Mobility of Particulate and Dissolved Munitions Constituents in the Vadose Zone at Operational Ranges

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The purpose of this project was to determine the extent to which munitions constituents could migrate in the subsurface due to colloid migration and/or via macropore flow. Both of these processes have the capability to bypass large proportions of subsurface media, resulting in faster or deeper migration that might be expected. The finding of a large plume of RDX at the Massachusetts Military Reservation is surprising because MC are sparsely distributed at low concentrations on surface soils at operational ranges, and because the vadose zone at MMR is quite deep. Consequently there is a need to explain the findings at MMR and to determine if groundwater contamination with MC is important at other operational ranges.

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MAY 2011 IPR COMMENTS

We have some concerns that the experimental plan as designed will not truly test the project hypotheses. Please provide a white paper (***due 5 August 2011***) that summarizes the results to date and provides a detailed experimental plan for the remainder of the study.

EXECUTIVE SUMMARY

Rationale and Goals

The purpose of this project is to determine the extent to which munitions constituents (MC) could migrate in the subsurface due to colloid migration and/or via macropore flow. Both of these processes have the capability to bypass large proportions of subsurface media, resulting in faster or deeper migration that might be expected. The finding of a large plume of RDX at the Massachusetts Military Reservation (MMR) is surprising because MC are sparsely distributed at low concentrations on surface soils at operational ranges, and because the vadose zone at MMR is quite deep. Consequently there is a need to explain the findings at MMR and to determine if groundwater contamination with MC is important at other operational ranges.

Macropores are a common feature of subsurface sediments and they are known to contribute to accelerated migration because they are capable of rapidly conducting large volumes of water to depth. Colloids are particles which are also known to contribute to accelerated migration because they do not effectively diffuse into the media which can normally retard contaminant migration. Colloids of importance in the subsurface consist of either microbes or minerals or contaminants that have become sorbed to minerals or microbes. The detonation of munitions at operational ranges could result in the production of MC colloids due to high- and/or low-order detonations, but there is little data on MC particles < 250 micrometers and previous conceptual models have only considered dissolution and migration of dissolved MC. If MC have the propensity to migrate as colloids then they may represent a unique class of colloids because they probably do not form strong attachment with mineral phases and because they dissolve during migration. Thus, modeling strategies and parameters applicable to MC colloids are potentially different than those used for other colloids (e.g., microspheres, microbes, viruses, and radionuclides strongly sorbed to soil organic matter or mineral particles).

Our goals are to investigate the transport of particulate and dissolved MC in intact samples of multiple soil types from operational ranges. MC particles distributed heterogeneously at operational range sites from low-order denotations are suspected to be the source of contamination to underlying aquifers. We will investigate the physical and chemical environments of these particles and determine how particles are dissolved and mobilized through natural soil samples, containing physical hydrological features such as macropores and a variety of reactive organic and mineral surfaces. We will apply this information to predict the transport of MC in various operational ranges to determine the risk of underlying aquifers to contaminated flux from the vadose zone.

Work Completed to Date

Our team collected soil core samples from three DoD facilities, two of which have groundwater contamination with MC – MMR and Joint Base Lewis-McChord (WA) – in addition to Aberdeen Proving Ground (MD). Two sizes of large columns (9 x 14 cm, 13 x 24 cm) of intact vadose zone material (B or C horizons) and bulk samples were collected from each of the three sites, in addition to bulk samples from overlying and underlying soil horizons. The columns are “intact,” meaning that they retain many macroporous properties that could lead to accelerated migration appropriate hydraulic conditions. The sediments have been characterized with respect to texture, carbon content (organic carbon (OC) and inorganic carbon (IC)), oxides, and pH, while clay mineralogy and cation/anion exchange capacity are in progress. We are willing to consider additional sites for collection, if desired.

Because the dissolved and particulate MC transport is fully coupled, we need to quantify the sorption and dissolved MC transport in order for us to quantitatively separate the dissolved MC transport from particle transport. Our team has conducted a variety of batch isotherm experiments to determine the role of reactive soil components, including OC and soil minerals (clays, iron oxides) in soils on the sorption of *dissolved* MC compounds. Initial results suggest that our range soil samples exhibited two major behaviors with respect to sorption of dissolved TNT and RDX that appeared to be dependent on the concentration of soil OC. For TNT, the Freundlich coefficient ranged from 40-70 for soils containing 3-6% OC (two sites at JBLM, and MMR-E horizon), while the Freundlich coefficient ranged from 25-30 for soils containing <1% OC (MMR-B horizon, Aberdeen B horizon). Similar results were observed for RDX, but with linear distribution coefficients having much lower magnitudes than observed for TNT, K_d ~7 and 3.4 for MMR-E and MMR-B, respectively. Subsequent and ongoing experiments are investigating the sensitivity of sorption to the type of organic matter (natural organic matter, humic acid (high aromaticity), and fulvic acid (high aliphaticity) and the type of clay (illite, kaolinite). Smectite may be considered in future experiments based on IPR panel response.

The partitioning of MC components in the supernatant (i.e. dissolved vs colloidal) at sorption equilibrium was quantified by filtering the supernatant with 0.45 µm and 2 nm filters resulting in three different size fractions: particulate (0.45 µm), colloidal (0.45 µm-2 nm), and dissolved (< 2 nm) fractions. Of samples in the colloidal range, it was found that 60-100% of the RDX and TNT was in the dissolved (2 nm) and 40-0%was in the colloidal (2 nm – 0.45 µm) fraction. Also, the affinity of RDX to particulates was substantially lower than that of TNT. Analysis of supernatant for OC and major cations will be used to determine the potential reactive components of soils that are responsible for sorption of NACs (OC, clays, oxides). We will compare our results with those in the literature (Ainsworth et al. 1993), revise sorption models, and use the improved models in flow through experiment studies.

It would be helpful to determine which components of soils associate with MC particles, so that intact columns may be dissected and MC particles isolated. To this end, we used Fourier transformed infrared spectroscopy (FTIR) to detect sorbed TNT and DNT (< 30 mg/L) onto Memphis soil, and particles of DNT in concentrations ranging from 0.01 to 1%. It was found that the 1% particles to soil mixture could be detected, and that the particles were not chemically associated with any reactive component of the soil. It is likely that lower particle detection limits and better spatial resolution may be developed in the future using novel sample preparation and synchrotron FTIR techniques.

Two sets of column experiments were designed to specifically interrogate the extent of particulate, colloidal, and dissolved MC when MC are applied in the dissolved and particulate forms. The role of soil organic matter was also investigated. Two soil horizons at MMR containing different concentrations of textural clays and OC (MMR-E is 3% OC and 1.5% clay; MMR-B is 0.2% OC and 10% clay) were selected to investigate specific sorption and transport mechanisms. The choice of these two soil horizons is based on the fact that MMR-B exhibited significantly less sorption than MMR-E, because the horizons are generally similar excepting clay and organic contents, and because they are each representative of the two populations of range soils with respect to observed magnitude of sorption of MC compounds. Both soils were packed into identical columns of 9 cm length x 2 cm diameter using a field-representative bulk density (~1.7 g/cm^3). The transport of dissolved TNT and RDX, and nonreactive tracer Br$^-$ were investigated simultaneously under saturated conditions at a flow rate of 30 mL/h. Influent concentrations of MC compounds were proportionally similar to that of Composition B and were of environmentally-relevant concentrations (TNT ~7 mg/L and RDX ~ 4.5 mg/L). We found breakthrough of total TNT and RDX was approximately twice as rapid in columns with MMR-B compared to MMR-E, and deterministic modeling to determine quantitative transport rates is in progress . Effluent samples were filtered to determine the extent of migration of particulate, colloidal (>0.45 µM), and dissolved (<2 nm) MC compounds, but results are incomplete at this time. Effluent samples were monitored for pH, major anions and cations, and dissolved OC to determine basic geochemical conditions. In the immediate future, particles of denotated Composition B residues will be applied to another set of duplicate columns of MMR-E and MMR-B horizons following the methods developed in Lavoie et al. (in review). Conditions and analyses will be identical to those described for the dissolved TNT/RDX column experiments. Following completion of the experiments, all columns will be flash-frozen and sectioned as a function of depth to determine the extent of mobility of MC particles and dissolved phase using bulk extractions.

The Lavoie et al. study (in review) involved the transport of analogue MC colloids (2,6-dinitrotoluene (DNT) and anionic microspheres) to columns consisting of clean sands and glass beads of different particle size distributions. The goal of the study was to determine the extent to which particles of MC could migrate through columns of sandy sediments, representing model aquifer materials. Transport experiments were conducted in saturated columns (2 x 20 cm) packed with different grain sizes of clean sand or glass beads (d_{50} of 0.4, 1, and 4 mm). Fine particles (~ 2-36 µm) of DNT were applied to the top 1 cm of sand or beads in the columns, and the columns were subsequently leached with artificial groundwater solutions. DNT migration occurred as both dissolved and colloidal phases. Concentration differences between unfiltered and filtered samples indicated that colloidal DNT accounted for up to 40% of the mass recovered in effluent samples. Proportionally, more colloidal than dissolved DNT was recovered in effluent solutions from columns with larger grain sizes, while total concentrations of DNT in effluent were inversely related to grain size. Of the total DNT mass applied to the upper most layer of the column, ≤ 2% was recovered in the effluent with the bulk remaining in the top 2 cm of the column. Our results suggest there is some potential for subsurface migration of MC particles and that most of the particles will be retained over relatively short transport distances.

We developed dissolution, particle and solute transport models to evaluate the coupled processes, analyze our experimental data, and assess potential contamination at operational ranges. At first, we formulated the dissolution rate as a function of molecular diffusion coefficient, film thickness, and surface area. This dissolution model is able to describe reported breakthrough curves (Webb et al., 2006) under various initial mass loading, MC particle sizes, and flow rates with an identical film thickness value. Our results indicated that breakthrough curves at concentrations less than the compound’s solubility is likely due to a small dissolution rate coupled with a relatively high flow rate.

With confidence in the dissolution model, we incorporated kinetic dissolution for the suspended, strained, and attached particulate residues in the colloid transport model. Filtration theory and empirical equations were used to determine the parameters for residues of different particle sizes. We used a particle transport model to analyze microsphere experiments to test the colloid transport models, and to provide a reference for particulate reside transport. Partitioning the microspheres into a number of groups according to the particle size distribution, PHREEQC (Parkhurst and Appelo, 1999) was used to simulate the simultaneous dissolution and movement of solute and particles of different sizes under flowing conditions. We used the model to analyze the DNT particle transport experiments. Our results suggested that the concentration of particulate residue in the effluent is mostly dependent on the initial mass of the small particles, and the filtration characteristics of the porous media. We attempted to implement a fully coupled model that explicitly accounts for the size decreases, and associated parameter changes as particles move through the porous media, but found it to be challenging. Such model capability would be helpful to examine the accelerated dissolution and particle transport near the contamination front where the dissolution will be fast due to low explosive saturation, and fast dissolution leads to more small particles, which can move fast.

For the application of our results to assess contaminations at field sites, we collected soil characteristics data (soil thickness, bulk density, texture, organic matter content, average water content, depth to seasonal saturation, drainage index, hydrologic index, slope, flooding frequency, and erodability) from USDA Natural Resource Conservation Service (NRCS) State Soil Geographic (STATSGO) Soils Database for most of the US Army bases. The susceptibility to munitions contamination were analyzed and ranked. In the future, we will select a number of bases representative of low to high susceptibility for scoping evaluation of potential of particular explosive residue contamination.

Planned Future Work

The nearly completed set of simplified column experiments was necessary to develop appropriate experimental and modeling methods for use in the intact soil column experiments. As we developed the dissolution, solute and particulate transport models, we are comparing our sorption experimental results with those in the literature (Ainsworth et al. 1993), and revising sorption models. The sorption models will be used to analyze the dissolved column experiment to provide another baseline in addition to the microsphere and DNT transport. With these results, we are ready to begin the intact column experiments.

Transport experiments will be conducted using both dissolved MC compounds and particulate MC residues in the intact cores from the three range sites. Saturated (e.g., stormflow) experiments will be conducted first, followed by unsaturated (vadose zone) experiments. If particle or colloid transport is not observed under saturated conditions, the unsaturated experiments will be limited and will focus on the transport of dissolved MC compounds. As in the repacked columns, effluent samples will be filtered to determine the extent of migration of particulate, colloidal, and dissolved MC compounds (as defined above). Effluent samples will be monitored for pH, major anions and cations, dissolved OC to determine basic geochemical conditions and to identify the formation of soil colloids associated with sorbed MC compounds. Following completion of the experiments, the columns will be flash-frozen and sectioned as a function of depth to determine the extent of mobility of MC particles and dissolved phase using either/or spectroscopic methods and bulk extractions.

The sorption models will be incorporated into our coupled dissolution, particle and solute transport to describe repacked and intact column experimental data. The dual continuum model will also be tested to evaluate the influence of preferential flow on residue transport, particularly, for intact cores. If the dual continuum model is not sufficient to describe accelerated particle transport, or size exclusion is found to be very important, we will implement size-dependent velocity in the particle transport model. Should we decide to investigate coupled transport in unsaturated experiments, we will add the trapping of particles by the air-water interface into the transport model. As our coupled models have many parameters to describe multiple processes, and significant uncertainty exists in some of the parameters, sensitivity and uncertainty analysis will be conducted for experiment design and reliable quantification (Tang et al. 2009).

