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# Measurement and Modeling of Energetic Material Mass Transfer to Soil Pore Water – Project CP-1227 FY03 Annual Technical Report

James M. Phelan, James L. Barnett and Dayle R. Kerr

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## Abstract

Military test and training ranges operate with live fire engagements to provide realism important to the maintenance of key tactical skills. Ordnance detonations during these operations typically produce minute residues of parent explosive chemical compounds. Occasional low order detonations also disperse solid phase energetic material onto the surface soil. These detonation remnants are implicated in chemical contamination impacts to groundwater on a limited set of ranges where environmental characterization projects have occurred. Key questions arise regarding how these residues and the environmental conditions (e.g., weather and geostratigraphy) contribute to groundwater pollution impacts. This report documents interim results of experimental work evaluating mass transfer processes from solid phase energetics to soil pore water. The experimental work is used as a basis to formulate a mass transfer numerical model, which has been incorporated into the porous media simulation code T2TNT. This report documents the results of the Phase III experimental effort, which evaluated the impacts of surface deposits versus buried deposits, energetic material particle size, and low order detonation debris. Next year, the energetic material mass transfer model will be refined and a 2-d screening model will be developed for initial site-specific applications. A technology development roadmap was created to show how specific R&D efforts are linked to technology and products for key customers.

## Acknowledgements

This work was sponsored by the Strategic Environmental Research and Development Program (SERDP), under the technical direction of Jeff Marqusee and programmatic direction of Brad Smith. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

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# 1.0 Introduction

SERDP is seeking techniques and knowledge that will permit assessment of the environmental impact of residual energetic material from test and training operations. Low-order detonations that disperse discrete solid phase particles onto and into the soil leave the greatest legacy of energetic material residues. One principal environmental impact is contamination of aquifers. The energetic material most likely to impact aquifers is RDX due to its low drinking water advisory limits, low retardation during soil transport and low rate of environmental degradation.

Understanding the mass transfer rate from discrete solid phase particles into the soil pore water is critical to the impact analysis of these residues for groundwater contamination. Weather is an important process that drives the mass transfer phenomena. This work seeks to analyze this mass transfer process using laboratory measurement and numerical simulation methods. The results from this work will create a new predictive ability to assess the migration potential of residual energetic materials. The transition plan will extend this work to evaluate groundwater impact and range management strategies.

*Objective*

This work seeks to develop an energetic material source release function that describes the mass transfer of solid phase energetic materials to a solute in soil pore water, and to incorporate this process in a solute transport model with linkages to time dependent weather phenomena. The ultimate objective of this work is to develop a screening level simulation tool, with data defining an energetic material source release function that can be used to assess groundwater pollution management strategies for residual energetic materials left by military testing and training operations.

# 2.0 Project Plan

This project began in FY01 as a two year effort to develop the preliminary data and mass transfer properties for use in a screening model. At the end of each year, the annual technical reports have documented the methods and results for work that occurred that year (Phelan et al., 2001; Phelan et al., 2003). At the Fall 2002 IPR, sufficient evidence was shown to extend the experimental work and explore certain mass transfer phenomena in more detail and create a screening model to evaluate the environmental impacts of low order detonation debris. The project extension proposal was for a one year extension; however funding constraints extended the task scope to three years. Table 1 shows the major project tasks in experimental and modeling areas for each year. Table 2 shows the detail tasks and milestones for the entire project.

Table 1. Project Task Schedule

| FY | Experimental | Modeling |
|---|---|---|
| 2001 | Method Development<br>Phase I, Test Group A and B | Initial Formulation |
| 2002 | Phase II, Test Group A and B | Revised Formulation and Data/Model Comparisons |
| 2003 | Phase III | |
| 2004 | | 2-d Model Enhancement |
| 2005 | | Screening Assessments |

Table 2. Master List of Tasks, Milestones and Deliverables

| Task Name | Milestone | Date | Status | Deliverable |
|---|---|---|---|---|
| 1 - Phase I Experiments | Complete solubility kinetics pretest | 8/01 | Completed | Phelan, J.M, J.L. Barnett, J.V. Romero, D.R. Parker, 2002. Solubility and Dissolution Kinetics of Composition B in Water. Sandia National Laboratories Report SAND2002-2420, December 2002. |
| | Complete Phase I, Test Group A | 11/01 | Completed | |
| | Complete Phase I, Test Group B | 01/02 | Completed | |
| 2- Initial Model Development | Develop Preliminary Form of Energetic Material Source Function | 8/01 | Completed | |
| | Integrate with T2TNT | 11/01 | Completed | |
| | Compare Modified T2TNT with Experimental Data | 02/02 | Completed | |
| 3 – Phase II Experiments | Phase II Test Plan | 02/02 | Completed | |
| | Complete Phase II, Test Group A | 06/02 | Completed | |
| | Complete Phase II, Test Group B | 09/02 | Completed | |
| 4 – Phase III Experiments | Complete Phase III Tests | 12/03 | This Report | |
| 5 – Revised Energetic Material Source Function | Complete New Energetic Material Source Function | 06/02 | Completed | |
| | Compare Energetic Material Source Function with Phase II Experimental Data | 11/02 | Completed | |
| | Revise Energetic Material Source Function with Phase III data | 9/04 | Not Started | |
| | Develop Screening Model Formulation | 12/04 | Not Started | |
| 6 – Applications Analysis Tools | Develop Screening Model Application and Analysis | 12/05 | Not Started | |
| 7 – Roadmap | Complete Development and Application Roadmap | 12/03 | This Report | |
| 8 – Technical Reports to SERDP | Annual Technical Report | 12/01 | Completed | Phelan, J.M., S.W. Webb, J.V. Romero and J.L. Barnett, 2001. FY01 Interim Technical Report, Strategic Environmental Research and Development Program, Project 1227, Measurement and Modeling of Energetic Material Mass Transfer to Soil Pore Water. |
| | Annual Technical Report | 12/02 | Completed | Phelan, J.M., S.W. Webb, J.V. Romero, J.L. Barnett, F. Griffin, M. Eliassi and J.L. Brainard, 2003. Measurement and Modeling of Energetic Material Mass Transfer to Soil Pore Water – Project CP-1227 Annual Technical Report. Sandia National Laboratories Report SAND2003-0153, January 2003. |
| | Annual Technical Report | 12/03 | This Report | Phelan, J.M., J.L. Barnett, and D.R. Kerr, 2004. Measurement and Modeling of Energetic Material Mass Transfer to Soil Pore Water – FY03 Project CP-1227 Annual Technical Report. Sandia National Laboratories Report SAND2004-XXXX, January 2004. |

# 3.0 Experimental Methods

## 3.1 Test Plans

Based on the results of the Phase I and Phase II tests, additional work was needed to define the impacts from three processes: 1) surface deposits versus buried deposits; 2) surface area effects; and 3) actual low order detonation debris. Test methods used for these Phase III tests were based on the saturated column methods described in Phelan et al., 2003. Phase III included nineteen tests and are shown in context with Phase I and II tests in Table 3.

Table 3. Experimental Test Phases and Principal Factors

| Test Phase | Principal Factors | Mass Transfer Test Designator |
|---|---|---|
| Phase I, Test Group A | Flow, temperature, EM particle size | MT1, MT2, MT3 |
| Phase I, Test Group B | Porous media saturation | MT5, MT12 |
| Phase II, Test Group A | Bed loading, bed depth, initial wetting rate | MT6, MT7, MT8, MT8b, MT8c, MT8d, MT9b2, 9b3 |
| Phase II, Test Group B | Flow, EM particle size, detonation debris | MT10, MT13, MT14, MT11, MT15, MT16, MT17, MT18 |
| Phase III | Surface vs. buried deposits, EM particle size, low order detonation debris | MT 19-1, 2, 3, 4; MT20-1, 2, 3; MT21-1, 2; MT22-1, 2, 3; MT23-1, 2; MT24-1; MT25-1; MT26-1, MT27-1; MT28-1. |

## 3.2 Chemical Analysis

*HPLC Method.*

The majority of the column effluent quantitative analysis was performed with the same Waters HPLC equipment and methods as described in Phelan et al., 2003. When the Waters HPLC was unavailable or out of order, an Agilent RP-HPLC was used as a backup and produced equivalent data.

The backup system consisted of an Agilent 1100 series controller, Agilent 1100 Autosampler, and an Agilent 1100 Diode Array Detector. The samples were injected (2.5μl) into an Agilent Hypersil BDX-C18 5μm guard column (4 mm x 4 mm) and then followed by an Agilent Hypersil BDS-C18 3μm column (4 mm x 100 mm). The samples were eluted with a 55:45 deionized water and acetonitrile eluant run in isocratic mode with a flow rate of 0.5 mL/min at approximately 38°C. The diode array detector accumulated all peaks found at the 210 nm, 254 nm, and 235 nm wavelengths. Calibration was performed as described for the Waters system in Phelan et al., 2003.

## 3.3 Energetic Material Preparation

*Source Material.*

The Composition B material used for Phase III was the same material that was used in Phase I and II.

