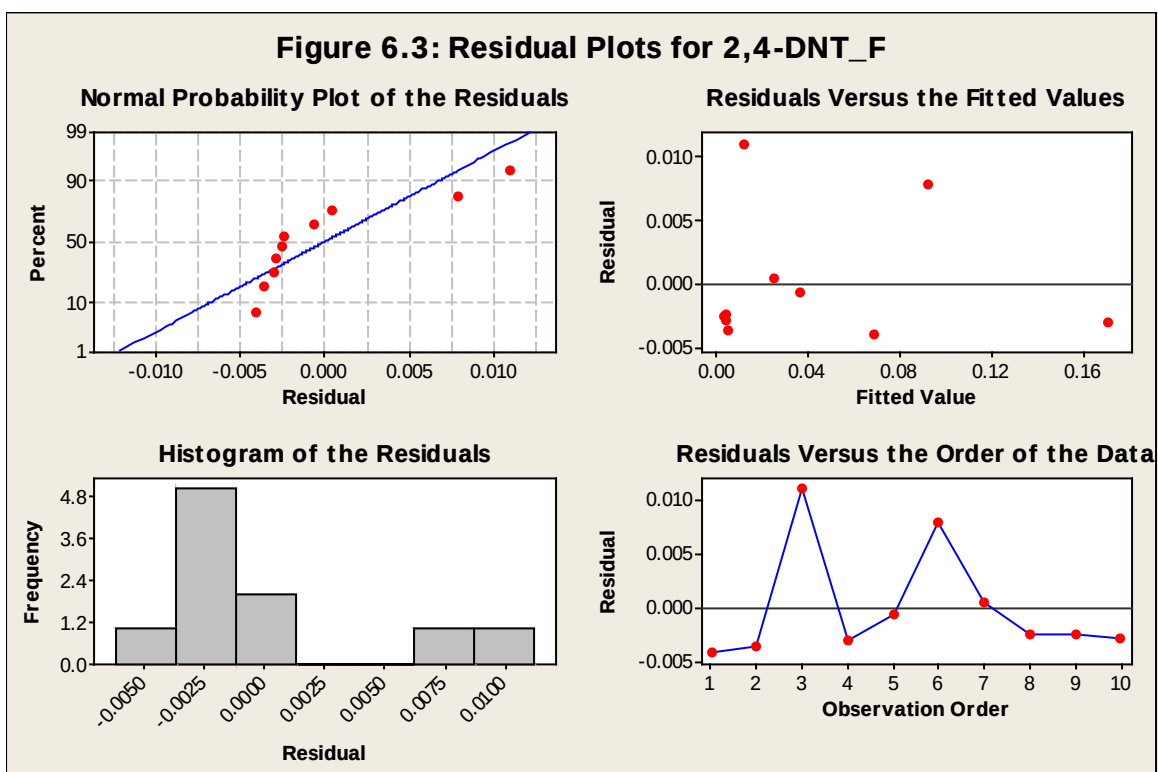


Figure B35. Residual plots for 2,4-DNT.

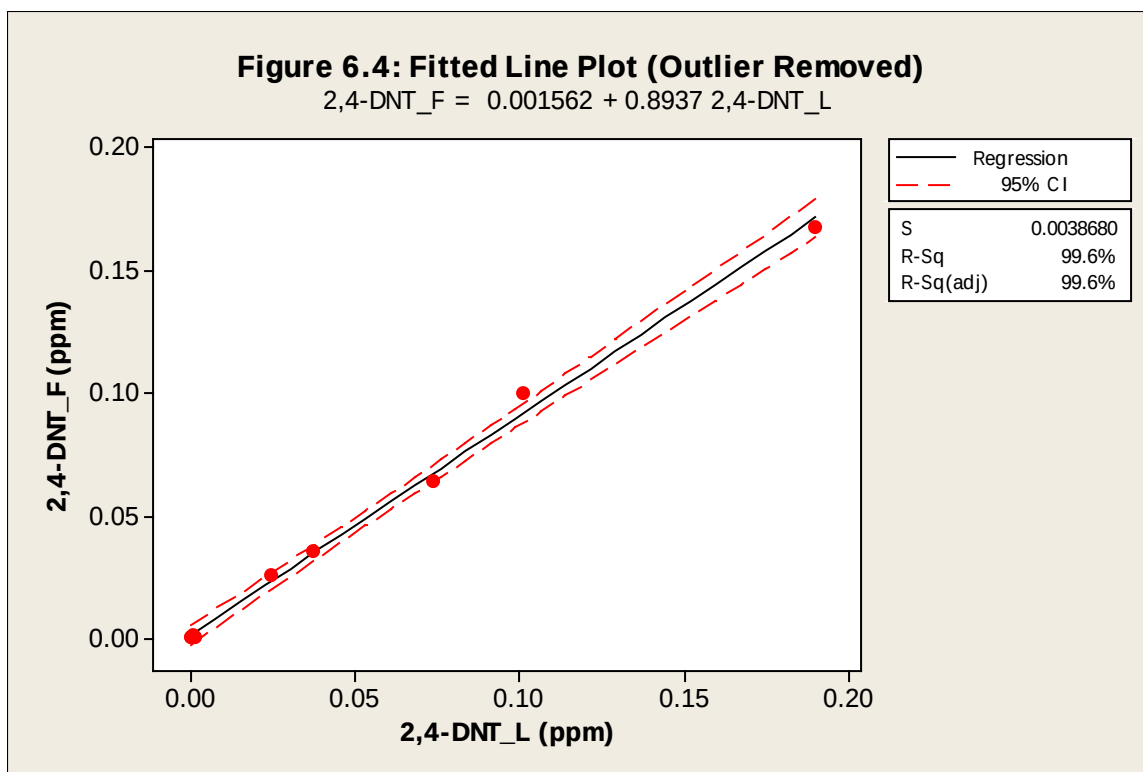


Figure B36. Regression fit for 2,4-DNT, outlier removed.

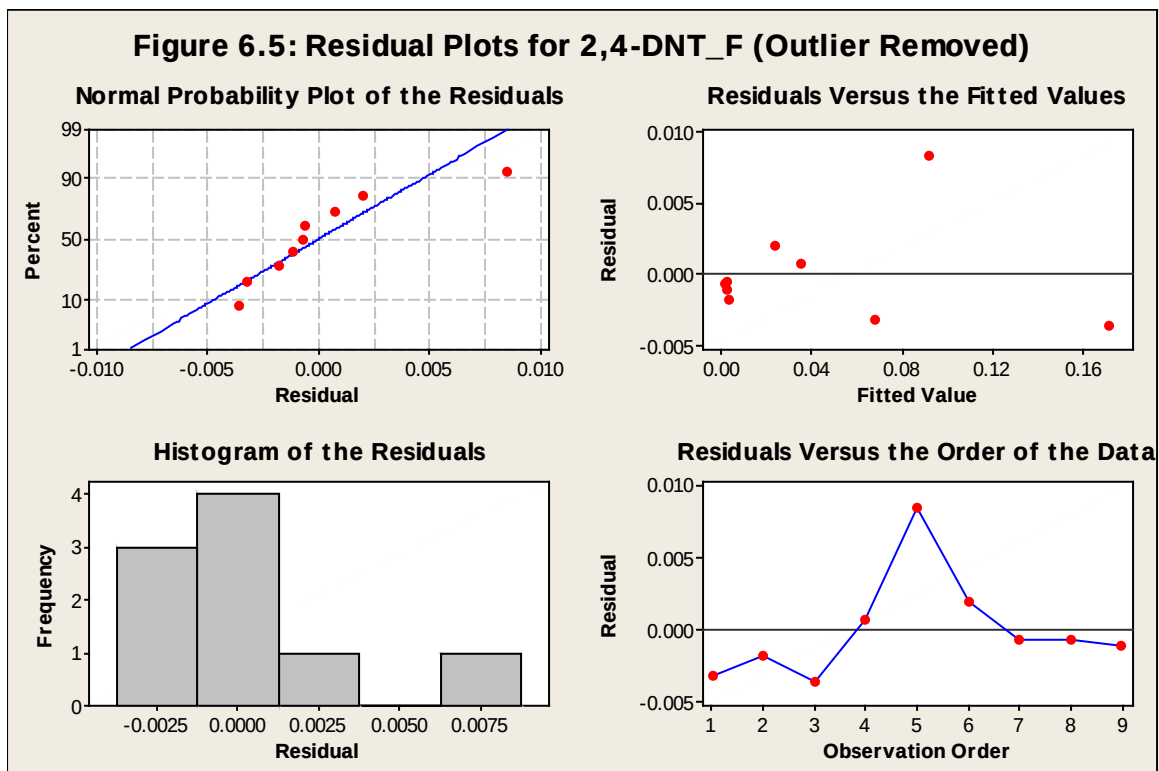


Figure B37. Residual plots for 2,4-DNT, outlier removed.

As the intercept is less than the reporting limit for the field method and is likely not statistically different from zero, the regression line was subsequently forced through the origin using the set of 10 uncensored results. The Minitab output is presented below.

The regression equation is

$$2,4\text{-DNT}_F = 0.909 \ 2,4\text{-DNT}_L$$

Predictor	Coef	SE Coef	T	P
Noconstant				
2,4-DNT_L	0.90865	0.02572	35.32	0.000
S = 0.00596866				

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	0.044452	0.044452	1247.78	0.000
Residual Error	9	0.000321	0.000036		
Total	10	0.044773			

Unusual Observations

Obs	2,4-DNT_L	2,4-DNT_F	Fit	SE Fit	Residual	St Resid
3	0.009	0.02266	0.00845	0.00024	0.01421	2.38R
4	0.190	0.16783	0.17273	0.00489	-0.00489	-1.43 X

R denotes an observation with a large standardized residual.

X denotes an observation whose X value gives it large influence.

The 95% confidence interval for the slope is:

$$0.909 \pm t_{97.5, 9} (0.0257) = 0.909 \pm 2.26 (0.0257) = 0.91 \pm 0.06 = [0.85 - 0.97].$$

The slope is statistically different from 1 with 95% confidence, but only marginally so. The non-parametric fits produced similar estimates for the slope. The Akritas-Theil-Sen slope for 2, 4-DNT is 1.0. The Turnbull estimate of the slope (Appendix B10) for 2, 4 DNT is about 0.94.

Conclusions: The field method for 2, 4-DNT produces results that are fairly comparable to the laboratory method to concentrations of at least 0.2 mg/L. The field method may possess a small negative bias as the slopes ranged from about 0.9–1 for the parametric and non-parametric linear fits. However, a correction factor for the field results would only increase the reported concentrations by 5% - 10%, which is within the range of instrumental error and well within the tolerance for total analytical error for chromatographic methods for explosives (e.g., laboratory control limits for explosives are usually considerable wider than 90% - 110%).

B.7 Evaluation of detected 1, 3-DNB results.

There are only seven paired uncensored values for 1, 3-DNB. A scatter plot of the results is presented in Figure B38. A regression line is presented in Figure B39.

The residuals deviate somewhat from normality but Figure B40 suggests that the regression line nevertheless gives a reasonably good fit. As the intercept is smaller than the RL for the field method, the y-intercept it is likely not significantly different from zero. Therefore, the regression line was forced through the origin. Forcing the line through origin also normalized the residuals (Figure B41). The output from Minitab is presented below.

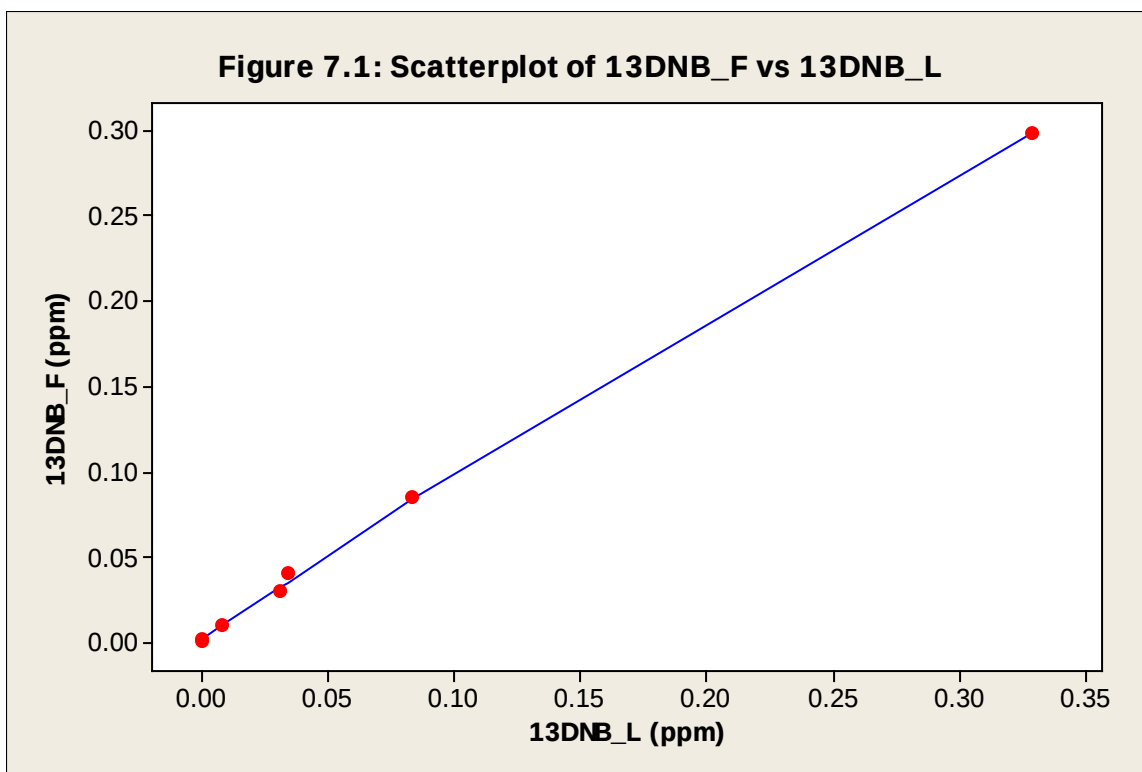


Figure B38. Scatter plot of detected 1,3-DNB results.

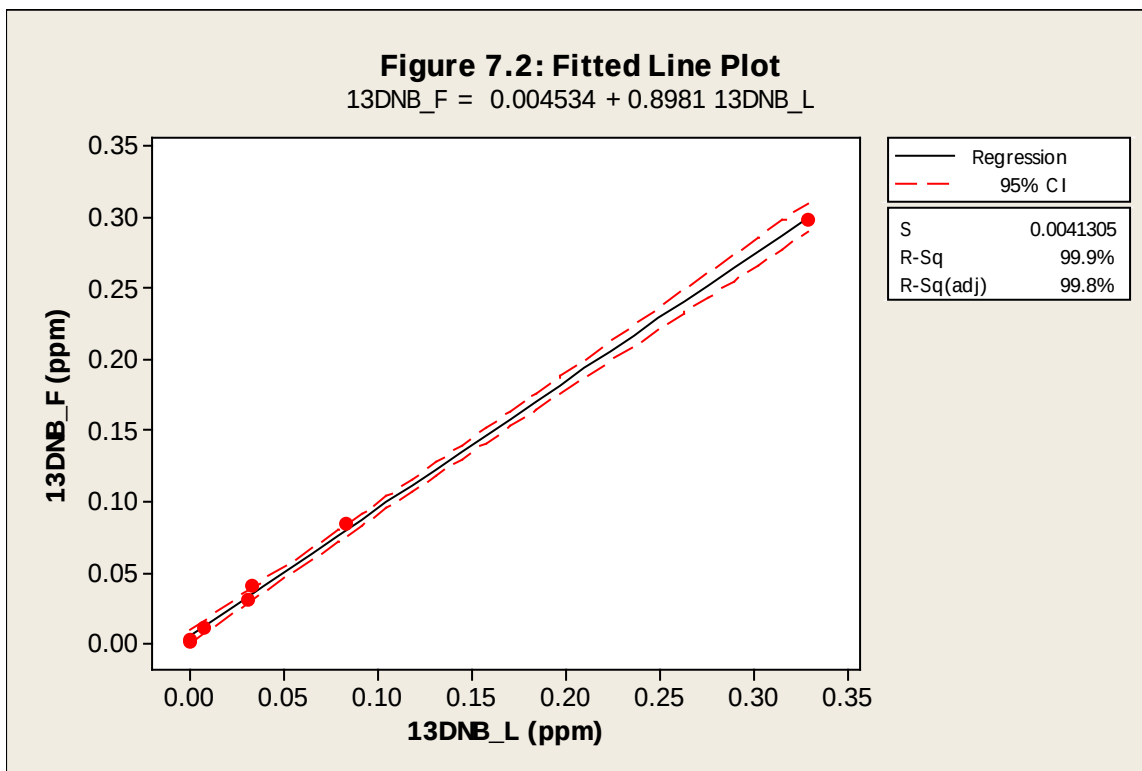


Figure B39. Fitted line plot for 1,3-DNB.