Ultimately, we will generalize our findings and parameter estimates to build models to assess potential contamination at operational ranges based on existing site characterization. We will assess the significance of particle transport at various site conditions (recharge, permeability, depth to groundwater, etc.) that might occur at the field scale. Preliminary fate and transport prediction will be made for the three selected ranges based on highly simplified aquifer models. A case modeling study will be conducted for MMR by incorporating our results and models with available characterization data.

BACKGROUND

In high-order detonations at DoD operational ranges, very little explosive residue remains to pose a risk to ground and surface waters (Clausen et al. 2006). In low-order detonations, however, particles of explosives remain on surface soils of operational ranges at relatively shallow depths. Particulate MC's consist of formulations of the following compounds which may be detected individually if they are dissolved: 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine (HMX), 2,4,6-trinitrotoluene (TNT), and 2,4-dinitrotoluene (2,4-DNT). MC concentrations, either dissolved or particulate, decrease rapidly as a function of depth (Jenkins et al. 2006). Compounds containing HMX and RDX, in particular, are sparingly soluble and are not expected to dissolve appreciably (Larsen et al. 2007). TNT and 2,4-DNT compounds, while having higher solubility, tend to photodegrade and biodegrade upon exposure to light and soil microorganisms, respectively (Clausen et al., 2006). Consequently, the risk of contamination to aquifers beneath military operational ranges was thought to be minimal. Recent findings at various military installations, however, have found large plumes of dissolved MC in groundwater aquifers (Clausen et al. 2006). Groundwater contamination beneath operational ranges poses a risk to long-term sustainability. Soil contamination in excess of MC solubility proves that particles are present and are likely contributing to the transport of MC (Clausen et al. 2006), either directly by particle transport or indirectly by particle dissolution. Previous research has quantified rates of particle dissolution and dissolved-phase transport under various scenarios (Selim et al. 1995; Xue et al. 1995; Lynch et al. 2002; Dontsova et al. 2006; Morley et al. 2006), but to our knowledge no one has investigated the physical and geochemical environments of the particles or the potential for transport of particles as colloids.

Because groundwater contamination was somewhat unexpected, accelerated flow through the vadose zone was suggested as a mechanism of MC transport into subsurface aquifers (Technical Exchange Meeting 2007). Older soils contain fractures, root traces, and macropores (Fig. 1), while younger soils (e.g., Inceptisols) contain alternating layers of widely variant hydraulic conductivity. Both soils are susceptible to preferential flow that may accelerate transport of MC through the vadose zone (Jardine et al. 1988, 1993a,b, 2006; Cumbie and McKay 1999; McKay et al. 2000; Mayes et al. 2000, 2003).

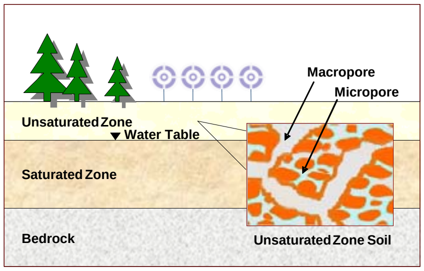


Fig 1. Conceptual model of subsurface consisting of macro- and micro-pores in the unsaturated zone.

Soils also contain micropores or regions of low hydraulic conductivity that are long-term reservoirs for dissolved contaminants (Fig. 1). Transport of dissolved contaminants into micropores is by diffusion. However, colloidal particles are too large to appreciably diffuse into micropores. Consequently, transport of particles through macropores and fractures may be several orders of magnitude more rapid than that of dissolved contaminants (Cumbie and McKay, 1999; McKay et al. 2000; McCarthy et al. 2002; Driese and McKay 2004).

Previous research has not determined if preferential flow associated with macropores, fractures, or root traces facilitates either dissolved or particulate transport nor has it examined the susceptibility to preferential flow by different soil types. The range of particle sizes that are mobile in various soil types is also unknown, as is the chemical and physical environment of MC particles. This proposal seeks to resolve the following questions:

1. Do preferential flow features, such as fractures and macropores, contribute to accelerated (i.e., preferential) transport of MC through the vadose zone at operational ranges?
2. To what extent does colloidal transport and concomitant particle dissolution contribute to preferential transport?
3. To what extent is preferential transport associated with migration of dissolved, individual compounds, e.g., RDX, HMX, 2,4-DNT, and TNT?
4. What is the role of stormflow in the transport of MC, either as particles or as dissolved compounds?
5. Are some soil types more likely to rapidly conduct MC into underlying aquifers than others; and if so, what soil characteristics are most important?

OBJECTIVES

Our goals are to investigate the transport of <u>particulate</u> <u>and</u> <u>dissolved</u> MC in intact samples of multiple soil types. MC particles distributed heterogeneously at operational range sites from low-order denotations are suspected to be the source of contamination to underlying aquifers. We will investigate the physical and chemical environments of these particles and determine how particles are dissolved and mobilized through natural soil samples. We will apply this information to predict the transport of MC in various operational ranges to determine the risk of underlying aquifers to contaminated flux from the vadose zone.

Our specific objectives include:

1. Collection of uncontaminated, intact, soil samples containing macropores, fractures, and root traces from several major soil types (e.g., Ultisol, Alfisol, Mollisol, and Inceptisol) in or near DoD operational ranges;
2. Application of MC as particles and as dissolved constituents to the intact soil samples to determine transport parameters under vadose and stormflow scenarios;
3. Analysis of the intact soil samples to determine the physical and chemical environment of MC particles with respect to soil pores, organic compounds, microbes, and minerals; and
4. Prediction of MC mobility at operational ranges by parameterizing a coupled hydrologic and geochemical model with site-specific data plus soil, hydraulic, and geochemical parameters obtained during our investigations.

Hypotheses

Aquifer contamination from low-order detonations is a result of transport of both <u>dissolved</u> <u>and</u> <u>particulate</u> explosive residues by infiltrating water in the soils. At sites with highly fractured or macroporous soils, there will be a tendency for more rapid transport of particulate munitions constituents relative to dissolved constituents because of their exclusion from the fine pore structure in the soil. To our knowledge, no previous studies have conducted an investigation to determine concomitant dissolution and transport of microscopic particles of explosives through soil samples that have macropores and other relevant natural features.

1. Preferential flow in natural, intact soil samples will result in rapid transport of particulate and dissolved munitions under saturated conditions that might occur during intense and infrequent storms. Under partially-saturated conditions typical of the vadose zone, preferential flow of colloids and dissolved munitions will be significantly less important.
2. A variety of straining, settling, size exclusion, and adsorption mechanisms will inhibit the transport of most particles, but these particles will be subject to dissolution by flowing water. Munitions particles of a select size may become mobilized as colloids and flushed through macropores and fractures during storm events.
3. Diffusion of dissolved MC into micropores will significantly delay transport of explosives to the groundwater but will result in the formation of a long-term source of dissolved contamination that may be reactivated under seasonally wet conditions.
4. Field-scale models of operational ranges will predict that colloidal and dissolved MCs may pose a risk to groundwater aquifers under prolonged storm-flow conditions in soil types that are conducive to preferential transport, i.e., those that have significant fractures and macropores. Most soil types, however, will not have preferential flow features that contribute to preferential flow of colloids or dissolved constituents.

TECHNICAL APPROACH

Overview

Experiments will be designed to enhance knowledge of the multiple processes influencing the transport of munitions particles, including the range of particle sizes over which colloids are mobile, rates of dissolution and reactive transport, and extent of sorption. Undisturbed soil samples containing natural root traces, fractures, and macropores will be used to determine the importance of preferential flow in each soil type under realistic vadose zone conditions, e.g., saturated and unsaturated flow. Munitions particles will be applied to the soil columns to determine the mobility of particulate MC and the evolution of dissolved-phase munitions constituents. Dissolved MC will also be applied to duplicate soil columns to isolate the control of particle dissolution. Following application of particulate MC, the soil columns will be flash-frozen and sliced as a function of depth. To the extent possible, the slices will be examined to determine the physical relationship of MC particles with preferential flow features and the chemical relationship of particles with mineralogical and biological components of the soil. The end result will be detailed knowledge of the range of particle sizes that are mobile in different soil types. Proportions of relatively mobile fractures and macropores susceptible to preferential flow and relatively immobile micropores that are long-term reservoirs for dissolved contaminants, and mass transfer kinetics between these two types of flow domains will be evaluated using a dual-domain reactive transport model coupled with nonlinear inverse solution code. All the reactive transport parameters obtained from these experiments will be applied to site-specific subsurface models of the DoD facilities from which the soil samples were collected to determine the risk of contamination in underlying aquifers.

CURRENT PROGRESS

Collection of MC Particles

MC particles were collected through Dr. Susan Taylor (20 g) and Dr. Mark Fuller (20 g). Dr. Fuller's project also involves colloid transport of MC, and in his proposal he has contracted Dr. Stephen Fallis of China Lake CA, to wet-mill Composition B munitions to produce colloid-sized particles. They provided some of these particles, and particle size and composition information to us (Fig. 2). Dr. Taylor also provided MC residues of a larger particle size to us and to Dr. Fuller's group. The advantage of this approach is coordination between projects to use the same source material. There is some question as to whether these MC particles are of sufficiently small particle size for our experiments, as particle sizes < 5 µm constitute the optimal size for transport in soil systems. Consequently, we will use these particles in our current experiments. In addition, we are investigating other avenues for obtaining smaller particles for our future work.

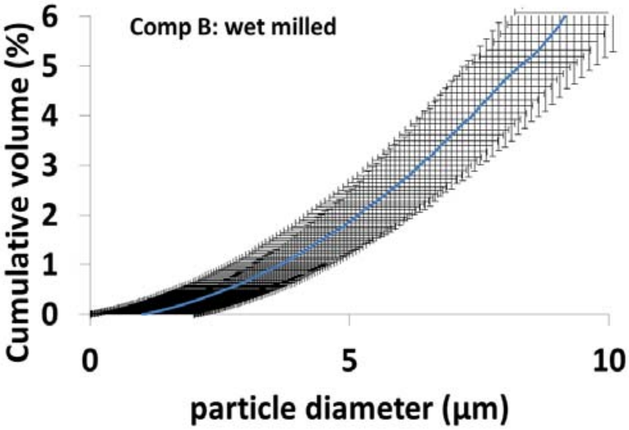


Fig. 2. Particle sizes of MC particles for use in repacked column transport experiments. Courtesy Stephen Fallis (China Lake) and Mark Fuller (Shaw Group).

Collection of Uncontaminated Soil Samples

Uncontaminated soil columns of two sizes and bulk samples were collected from operational ranges at three DoD sites: Massachusetts Military Reservation (MMR) (Fig. 3), Joint Base Lewis-McChord (JBLM) (Fig. 4), and Aberdeen Proving Ground (APG) (Fig. 5). At Camp Edwards, located on Cape Cod in Massachusetts, both TNT and RDX have been detected in the groundwater (Clausen et al., 2006). The results of extensive soil sampling at Camp Edwards indicate that TNT and RDX contamination is limited to widely dispersed, shallow sources. The TNT detected in groundwater appears to be limited to within 100 feet of identified source areas, likely due to sorption and degradation. However, a nearly two mile long RDX plume has been delineated using groundwater samples, indicating its migration through a relatively thick (~ 35 meters) vadose zone to the water table (Clausen et al, 2006). Our access to MMR was facilitated by Dr. Chuck Coyle as suggested during our IPR in February 2009. The soils at MMR are derived from Pleistocene-age glacial tills and could be characterized as a silt loam. Few gravels or cobbles were observed in MMR soils (Fig. 3). The undisturbed cores were collected from the B horizon, and buckets of disturbed soil were collected from the B horizon and the overlying burn layers and A horizons (Fig. 3).

Low concentrations (< 1 μg/L) of RDX have also been detected in groundwater samples from Ft. Lewis (now JBLM), Washington (Jenkins et al., 2001). The soils at Ft. Lewis are coarse gravelly sands derived from Pleistocene-age glacial tills and weathering of these materials has not progressed to the degree observed at MMR. JBLM samples in the upper horizons contain many roots and organic concentrations are high, while gravel content is also very high (Fig. 4). Below the root zone (60 cm), unweathered glacial tills consisting of sands are gravels are encountered. The undisturbed cores were taken from the root zone (Fig. 4) and buckets of gravelly sand were collected from below the root zone. Columns will be repacked with the material from below the root zone since it was not sufficiently cohesive to support collection of undisturbed cores.

The soils at APG are a sandy loam Sassafras Series soil (Fig. 5). These soils are have been used by other investigators (Drs. Ron Checkai, Roman Kuperman, Mike Simini) for studying the transport of explosives. The suggestion for this site also came from the ESTCP/SERDP meeting at our focused SON luncheon, and sample collection was facilitated by Dr. Checkai and others. Groundwater contamination at APG is suspected, and the characteristics of the site and soils (sandy soils and shallow vadose zone) are likely to promote mobility of Comp B components. Undisturbed samples were collected from the B horizon, and buckets of disturbed soil were collected from the B and the overlying B/A horizons (Fig. 5).