*Low Order Detonation Debris*

As part of the companion project to this effort, the US Army Engineer Research and Development Center (SERDP Project CP-1155) evaluated the nature and distribution of low order detonation debris (Pennington et al., 2003; Taylor et al., 2004). Low order detonation debris from the May 2002 Blossom Point tests was provided by S. Taylor of the US Army, Engineer Research and Development Center, Cold Regions Research and Development Laboratory. Table 4 shows the type and mass of material received.

Table 4. Low order detonation debris, 81 mm mortar, Blossom Point, May 2002

| | |
|---|---|
| **5m or closer to the detonation** | |
| Bag 1 | Single particle (2.2292 g) |
| Bag 2 | Single particle (2.1536 g ) |
| Bag 3 | 6 grains (1.0295g ) |
| Bag 4 | 23 grains (1.0292g ) |
| Bag 5 | >500μm (0.9501 g ) |
| Bag 6 | <500μm not sized (1.2727 g, CompB + soil) |
| **5m or farther from the detonation** | |
| Bag 7 | Bag 7. >500μm (0.9162 g CompB) |
| Bag 8 | Bag 8. <500μm (0.4079 g, CompB + soil) |

The specific surface area of each material was measured using the same method for the Comp B particles described in Phelan et al., 2003. The instrument used was a Micromeritics Accelerated Surface Area and Porosimetry 2405 Instrument that measures BET surface area with Kr or $N_2$ gas. The results for the BET specific surface area measurements are shown in Table 5.

Table 5. BET Specific Surface Area Measurements, Low Order Detonation Debris, 81 mm mortar, Blossom Point May 2002

| | Bag #1 | Bag #2 | Bag #3 | Bag #4 | Bag #5 | Bag #6 | Bag #7 | Bag #8 |
|---|---|---|---|---|---|---|---|---|
| Sample Description | Single particle | Single particle | 6 grains | 23 grains | > 500 μm | < 500 μm, with soil | > 500 μm | < 500 μm, with soil |
| Sample Location from Detonation | < 5 m | < 5 m | < 5 m | < 5 m | < 5 m | < 5 m | > 5 m | > 5 m |
| Sample Wt, before degas (g) | 2.2152 | 2.1518 | 1.0266 | 1.0185 | 0.9262 | 1.1236 | 0.9056 | 0.3866 |
| Degas Time (hrs) | 24.0 | 30.0 | 24.0 | 26.5 | 21.75 | 24.0 | 21.75 | 27.0 |
| Degas Temp (C) | 23 | 23 | 23 | 23 | 60 | 23 | 60 | 23 |
| Gas | Kr | Kr | Kr | Kr | $N_2$ | Kr | $N_2$ | Kr |
| Single Point BET Surface Area ($m^2/g$) | 0.0472 | 0.0405 | 0.0716 | 0.0608 | 0.4340 | 0.3700 | 0.4404 | 0.5557 |
| Multi Point BET Surface Area ($m^2/g$) | 0.0886 | 0.0667 | 0.1244 | 0.1039 | 0.6198 | 0.5065 | 0.7028 | 0.7751 |
| +/- | 0.0009 | 0.0003 | 0.0009 | 0.0005 | 0.0860 | 0.0051 | 0.1243 | 0.0048 |

For reference, Table 6 shows the specific surface area results for the reference CompB particles used in these tests (Phelan et al., 2003).

Table 6. Specific Surface Area of Composition B Size Separates

| Size Fraction | BET Single Point ($m^2/g$) | BET Multi Point ($m^2/g$) | Spherical Calculated ($m^2/g$) |
|---|---|---|---|
| 90 to 106 μm | 0.3283 | 0.4961 (± 0.0052) | 0.0371 |
| 500 to 600 μm | 0.1566 | 0.2071 (± 0.0013) | 0.0066 |
| 1000 to 1180 μm | 0.1750 | 0.2293 (± 0.0012) | 0.0033 |

Of the low order detonation debris provided, the materials in Bags #5 through #8 were most similar to the particle sizes of CompB used in the mass transfer tests. The multi-point BET surface areas of Bags #5 and #7 were significantly greater (~3X) than the 500-600 μm and 1000-1180 μm CompB particles. The multi-point BET surface area from Bags #6 and #8 were more similar (~ same for Bag #6 and ~1.5X for Bag #8) to the 90-106μm CompB particles. Therefore, material from Bag #6 and #8 were selected for use in mass transfer tests.

The low order detonation debris from Bag 6 and Bag 8 were analyzed quantitatively to determine the RDX and TNT content. Approximately 0.1 g of material was placed into 4 mL of acetonitrile and sonicated at 10°C for 1 hour. An aliquot was removed, filtered through a 0.45μm nylon syringe filter and placed into an autosampler vial. The RDX and TNT content was quantified using HP6890 Gas Chromatograph using the conditions described in Phelan et al., 2003. Table 7 shows the ratio of RDX, TNT and CompB (sum of RDX and TNT) for Bag 6 and 8. Comparison of Bag #6 to Bag #8 shows the same proportion of RDX to TNT, although slightly enriched in RDX (depleted in TNT) when compared to Comp B source material (60% RDX, 40% TNT).

Table 7. RDX, TNT and Comp B Content of Bag 6 and Bag 8 Low Order Detonation Debris

| Material | RDX (%, m/m) | TNT (%, m/m) | Comp B (%, m/m) |
|---|---|---|---|
| Bag #6 | 73 | 27 | 54 |
| Bag #8 | 74 | 26 | 26 |

3.4 Test Conditions

The test equipment used in the Phase III tests were the same as the saturated flow tests described in Phelan et al., 2003. For the surface deposit evaluation, water was introduced as a fine mist from the top using a Meinhard® Nebulizer (Model # HEN-170-AA), designed to function at 1 L/min argon and approximately 170 psig for inductively coupled plasma chemical analysis systems. The nebulizer can function reliably at liquid flow rates from 10 to 1200 μl/min. The nebulizer was operated at 1.75 mL/hr (~30 μL/min) water flow and 70 mL/min air flow to generate a spray mist that contacted the surface deposits of CompB over the full inner diameter of the column from a distance of 3.4 cm.

# 4.0 Experimental Results

Each set of experiments was performed to evaluate a specific mass transfer process. Nineteen experiments were completed and included: surface deposits versus buried deposits; surface area effects; and actual low order detonation debris. In addition, replicate tests were completed to assess variability of the experimental approach. Tests with the same prefix were replicates and the suffix shows the replicate run number.

The tests ran for different periods of time. In general, the test duration was longer for greater initial mass of test material in order to evaluate the depletion stage until exhaustion. Table 8 shows the duration for each experiment.

Table 8. Experiment Duration (hours)

| MT19-1 | MT19-2 | MT19-3 | MT19-4 | MT20-1 | MT20-2 | MT20-3 | MT21-1 | MT21-2 |
|---|---|---|---|---|---|---|---|---|
| 192 | 153 | 134 | 120 | 202 | 155 | 159 | 155 | 151 |
| **MT22-1** | **MT23-1** | **MT24-1** | **MT25-1** | **MT26-1** | **MT27-1** | **MT28-1** | | |
| 135 | 897 | 203 | 1456 | 273 | 1093 | 539 | | |

## 4.1 Data Analysis Methods

Analysis of the data from the Phase III tests were performed in a similar approach as for Phase I and II. Due to the restricted project budget for the FY03 effort, the results presented in this report only show general trends and qualitative comparisons. The focus of the FY04 effort will be a more detailed analysis of all data in Phases I, II and III; revision of the mass transfer model and development of a 2-d screening model with specified data input requirements. The follow describes data transformations for analysis and plotting.

*$C/C_{max}$.* Often the ratio of concentration values to their maximum temperature value ($C_{max}$) better describes data where small changes in temperature may influence the maximum capacity of the chemical in the water. As each effluent sample was collected, a temperature measurement was recorded using a thermocouple attached to the outside of the column and recorded with a datalogger. With this temperature, $C_{max}$ was calculated for RDX and TNT using empirical data correlations from Phelan et al., 2002.

*Cumulative Discharge.* The cumulative discharge datum is another derived value that describes how much of the initial mass placed into the column has been discharged in the effluent. Concentration values with each aqueous effluent sample mass define a chemical discharge mass. When summed and referenced to the initial mass, the cumulative discharge defines the fraction of chemical mass discharged from the column. With the uniformity of the TNT and RDX in the CompB used, this approach shows well how much of the initial mass discharges out of the column. Unfortunately, amount of TNT and RDX in the low order detonation debris is not as uniform and a single sub-sample (with unknown variance) led to non-real cumulative discharge values (i.e. > 100%). For the low order detonation debris,

the cumulative discharge charts use the total mass of chemical discharged from the column as the fractional basis – not the total mass placed into the column.

*Effluent Discharge Profiles.* The effluent concentration versus time or pore volume plots show several characteristic features that were frequently encountered. A plateau of high effluent $C/C_{max}$ was evident under certain conditions. This has been termed an excess mass capacity stage. At the end of this plateau, the effluent $C/C_{max}$ began a decline that has been termed a mass depletion stage. The nature of the magnitude and duration of the excess mass capacity stage and the rate of decline of the depletion stage were described by a numerical model in Phelan et al., 2003.