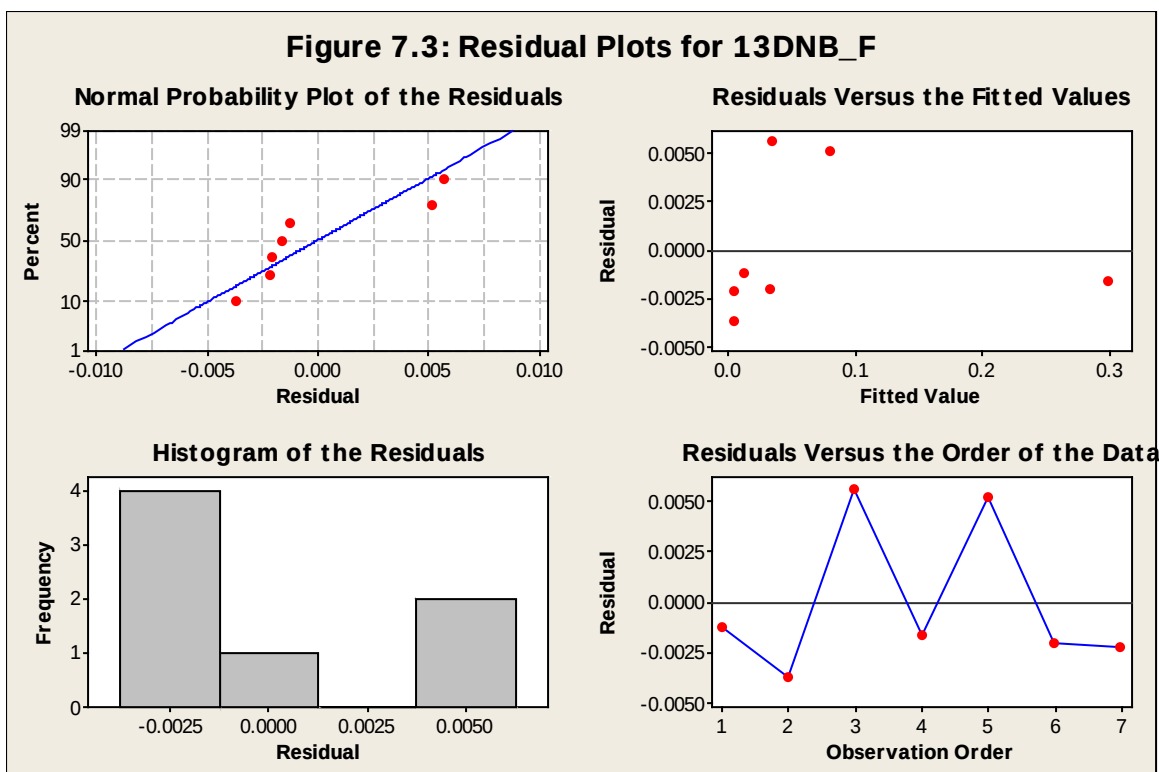


Figure B40. Residual plots for 1,3-DNB.

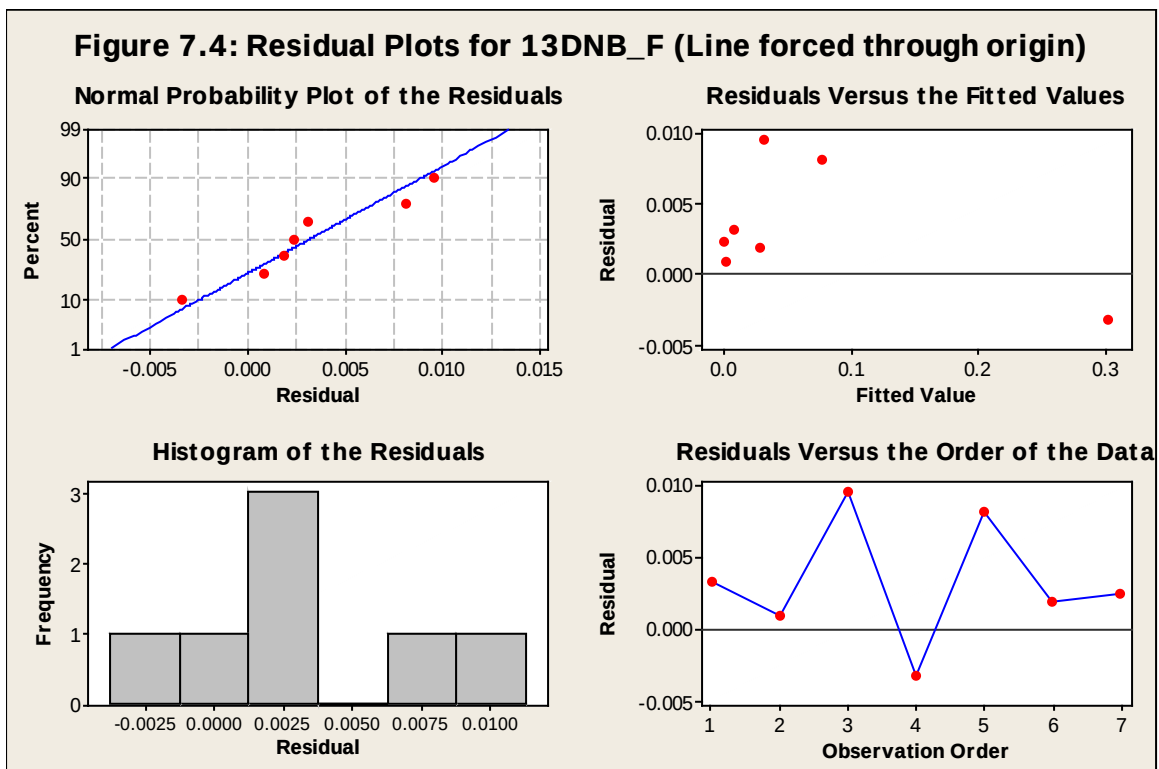


Figure B41. Residual plots for 1,3 DNB, line forced through origin.

The regression equation is

$$13\text{DNB}_F = 0.917 \ 13\text{DNB}_L$$

Predictor	Coef	SE Coef	T	P
Noconstant				
13DNB_L	0.91693	0.01635	56.08	0.000

S = 0.00559490

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	0.098448	0.098448	3145.01	0.000
Residual Error	6	0.000188	0.000031		
Total	7	0.098636			

Unusual Observations

Obs	13DNB_L	13DNB_F	Fit	SE Fit	Residual	St Resid
4	0.329	0.29796	0.30127	0.00537	-0.00331	-2.12RX

R denotes an observation with a large standardized residual.

X denotes an observation whose X value gives it large influence.

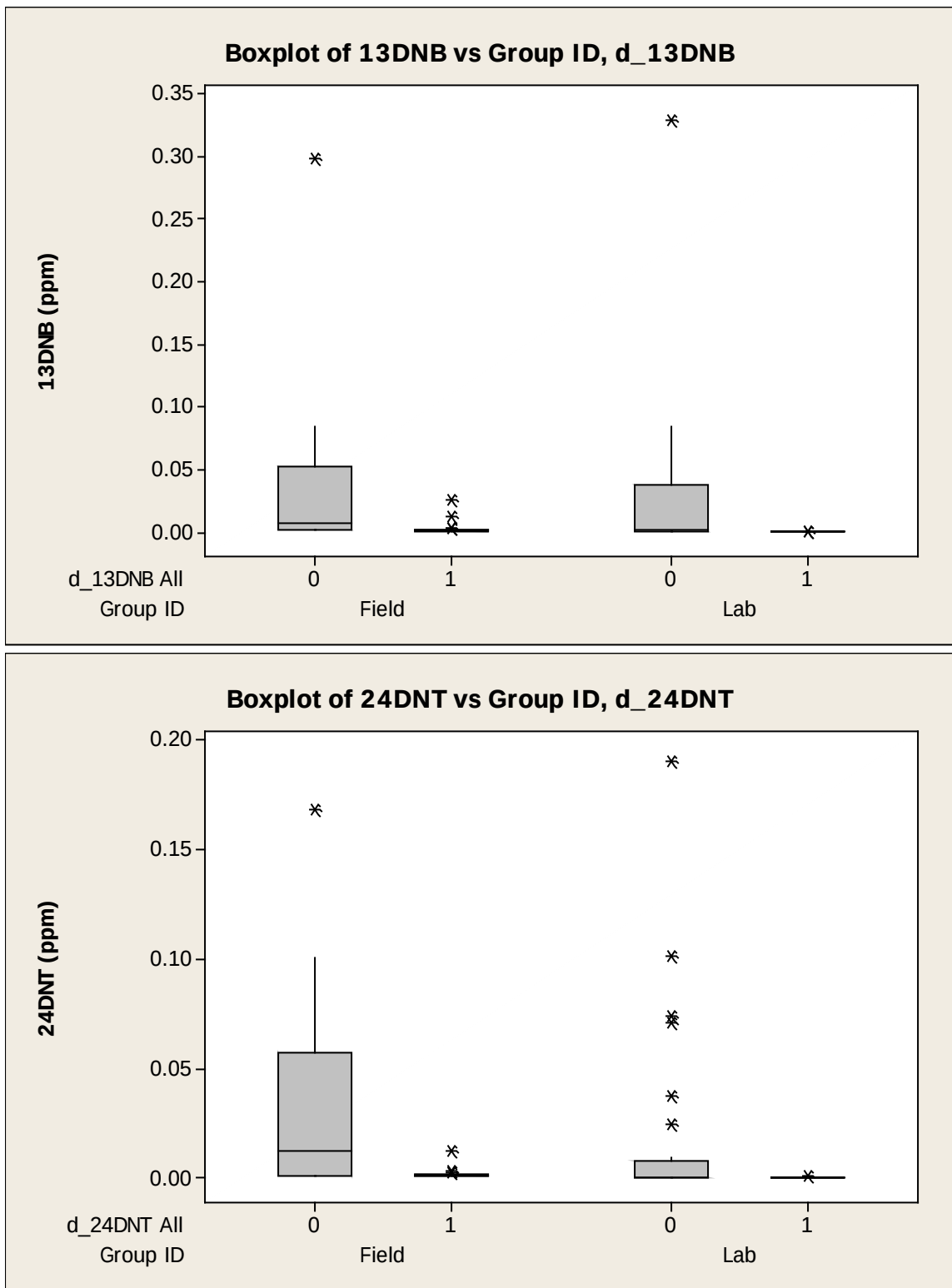
There is little scatter about the regression line; $r^2 > 0.99$. The slope of the line is about 0.92. The 95% confidence interval for the slope is

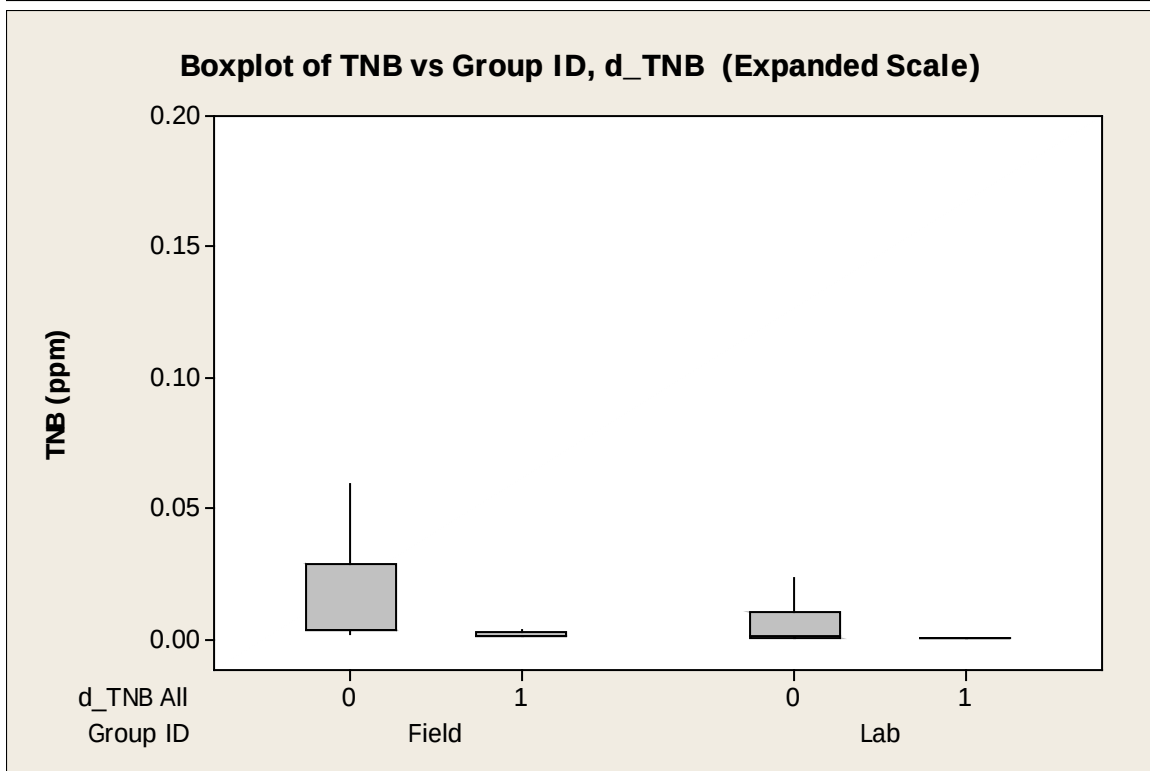
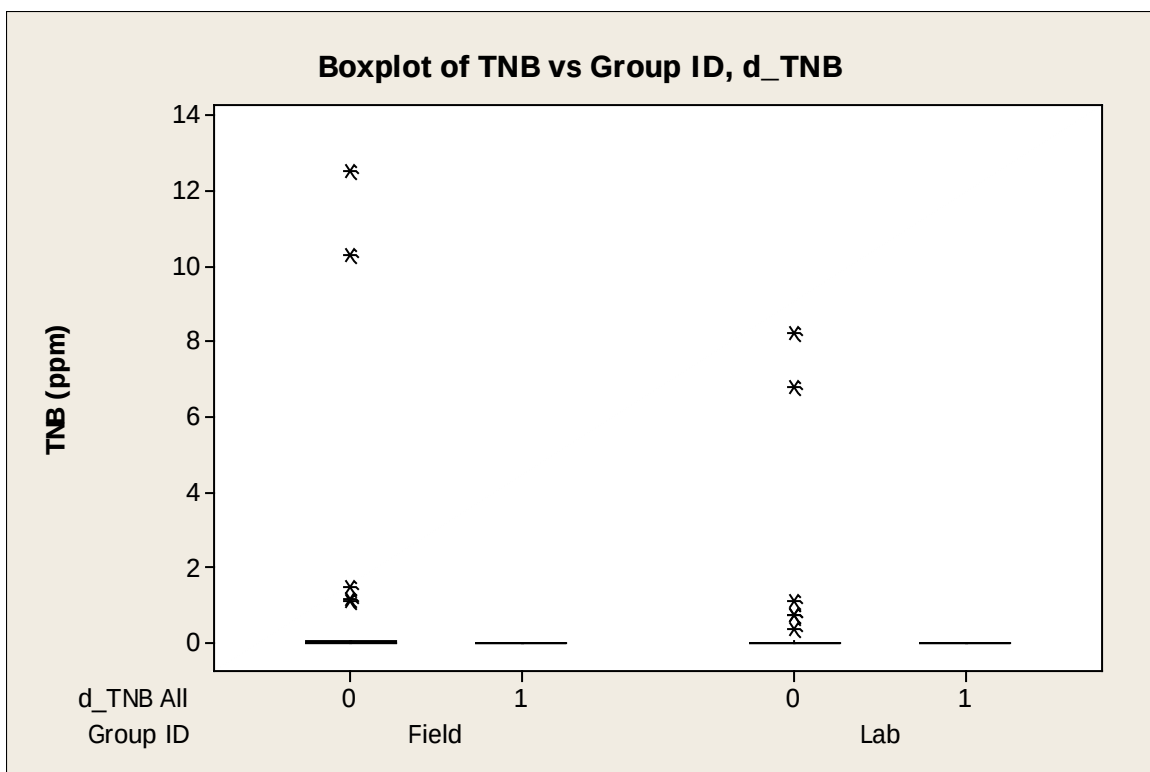
$$0.92 \pm t_{97.5, 6} (0.0164) = 0.92 \pm 2.45 (0.0164) = 0.92 \pm 0.04 = [0.88 - 0.96].$$