There are two sizes of laboratory-scale columns: 9 cm diameter x 14 cm length, and 13 cm diameter x 24 cm length. Approximately 6 small columns and 5 large columns were collected from each site. The samples are *intact* soil B or C horizons that retain natural soil features such as macropores, root traces, fractures, and worm burrows that might influence contaminant mobility. We excavated a small trench in the subsurface and shaped the samples to the desired size and shape using hand tools, e.g., rock hammer and knives (Figs. 3-5). Subsequently, the soil columns were encased in PVC pipes using expandable foam. Bulk samples were also collected from each site: JBLM root zone, JBLM C horizon, MMR A horizon, MMR "burn" layer (potentially from older firing range activities) (dubbed MMR-E), MMR B horizon, APG B/A horizon, and APG B horizon. As discussed in the December lunch at the ESTCP/SERDP meeting, we transferred some bulk soil samples to Dr. Herb Allen of University of Delaware and Dr. Mark Fuller of Shaw Group for use in their projects.

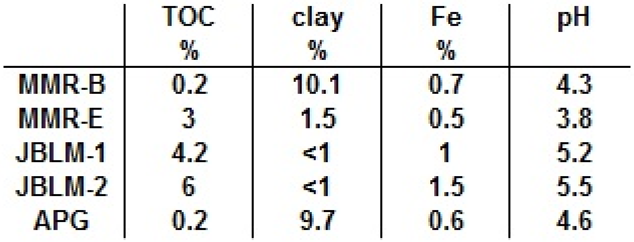
We are using a variety of conventional soil characterization techniques to determine the physical and chemical properties of the samples, including particle size (texture), pH, metal-oxide content, bulk density, cation exchange capacity (CEC), clay content and mineralogy, and soil organic carbon content (Table 1). Clay mineralogy and CEC are in progress.

Figure 3. Soil sample collection at Massachusetts Military Reservation (MMR) Operational Range near Sandwich, MA.

Figure 4. Soil sample collection at Joint Base Lewis-McChord (JBLM) near Tacoma,WA. Note high percentage of gravels.

Figure 5. Soil sample collection at Field M of Aberdeen Proving Ground (APG) near Lakewood, MD.

Table 1. Total organic carbon (TOC), textural clay, and Fe (total) content in DoD soils.



	TOC %	clay %	Fe %	pH
MMR-B	0.2	10.1	0.7	4.3
MMR-E	3	1.5	0.5	3.8
JBLM-1	4.2	<1	1	5.2
JBLM-2	6	<1	1.5	5.5
APG	0.2	9.7	0.6	4.6

Sorption of Dissolved MCs (TNT and RDX) to DoD Soils

The fate of nitroaromatic compounds (NACs) have been found to be affected by clay minerals and soil organic matter (SOM) (Haderlein et al., 1996; Hatzinger et al., 2004; Singh et al., 2008). In this study, soils with varying textural clay and organic carbon content (Table 1) were collected from B- and adjacent horizons from operational ranges MMR (MMR-E and MMR-B), APG and JBLM (1-sands and gravels, 2-root zone). Soils from MMR-E and JBLM-1 and 2 sites have high OC content of 3-6% but very low textural clay content (<1.5%) where as MMR-B and APG soils have high clay content (9-11%) and negligible OC content(<0.2%). TNT and RDX sorption was carried out in the e 0-60 mg/L and 0-15 mg/L respectively. 0.5 g soil was added to 30 mL solutions of TNT and RDX adjusted for respective soil pH in a background solution of 10 mM NaCl.

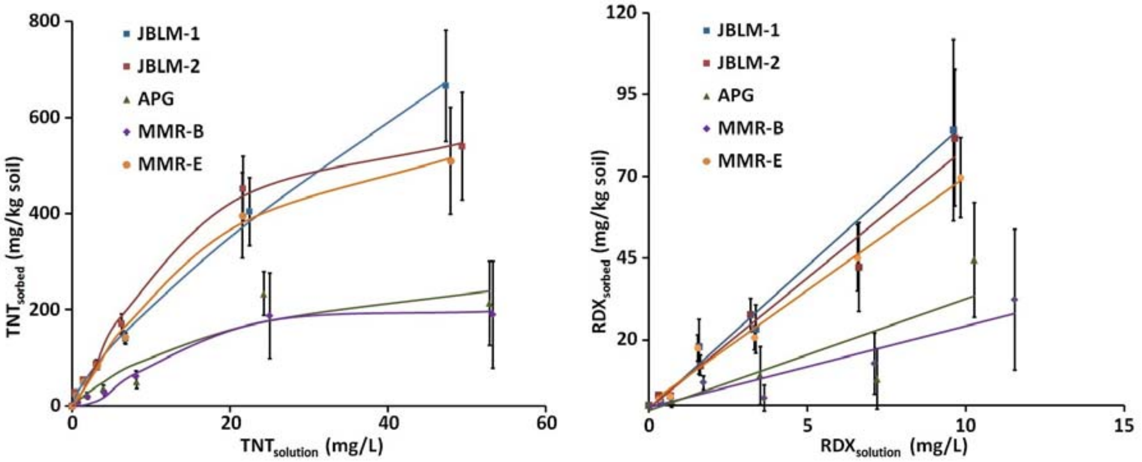


Figure 6. Sorption of TNT and RDX in soils from different operational ranges.

Results from TNT and RDX sorption (Fig. 6) show that TNT and RDX sorption was two to three times higher in soils MMR-E, JBLM-1 and JBLM-2, which have higher TOC compared to APG and MMR-B soils which have lower TOC. With respect to textural clay content, the sorption of both TNT and RDX was inversely proportional. Sorption values for TNT and RDX are in the same magnitude as reported in literature for minerals and soils (Haderlein et al., 1996; Hatzinger et al., 2004). Although most literature values report higher NAC sorption generally to clay minerals and soil enriched with clay, for our soils we found that OC content of soils plays a more important role in attenuating TNT and RDX than does textural clay content. MMR-B (~10%) soil was enriched in clay content compared to MMR-E (~1.5%). Analyses to determine the *mineralogy* of the clays present is in progress. As expected, an order of magnitude higher sorption of TNT compared to RDX which shows that of the two MCs, RDX may be transported in the soils with less retardation.

Table 2. Parameters describing the Freundlich equation fit to sorption isotherm data (K_f: affinity coefficient, K_d: adsorption coefficient, n: unitless Freundlich coefficient, r^2:goodness of fit).

	TNT			**RDX**	
Soils	***K_f(L/Kg)***	***n***	***R^2***	***K_d(L/Kg)***	***R^2***
JBLM-1	**68**	**0.6**	**0.96**	**8.7**	**0.98**
JBLM-2	**42**	**0.7**	**1.00**	**7.9**	**0.97**
APG	**30**	**0.5**	**0.99**	**6.9**	**0.98**
MMR-B	**25**	**0.6**	**0.97**	**3.4**	**0.79**
MMR-E	**54**	**0.6**	**0.91**	**2.5**	**0.90**

In a separate study conducted for MMR-E (high OC, low textural clay) and MMR-B (low OC, high textural clay) the supernatant at sorption equilibrium was divided into dissolved (<2 nm) and colloidal (2 nm – 0.45 µm) fractions to determine with which fraction are TNT and RDX associated. In systems where 2.5 mg/L and 10 mg/L of TNT and RDX was initially added, 75-80% of TNT and 80-100% of RDX was present in the dissolved fraction in both the systems. The results show that the NACs in dissolved form are more likely to stay dissolved rather than interacting or associating themselves with organic or mineral colloids from the soil. Although, literature suggests RDX is retarded less in soils than TNT, a comprehensive study determining the fractionation of dissolved MCs in dissolved and colloidal fraction has not previously been covered. Also, colloids have previously been reported to play a major role is transport of organic and inorganic contaminants (McCarthy and Zachara, 1989). However, as shown by our results (Fig. 7, the fractionation of these contaminants in the dissolved (<2 nm) or particulate phase (>0.45 μm) shows that effect of colloids may be secondary when the MC are initially present in the dissolved phase.

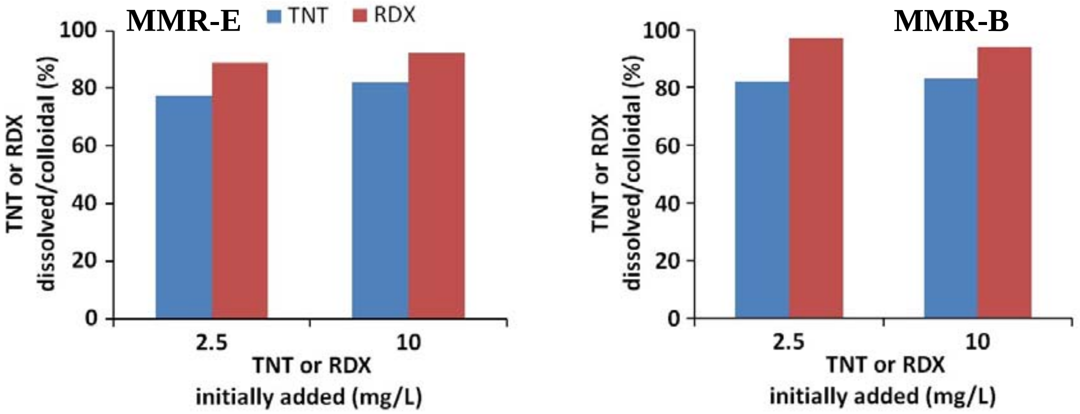


Figure 7. The ratio of dissolved (< 2nm) to colloidal (2 nm – 0.45 μm) in supernatants of MMR-B (right) and MMR-E (left) soils at sorption equilibrium.

Currently, further measurements of dissolved to colloidal ratios of TNT and RDX in MMR-B and MMR-E soils is being carried out for lower initial added concentrations (0.25. 0.5, 1.0 and 2.5 mg/L of TNT and RDX) to represent environmentally relevant dissolved MC concentrations. In addition sorption of another significant MC, HMX is being studied with the DOD soils in context. We will compare our results with those in the literature (Ainsworth et al. 1993), revise sorption models, and use the improved models in flow through experiment studies.

Transport of Dissolved MCs TNT and RDX in Soils from MMR

After having quantified sorption of TNT and RDX in soils with varying OC and clay content from operational ranges, an obvious question was whether OC plays a role in transport of dissolved TNT and RDX in flow-through systems. There have been several studies where the importance of organic matter has been prioritized in both sorption and transport experiments (Hatzinger et al., 2004; Singh et al, 2008; Alavi et al., 2011). However, a cohesive understanding of the importance of OC in environmental conditions (such as soils directly from contaminated field sites) is lacking. Therefore, following sorption experiments of TNT and RDX on the five DoD soils, the two soils from the same profile (MMR-E and MMR-B) which have different textural clay and OC content were chosen to the extent to which both OC and textural clay are important for the transport of dissolved MCs. Plexi-glass columns (9 cm length by 2 cm diameter) were filled with the MMR-E and MMR-B soils using a field representative bulk density of ~1.7 g/cm^3. The transport of TNT (~7 mg/L) and RDX (~ 4.5 mg/L) and a nonreactive tracer (Br^-) were conducted at a flow-rate of 30 mL/h. The solutions were readjusted for soil pH accordingly (Table 1) and prepared in a background of 10 mM NaCl.

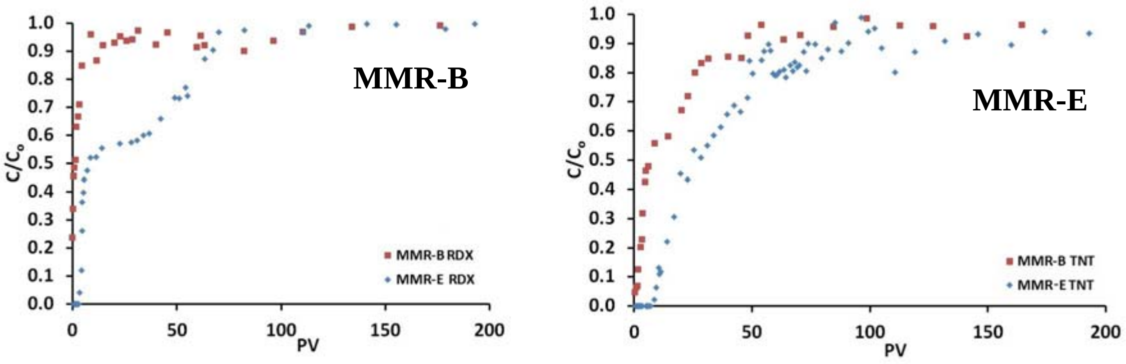


Figure 8. Breakthrough curves of TNT (7 mg/L) and RDX (4.5 mg/L) in MMR-B (left panel) and MMR-E (right panel) soils.

From breakthrough experiments (Fig. 8), we see that the breakthrough curves for both TNT and RDX show a rate-limited behavior. The breakthrough in MMR-E and MMR-B soils is given as the mean arrival time of the advective front (arrival time of 50% of the influent TNT and RDX concentrations) of TNT and RDX was delayed significantly by 3.3 and 6 times in column filled with MMR-E soil (Fig 8(right panel) compared to MMR-B (Fig. 8 (left panel)). Following the results from the sorption experiment (higher sorption in columns with higher OC content), we may conclude that OC played a role in the delayed breakthrough of TNT and RDX in the columns. This is complemented by a recent study where topsoil was mixed with compost to obtain soils with different TOC content (Singh et al., 2008). Soil with higher OC content led to higher sorption and delayed breakthrough of NACs such as TNT and RDX.