## 4.2 Effect of Test Replication

Four replicates of a test that mimicked test MT-10 (Phelan et al., 2003) were completed to evaluate the variability of effluent concentration profiles while keeping test conditions constant. Table 9 shows the test parameters. The flow rate was set at ~ 40% of the saturated hydraulic conductivity, which was the intermediate flow rate from Phase II tests.

Table 9. Test Parameters – Effect of Test Replication

| | |
|---|---|
| MT Test No. | 19-1, 2, 3, 4 |
| Source Material | 100 μm Comp B |
| Constant flow rate (ml/hr) | 1.75 |
| Bed depth (cm) | 0.59 - 0.60 |
| Initial RDX (mg) | 3.56 - 3.73 |
| Initial TNT (mg) | 2.64 - 2.76 |
| Bed Location | Center |
| Flow | Up |

Figure 1 shows the effect of test replication for the RDX $C/C_{max}$ effluent concentration and Figure 2 shows the same for TNT. An average for each is shown in black. For RDX, the plateau period ranged from 50 to 80% $C/C_{max}$ and ended at about 20 hours. The decline phases were very similar for all four tests. For TNT, the plateau phase peaked at 9 to 15% and started earlier than RDX at about 12 hours. The TNT declining phase was similar for three of the tests – only MT19-3 had a slightly reduced rate of decline.

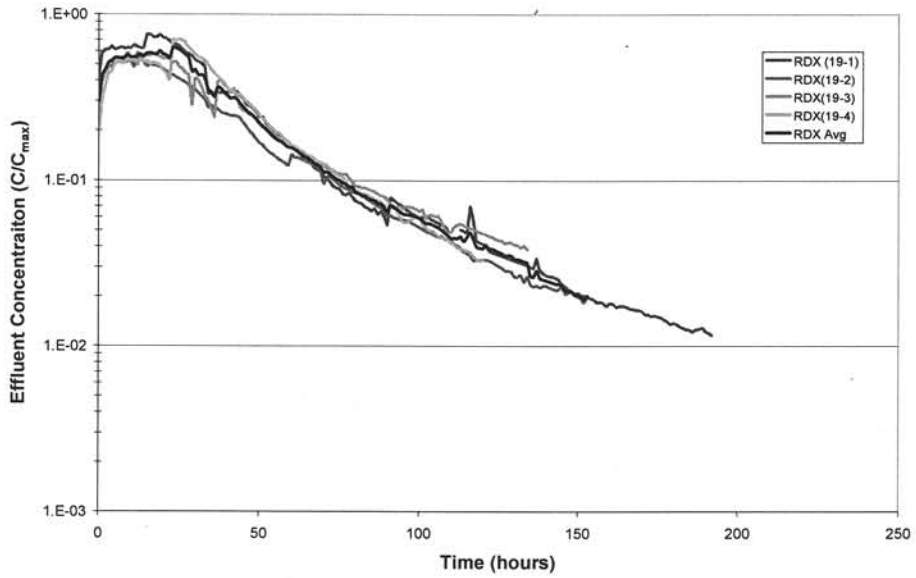


Figure 1. Effect of Test Replication – Effluent Concentration ($C/C_{max}$), RDX

The cumulative discharge profiles for RDX and TNT (Figures 3 and 4, respectively) were very similar for three out of the four tests – only MT19-2 showed a much reduced discharge rate and cumulative discharge. The RDX reached a cumulative discharge of 70 to 80%, whereas the TNT was much lower, at about 30%.

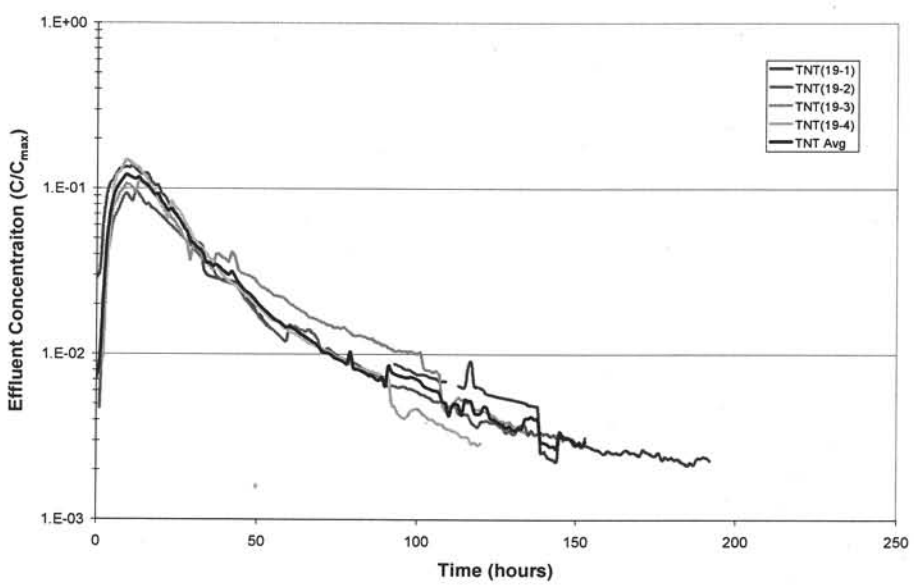


Figure 2. Effect of Test Replication – Effluent Concentration ($C/C_{max}$), TNT

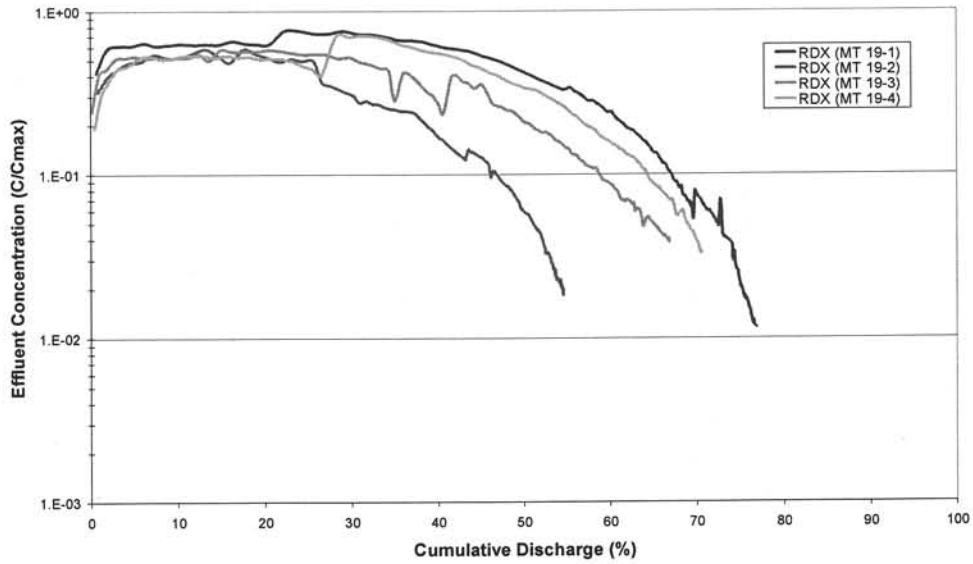


Figure 3. Effect of Test Replication – Cumulative Discharge, RDX

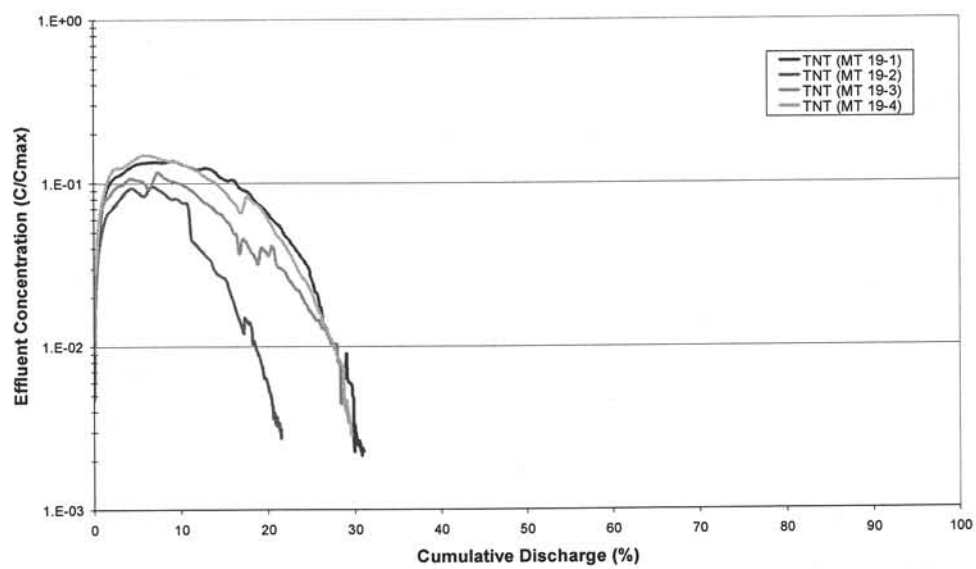


Figure 4. Effect of Test Replication – Cumulative Discharge, TNT

## 4.3 Effect of Bed Location

All previous tests used deposits that were buried beneath ~6 cm of glass bead mix. In this group of tests, a deposit of glass bead/CompB mixture was placed at the top and the water was sprayed onto the material for even distribution across the column surface area (MT 20-1, 2 and 3). A surface deposit up flow test was also completed for comparison to previous up flow tests (MT-21). Table 10 shows the test parameters for each.