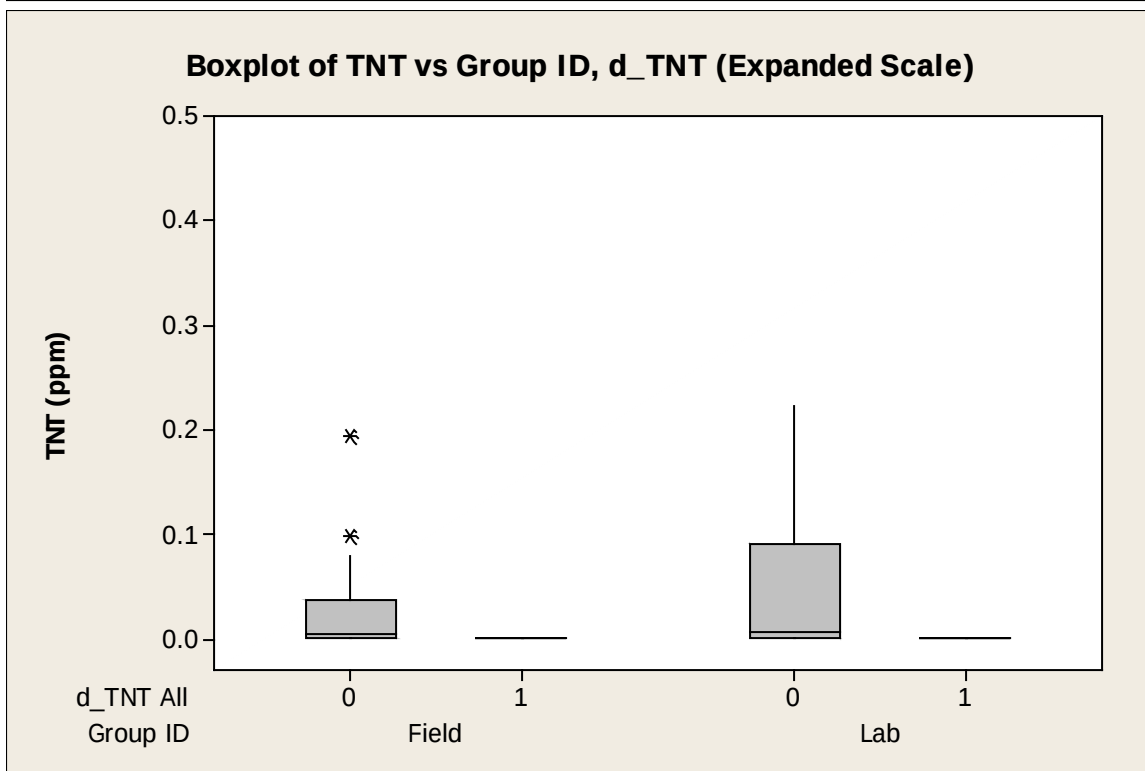
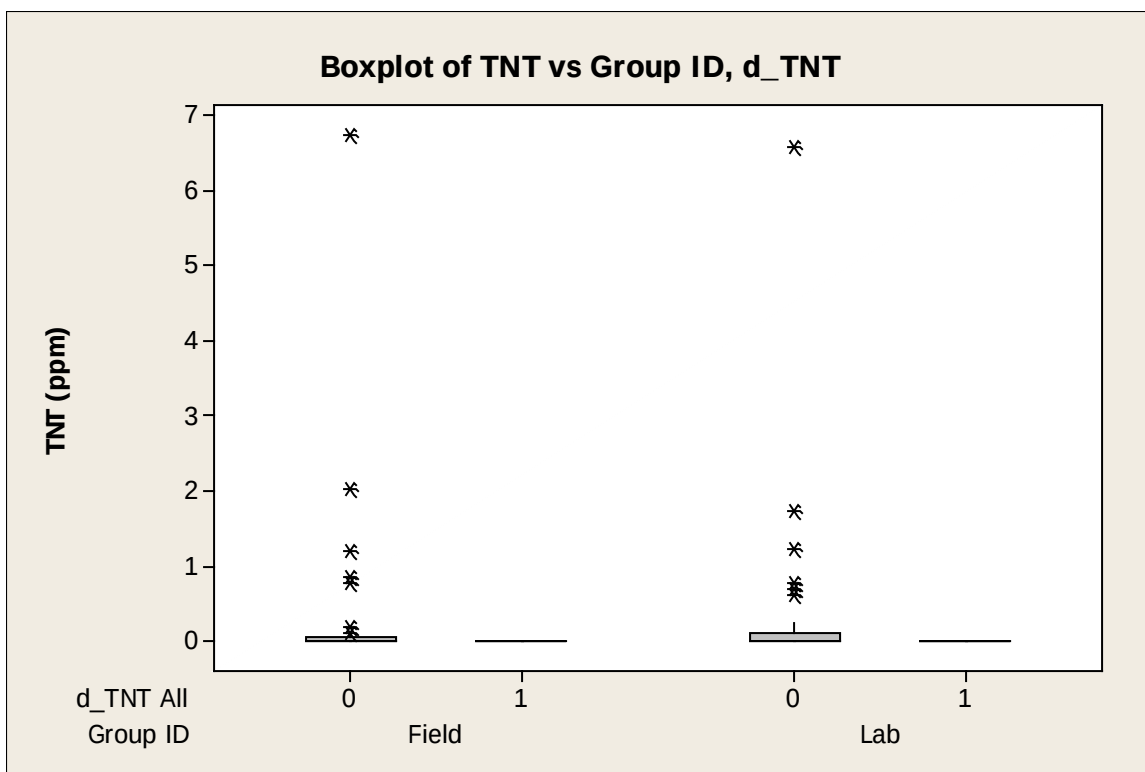
The slope is significantly different from one but only marginally so. The slope may not actually be different from one, as the regression line was calculated from a relatively small number of points. The non-parametric methods also produced slopes that ranged from 1 – 1.2. A consistent direction of bias (as measured by the slope) was not observed.

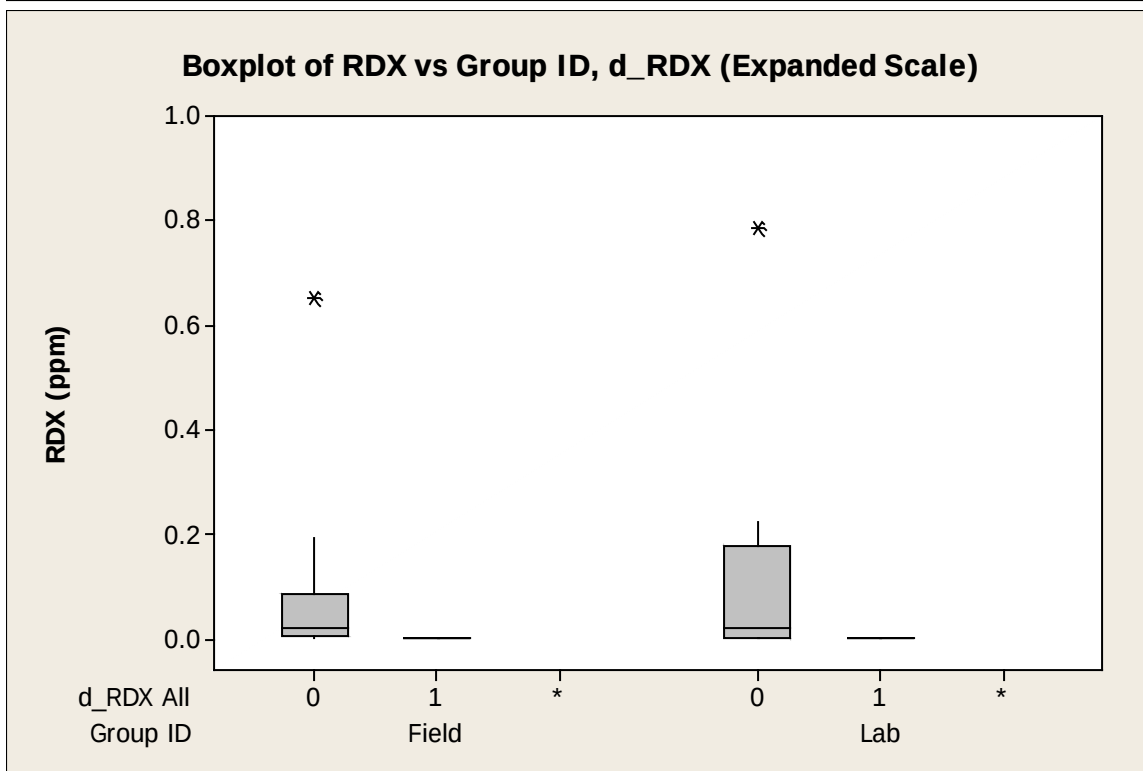
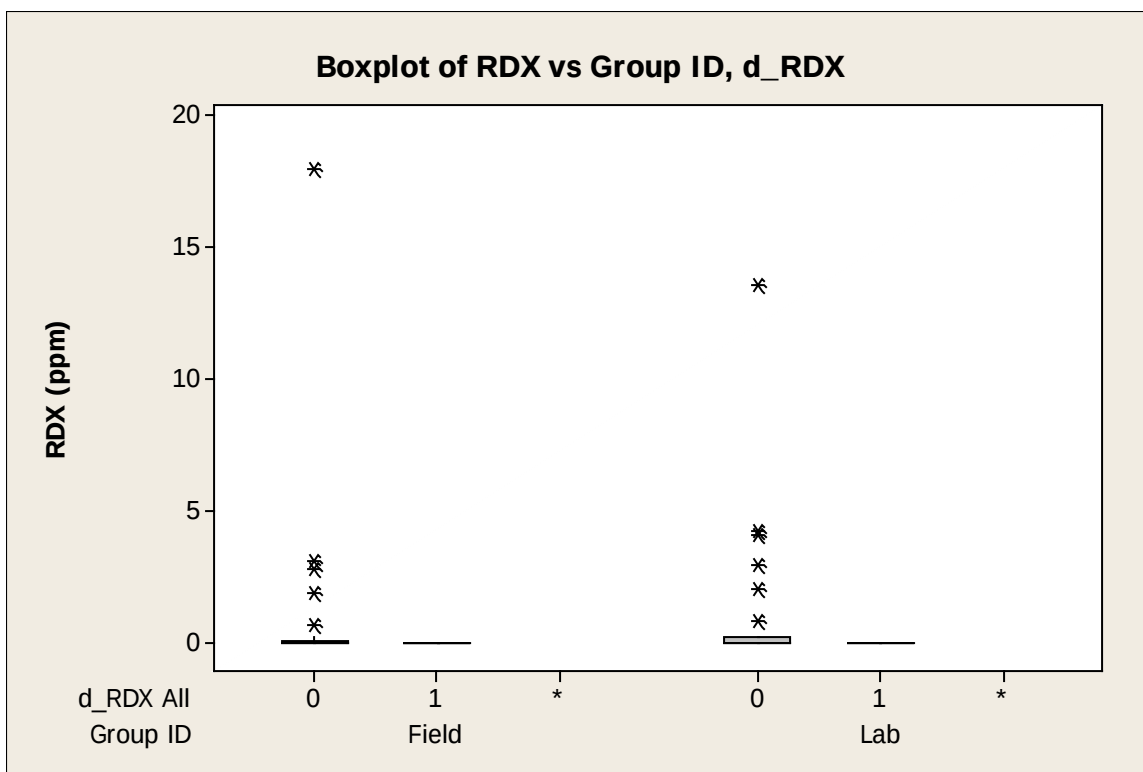
Conclusions: The field method seems to produce results comparable to the laboratory method for 1, 3-DNB at least for concentrations as large as about 0.3 mg/L. A correction factor for the field results would only change reported concentrations by about 10%, which is well within typical error tolerances for analytical uncertainty for chromatographic methods for explosives.

B.8 Box Plots









Key

0 = Detects

1 = Non-detects

Field = Results from field method

Lab = Results from fix-lab method

B.9 Sign Tests

Sign Test for Median: 13DNB_F-13DNB_L

Sign test of median = 0.00000 versus not = 0.00000

	N	Below	Equal	Above	P	Median
13DNB_F-13DNB_L	36	3	0	33	0.0000	0.00091

p-value (adjusted for 'Equal' ties) = 0

Median difference adjusted for nondetects = 0.000769

Field method is biased high relative to laboratory method.

Sign Test for Median: 24DNT_F-24DNT_L

Sign test of median = 0.00000 versus not = 0.00000

	N	Below	Equal	Above	P	Median
24DNT_F-24DNT_L	36	6	0	30	0.0001	0.00089

p-value (adjusted for 'Equal' ties) = 0

Median difference adjusted for nondetects = 0.000459

Field method is biased high relative to laboratory method.

Sign Test for Median: TNB_F-TNB_L

Sign test of median = 0.00000 versus not = 0.00000

N Below Equal Above P Median

TNB_F-TNB_L 36 4 0 32 0.0000 0.00250

p-value (adjusted for 'Equal' ties) = 0

Median difference adjusted for nondetects = 0.002350

Field method is biased high relative to laboratory method.

Sign Test for Median: TNT_F-TNT_L

Sign test of median = 0.00000 versus not = 0.00000

N Below Equal Above P Median

TNT_F-TNT_L 36 14 0 22 0.2430 0.00057

p-value (adjusted for 'Equal' ties) = 0.243

Median difference adjusted for nondetects = 0.000523

Sign Test for Median: RDX_F-RDX_L

Sign test of median = 0.00000 versus not = 0.00000

```
N Below Equal Above P Median
RDX_F-RDX_L 34 18 0 16 0.8642 -0.00030
```