In addition to breakthrough experiments, desorption was also carried out for the MMR-B and MMR-E systems once breakthrough reached a steady state (~200 pore volumes) (Fig 9). For both systems, desorption was conducted by 10 mM NaCl solutions. Differences between MMR-B and MMR-E soils for TNT is evident. In MMR-E, the desorption of TNT is gradual and equilibrates at ~2.5 mg/L. In MMR-B, the desorption is drastic and equilibrated at 0.4 mg/L. In the case of RDX, the difference in MMR-E and MMR-B is not directly evident. RDX concentration at desorption equilibrium was around 0.3 mg/L. The values of TNT and RDX when desorption reached steady state suggests that a significant portion of TNT and RDX is strongly sorbed, particularly in MMR-E soil.

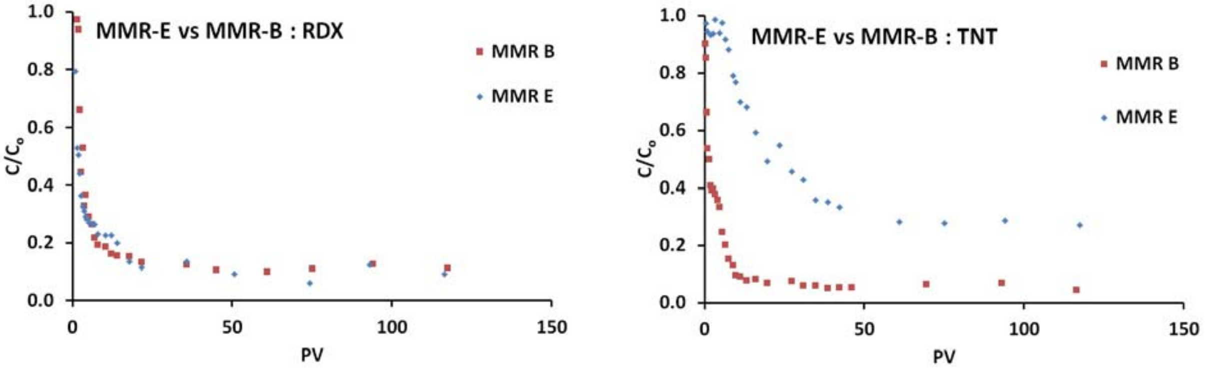


Figure 9. Desorption curves of TNT (right) and RDX(left) conducted after breakthrough of TNT and RDX reached steady state in MMR-B and MMR-E soils.

For further studies various tasks are in progress. Transport of another significant MC, dissolved HMX, is currently being carried out. For TNT and RDX related experiments, we are determining the dissolved to colloidal ratio (e.g., Fig. 7) of TNT and RDX in breakthrough and desorption systems. The retardation coefficient (and calculated distribution coefficient) will be calculated with transport modeling once the analyses of nonreactive tracer Br are complete.

Following these, the transport of particulate MCs will be conducted in (repacked) columns filled with MMR-B and MMR-E soils. These experiments will be used to determine the rate and extent of particle versus dissolved phase Composition B in simple soil systems. This set of experiments is necessary to complete methods development for dissolved, and especially, for particulate, MC influents. Further, the experiments are necessary to generate model parameters for reaction of dissolved and particulate MC in soil systems devoid of macropores, fractures, and other complex hydrological characteristics present in the intact cores.

MC Particle Transport Experiments in Clean Sands

Previous studies examining the size distribution of explosives residues have focused almost exclusively on the centimeter to millimeter pieces as potential sources of contamination (Jenkins et al., 2006, Taylor et al., 2004). However, the same studies also reported the occurrence of fine explosives residues (< 250 µm) coincident to the deposition of the larger fragments (Jenkins et al., 2006, Taylor et al., 2004, 2009). In addition, experiments examining the fate of MC residues on ranges provide anecdotal evidence that larger pieces of MC tend to disaggregate into smaller particles due to weathering (Taylor et al., 2009). Given the low solubility values for MC, it is possible that micron to sub-micron sized particles could be mobilized as colloids. The transport of fine MC particles could contribute to the downward migration of explosives compounds through the vadose zone to underlying aquifers. Because this conceptual model has not been investigated with respect to MC, the primary goal of this study was to determine the potential for solid-phase transport of MC in a simple model aquifer system. A secondary objective was to determine the influence of grain size on the mobility of MC in granular sediments.

Transport experiments were conducted in saturated columns (2 x 20 cm) packed with different grain sizes of clean sand or glass beads (Table 3). Fine particles (2-36 μm) of 2,6-dinitrotoluene (DNT) were used as a surrogate for MC. DNT particles were applied to the top 1 cm of sand or beads in the columns, and the columns were subsequently leached with artificial groundwater solutions. DNT migration occurred as both dissolved and particulate phases (Fig. 10).

Concentration differences between unfiltered and filtered samples indicate that particulate DNT accounts for approximately 40% of the DNT mass recovered in the effluent from the glass bead column, 31% for the medium sand column and less than 15 % for fine sand column. Proportionally, more particulate than dissolved DNT was recovered in effluent solutions from columns with larger grain sizes, while total concentrations of DNT in effluent were inversely related to grain size (Table 4). Paired t-test statistical analysis was used to compare the dissolved and total effluent aliquots from each experiment. A difference in means across the paired observations was considered significant for p-values <0.05. The statistical analysis and the mass balance calculations suggest that as grain size increases, particulate transport accounts for a larger portion of the DNT detected in the effluent. Conversely, lower effluent concentrations of total and dissolved DNT were observed in glass beads versus the both sands (Fig. 10), and total DNT mass recovered in the effluent decreased with increasing grain size, from 2% in fine sand to 0.2% in glass beads with medium sand being intermediate (Table 4).

Table 3: Summary of column transport experimental conditions.

ID	Pack Type	Median Grain Size (mm)	Porosity	Ks (m/s)	Flow Velocity (m/s)
FS	Fine Sand	0.4	0.33	1.18E-03	1.07E-03
MS	Medium Sand	1.0	0.31	3.55E-03	1.14E-03
GB	Glass Beads	4.0	0.43	2.66E-03	8.29E-04

Table 4: Mass balance results for DNT tracer experiments.

	FS	MS	GB
Total Mass Applied to Column (mg)	468	431	437
Mass Recovered in Effluent (mg)			
- Total	9.25 (2 %)	6.98 (1.6 %)	0.82 (0.2%)
- Dissolved	7.89 (1.69 %)	4.85 (1.13%)	0.49 (0.11 %)
- Particulate	1.36 (0.29 %)	2.13 (0.49 %)	0.33 (0.08%)
Mass Recovered in Sand (mg)	549.0 (117.3%)	428.9 (99.4 %)	336.6 (77.1%)
Total Mass Recovered in Effluent and Sand (mg)	559.2 (119 %)	435.9 (101 %)	337.4 (77.3%)

Of the total DNT mass applied to the upper most layer of the column, ≤ 2% was recovered in the effluent with the bulk remaining in the top two cm of the column (Fig. 11).

It is not possible to determine via the analytical methods used in this study whether the DNT in the slices of column material occurs as dissolved/adsorbed or particulate DNT. The occurrence of dissolved and particulate DNT transport, as evidenced from our effluent results, suggests the column solid phase should contain a combination of both. Most of the solid phase samples in the upper portions of the columns (~2-8 cm) exceeded the solubility of DNT, suggesting that particulate DNT is present. Therefore, the observed spatial distribution of DNT may be largely attributed to the transport and subsequent retention of DNT particles at depth in the column material. Results for our sand samples are consistent with the findings of Bradford et al. (2002) and Johnson et al. (2007) in which microsphere retention profiles in porous media exhibited a non-linear decrease in colloid concentration with mass retention strongest near the point of input. Bradford et al. (2002) attributed this initial removal to physical straining of larger particles in blocked or dead end pores.

There are very few transport experiments using particulate explosives materials present in the literature for comparison. Dontsova et al. (2006) performed transport experiments using Composition B (CB) residues from low order detonations which were applied to column materials in both the dissolved and solid phase. However, the size of the Composition B particles was relatively large (0.25 to 2 mm), which is expected to lead to high retention in soil pores. The effluent samples were not analyzed for the presence of particulate material (e.g. using filtered aliquots) so it is unknown whether particle phase transport of Composition B occurred in these experiments.

The conceptual model presented by previous studies investigating the mass transfer of MC from surface soils to underlying aquifers is based on the premise that transport occurs solely in the dissolved phase. However, our results show that transport of DNT, a surrogate for MC, can occur as both a dissolved phase and particulate. This suggests that it may be possible for fine explosives residues, produced directly by detonation or though the weathering of larger MC fragments, to migrate as particulate material.

The findings of this study are preliminary because many uncertainties remain regarding the mechanisms governing the dissolution and mobility of particulate MC material. More study is needed to determine if residues of Composition B or other explosives residues exhibit the same potential for transport as the MC surrogate used in this study or whether the conventional conceptual model for MC should be expanded to include particulate transport.

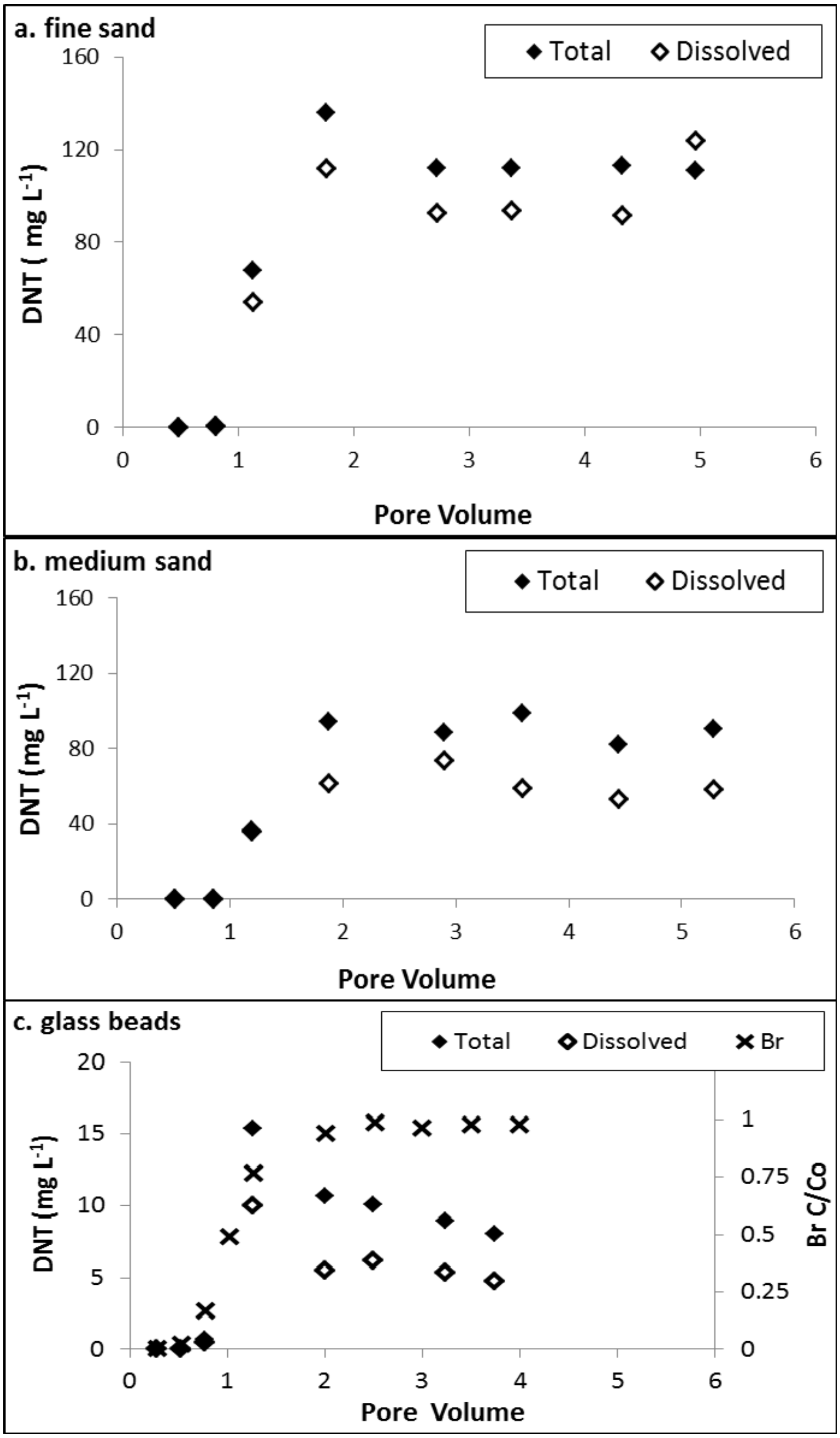


Figure 10. DNT concentrations for unfiltered and filtered effluent samples presented as unfiltered and filtered sample DNT concentration versus pore volume of effluent (10a – fine sand, 10b – medium sand and 10c – glass beads). Fig. 10b also includes Br breakthrough data presented as sample concentration normalized to the influent concentration (C/C_o) versus pore volume of effluent. Note scale difference for Fig. 10b DNT concentrations.