Table 10. Test Parameters – Effect of Bed Location

| MT Test No. | 19-1, 2, 3, 4 | 20-1, 2, 3 | 21-1, 2 |
|---|---|---|---|
| Constant flow rate (ml/hr) | 1.75 | 1.75 | 1.75 |
| Bed depth (cm) | 0.59 - 0.60 | 0.52 – 0.59 | 0.58 – 0.59 |
| Initial RDX (mg) | 3.56 - 3.73 | 3.62 - 3.73 | 3.67 – 3.89 |
| Initial TNT (mg) | 2.64 - 2.76 | 2.68 - 2.76 | 2.72 – 2.88 |
| Bed Location | Center | Top | Top |
| Flow | Up | Down (nebulizer) | Up |

Figure 5 shows the effect of bed location (surface or buried) for RDX with a compilation of all comparison tests. All MT19 tests are in red, all MT20 tests are in magenta, and all MT21 tests are in green. The plateau period for all tests appears very similar with values ranging from 50 to 80% and lasting for 15 to 20 hours. During the declining phase, the surface deposit with nebulizer spray showed slightly extended period with higher concentrations and then a faster drop off. The up flow surface deposit of test MT21 did not show this effect and was more similar to the up flow buried deposit of test MT19. The same pattern was observed for TNT as shown in Figure 6.

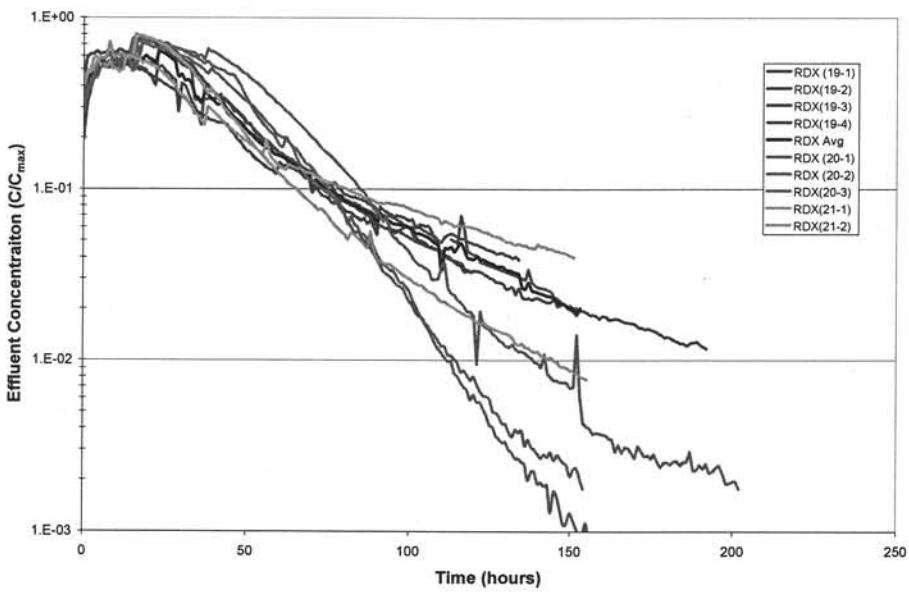


Figure 5. Effect of Bed Location – Effluent Concentration ($C/C_{max}$), RDX

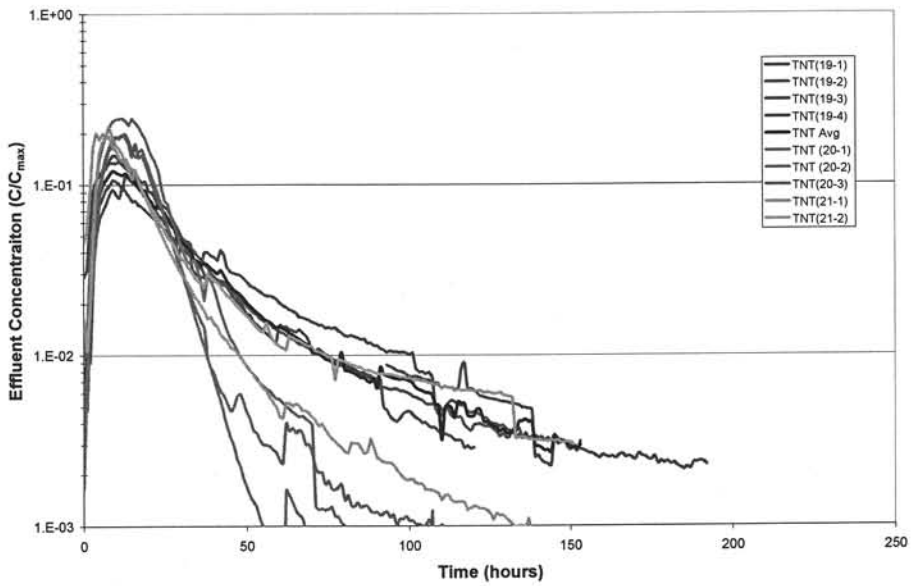


Figure 6. Effect of Bed Location – Effluent Concentration ($C/C_{max}$), TNT

The cumulative discharge profiles for RDX (Figure 7) and TNT (Figure 8) show the sustained higher effluent concentrations of the surface deposit tests with down spray (MT20) and a more rapid drop off. The cumulative discharge for the up flow tests also seem to reach the same or slightly lower magnitude at a slower rate.

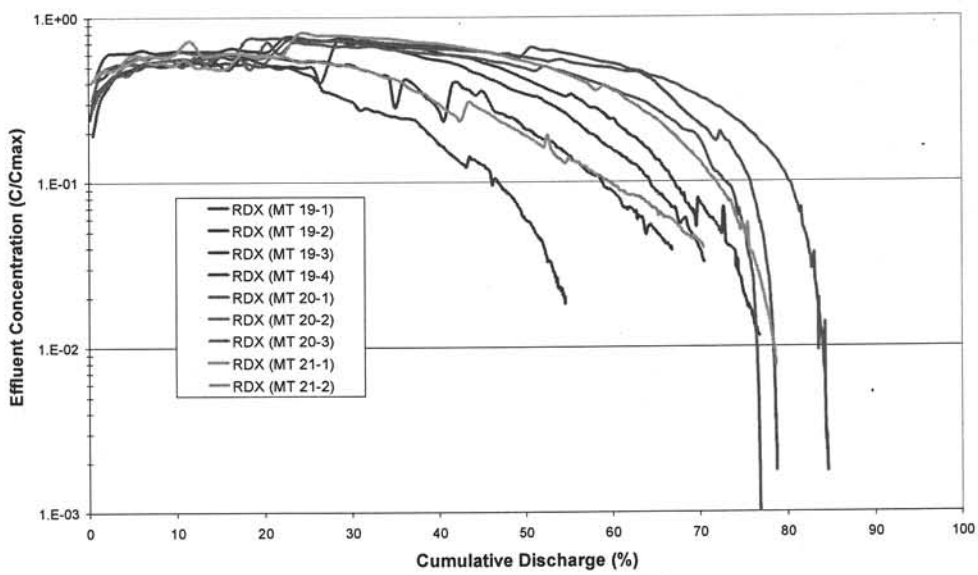


Figure 7. Effect of Bed Location – Cumulative Discharge, RDX

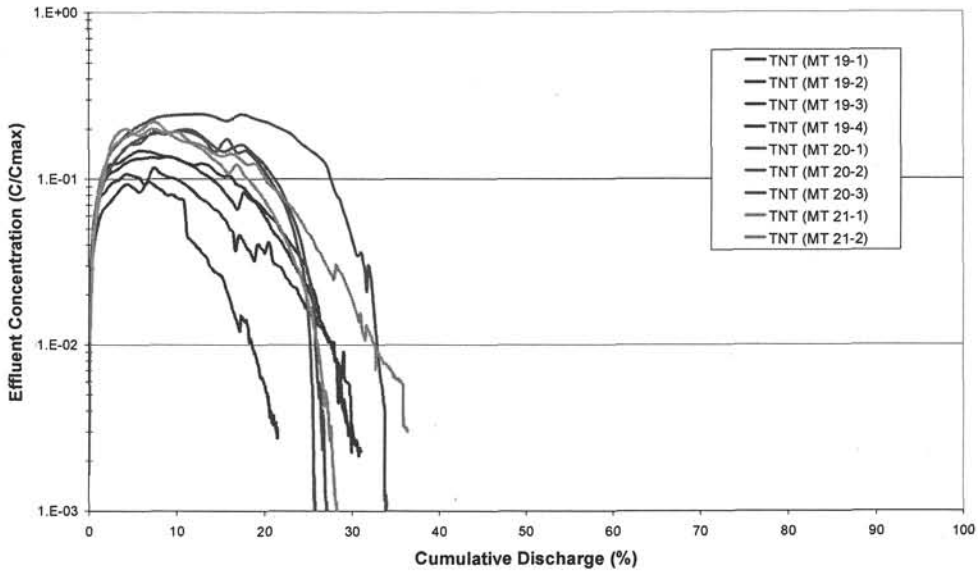


Figure 8. Effect of Bed Location – Cumulative Discharge, TNT

## 4.4 Effect of Energetic Material Particle Size

In the Phase II tests, the effect of energetic material particle size was first explored. Those tests showed that for the same initial mass, the effluent discharge concentrations of both RDX and TNT were significantly decreased for a 10X increase in particle size (100 μm to 1000μm diameters). For the Phase III tests, the intermediate size 500 μm particles were evaluated. Table 11 shows four tests were performed varying bed depth and initial mass.