p-value (adjusted for 'Equal' ties) = 0.8642

Median difference adjusted for nondetects = -0.0005

B.10 Paired Prentice-Wilcoxon tests and box plots of field – lab results

PPW test for 1,3 DNB

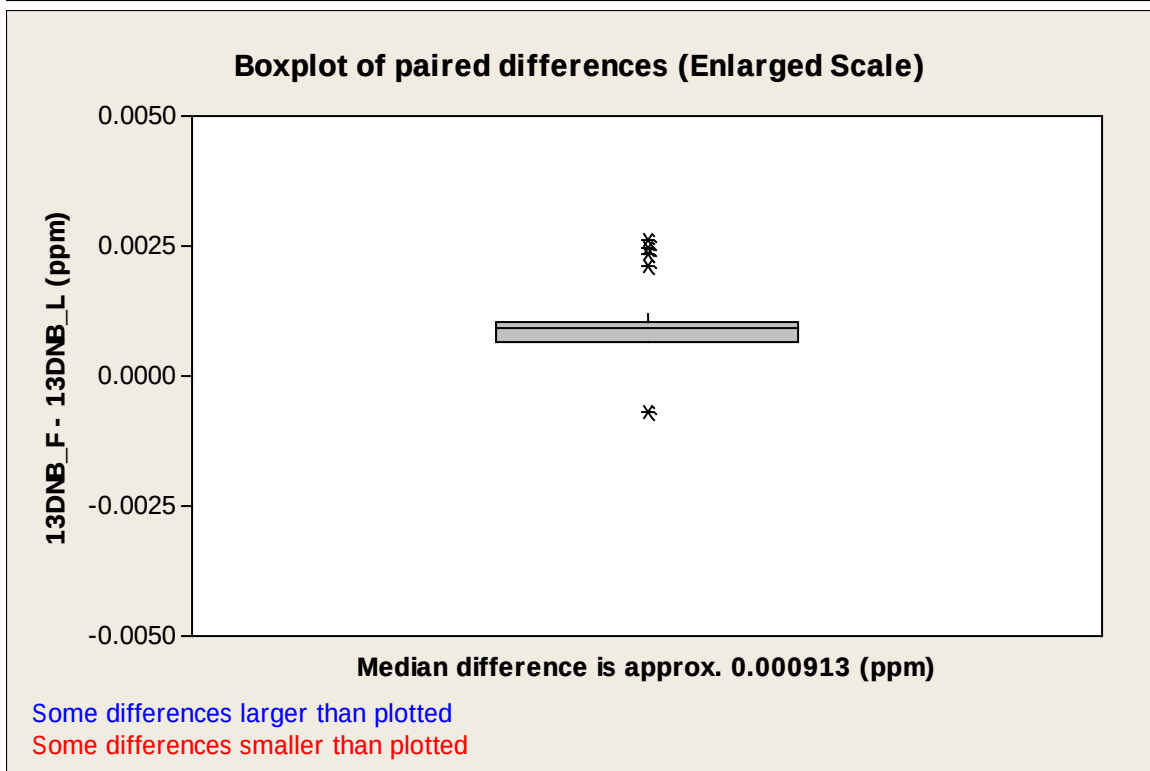
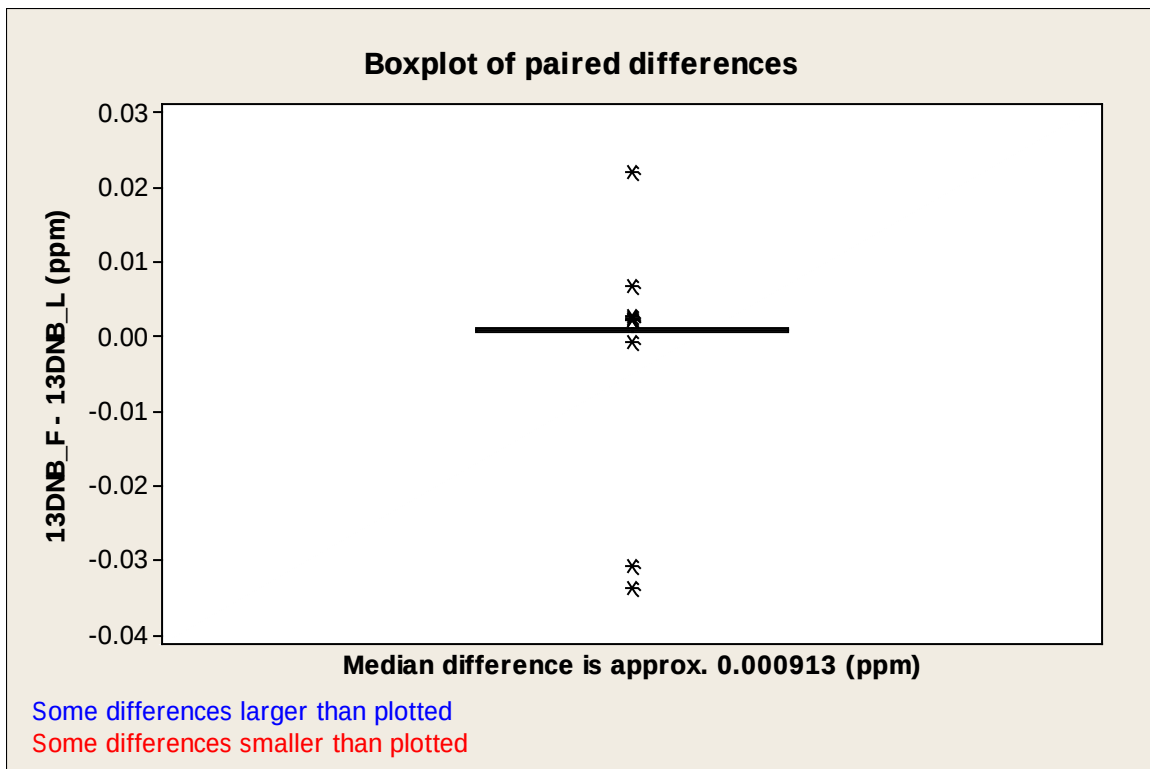
Paired Prentice-Wilcoxon test
(NonPar test for equality of paired left-censored data)

Ho: distribution of 13DNB_F = 13DNB_L

vs Ha: not =

Test Statistic: 1.594

p value: 0.111



PPW test for 2, 4-DNT

Paired Prentice-Wilcoxon test

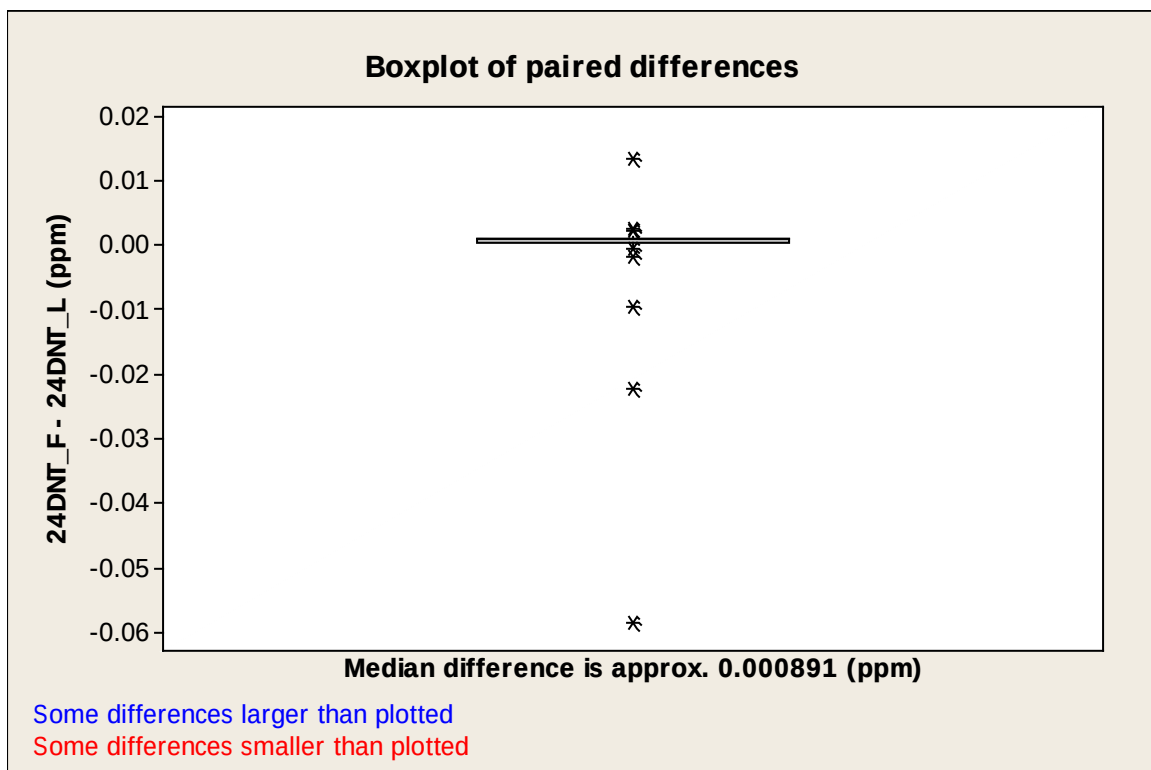
(NonPar test for equality of paired left-censored data)

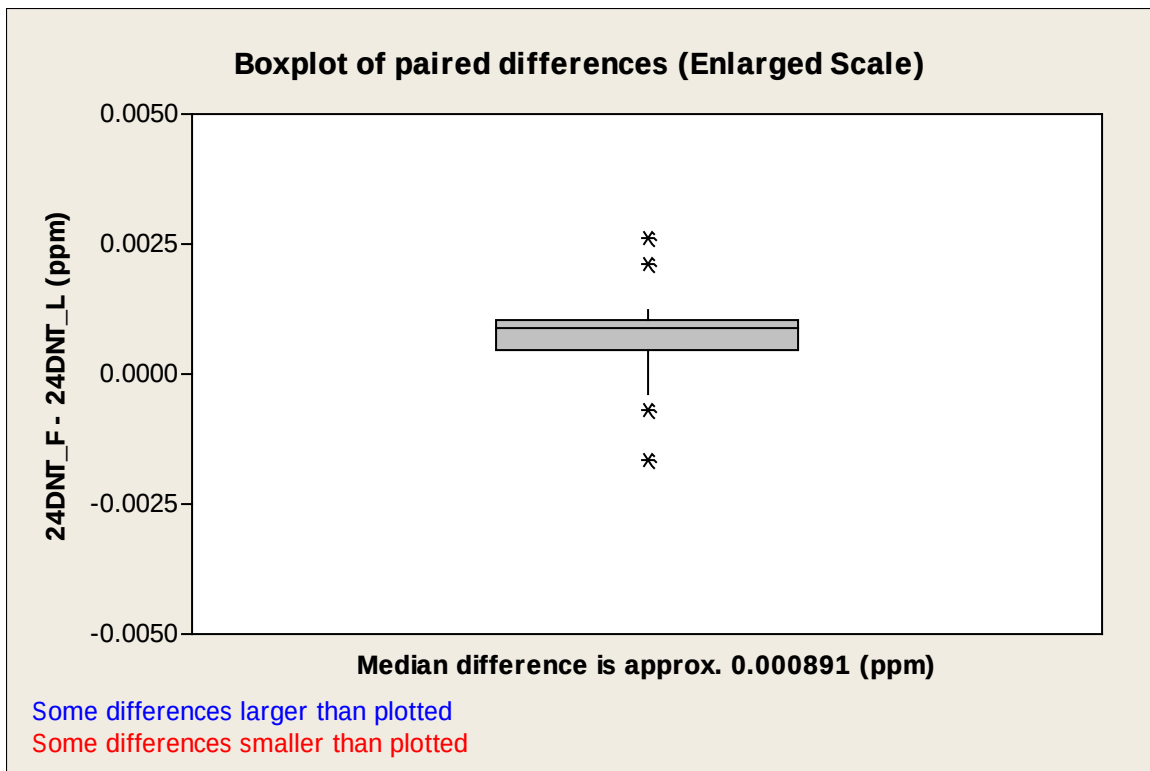
Ho: distribution of 24DNT_F = 24DNT_L

vs Ha: not =

Test Statistic: 1.931

p value: 0.053





PPW test for TNB

Paired Prentice-Wilcoxon test

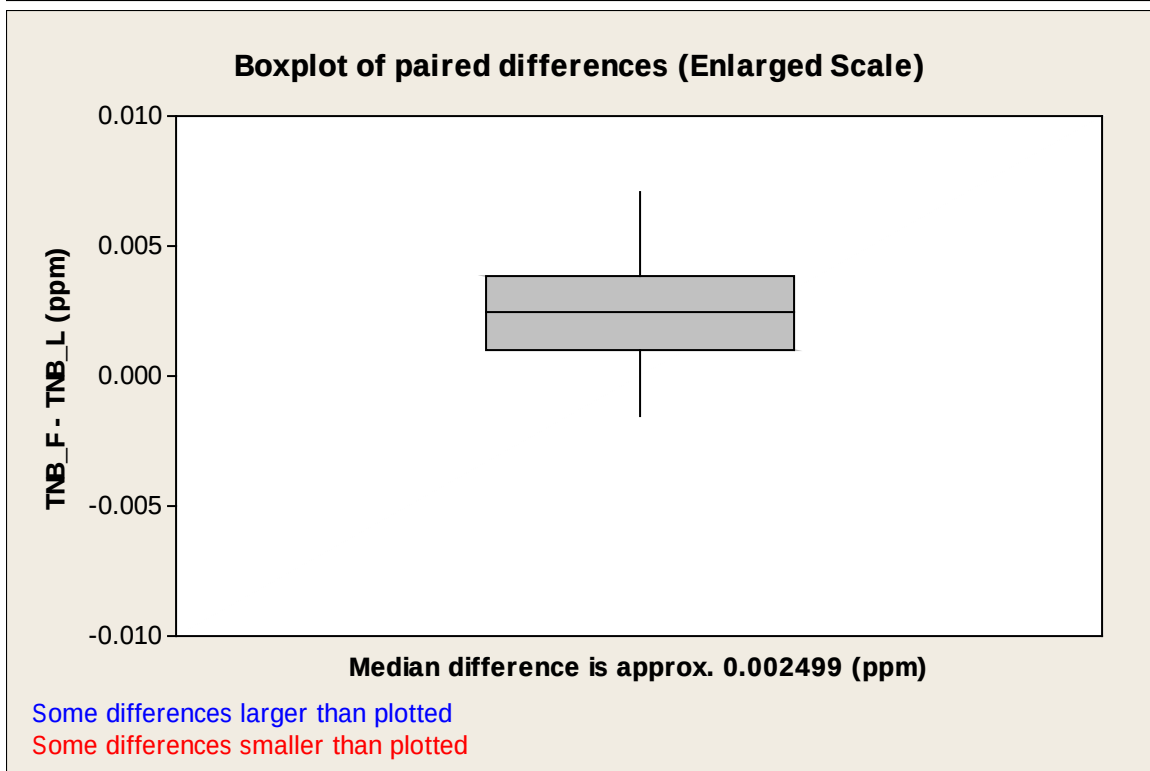
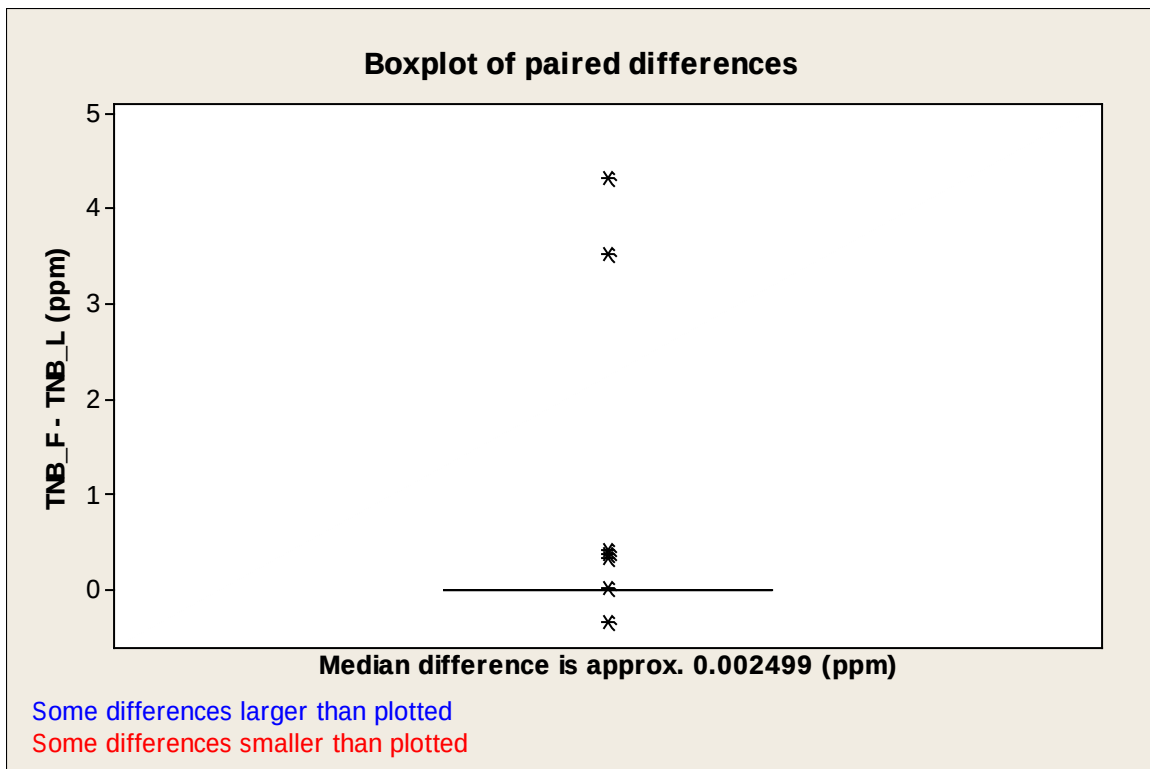
(NonPar test for equality of paired left-censored data)