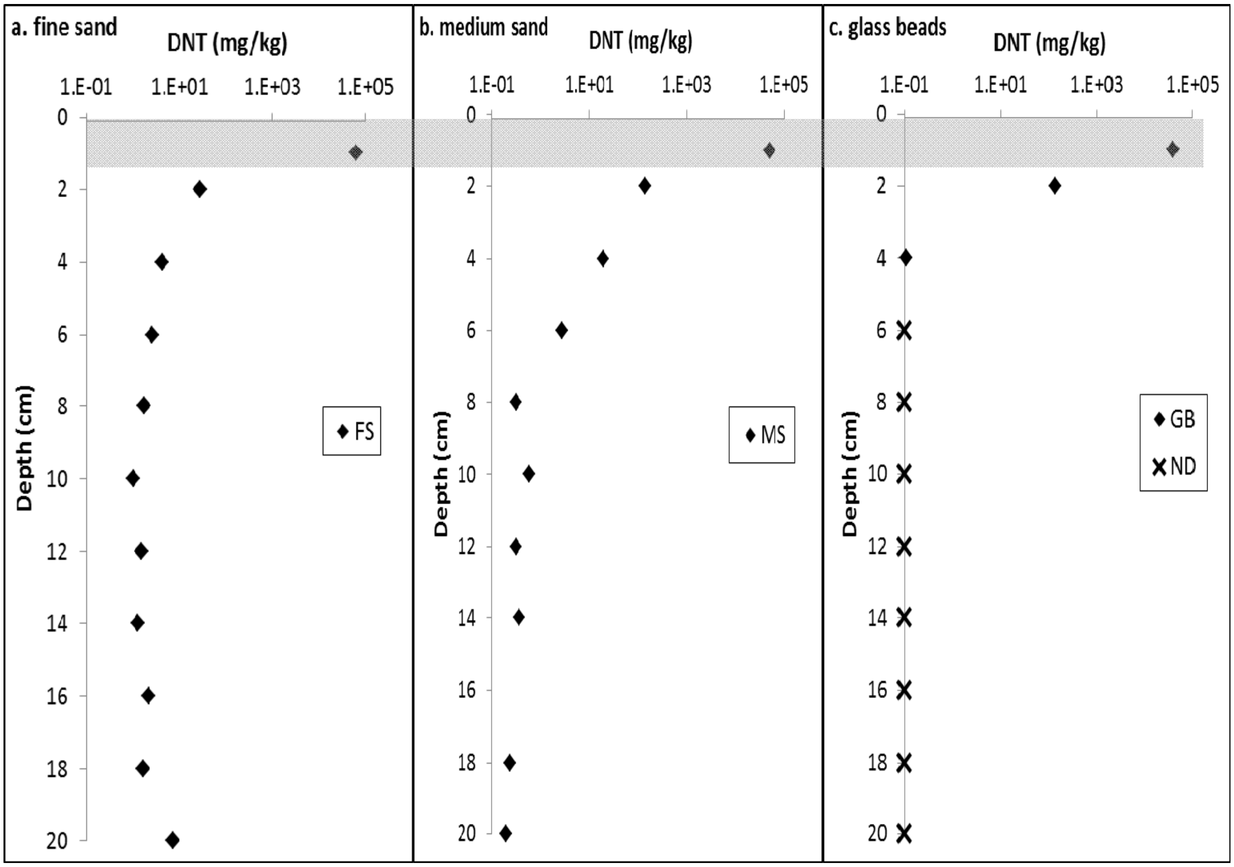


Figure 11. DNT distribution in sand samples from experiments in fine sand (FS), medium sand (MS), and glass beads (GB), presented as DNT concentration in each 1 cm segment of sand (mg/kg) versus depth, in Figures 11a, 11b, and 11c, respectively. Shaded area indicates approximate depth of DNT surface application. Analytical results indicate that GB samples below 4 cm were non-detect ND (MDL = 0.04 mg/kg).

Dissolution, Particle, and Solute Transport Modeling

The goal was to develop a coupled particle and solute transport model with kinetic dissolution to quantify the coupled processes, analyze experiments data, and assess the potential contamination at operational range conditions. The dissolution rate is formulated as (Lynch et al., 2003)

$$k_{dis} = \frac{D_m}{h} a$$

Where D_m is the diffusion coefficient, h is the boundary layer film thickness and a is the surface area per liter, which decreases as particulate explosives dissolve. To dissolve m_0 mole explosives with sphere particle of diameter $r_0$cm in 1 liter pure water, we derived the dissolved concentration to be described by

$$\frac{\partial c}{\partial t} = \frac{3m_w D_m m_0^{\frac{1}{3}}}{1000\rho h r_0}(m_0 - c)^{\frac{2}{3}}(c_{sat} - c)$$

Where m_w is the molecular weight (g/mole), ρ is the density (g/cm^3), and c_{sat} is the solubility. This was solved using the Runge-Kutta method using Excel to describe the dissolution process. Assuming a film thickness of 0.01 cm, the model predictions (Fig. 12) are similar to experimental results in (Webb et al., 2006).

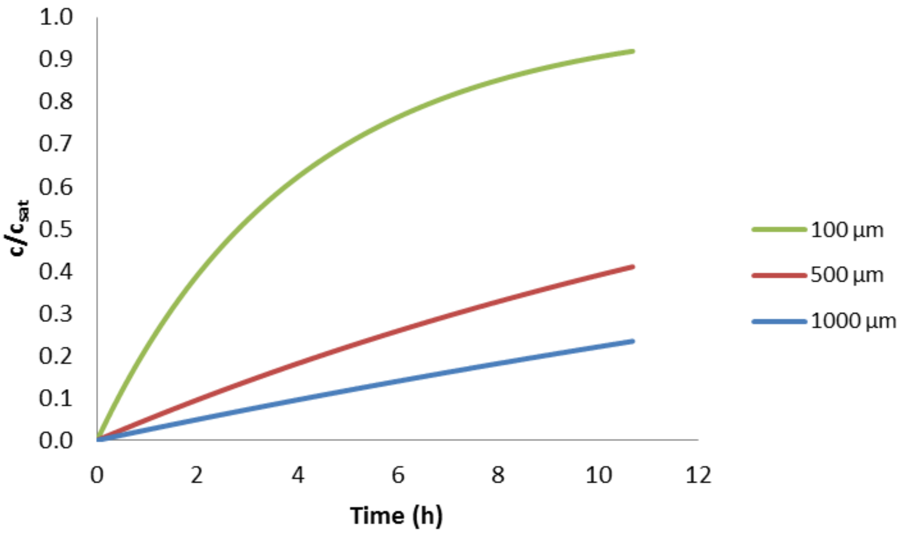


Figure 12. Predicted dissolved concentration time series for dissolving 0.01 g RDX with particles of 100, 500, or 1000 µm in 20 mL water.

In reality, explosive residue consists of particles of a range of sizes (Taylor et al. 2004, 2006). Large particles are expected to be strained while small particles may move through the porous media. The size of particles can decrease with dissolution so that strained particles can be mobilized when they are small enough. Here we conducted numerical dissolution experiments to examine the size changes when DNT of known distributed particle sizes are dissolved in water. The dissolution model was implemented in PHREEQC (Parkhurst and Appelo 1999) using each kinetic reactants to represent particles of a particular size. As m and m_0 can be accessible in the rate formula in the code to specific user-defined kinetic rates, and $r/r_0 = (a/a_0)^{1/2} = (m/m_0)^{1/3}$ for sphere particles, the dissolution rate is parameterized as

$$k_{dis} = k_{dis,ini}\, a_0 \left(\frac{m}{m_0}\right)^{\frac{2}{3}}$$

where a_0, and m_0 are the initial surface area and moles of particulate munitions compounds per liter pore fluid, and m is the moles per liter pore fluid at calculated time. As discussed in the previous subsection, $a_0 = 3mm_w/\rho r$ for spherical particles.

Suppose we dissolve in water DNT with identical mass fraction of particles with size of 1, 2, 5, and 10 µm, the dissolved concentration increases with time, with the rate dependent on the total surface area, or amount of particles (Fig. 13). More mass (particles) means higher surface area, higher dissolution rate, and reaches equilibrium (either reaches saturation or all particles are dissolved) earlier. With the same mass amount for particles of different sizes, the diameter of the smaller particles decreases faster as the relative surface areas are greater (Fig. 14-16). In the case of less than enough amount of DNT to saturate the solution, smaller particles disappear earlier than larger particles (Fig. 14). When abundant DNT particles are added, the solution reaches equilibrium before all of the particles are dissolved, inhibiting further dissolution and particle size decreases. The extent of particle size decrease is dependent on the initial total mass, where moderate mass leads to complete dissolution of small particles and little decrease for large particles (Fig. 15), and where abundant mass results in small diameter decreases as the solution reaches solubility with the dissolution of only a small fraction of the total initial mass (Fig. 16). These modeling exercises suggest that the particle size decreases are highly dependent on the particle size, surface area, and mass distribution as well as the abundance of initial total mass.

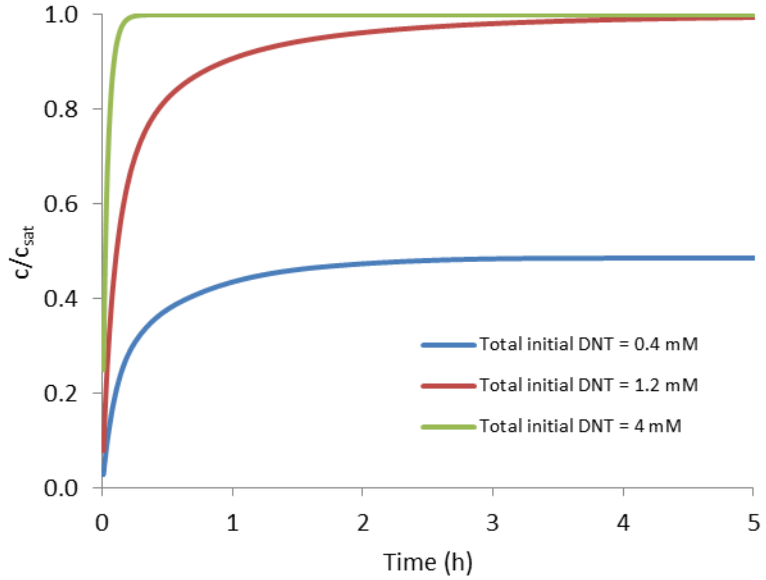


Figure 13. DNT Concentration time series for dissolving 0.4, 1.2, and 4 mM of DNT particles with equal mass fraction of 1, 2, 5, and 10 μm diameters.

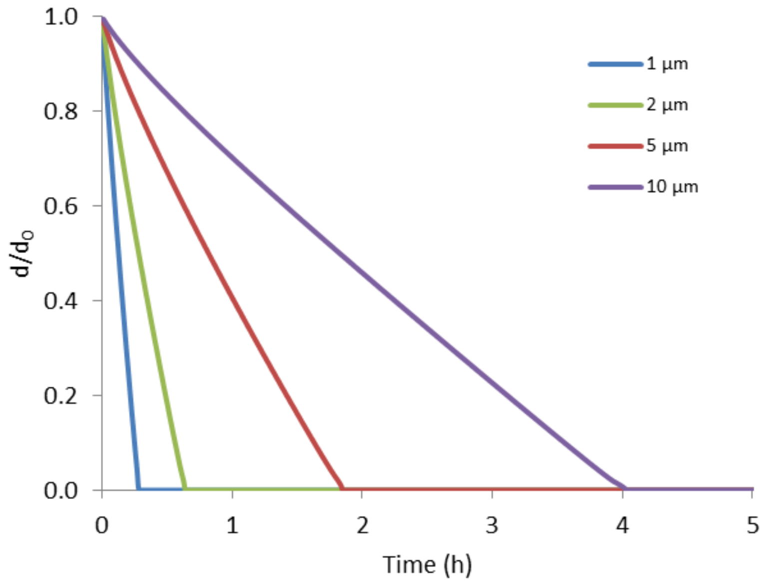


Figure 14. DNT particle size decreases for dissolving 0.4 mM DNT particles with equal mass fraction of 1, 2, 5, and 10 µm diameters.

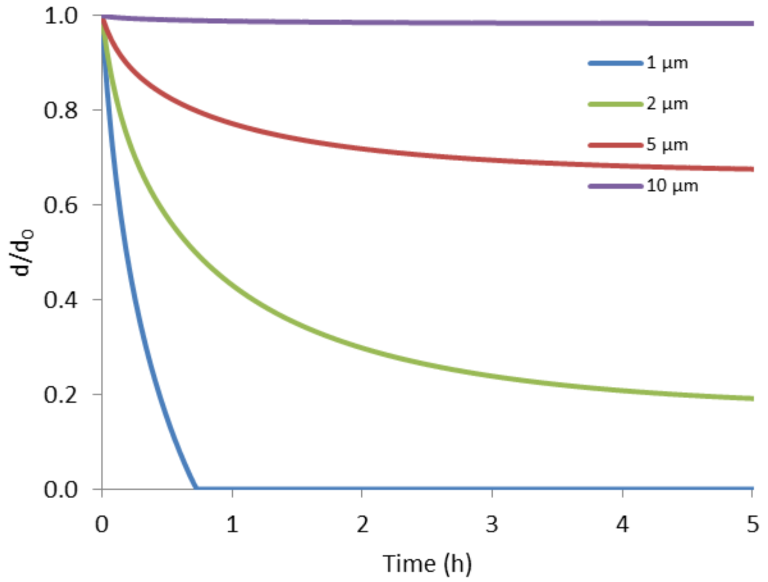


Figure 15. DNT particle size decreases for dissolving 4 mM DNT particles with equal mass fraction of 1, 2, 5, and 10 µm diameters.