Table 11. Test Parameters – Effect of Energetic Material Particle Size

| MT Test | 22-1 | 23-1 | 24-1 | 25-1 |
|---|---|---|---|---|
| Constant flow rate (ml/hr) | 1.75 | 1.75 | 1.75 | 1.75 |
| Bed depth (cm) | 0.48 | 0.58 | 3.44 | 3.47 |
| EM Particle Size | 500 μm | 500 μm | 500 μm | 500 μm |
| Initial RDX mgs | 3.89 | 37.8 | 3.73 | 37.85 |
| Initial TNT mgs | 2.88 | 28.0 | 2.76 | 28.04 |
| Bed Location | Center | Center | Center | Center |
| Flow | Up | Up | Up | Up |

Figure 9 shows the effect of energetic material particle size for the 500 μm particles. For the same initial mass as in the other Phase III tests (MT 19, 20 and 21), the RDX effluent concentration with the 500 μm particle sizes showed significantly reduced effluent concentrations. For the low initial mass test cases (MT22-1 and MT24-1), there was little if any plateau phase and the effluent concentrations were much lower than for the higher mass cases (MT23-1 and MT25-1).

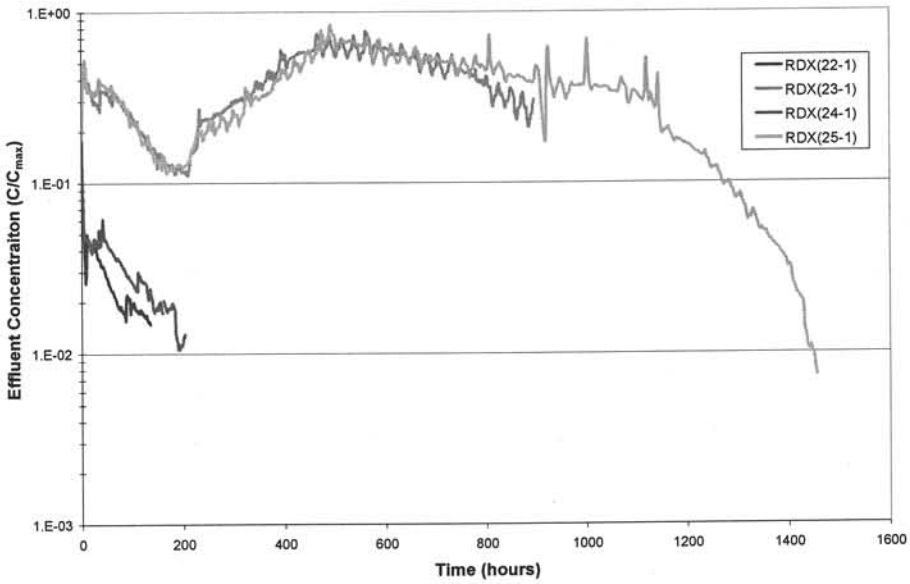


Figure 9. Effect of Energetic Material Particle Size - Effluent Concentration ($C/C_{max}$), RDX

The TNT effluent discharge profiles (Figure 10) showed the same behavior as the RDX (Figure 9). For both RDX and TNT, an unusual profile occurred where after ~200 hours in a decline phase, the concentrations increased back up to or above the initial plateau phase. This behavior was repeated in both the thin bed and thick bed depth tests and also occurred with the TNT effluent discharge profiles. No explanation can be given at this time for this behavior and more work is likely needed to better understand this phenomenon.

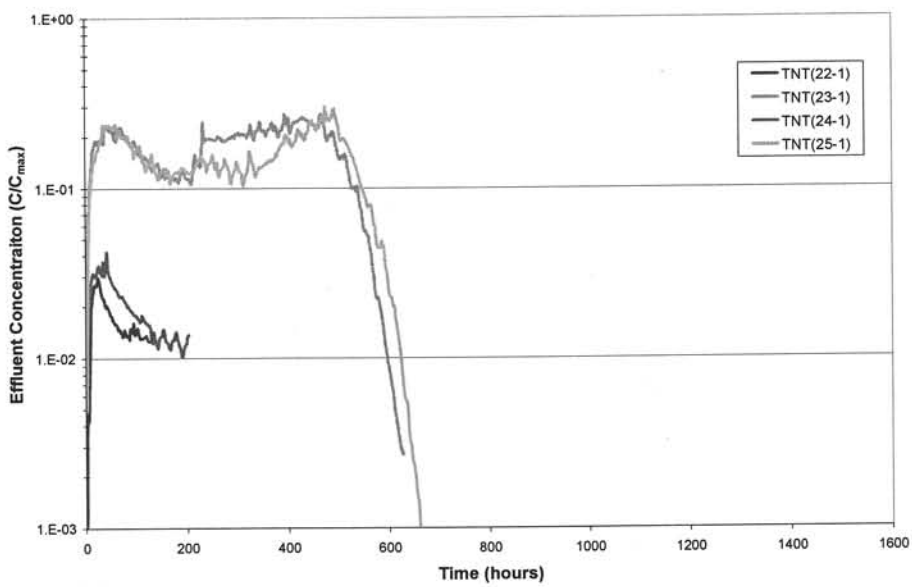


Figure 10. Effect of Energetic Material Particle Size - Effluent Concentration ($C/C_{max}$), TNT

The cumulative discharge profiles for the low initial mass 500 μm CompB particles showed a very low cumulative discharge (Figure 11). However, a significant mass still remained in the column as determined by the mass balance (see Section 4.6, Tables 14 and 15). For the larger initial mass tests (MT23-1 and MT25-1), most of the mass was discharged via the effluent. To evaluate the discharge profile until exhaustion, test MT25-1 was run for 1450 hours (60 days). As shown in Figure 11, the effluent concentration remained high until the 90% of the initial mass had been discharged. The TNT behavior was similar (Figure 12); however the maximum cumulative discharge was less, at about 70 to 80%.

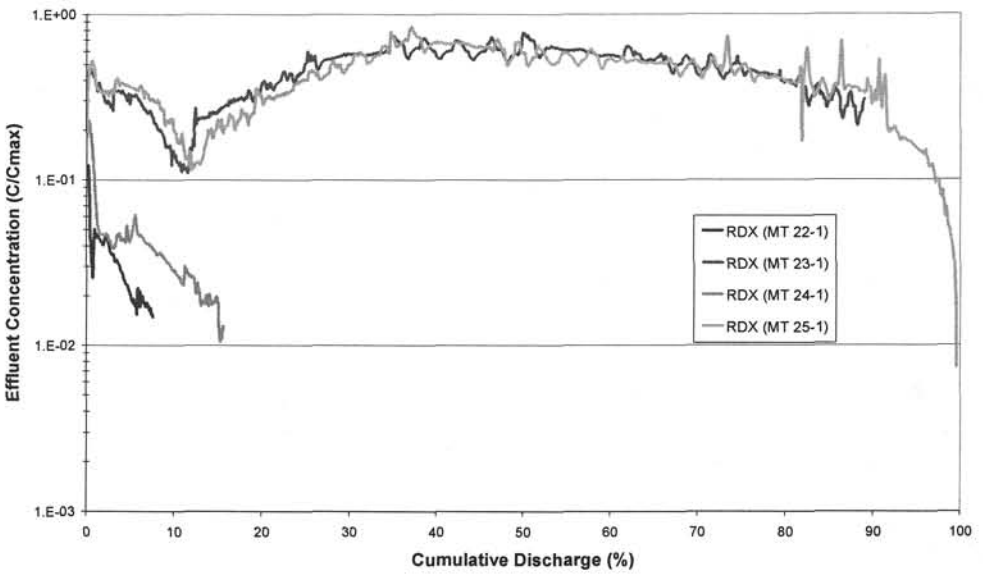


Figure 11. Effect of Energetic Material Particle Size – Cumulative Discharge, RDX