Ho: distribution of TNB_F = TNB_L

vs Ha: not =

Test Statistic: 4.123

p value: **0.000**



PPW test for TNT

Paired Prentice-Wilcoxon test

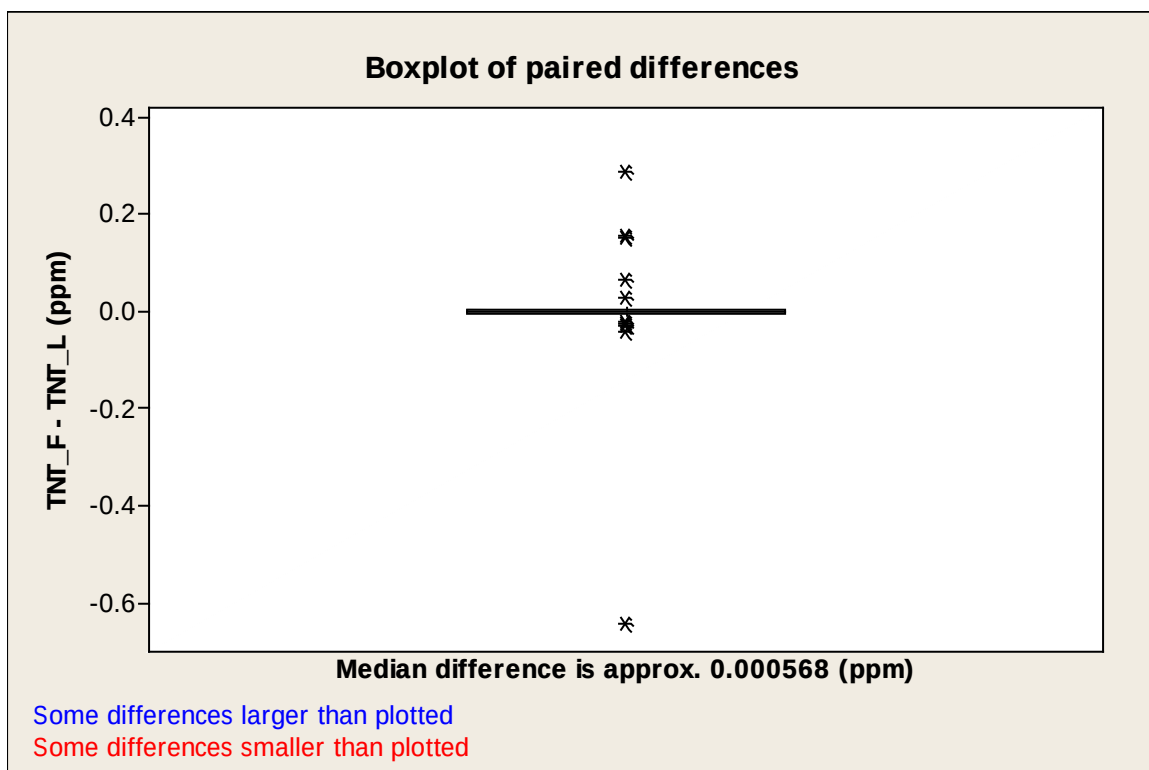
(NonPar test for equality of paired left-censored data)

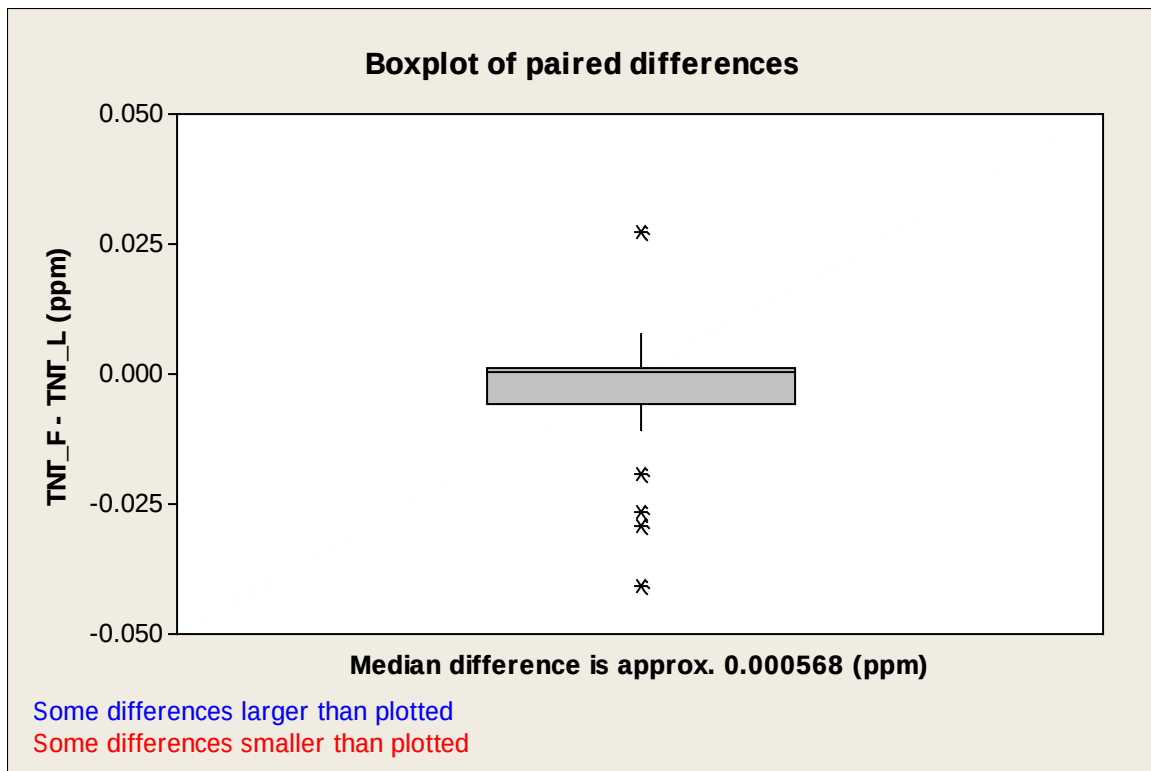
Ho: distribution of TNT_F = TNT_L

vs Ha: not =

Test Statistic: 2.129

p value: 0.033





PPW test for RDX

Paired Prentice-Wilcoxon test

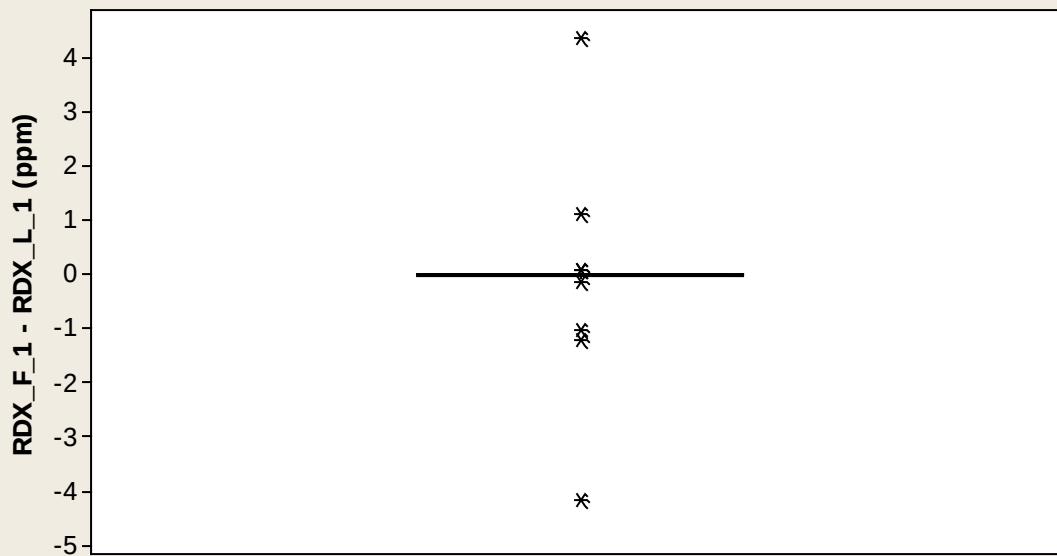
(NonPar test for equality of paired left-censored data)

Ho: distribution of RDX_F_1 = RDX_L_1

vs Ha: not =

Test Statistic: 0.343

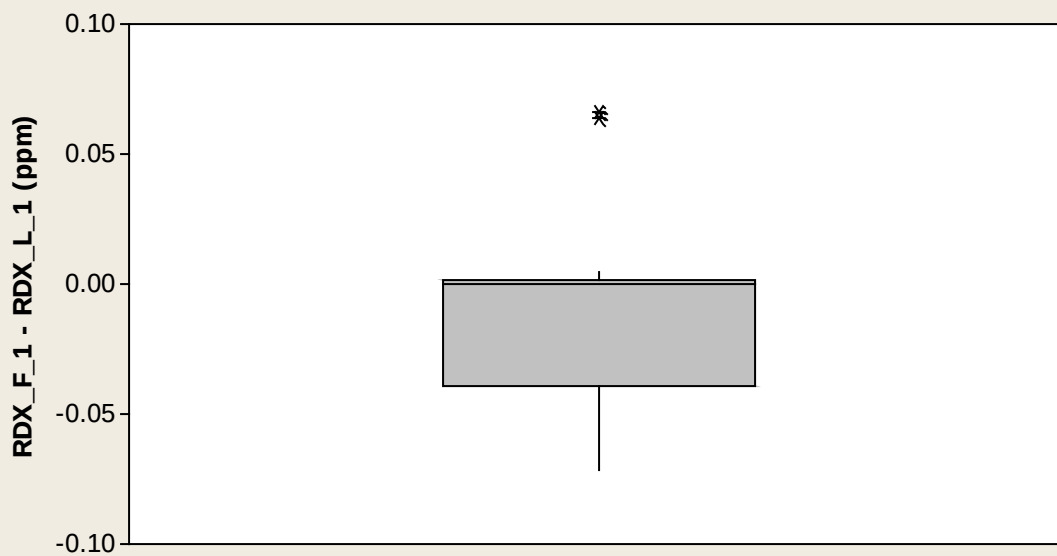
p value: 0.732

Boxplot of paired differences

Median difference is approx. -0.0003 (ppm)

Some differences larger than plotted

Some differences smaller than plotted

Boxplot of paired differences (Enlarged Scale)

Median difference is approx. -0.0003 (ppm)