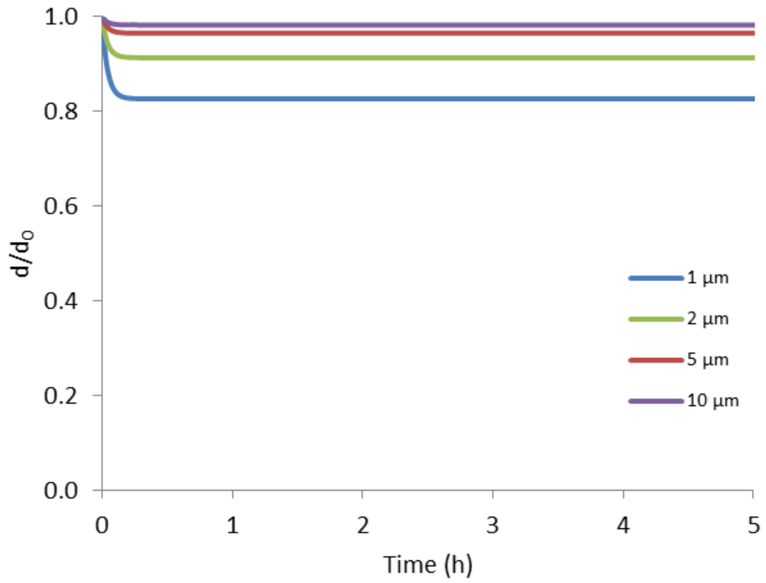


Figure 16. DNT particle size decreases for dissolving 10 mM DNT particles with equal mass fraction of 1, 2, 5, and 10 µm diameters.

The coupled dissolution and solute transport is described by

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} + k_{dis}(c_{sat} - c)$$

This was implemented in PHREEQC (Parkhurst and Appelo, 1999) to simulate the effluent RDX concentrations under various loading, flow rates, and particle size when particulate RDX was embedded in a column (Figs. 17-19). The predictions are in qualitative agreement with reported experimental results (Webb et al., 2006).

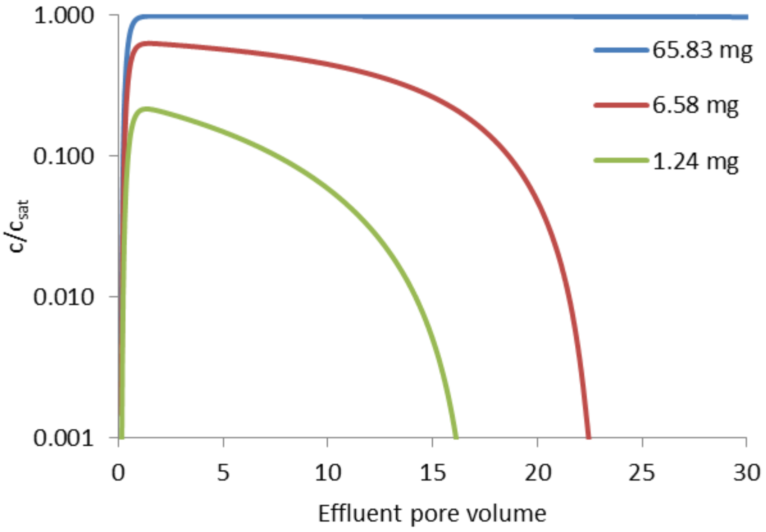


Figure 17. Predicted RDX breakthrough curves with various initial masses.

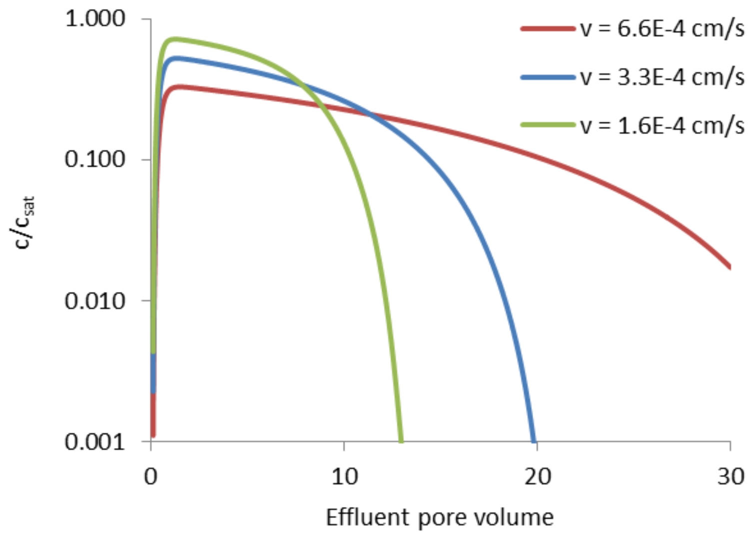


Figure 18. Predicted breakthrough curves with various flow rates.

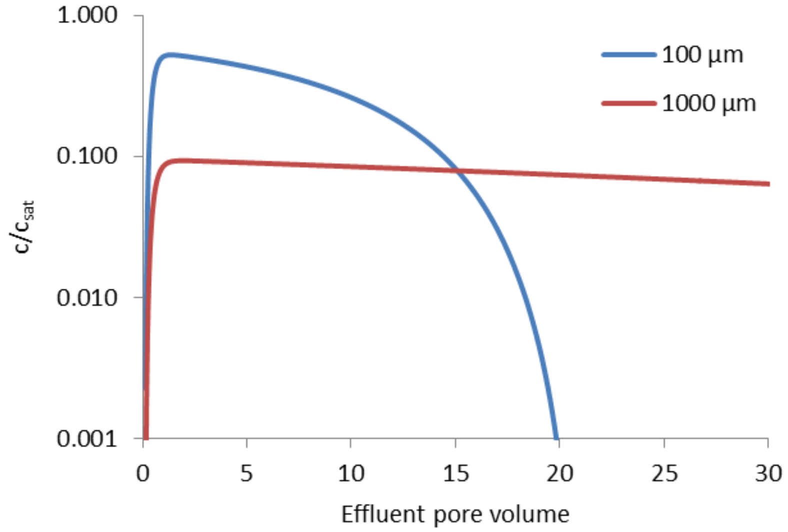


Figure 19. Predicted breakthrough curves with various particle sizes.

The coupled dissolution, particle and solute transport is modeled by

$$\frac{\partial p}{\partial t} + \frac{\partial p_{str}}{\partial t} + \frac{\partial p_{att}}{\partial t} = D_p \frac{\partial^2 p}{\partial z^2} - v_p \frac{\partial p}{\partial z} - k_{dis,p}(c_{sat} - c)$$

$$\frac{\partial p_{att}}{\partial t} = k_{att} p - k_{det} p_{att} - k_{dis,a}(c_{sat} - c)$$

$$\frac{\partial p_{str}}{\partial t} = k_{str} \Psi_{str} p - k_{dis,s}(c_{sat} - c)$$

where p, p_{str}, and p_{att} are the concentration of the aqueous, strained, and attached particles normalized by pore fluid volume, D_p, v_p and $k_{dis,p}$ are the dispersion coefficient, superficial velocity and dissolution rate of particles, k_{att}, k_{det} and k_{str} are the attachment and detachment coefficients. k_{att} was calculated using filtration theory (Logan et al., 1995; Yao et al., 1971). k_{str} was approximated by (Bradford et al., 2003)

$$k_{str} = 4.495\,(d_p/d_{50})^{1.42}\left(\frac{d_{50}+z-z_0}{d_{50}}\right)^{-\beta}$$

The model was used to the breakthrough curves and final profile concentration of microspheres of 0.5, 1.0, and 2.0 μm in the particle transport experiments (Lavoie, 2010) (Figs. 20-21).

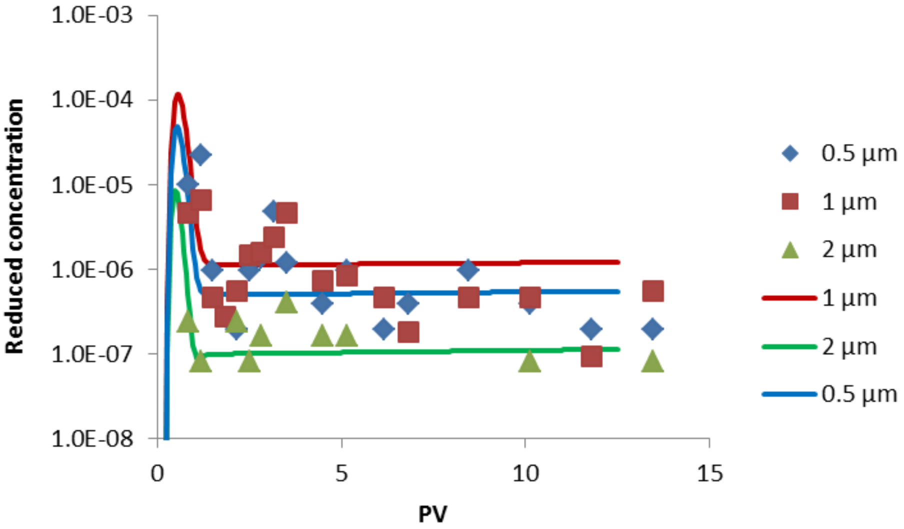


Figure 20. Breakthrough curves for microsphere transport in fine sand column (discrete symbols represent observation, and continuous curves are for model calculations).

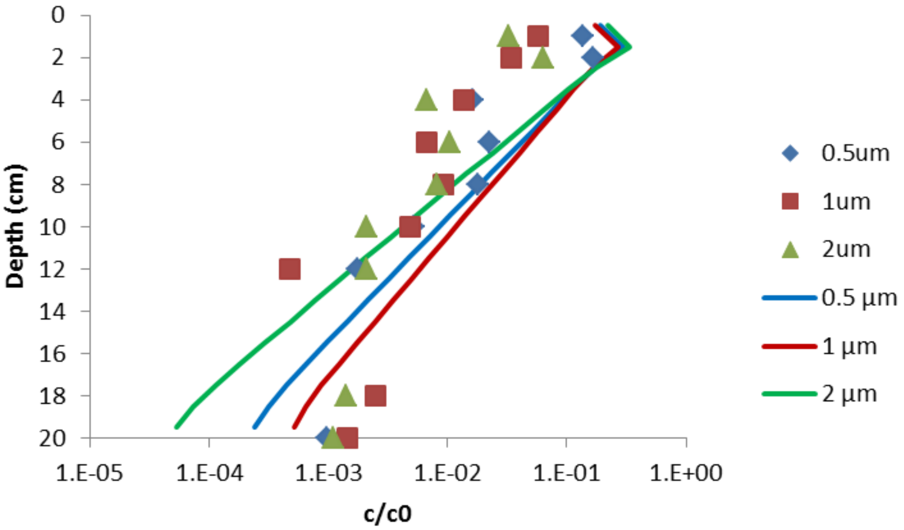


Figure 21. Profile concentration for microsphere transport in fine sand column at the end of the experiment (discrete symbols represent observation, and continuous curves are for model calculations).

As a large amount of DNT was placed in the influent of the columns (Fig. 10), dissolution calculations indicated very small diameter decreases in the short period of the flow through experiments (similar to Fig. 16). Therefore, the diameter was assumed to be constant, and the initial DNT particles were partitioned into 5 groups with representative sizes of 1, 2, 4, 8, 16 and 32 µm according to the initial DNT particle size distributions (Lavoie, 2010). Preliminary results suggested that the model over predicts the dissolution (Fig. 22). The reason is that all of the surface area of the initial DNT was used for the dissolution. The interfacial area between water and DNT particles are expected to be much smaller than the total surface area of DNT particles because a large amount of DNT particles was placed in the small pore volume in the top 1 cm of the column. The model also under predicts effluent particle concentrations (Fig. 23) because only a small amount of particles are smaller than 10 µm, accounting for less than 0.5% of the total mass, and they are subject to filtration. Due to overprediction in the dissolution, the profile concentration is also over predicted (Fig. 24). The model also provides profile concentration distribution for the suspended, strained, and attached particles (Figs. 25-27).

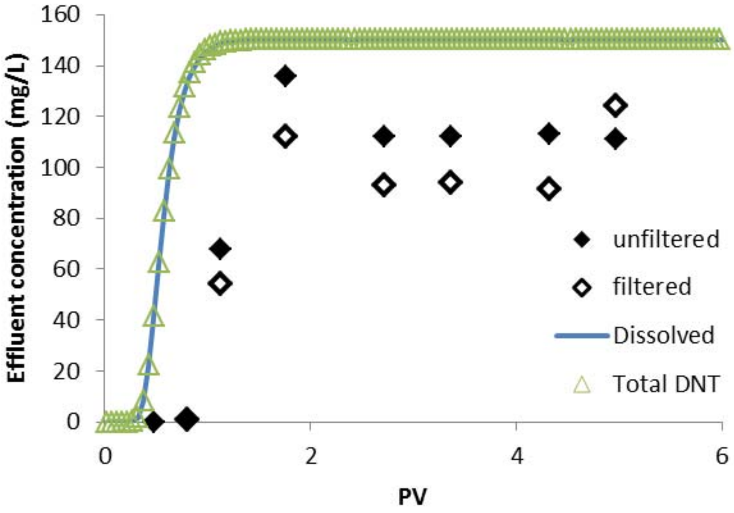


Figure 22. Predicted vs. observed breakthrough curves for the fine sand column experiments (Lavoie et al., in review).