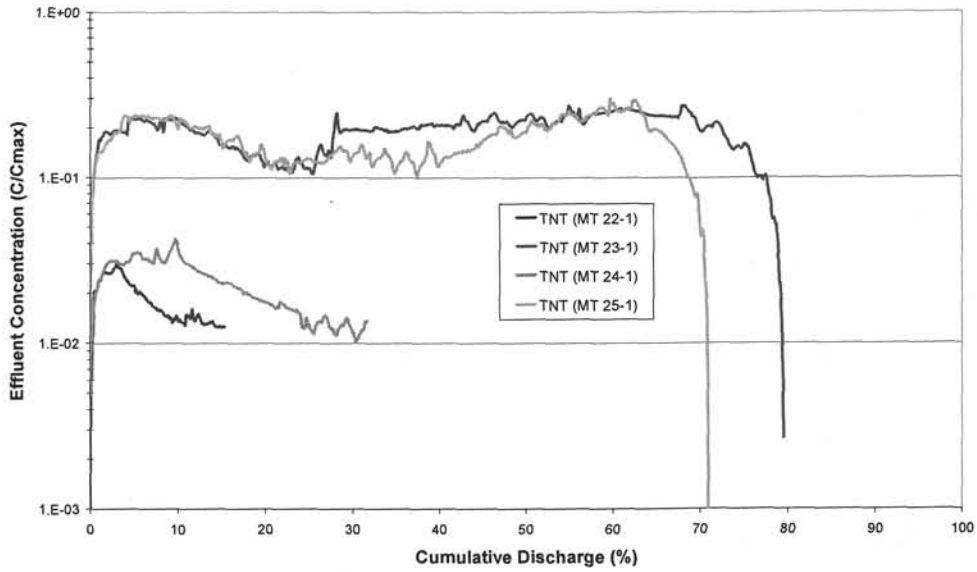


Figure 12. Effect of Energetic Material Particle Size – Cumulative Discharge, TNT

## 4.5 Effect of Low Order Detonation Debris

The low order detonation debris selected for these tests contained about 54% (Bag #6) and 26% (Bag #8) energetic material (Table 7). The balance of the material is assumed to be soil. The initial mass selected to place in the columns was an amount to mimic the previous tests in Phase III (~ 3.7 mg RDX and 2.7 mg TNT). Table 12 shows the details of these tests.

Table 12. Test Parameters – Effect of Energetic Material Particle Size

| MT Test | 26-1 | 27-1 | 28-1 |
|---|---|---|---|
| Constant flow rate (ml/hr) | 1.75 | 1.75 | 1.75 |
| Bed depth (cm) | 0.53 | 0.57 | 0.55 |
| Detonation Debris | Bag #6 | Bag #6 | Bag #8 |
| Initial RDX (mg) | 5.46 | 55.25 | 5.33 |
| Initial TNT (mg) | 2.02 | 20.49 | 1.83 |
| Bed Location | Center | Center | Center |
| Flow | Up | Up | Up |

For the low initial mass tests (MT26-1 and MT28-1), the effluent discharge profiles showed low $C/C_{max}$ values, no discernable initial plateau and a declining phase similar to the CompB particles (Figure 13 and 14). For the high initial mass test (MT28-1) with 10X the mass, the initial plateau was evident and the effluent concentrations remained high for the duration of the test.

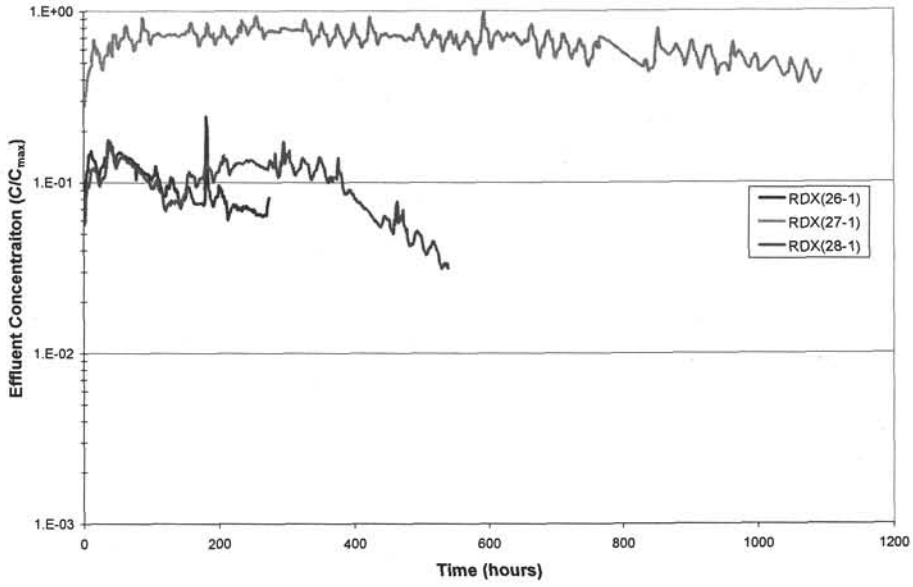


Figure 13. Effect of Low Order Detonation Debris – Effluent Concentration ($C/C_{max}$), RDX

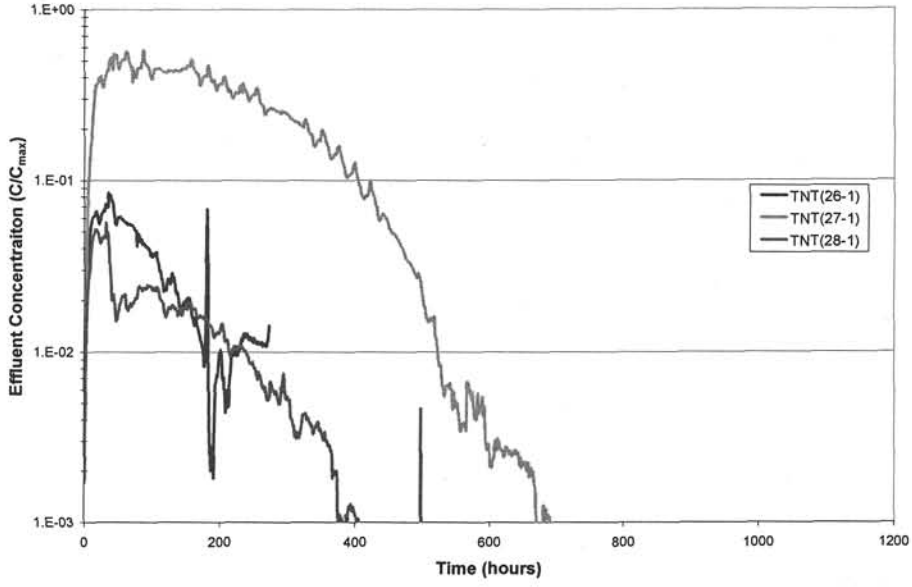


Figure 14. Effect of Low Order Detonation Debris – Effluent Concentration ($C/C_{max}$), TNT

After completion of tests with the low order detonation debris, we noted that sum of the cumulative mass discharged and mass extracted upon test completion was slightly or significantly different than the amount based on the single subsample of the bag. The single subsample mass was derived from the fraction of CompB (RDX + TNT) and ratio of RDX and TNT in the detonation debris (Table 7). Table 13 shows this comparison for all three tests. Tests MT26-1 and MT28-1 seem reasonable given the limited basis of a single subsample. However, test MT27-1 significantly deviated from the single subsample basis of Bag #6. The most likely explanation is that the ratio of CompB to soil was greater in the sample used in test MT27-1 than in the single subsample. Due to the limited mass of

low order detonation debris, we hesitated to sample and analyze more material to better estimate the heterogeneity. Therefore, for the cumulative discharge charts, the basis mass is the sum of the effluent and extraction masses rather than the subsample proportions used in all other tests in Phase III.

Table 13. Heterogeneity of Low Order Detonation Debris

| | | Bag #6 | | Bag #8 |
|---|---|---|---|---|
| | Component | MT26-1 | MT27-1 | MT28-1 |
| Subsample | RDX (mg) | 5.46 | 55.25 | 5.33 |
| | TNT (mg) | 2.02 | 20.49 | 1.83 |
| Effluent | RDX (mg) | 2.29 | 57.07 | 4.87 |
| | TNT (mg) | 1.63 | 29.06 | 1.28 |
| Extraction | RDX (mg) | 3.81 | 40.12 | 0.38 |
| | TNT (mg) | 0.52 | 0.01 | 0.01 |
| Test Sum | RDX (mg) | 6.10 | 97.19 | 5.25 |
| | TNT (mg) | 2.15 | 29.06 | 1.30 |
| % Diff | RDX (%) | 112 | 176 | 99 |
| | TNT (%) | 106 | 142 | 71 |