Some differences larger than plotted

Some differences smaller than plotted

B.11 Akritas-Theil -Sen Lines

A-T-S line for 1, 3-DNB

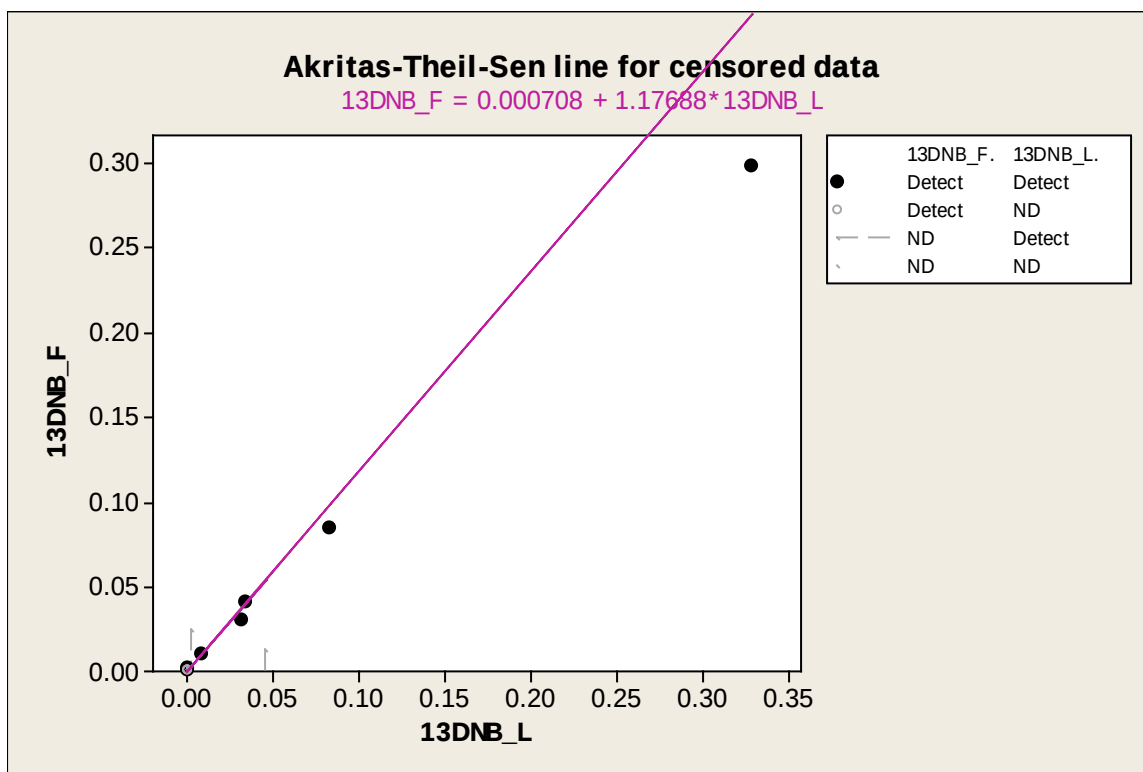
stau 189.000

tau 0.300000

$$13\text{DNB_F} = 0.000708 + 1.17688 \cdot 13\text{DNB_L}$$

Slope 1.17688

Intercept 0.000708025



A-T-S line for 1, 3-DNB

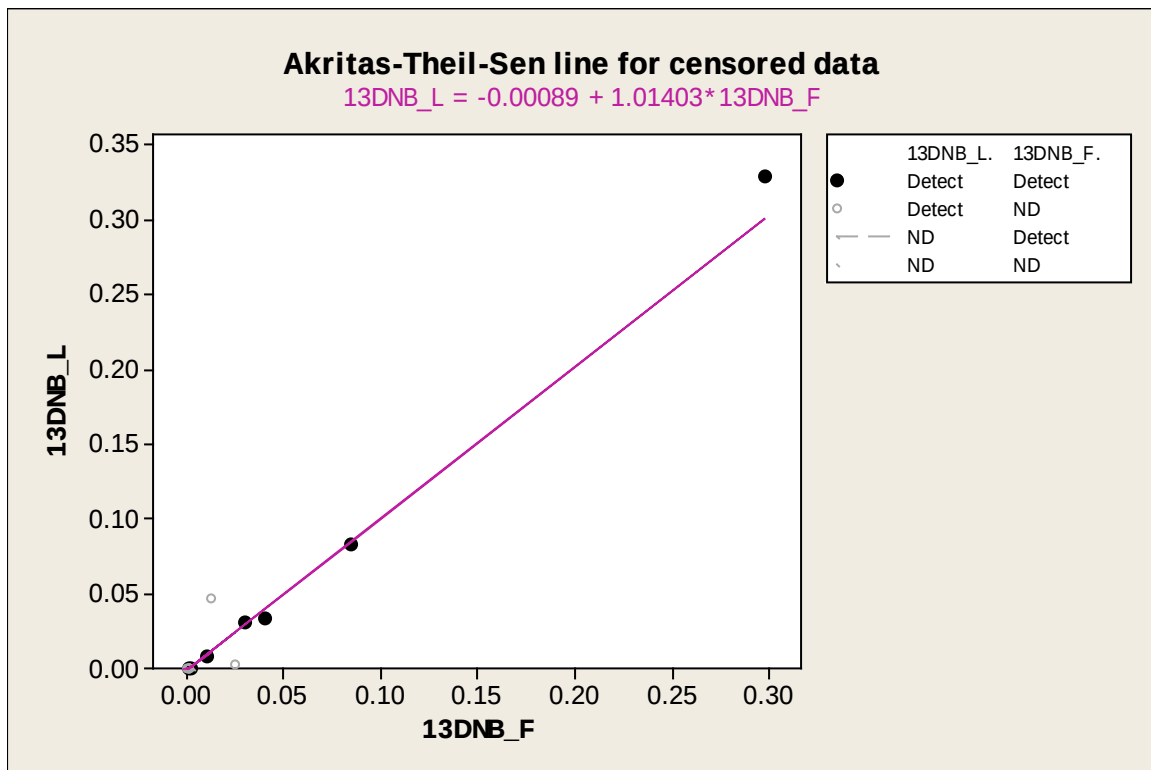
stau 225.000

tau 0.357143

$$13\text{DNB_L} = -0.00089 + 1.01403 \cdot 13\text{DNB_F}$$

Slope 1.01403

Intercept -0.000889576



A-T-S line for 2, 4-DNT

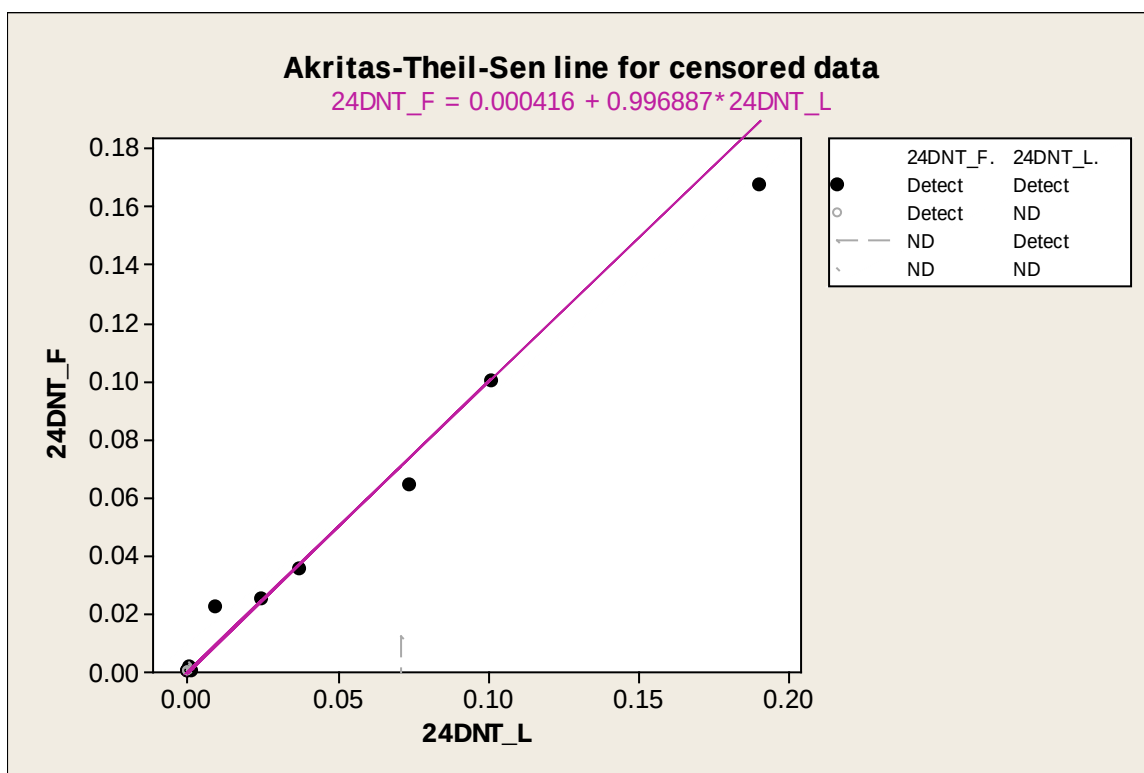
stau 210.000

tau 0.333333

$$24DNT_F = 0.000416 + 0.996887 * 24DNT_L$$

Slope 0.996887

Intercept 0.000416095



A-T-S line for 2, 4-DNT

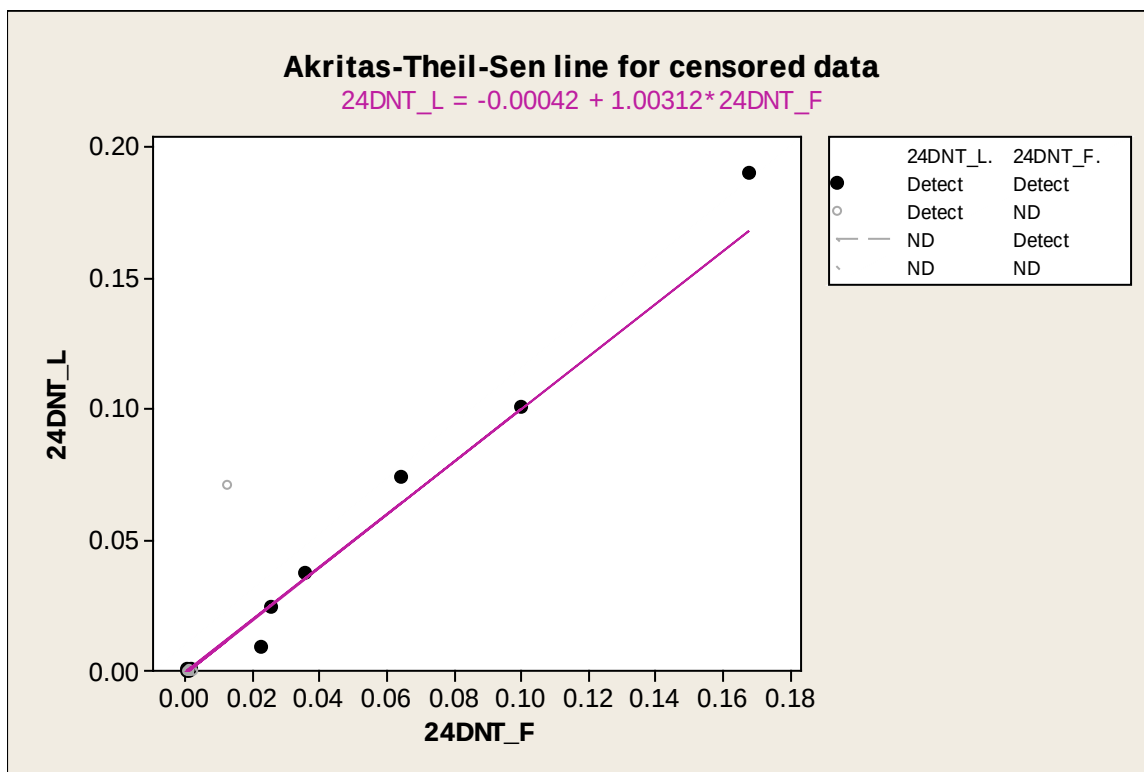
stau 257.000

tau 0.407937

$$24\text{DNT_L} = -0.00042 + 1.00312 \cdot 24\text{DNT_F}$$

Slope 1.00312

Intercept -0.000417392



A-T-S line for TNB

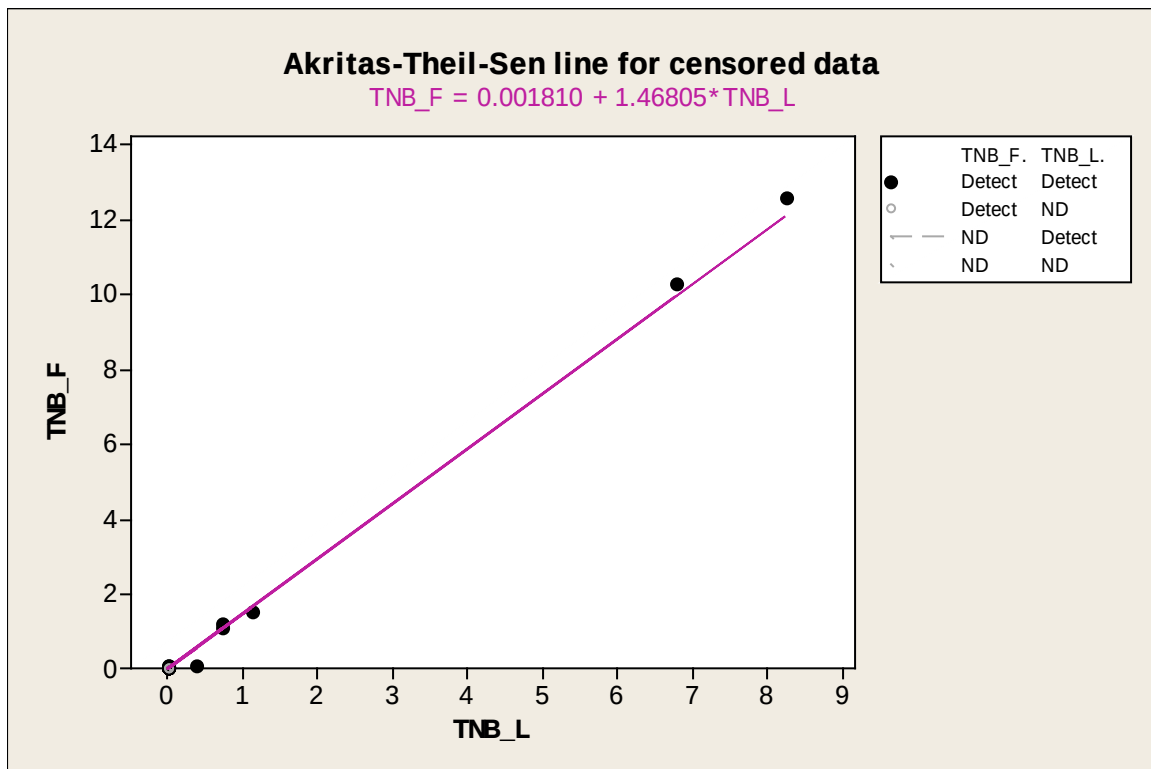
stau 380.000

tau 0.603175

$$\text{TNB}_F = 0.001810 + 1.46805 * \text{TNB}_L$$

Slope 1.46805

Intercept 0.00181044



A-T-S line TNB

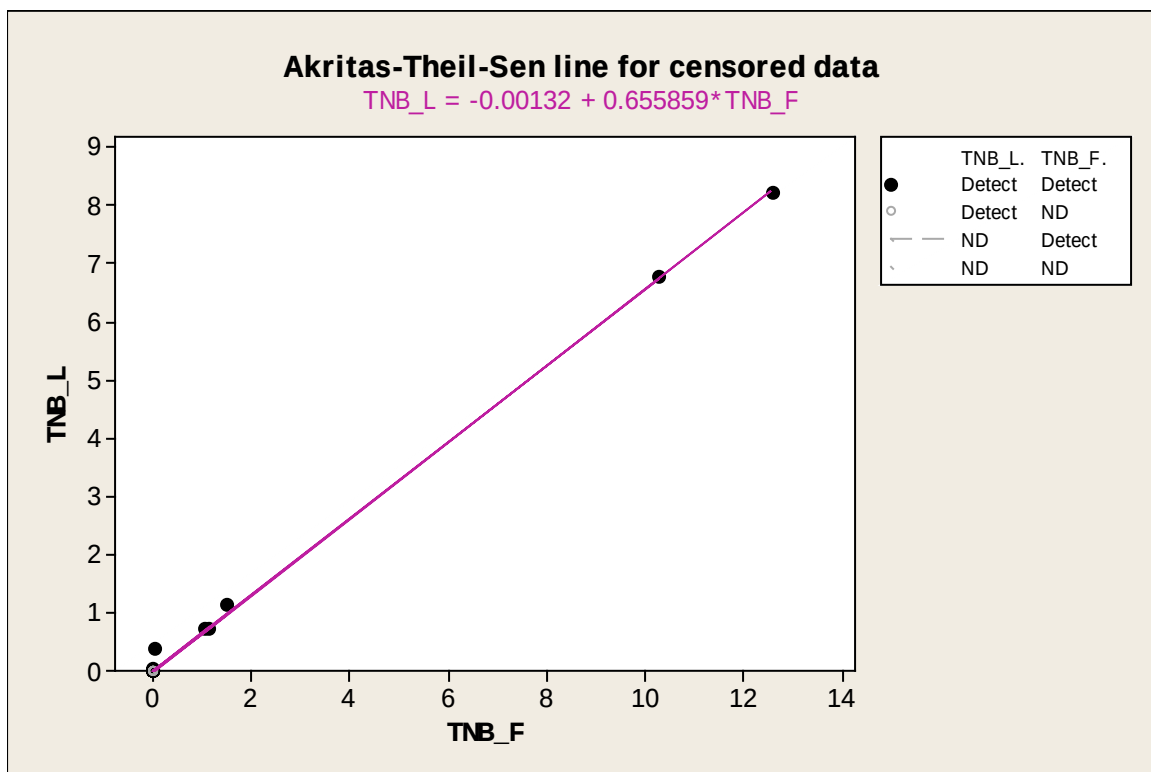
stau 379.000

tau 0.601587

$$\text{TNB_L} = -0.00132 + 0.655859 * \text{TNB_F}$$

Slope 0.655859

Intercept -0.00131650



A-T-S line for TNT

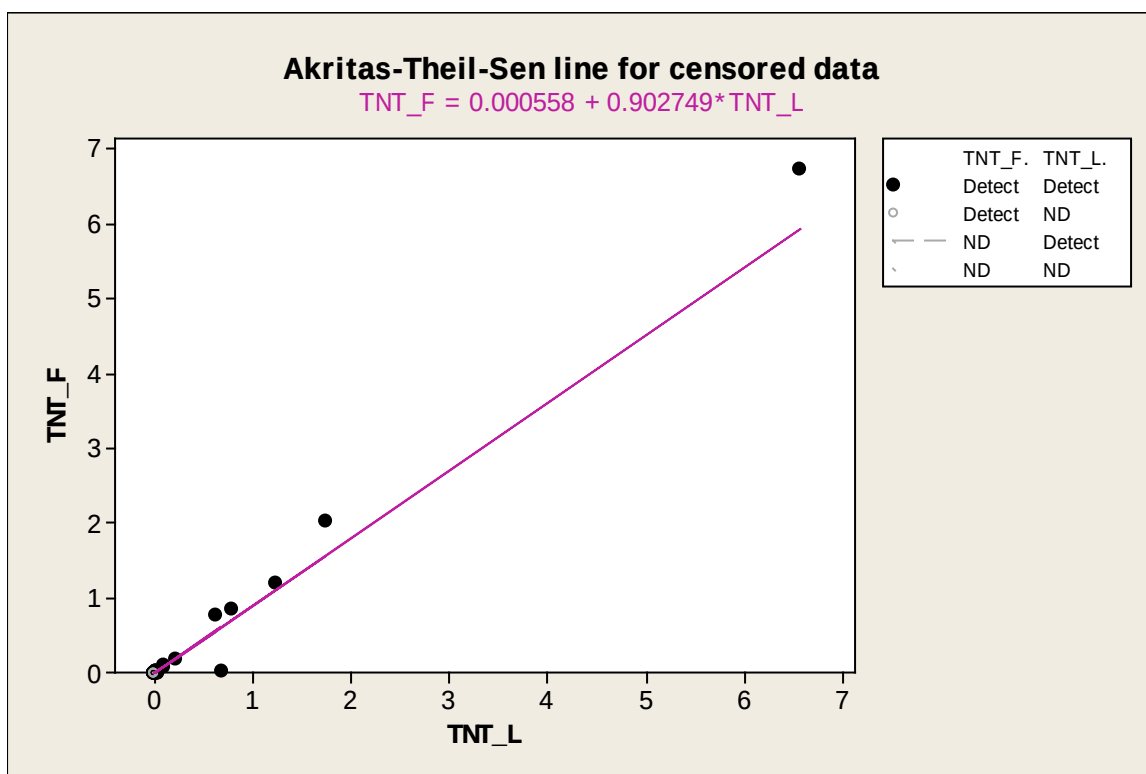
stau 511.000

tau 0.811111

$$\text{TNT}_F = 0.000558 + 0.902749 \cdot \text{TNT}_L$$

Slope 0.902749

Intercept 0.000558141



A-T-S line for TNT

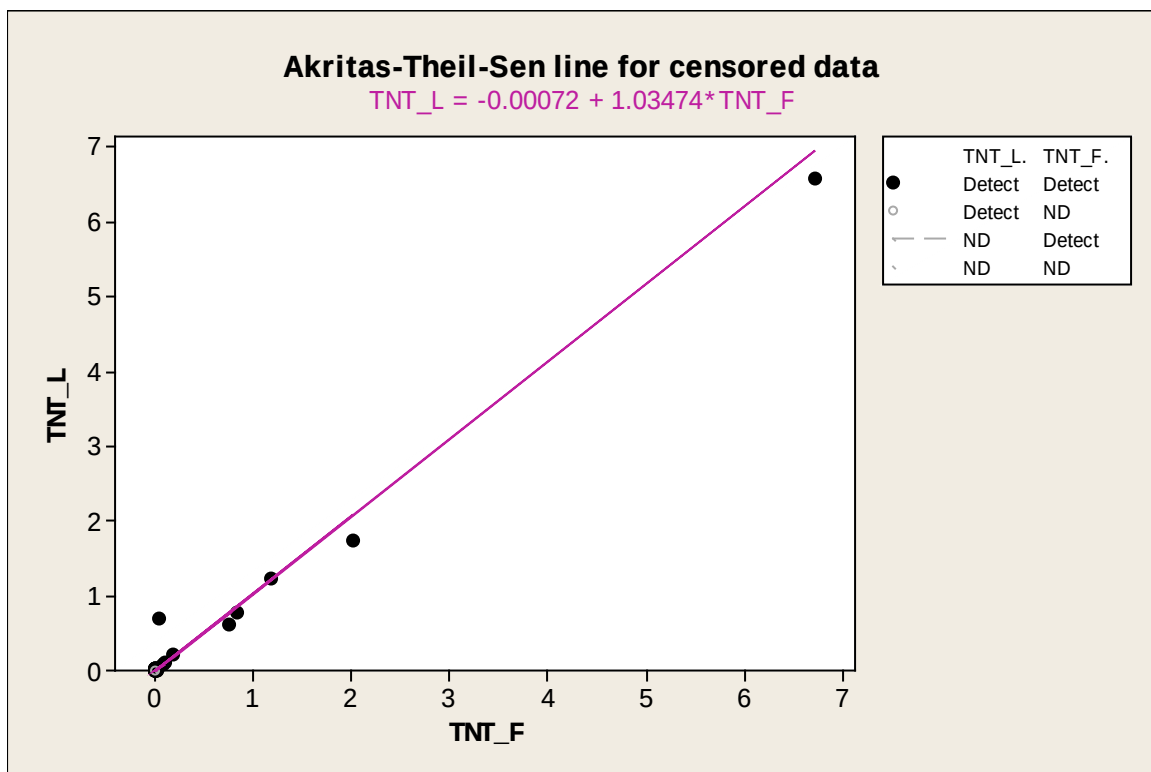
stau 513.000

tau 0.814286

$$\text{TNT_L} = -0.00072 + 1.03474 * \text{TNT_F}$$

Slope 1.03474

Intercept -0.000719215



A-T-S line for RDX

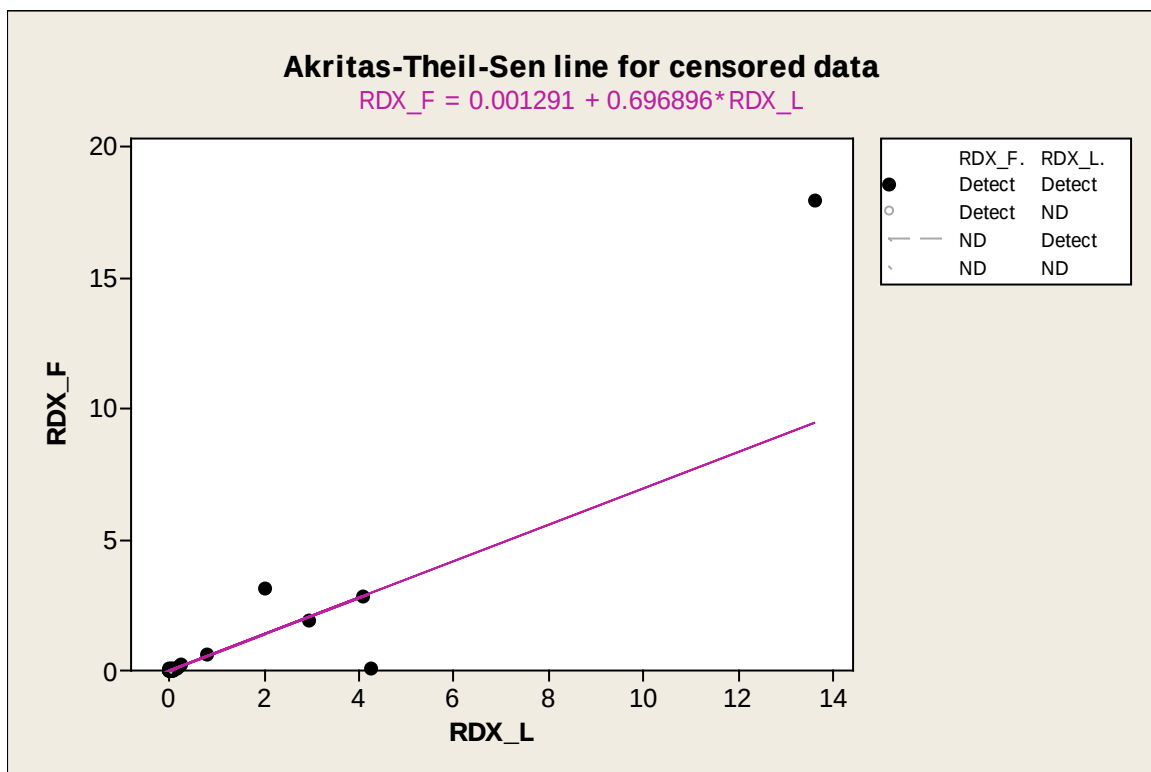
stau 433.000

tau 0.771836

$$\text{RDX_F} = 0.001291 + 0.696896 \cdot \text{RDX_L}$$

Slope 0.696896

Intercept 0.00129093



A-T-S line

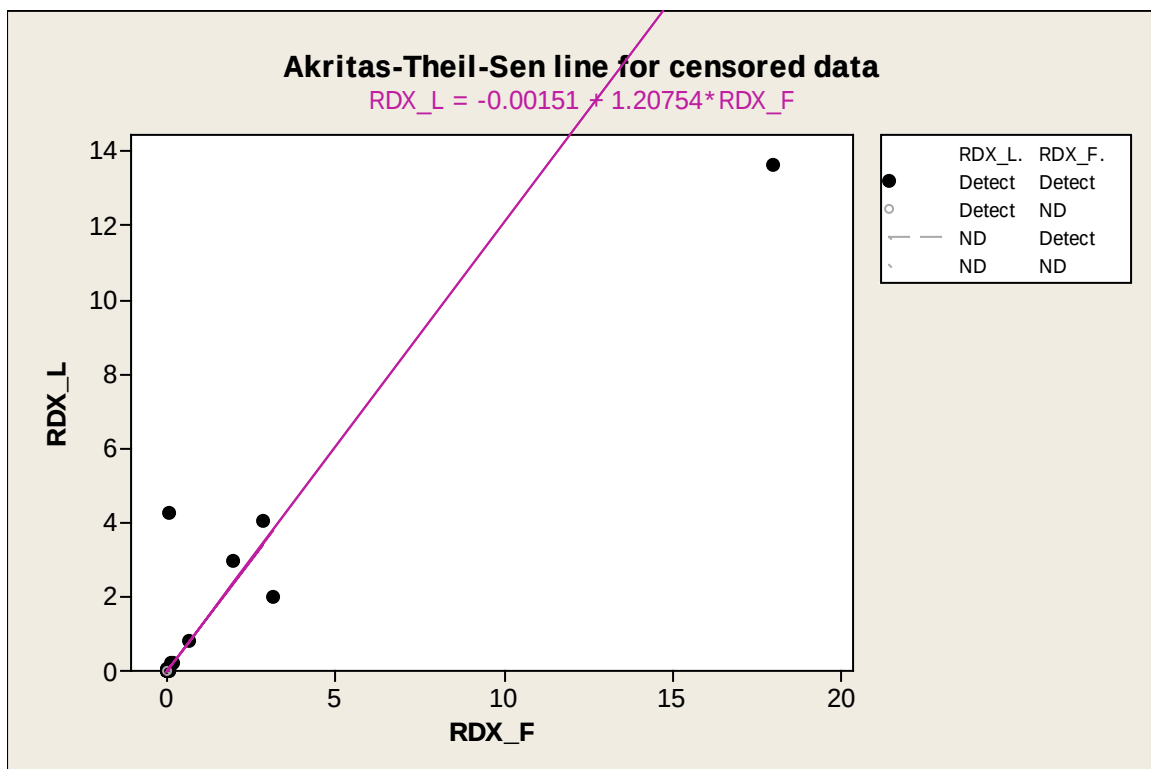
stau 435.000

tau 0.775401

$$\text{RDX_L} = -0.00151 + 1.20754 \cdot \text{RDX_F}$$

Slope 1.20754

Intercept -0.00151131



B.12 Kendall-Theil lines

Kendall's tau for 1, 3-DNB

S 179.000

tau 0.284127

taub 0.711265

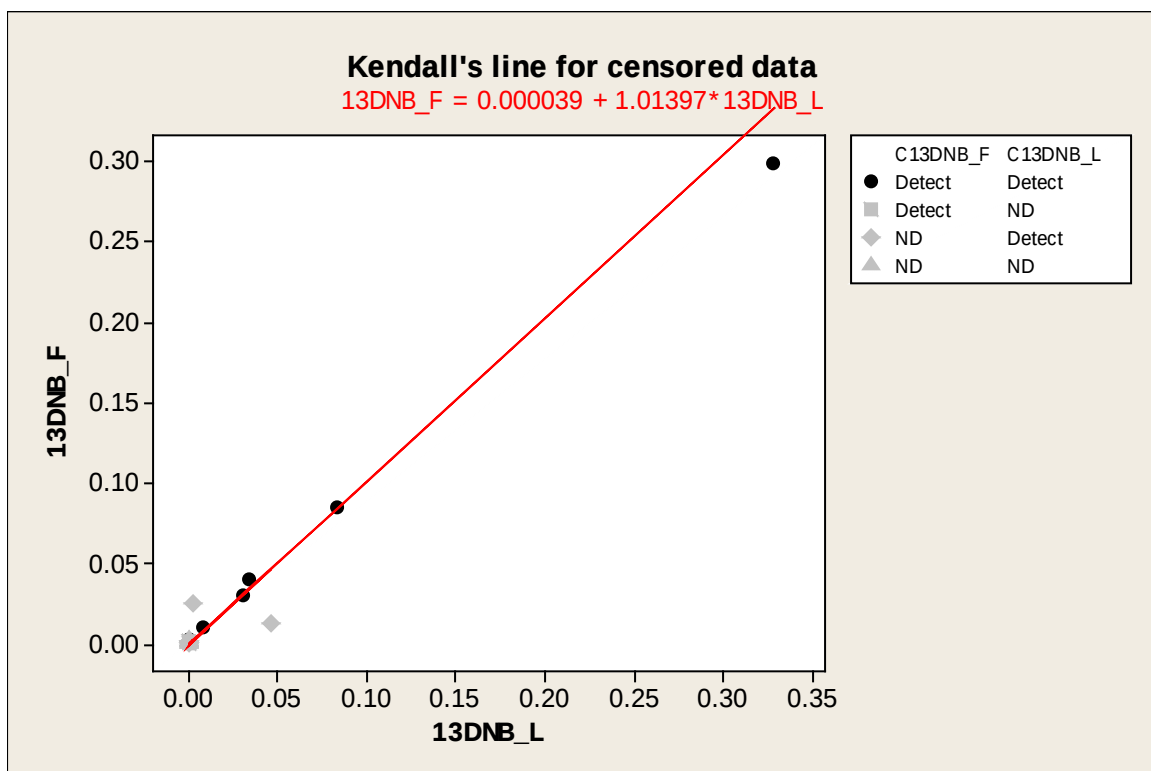
z 2.61367

pval 0.00895767

The median slope is between 1.00184 and 1.01443

Turnbull estimates of median slope and intercept

$13DNB_F = 0.000039 + 1.01397 \cdot 13DNB_L$



Kendall's tau for 2, 4-DNT

S 215.000

tau 0.341270

taub 0.626593

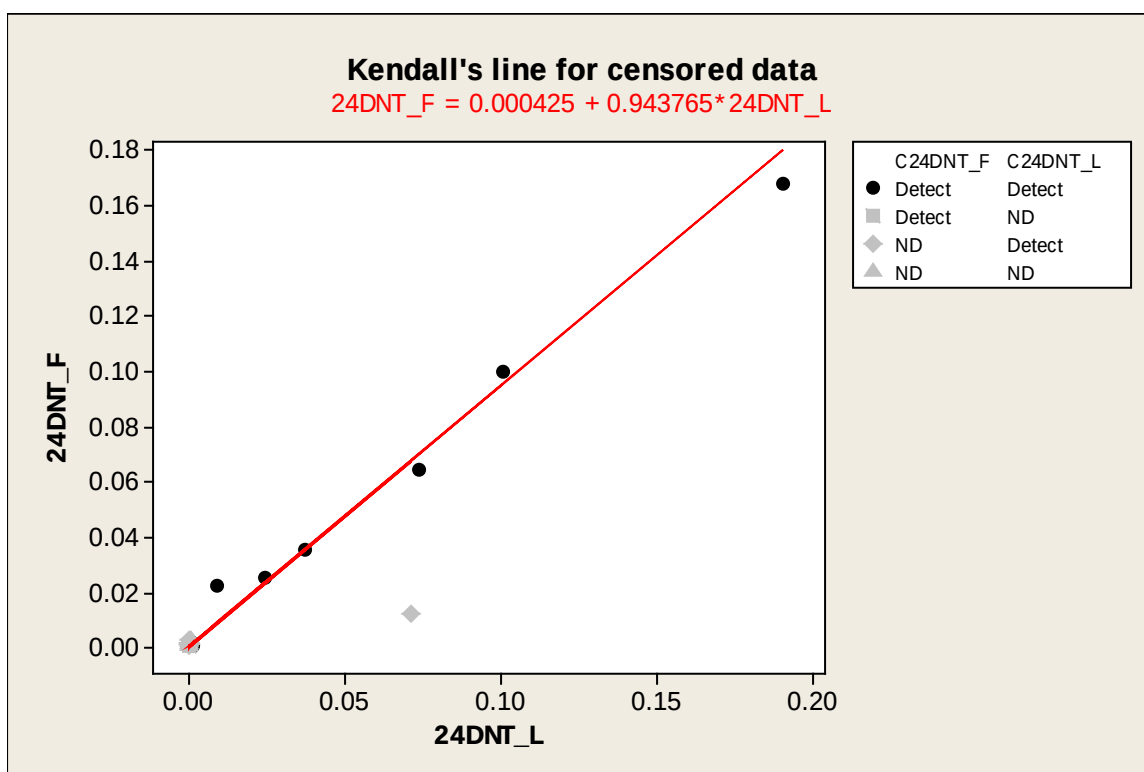
z 3.08647

pval 0.00202549

The median slope is between 0.930985 and 0.988869

Turnbull estimates of median slope and intercept

$$24DNT_F = 0.000425 + 0.943765 * 24DNT_L$$



Kendall's tau for TNB

S 372.000

tau 0.590476

taub 0.623137

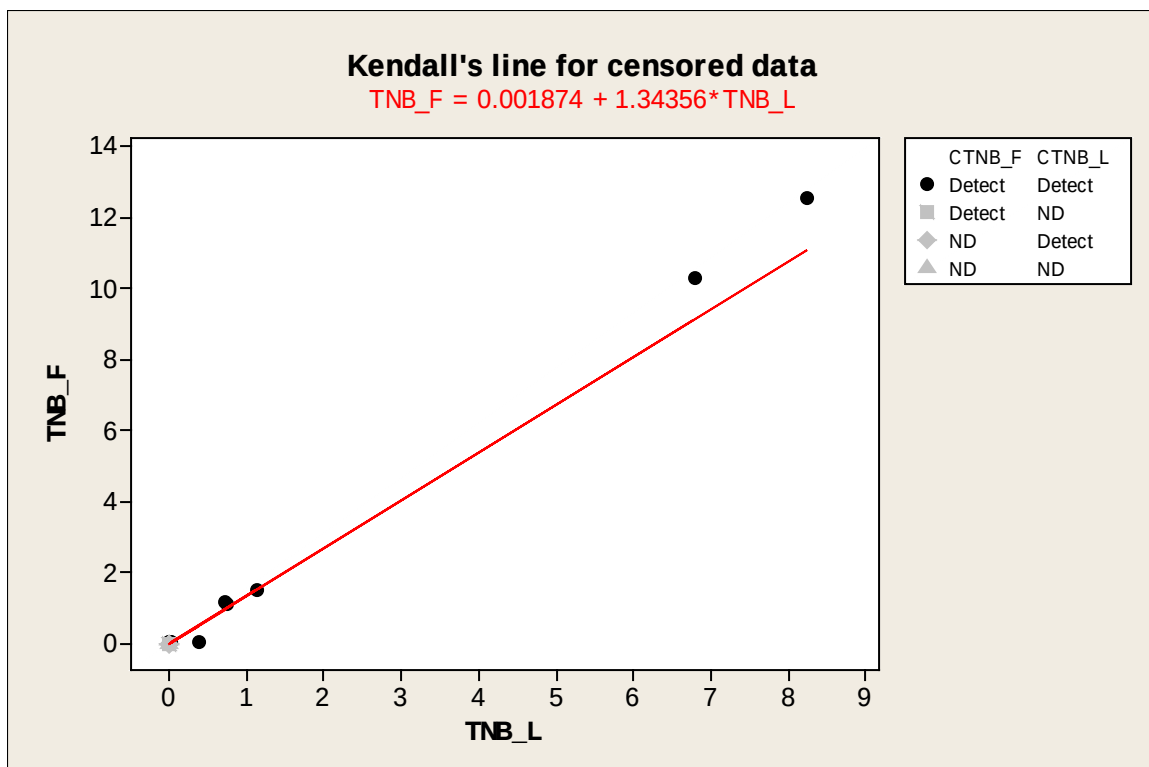
z 5.08457

pval 0.000000368

The median slope is between 1.34287 and 1.34460

Turnbull estimates of median slope and intercept

$$\text{TNB}_F = 0.001874 + 1.34356 \cdot \text{TNB}_L$$



Kendall's tau for TNT

S 510.000

tau 0.809524

taub 0.819937

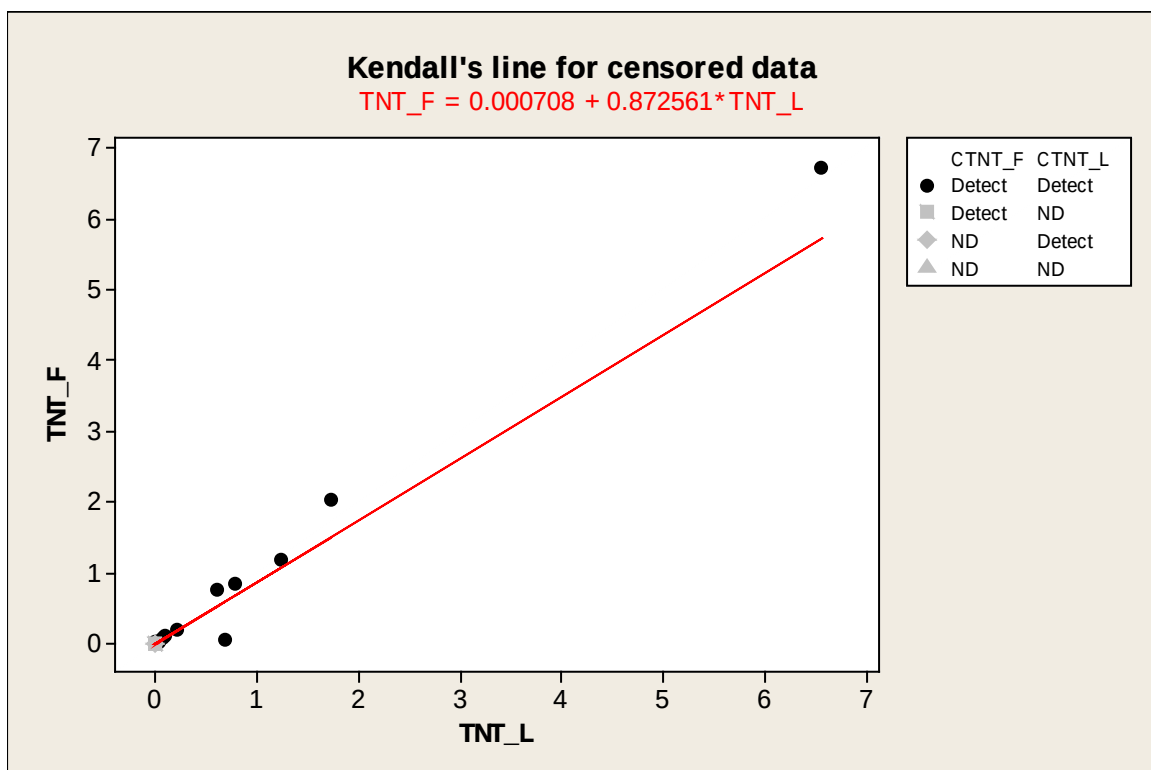
z 6.94328

pval 0.000000000

The median slope is between 0.872197 and 0.891511

Turnbull estimates of median slope and intercept

$$\text{TNT_F} = 0.000708 + 0.872561 * \text{TNT_L}$$



Kendall's tau for RDX

S 434.000

tau 0.773619

taub 0.774309