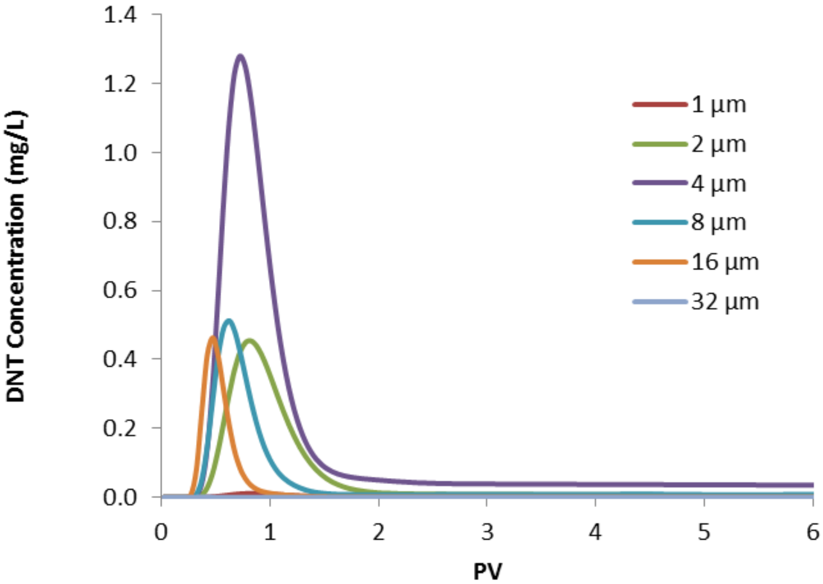


Figure 23. Predicted breakthrough curves for different particles for the fine sand column experiments (Lavoie et al., in review).

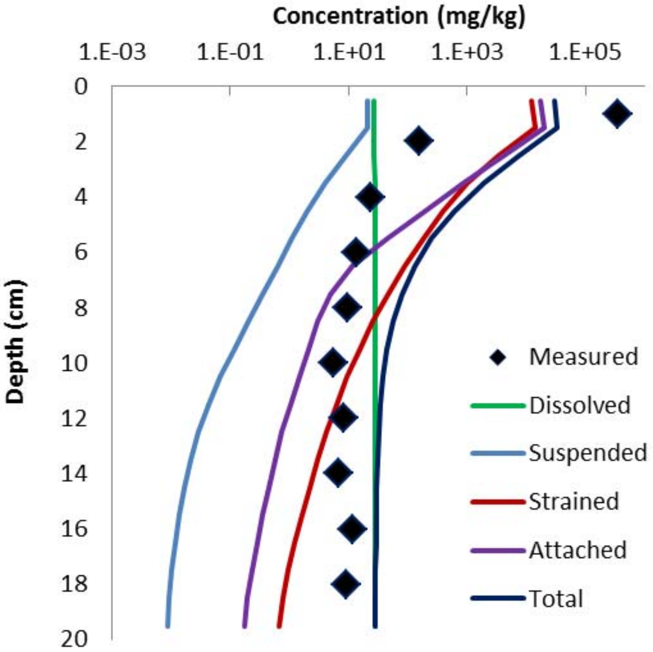


Figure 24. Predicted and observed profile concentration in the fine sand column at the completion of the experiment (Lavoie et al., in review).

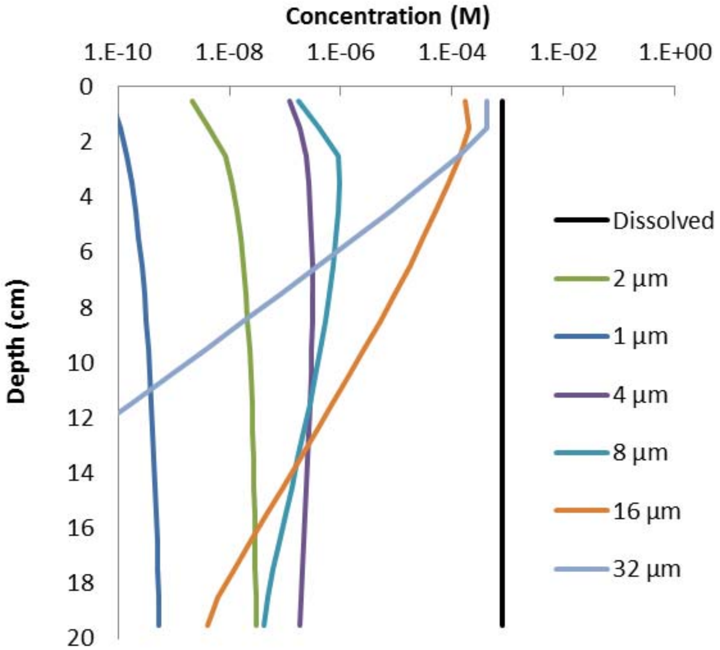


Figure 25. Predicted suspended profile concentrations in the fine sand column at the completion of the experiment.

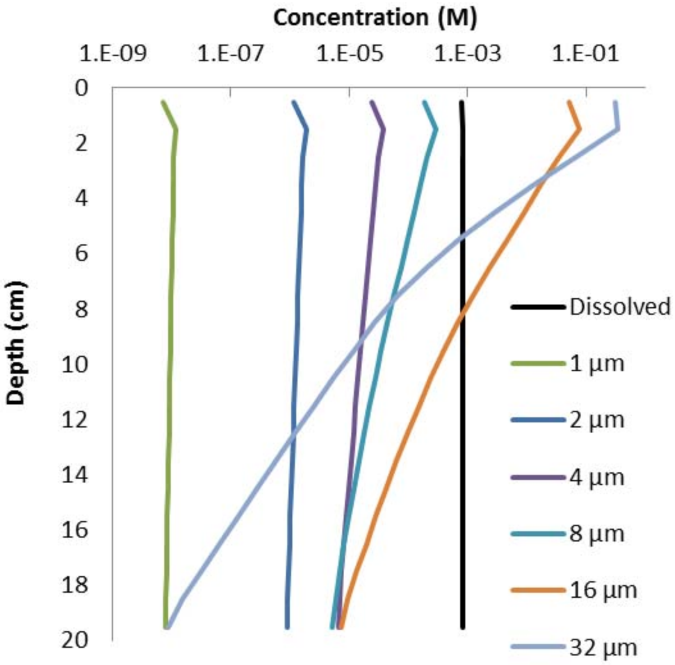


Figure 26. Predicted strained profile concentrations in the fine sand column at the completion of the experiment.

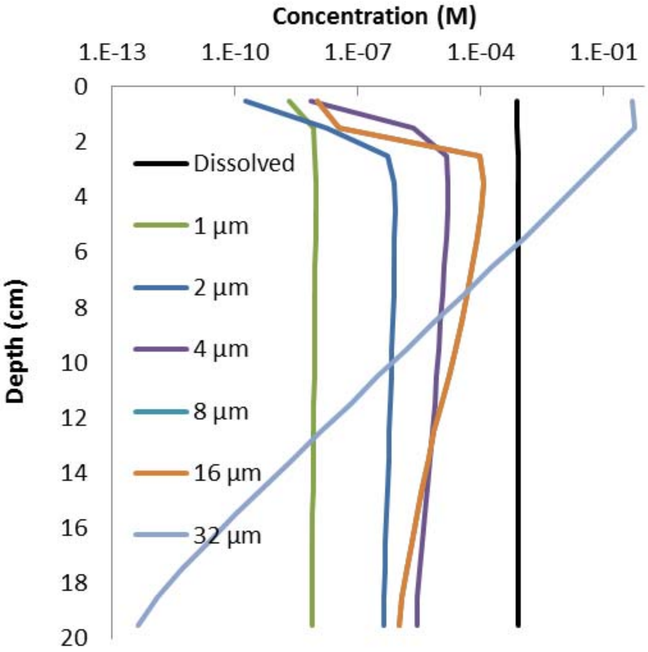


Figure 27. Predicted attached profile concentrations in the fine sand column at the completion of the experiment.

Detection of MC Compounds in Soils

We conducted some initial investigations to determine which components of soils associate with MC particles, so that intact columns may be dissected and MC particles isolated. To this end, we used Fourier transformed infrared spectroscopy to detect sorbed TNT and DNT (< 30 mg/L) onto Memphis soil, and particles of DNT in concentrations ranging from 0.01 to 1%. It was found that the 1% DNT particles to soil mixture could be detected at the wavelength of 1526 cm^{-1}, and that the particles were not chemically associated with any reactive component of the soil (Fig. 28). It is likely that lower particle detection limits and better spatial resolution may be developed using novel sample preparation and synchrotron FTIR techniques.

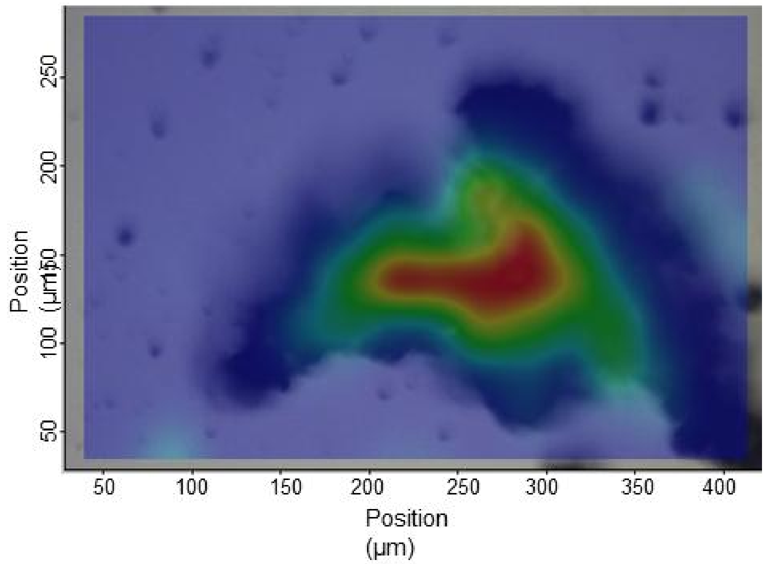


Figure 28. Overlay of microscopic image of Memphis silt mixed with DNT (1%) showing the location of DNT particle(s) as indicated by presence of peak intensity at 1526 cm^{-1}.

FUTURE WORK

Application Method For Colloids in Suspension

We believe that improved methods for applying particles to the intact columns will be needed. Comparison of dissolved and particulate MC will be facilitated by a similar application method, e.g., in the influent solution as opposed to direct application to the soil. Modeling experiments of the Lavoie et al. (in review) paper demonstrated that particles tend to aggregate when applied directly to soils, which may have minimized the migration of colloidal particles through the glass beads, in particular. In addition, the Composition B particles currently available to ORNL (Fig. 2) are too large (i.e., mostly > 5 µm) to be appreciably transported through soil pores. Consequently, we are currently developing an improved method for applying suspensions of Composition B particles to the soils. The following experiments will be performed at the U.S. Army Engineer Research & Development Center by Dr. Mark Chappell.

Experiments will be conducted to investigate the potential of dispersed Composition B particles to be transported through a porous media. These systems will be conducted under highly controlled conditions in order to quantify the potential of the originally dispersed particles to be transported and/or readily dissolved and forming adsorbed phases. Composition B flakes will be carefully milled and dispersed in 10 mM $NaNO_3$ background electrolyte to create the initial suspension. This suspension will then be continuously leached at 0.05 mL min^{-1} using a peristaltic pump to duplicate Spectrum C10/20 glass chromatography columns packed with acid-washed Ottawa sand. The state of the initial dispersion will be periodically monitored via dynamic light scattering (DLS) by flowing the influent through a Malvern Nano Zetasizer S equipped with a flow-cell prior to splitting the influent and pumping to the duplicate columns from the bottom upward. Effluent will be collected using a fraction collector. Dispersion size distribution will be determined by DLS and particle number density in the collected effluent will be calculated from the modeled data using measurements of the suspension refractive index (via a refractometer) and viscosity (via a vibrating viscometer) of the original suspensions. Subsamples of the collected eluant will be ultracentrifuged at 100,000 xg to remove particles and then the dissolved constituents will be quantified as described in Method 8330B using HPLC with UV-vis detection. Breakthrough data of both dissolved and particulate Composition B will be quantified via statistical mechanical modeling. Dissolved solute dispersion coefficients and retention factors will be quantified using an equilibrium steady-state model (van Genuchten, 1980; van Genuchten, 1981) while the dispersion attachment and straining coefficient for Composition B particulates will be modeled using a steady-state colloid model (Bradford et al., 2003; Simunek et al., 2006). In addition, we will attempt to determine the distribution of particles within the collector by removing the material at 2 cm increments and analyzing the collected sand for nitrogen using EDX.

Successful development of the suspension application method will be utilized in the intact column experiments at ORNL, and ERDC will provide the milled materials of necessary sizes (i.e., mostly < 5 µm) to ORNL.