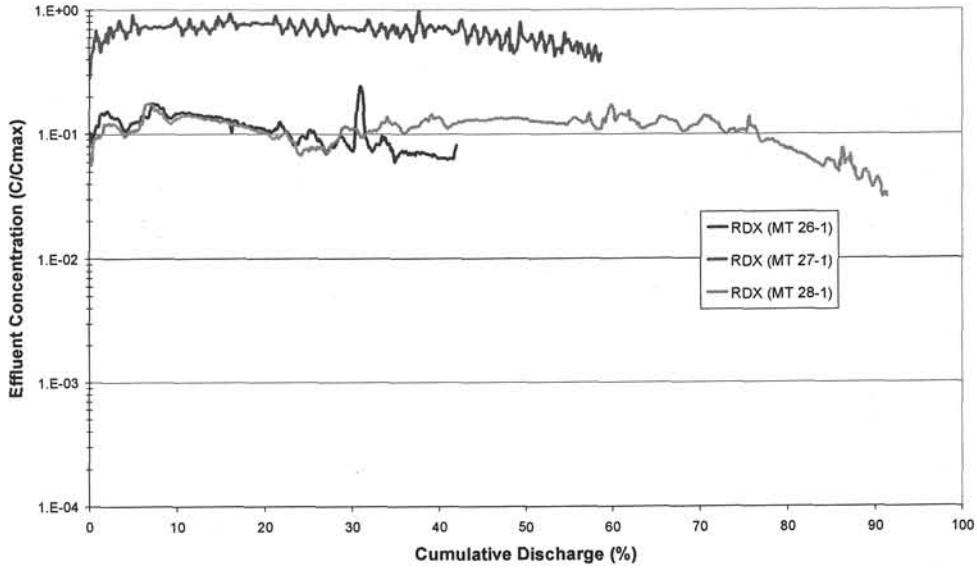


Figure 15. Effect of Low Order Detonation Debris – Cumulative Discharge, RDX

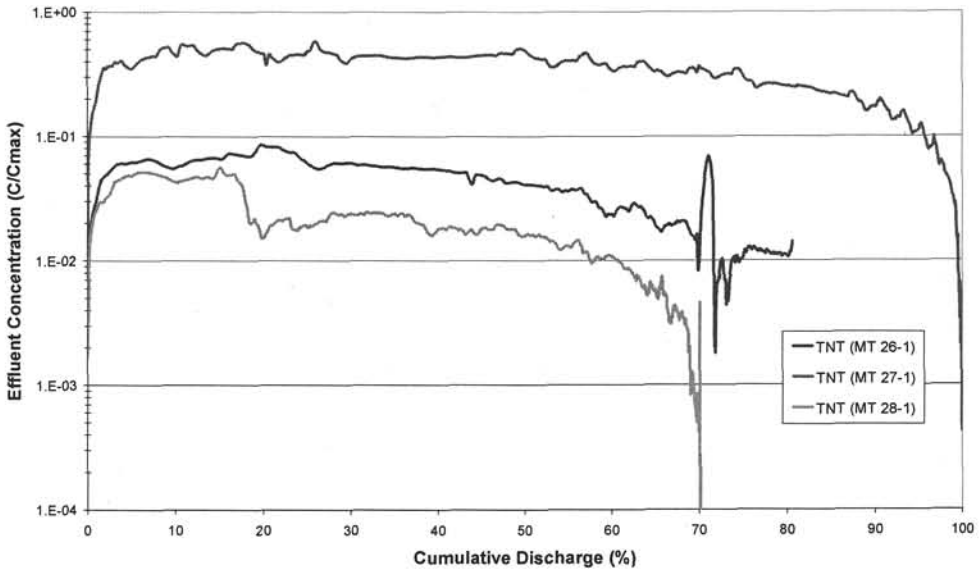


Figure 16. Effect of Low Order Detonation Debris – Cumulative Discharge, TNT

## 4.6 Mass Balance

At the end of each test, the amount of RDX and TNT remaining in the column was quantified. The contents of the column were removed and placed into a large sample container. A 1:1 sample mass to acetonitrile volume mixture was sonicated overnight at 10°C. A 5 mL sample of the extract was collected, filtered through a 0.45 μm syringe filter, and quantified on the GC/ECD. The total mass of RDX and TNT remaining in the column at the end of the test was determined and shown as the extraction row in Tables 13 and 14. The effluent row is the sum total mass of RDX or TNT in the effluent as measured in each effluent sample.

The results in Tables 14 and 15 show that mass balance results were generally very good. RDX values ranged from 68 to 100% and TNT values ranged slightly lower, from 27% to 80%. The tests with the 100 μm particles were generally lower than the 500 μm particles. Degradation is the most likely explanation for the low mass balance of TNT.

Table 14. Mass Balance of RDX

| | **MT19-1** | **MT19-2** | **MT19-3** | **MT19-4** | **MT20-1** | **MT20-2** | **MT20-3** | **MT21-1** | **MT21-2** |
|---|---|---|---|---|---|---|---|---|---|
| Effluent | 76.85 | 54.58 | 66.86 | 70.55 | 84.59 | 78.74 | 76.86 | 78.68 | 70.45 |
| Extraction | 5.94 | 13.47 | 9.63 | 7.51 | 0.32 | 1.14 | 0.71 | 3.53 | 3.80 |
| Total | 82.79 | 68.05 | 76.49 | 78.06 | 84.91 | 79.87 | 77.57 | 82.20 | 74.25 |
| | **MT22-1** | **MT23-1** | **MT24-1** | **MT25-1** | **MT26-1** | **MT27-1** | **MT28-1** | | |
| Effluent | 7.56 | 88.98 | 15.63 | 99.59 | 37.58 | 58.72 | 92.74 | | |
| Extraction | 76.83 | 9.36 | 76.68 | 0.18 | 62.42 | 41.28 | 7.26 | | |
| Total | 84.38 | 98.34 | 92.30 | 99.77 | 100.00 | 100.00 | 100.00 | | |

Table 15. Mass Balance of TNT

| | **MT19-1** | **MT19-2** | **MT19-3** | **MT19-4** | **MT20-1** | **MT20-2** | **MT20-3** | **MT21-1** | **MT21-2** |
|---|---|---|---|---|---|---|---|---|---|
| Effluent | 31.04 | 21.46 | 29.29 | 29.61 | 34.12 | 27.30 | 25.87 | 28.33 | 36.32 |
| Extraction | 2.30 | 7.02 | 2.25 | 3.86 | 0.36 | 1.09 | 0.42 | 0.94 | 0.92 |
| Total | 33.35 | 28.48 | 31.54 | 33.47 | 34.48 | 28.39 | 26.29 | 29.27 | 37.24 |
| | **MT22-1** | **MT23-1** | **MT24-1** | **MT25-1** | **MT26-1** | **MT27-1** | **MT28-1** | | |
| Effluent | 15.32 | 79.53 | 31.62 | 70.97 | 75.91 | 99.97 | 99.05 | | |
| Extraction | 56.77 | 0.00 | 46.16 | 0.00 | 24.09 | 0.03 | 0.95 | | |
| Total | 72.09 | 79.53 | 77.77 | 70.97 | 100.00 | 100.00 | 100.00 | | |

# 5.0 Science and Technology Roadmap

## 5.1 Background

The environmental impacts of military range detonation debris is an emerging issue that military environmental planners are working to understand. The technical information and decisions regarding this issue are complex, requiring a comprehensive understanding of the numerous technology options, development paths, and end-products necessary to reach specific goals. One method to develop this understanding is through a science and technology roadmap – a popular metaphor that describes a process for planning complex systems. The process of roadmapping identifies, evaluates and selects strategic alternatives that can be used to achieve a desired S&T objective (Kostoff and Schaller, 2001; Probert et al., 2003).

There are several types of roadmaps emerging in business planning practices. For the military range sustainability issue, a product-technology roadmap appears the most appropriate approach to represent the structural and temporal relations among S&T elements that evolve into practical product applications (Kostoff and Schaller, 2001; Probert et al., 2003). Section 5.2 describes a preliminary S&T roadmap of the environmental impacts of military range detonation debris. For full acceptance of this roadmap, the concepts need to be reviewed and revised (as needed) by the key players and decision makers in this field.

## 5.2 Environmental Impacts of Military Range Detonation Debris – A Science and Technology Roadmap

The product-technology roadmap consists of nodes and links with both spatial and temporal relations. In Figure 17, there are four main threads depicting specific markets, individual products, the technology base that feeds these products, and R&D projects necessary to improve the technology base for this particular product and market application.

The principal markets for military range sustainability are Installation Environmental Management and Range Operations Management. The Installation Environmental Market is targeted with a Screening Toolset to evaluate the interactions and attributes of military range operations, detonation residues, mass transfer and weather driven flow/transport models. This Screening Toolset will allow environmental specialists to identify key parameters that may cause a specific range site to exceed environmental criteria (e.g., groundwater maximum contaminant levels or drinking water standards).

Figure 18 shows a conceptual depiction of the Screening Toolset model. The key parameters include: surface weather conditions, nature of the detonation debris, mass transfer of solid phase energetics to soil pore water, distance to groundwater, and groundwater velocity. Installation

environmental specialists will be able to assess vulnerabilities at a specific range and determine if improved data or processes are needed to better discriminate the impacts.

If the Installation Environmental Management market finds value in the screening toolset, this roadmap envisions development of an Analysis Toolset that would serve Range Operations Management. If specific military range locations appear vulnerable to environmental impact with the Screening Tool, then major decisions may be needed regarding changes in range operations. To support these major decisions, the Analysis Toolset will require Integrated Validation with Meso-Scale Tests to mimic the threats to the environment. Then application modules need to be developed that provide improved data input and model output/post-processing algorithms. Range Operations Management can then use the Analysis Toolset with confidence to make changes to training operations or develop mitigation methods that can be modeled before implementation.