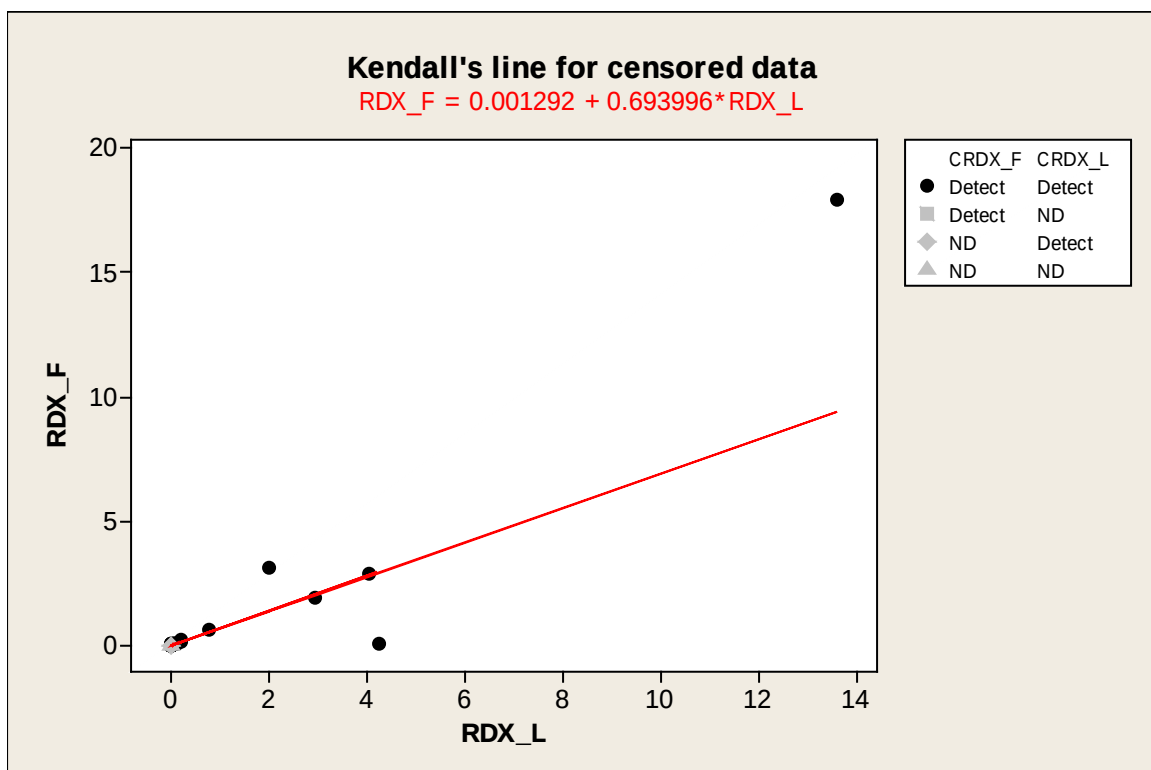
z 6.41969

pval 0.000000000

The median slope is between 0.692399 and 0.695160

Turnbull estimates of median slope and intercept

$$\text{RDX_F} = 0.001292 + 0.693996 * \text{RDX_L}$$



Appendix C: Data from Griffin 450 and HPLC

Field analysis results for the LAAP and MAPP are shown in Table C1.

Control sample recoveries for both sites are shown in Tables C2 and C3.

Table C4 contains the HPLC laboratory results for groundwater collected at the LAAP and MAAP during field analysis.

Table C1. Griffin 450 results for wells at LAAP and MAAP. Results shown are mg/L in groundwater. Results shown are mg/L in groundwater.

Well #	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
108	<0.0178	0.0107	0.0643	1.1542	0.7663	3.1228
111	<0.0016	0.0009	<0.0007	0.0031	0.0015	<0.0006
112	<0.0015	0.0011	0.0007	0.0030	0.0027	0.0292
105	<0.0356	0.0407	0.0227	1.0887	0.1939	0.1939
104	<0.0356.	0.2980	0.1678	12.5725	6.7263	17.9812
140	<0.0089	0.0846	0.0355	0.0283	0.8421	1.9238
141	<0.0089	0.1059	0.1002	1.5073	1.1937	0.6502
142	<0.0015	<0.0006	<0.0007	0.0033	0.0008	0.0029
85	<0.0356	<0.0133	0.0256	10.2946	2.0208	2.8327
110	<0.0178	<0.0067	<0.0080	0.0594	0.0376	0.0442
MI660	<0.0036	<0.0013	<0.0016	<0.0006	0.0289	0.0285
MI658	<0.0030	0.0025	0.0017	0.0081	0.0977	0.0890
MI653	<0.0015	0.0010	<0.0007	<0.0002	0.0018	0.0040
MI645	<0.0015	<0.0006	<0.0007	<0.0002	0.0012	0.1384
MI531	<0.0011	<0.0004	<0.0005	<0.0002	0.0010	0.0030
MI570	<0.0045	<0.0017	<0.0020	<0.0007	0.0054	0.0091
MI533	<0.0011	<0.0004	<0.0005	<0.0002	0.0188	0.0680
MI536	<0.0018	<0.0007	<0.0008	0.0042	0.0028	0.0368
MI537	<0.0015	<0.0006	<0.0007	0.0037	0.0084	0.0146
MI538	<0.0015	<0.0006	<0.0007	0.0035	0.0127	0.0155
MI654	<0.0018	<0.0007	<0.0008	0.0282	0.0181	0.0367
MI355	<0.0011	<0.0004	<0.0005	0.0019	0.0012	0.0285
MI514	<0.0018	<0.0007	<0.0008	0.0052	0.0788	0.0042
MI516	<0.0018	<0.0007	<0.0008	0.0032	0.0094	0.0016
MI534	<0.0011	<0.0004	<0.0005	0.0020	0.0021	0.0133
MI569	<0.0011	<0.0004	0.0005	0.0022	0.0008	0.0015
MI571	<0.0011	<0.0004	<0.0005	<0.0002	0.0008	0.0014
MI573	<0.0011	<0.0004	0.0006	0.0023	0.0309	0.0708

Table C2. Griffin 450 LCS % recoveries. Values in bold are outside DoD QSM limits

	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	78.0	72.8	82.3	82.5	74.1	57.4
LAAP Day 2	57.5	46.8	60.3	72.5	59.0	32.7
LAAP Day 3	109.1	64.6	95.8	90.5	83.1	69.3
MAAP Day 1	99.6	97.9	91.0	81.2	81.8	55.2
MAAP Day 2	107.2	92.6	103.6	72.2	66.6	41.3
MAAP Day 3	99.5	102.2	110.7	61.7	69.8	56.7
MAAP Day 4	76.9	107.7	104.1	78.6	88.4	113.0

Table C3. Griffin 450 MS % recoveries. Values in bold are outside DoD QSM limits

	Sample ID	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	111MS	95.8	86.3	91.4	74.1	62.8	44.9
	111MSD	100.9	74.1	118.7	103.1	92.2	38.3
LAAP Day 2*	104MS	92.2	176.2	168.4	7040.8	3558.1	-2179.5
	104MSD	98.8	236.2	195.0	5289.7	2168.4	-3781.0
LAAP Day 3	142MS	80.3	71.8	72.5	74.8	71.5	53.6
	142MSD	96.1	103.8	93.3	88.5	81.3	49.5
MAAP Day 1	MI531MS	120.2	108.7	105.1	65.9	54.8	9.8
	MI531 MSD	122.6	77.0	95.7	79.2	58.3	26.2
MAAP Day 2	MI536MS	107.3	68.0	104.8	59.2	54.4	259.3
	MI536 MSD	116.5	99.4	120.8	88.6	81.0	205.5
MAAP Day 3	MI355MS	159.3	105.8	113.5	22.1	60.6	20.1
	MI355MSD	144.9	92.5	105.7	22.7	66.2	36.9
MAAP Day 4	MI569MS	70.1	99.0	93.6	65.9	85.5	32.7
	MI569MSD	97.7	129.9	102.5	76.4	95.7	34.5

* The well sample chosen was highly contaminated with the MCs of interest except for NB, therefore the spike was insignificant compared to the amount of analyte present, resulting in poor recoveries.

Table C4. HPLC results for wells at LAAP and MAAP. Results shown are mg/L in groundwater.

Well #	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
108	<0.0005	0.0082	0.0738	0.7259	0.6142	2.0165
111	<0.00005	<0.00005	<0.00005	<0.00005	<0.00005	<0.00005
112	<0.00004	0.0003	0.0011	0.0003	0.0004	0.0248
105	<0.0010	0.0340	0.0093	0.7398	0.2231	0.2231
104	<0.0010	0.3286	0.1901	8.2453	6.5697	13.6107
140	<0.00025	0.0834	0.0372	0.0234	0.7790	2.9515
141	<0.00025	0.0311	0.1009	1.1211	1.2344	0.7841
142	<0.00004	<0.00004	<0.00004	<0.00004	<0.00004	<0.00004
85	<0.0010	0.0029	0.0247	6.7785	1.7333	4.0635
110	<0.0005	0.0461	0.0710	0.3817	0.6814	4.2326
MI660	<0.0001	<0.0001	0.0004	0.0007	0.0398	0.0681
MI658	<0.00008	0.0001	0.0009	0.0009	0.0958	0.1426
MI653	<0.00004	<0.00004	0.0001	0.0001	0.0011	0.0045
MI645	<0.00004	<0.00004	0.0002	0.0001	0.0004	0.2103
MI531	<0.00003	<0.00003	<0.00003	0.0001	0.0009	0.0011
MI570	<0.0001	<0.0001	<0.0001	0.0004	0.0047	0.0076
MI533	<0.00003	0.0001	0.0003	0.0008	0.0225	0.0711
MI536	<0.00005	<0.00005	0.0002	0.0002	0.0034	0.0348
MI537	<0.00004	<0.00004	0.0001	0.0035	0.0349	0.0341
MI538	<0.00004	<0.00004	0.0001	0.0018	0.0321	0.0700
MI654	<0.00005	<0.00005	0.0004	0.0006	0.0103	0.0755
MI355	<0.00003	<0.00003	<0.00003	0.0001	<0.00003	<0.00003
MI514	<0.00005	<0.00005	0.0003	0.0068	0.0857	0.0097
MI516	<0.00005	<0.00005	0.0001	0.0004	0.0160	0.0206
MI534	<0.00003	<0.00003	<0.00003	0.0004	0.0032	0.0026
MI569	<0.00003	<0.00003	<0.00003	0.0001	0.0001	0.0003
MI571	<0.00003	<0.00003	<0.00003	<0.00003	0.0001	0.0001
MI573	<0.00003	<0.00003	0.0002	0.0003	0.0037	0.0048

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14. ABSTRACT This effort demonstrated the use of field-portable instrumentation for the quantification of munitions constituents in groundwater, without the need to ship water samples to a fixed analytical laboratory. The results indicate that similar reporting limits can be obtained using the field-portable instrument when coupled to solid phase extraction sample preparation, yet instrument stability at the low concentration range is an issue. The instrumentation was tested on 28 groundwater samples for a variety of analytes with concentrations ranging up to 3 orders of magnitude. Detection limits for the field instrumentation are generally below regulatory thresholds. Linear regression comparison of the field results to laboratory-based analysis suggest comparability between the techniques, with the slope of the regression for all analytes being between 0.8 and 1.2, except for TNB and RDX. The field results were about 70% of the laboratory results on the average. The field method consistently exhibits a significant positive bias for TNB. The field and laboratory NB results were consistent in that both the field and laboratory methods reported non-detects.					
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