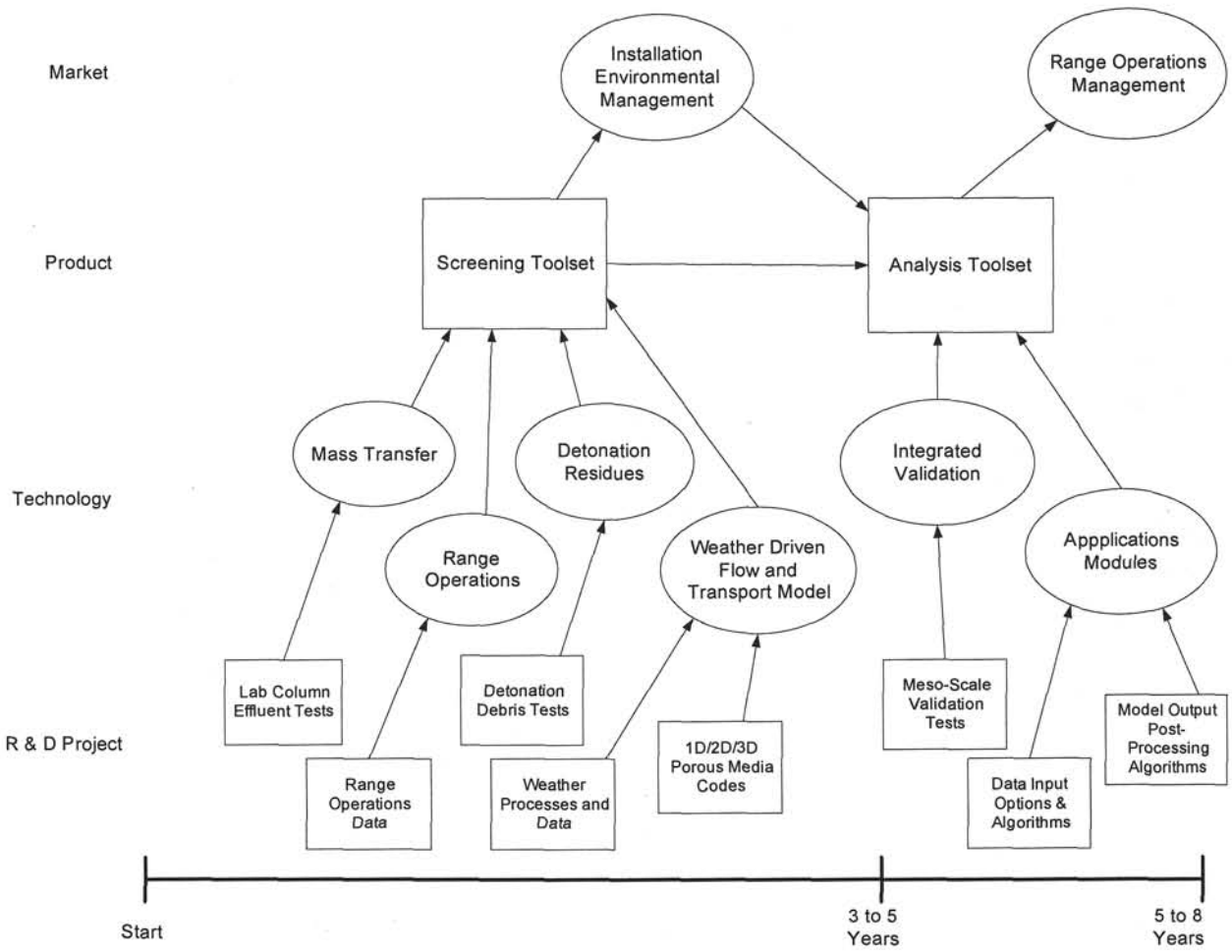


Figure 17. Science and Technology Roadmap

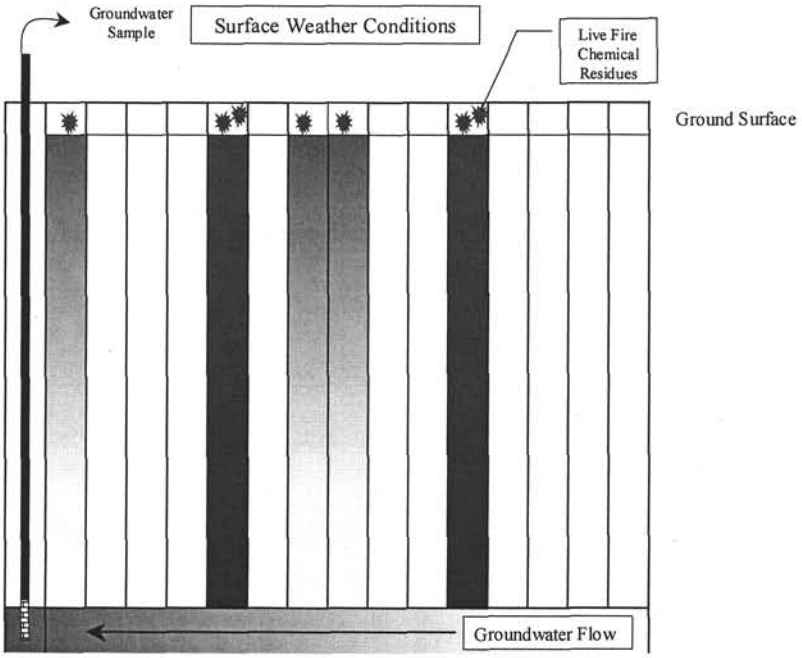


Figure 18. Two-dimensional conceptual embodiment of the Screening Toolset model

# 6.0 Summary

## 6.1 Phase III Results

This effort continued previous experimental measurements of solid phase energetic material mass transfer processes using laboratory porous media columns. The key factors of surface deposits versus buried deposits, energetic material particle size and low order detonation debris were explored during this years' effort. In addition, test replicates were completed to assess experimental variability that will help better understand true differences due to changes in experimental conditions.

As in Phases I and II, under most circumstances the effluent concentrations were very high, near the maximum controlled by temperature dependent water solubility. Differences in $C/C_{max}$ peak levels and duration during the excess mass capacity stage and the slope of the depletion phase continue to provide important features that need to be incorporated in the mass transfer model.

The effect of test replication test series showed that effluent concentration profiles of replicate tests were fairly uniform and that RDX profiles appeared more uniform than the TNT profiles. Plots of the cumulative discharge profiles showed more discrimination of the net mass discharge and also revealed that one test (MT19-2) was significantly lower than the rest. This will provide the reader with a better understanding of normal test variation and provide a guide for comparison with changes in experimental conditions.

The effect of bed location showed that in general, surface deposits showed slightly sustained greater effluent concentrations for both RDX and TNT. However, as is shown in the cumulative discharge profiles, as the mass became depleted the effluent concentrations declined more rapidly. The cumulative discharge of RDX showed high values of 70 to 85%; however, TNT values were significantly lower, at 25 to 40%. The remaining mass in the column after test termination showed very small amounts. Thus, degradation losses must account for the difference.

The initial mass and total surface area of energetic material particles plays a key role in the effluent concentrations of RDX and TNT. With a similar mass, but a 5X increase in particle diameter, the effluent concentrations never reach peak concentrations as with the smaller particles. Increasing the mass (and the total surface area) with the larger particles creates an effluent profile similar to that with the smaller particles. Investigating how the surface area affects the mass transfer function will be a key effort in next years technical workscope. A new feature appeared during tests MT23-1 and MT25-1 (high mass for both, with a thin bed in one and a thick bed in the other) where, after 200 hours and well into a depletion phase, the effluent concentrations increased back up to and slightly above the initial peak concentrations. This bi-modal response needs more evaluation and additional tests to understand this new phenomenology.

The low order detonation debris used in the Phase III tests contained both soil and energetic material. With similar initial mass buried deposits, the low order detonation debris showed significantly lower peak effluent concentrations and a slower decline in the mass depletion stages. These effects may be due to partitioning onto the soil solid phase or may be an effect of the detonation on the energetic material. Taylor et al., 2003 describes visual interpretations that some of the low order detonation debris may have been melted and resolidified upon cooling. Bag #8 (>500 μm) showed a similar bimodal effluent concentration profile as the 500 μm particles in MT23-1 and MT25-1. With a 10X increase in initial mass, the effluent concentrations of Bag #6 remained very high, consistent with the CompB high initial mass test in Phase II (MT17 and MT18).

### 6.2 Path Forward – Near Term

The tests completed in Phase III have answered several key questions, but of course have raised several more. However, sufficient data are now available to refine the energetic material mass transfer model for use in screening assessments. The technology roadmap shows how specific R&D efforts are linked to key technologies, which can be incorporated into products that serve key customers. Most of the R&D efforts have sufficient data that can now be compiled for use in a screening model toolset. Development and application of the screening model toolset will provide new insight into the processes and parameters that have a significant influence on detonation debris impact to groundwater quality. The FY04 and FY05 task scope is directed to fill these near term goals.

### 6.3 Path Forward – Long Term

If applications of the screening model toolset show important range operations vulnerabilities, then the screening model will need validation with meso-scale tests. These meso-scale tests need to demonstrate at scale the integrated processes that have significant influence on mass transfer, solute transport and environmental dispersion. The screening model will need to be improved to provide data input and pre-processing algorithms and model output post-processing methods to streamline applications.

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