Intact Column Experiments

In the vadose zone, unsaturated conditions in which soil, water, and air are present prevail under normal conditions. When rainstorms or snowmelt occurs, the vadose zone may become fully saturated, i.e. only soil and water are present, for short time periods. It is during stormflow scenarios that fractures or macropores become fully saturated and are highly conductive to water and contaminants (Mayes et al., 2003; Jardine et al., 2006). Transport of colloidal particles, however, may be more rapid than dissolved solute tracers because the particles are too large to appreciably diffuse into fine pores (Cumbie and McKay 1999; McKay et al. 2000). In field-scale tracer experiments, the breakthrough of colloidal microspheres and viruses 18 m away from the injection point was much more rapid than that of dissolved tracers He, Ne, and dye (McKay et al. 2000). The difference in arrival times was a factor of 10-20 times faster for colloidal versus dissolved solutes, indicating the tremendous potential for preferential migration of particles. Further, it was found that particles of a certain size (0.5μm) were more mobile than larger particles, which were subject to gravitational settling, and also more mobile than smaller particles, which were subject to minor diffusion into fine-grained pores (McCarthy et al. 2002). The "optimal" size range for particle transport is likely to be dependent upon macropore/fracture diameter, flow velocity, and degree of saturation (water content) (Morley et al. 2006). Consequently, the size of mobile particles will probably be different in different soils. Further, even the relatively "immobile" particles will continue to be dissolved by flowing water.

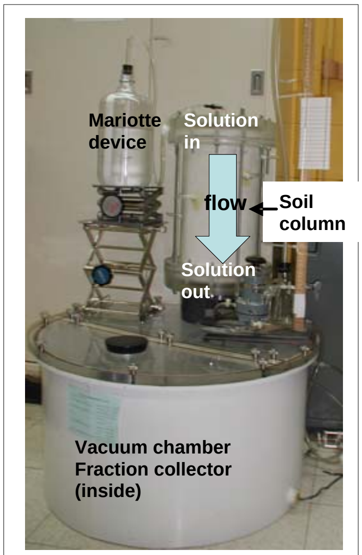


Fig. 29. Experimental configuration of flow experiments.

In order to reproduce these scenarios in the laboratory, experiments will be conducted under saturated (water + soil) and unsaturated (water + air + soil) conditions (Fig. 29) on intact soil samples (Figs. 3-5). Intact soil samples retain features that might contribute to preferential flow through the vadose zone and lead to aquifer contamination, such as fractures, macropores, root traces, and worm burrows. The soil columns will be affixed with a porous glass frit at the top and bottom in order to control the degree of saturation, i.e., water content, inside the cores (Mayes et al. 2003). A pump or Mariotte device will be attached to the upper boundary to supply solution at a steady rate "Solution in" . A fraction collector will be emplaced at the bottom to collect solutions eluted from the cores "Solution out". Under unsaturated conditions, a vacuum chamber containing a fraction collector will be affixed at the lower boundary in order to apply suction and induce the migration of air into the columns "Vacuum chamber".

Suspensions of Composition B particles will be applied to the soil columns under saturated conditions to simulate particle dissolution and transport under storm-flow scenarios. These experiments will be compared with those in duplicate columns in which dissolved TNT/RDX/HMX solutions are applied, in order to determine the rates of transport and reaction for dissolved versus particulate Composition B. Under saturated conditions, when these types of macropores are most conductive, soils will be most capable of transmitting contaminants into underlying aquifers.

If mobility is observed in the saturated flow experiments, a complete second set of experiments will be conducted under partially saturated conditions, in which the most conductive macropores will become air-filled and will not contribute to preferential transport of contaminants. These experiments represent typical vadose zone conditions. The effluent solutions will be collected and analyzed as a function of time (e.g., Fig. 8-10). All effluents will be monitored for three different size fractions: particulate (>0.45 µm), colloidal (0.45 µm-2 nm), and dissolved (< 2 nm) fractions (e.g., Fig. 7). Additionally, major anions and cations, pH, and total OC will be monitored. In all cases, nonreactive tracer (Br) will be applied simultaneously with the leaching solutions in order to determine the basic hydraulic parameters governing transport, i.e., dispersivity. In the experiments, the elution of the nonreactive tracer will be compared with that of the reactive tracers, i.e., MC, in order to determine the degree of chemical reactivity of the MC. Each applied solution will be similar in pH as the native soil in order to isolate chemical reactivity of the MC compounds.

Following completion of the experiments, the columns will be flash-frozen and sectioned as a function of depth to determine the extent of mobility of MC particles and dissolved phase using spectroscopic methods (Fig. 28) and/or bulk extractions (Fig. 11). This set of experiments will determine the extent of mobility of particulate and dissolved-phase MC in intact soil columns from the various operational ranges.

FTIR Spectromicroscopy of Comp-B in Column Experiments

Preliminary studies have shown that DNT particles can be detected in soils when loaded at 1% DTN (by weight) (Fig. 28). However, the FTIR signal observed for DNT (mixed with soil) in preliminary experiments was not sufficient to differentiate particulate from dissolved/sorbed DNT using traditional methods (i.e measuring changes in peak position and shape). Even though FTIR spectromicroscopy could not be used to determine DNT binding complexes in soil in preliminary experiments, detection of DNT particles was possible because they were present as ‘hot spots’ in FTIR maps. The presence of DNT ‘hot spots’ allowed detection of DNT in samples with low bulk DNT concentrations because the ‘hot spots’ represented a locally high concentration of DNT. Based on these preliminary results and the work done by Schafer et al (2007), we predict that when Comp-B is present in particulate form, it (specifically TNT within Comp-B particles) will also be detectable when present in future experiments.

The feasibility of detecting Comp-B particles via FTIR spectromicroscopy in future soil transport studies will be tested in two experiments. Initially, a dispersion containing only Comp-B particles will be dried on an aluminum-coated microscope slide at room temperature, and analyzed by FTIR spectromicroscopy to determine the ability of this technique to detect pristine Comp-B particles to be used in future column experiments. If Comp-B particles from the pure dispersion are detectable using FTIR spectromicroscopy, a second feasibility study will be conducted. In this study, surface soil from a column study (representing the highest potential concentration of Comp-B particles in future column experiments) will be analyzed by FTIR spectromicroscopy to determine this techniques’ ability to detect Comp-B particles in soils. If the second feasibility study shows that Comp-B particles can be detected in soils by FTIR spectromicroscopy, this technique will be used in future column studies to differentiate movement of particulate Comp-B from movement of dissolved Comp-B in soil column studies.

Multiscale Modeling

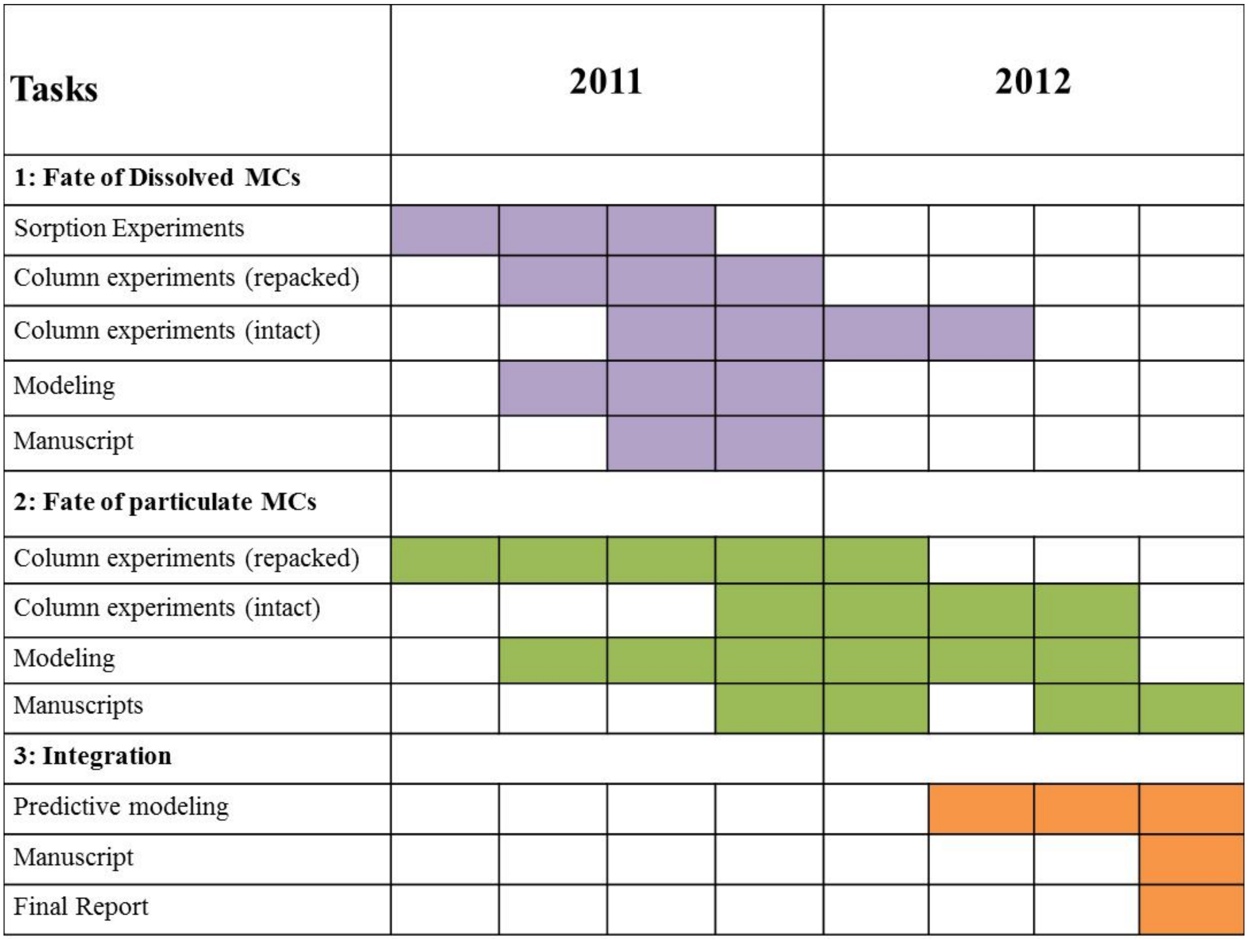
We will compare our sorption batch experiment results with those in the literature (Ainsworth et al. 1993) and revise sorption models. The revised sorption models will be incorporated into our dissolution, particle and solute transport models to describe repacked and intact column experimental data, quantify the processes, and evaluate the role of particle transport. The dual continuum model will also be tested to evaluate the influence of preferential flow on residue transport, particularly, for intact cores.

If the dual continuum model is not sufficient to describe accelerated particle transport, or size exclusion is found to be very important, we will implement size-dependent velocity in the particle transport model. Should particle transport in unsaturated experiments be found to be significant, we will add the trapping of particles by the air-water interface into the transport model. As our coupled models have many parameters to describe multiple processes, and significant uncertainty exists in some of the parameters, sensitivity and uncertainty analysis will be conducted for experiment design and reliable quantification (Tang et al., 2009).

Ultimately, we will integrate and generalize our findings and parameter estimates to build models to assess potential contamination at operational ranges based on existing site characterization. Based on our analysis and ranking of contamination susceptibility of various operational ranges using soil characteristics from the NRCS database, we will select a number of bases representative of low to high susceptibility for scoping our evaluation of potential munitions contamination. We will use our coupled process models to conduct preliminary simulations for the selected sites with a range of recharge, depth to ground water table/vadose zone thickness, permeability, soil characteristics, etc., to examine how these processes influence mobility and attenuation on different operational range conditions. One-dimensional saturated and unsaturated flow and transport models will be used to approximate potential migration through the vadose zone, and into the aquifer. These results will quantitatively indicate the implications of deposition of explosive residues at many operational ranges.

As extensive characterization and groundwater modeling research have been conducted for contaminant fate and transport studies at MMR, we will conduct a case modeling study of the MMR site to evaluate the coupled dissolution, particle and solute transport. The long-term monitoring and subsurface characterizations data, and previous models will be used to develop coupled hydrological and geochemical models to predict the concentration, and onsite and offsite migration. The widely used groundwater flow, and reactive transport codes (MODFLOW, MT3DMS, and PHT3D) will be used to solve the flow, transport, and reaction equations.

GANTT CHART



Tasks	2011				2012			
1: Fate of Dissolved MCs								
Sorption Experiments	🟪	🟪	🟪					
Column experiments (repacked)		🟪	🟪	🟪				
Column experiments (intact)			🟪	🟪	🟪	🟪		
Modeling		🟪	🟪	🟪				
Manuscript			🟪	🟪				
2: Fate of particulate MCs								
Column experiments (repacked)	🟩	🟩	🟩	🟩	🟩			
Column experiments (intact)				🟩	🟩	🟩	🟩	
Modeling		🟩	🟩	🟩	🟩	🟩	🟩	
Manuscripts				🟩	🟩		🟩	🟩
3: Integration								
Predictive modeling						🟧	🟧	🟧
Manuscript								🟧
Final Report								🟧

MILESTONES

(complete = green; in progress = orange; incomplete = black; change in scope = purple)

Year 1

- Initial coordination and planning meeting with all ERSON 4 projects and SERDP Program Office
- Monthly Financial Reports (MFR)
- Quarterly Progress Report (QPR)
- Attend SERDP/ESTCP annual meetings
- Collect or receive MC colloids and/or MC-contaminated soil samples
- Microscopic analysis of MC-contaminated soil samples
    - This effort appears to be unsuccessful and we have changed scope to pursue FTIR and other methods with new collaborators (US ACE EDRC)
- Collect uncontaminated samples from Site 1
- Conduct batch experiments and preliminary geochemical modeling, Site 1
- Begin saturated flow experiments using dissolved MC and MC colloids, Site 1
    - Note, first round of experiments used Ottawa sand =Site 1

Year 2

- Monthly Financial Reports (MFR)
- Quarterly Progress Report (QPR)
- Interim Report
- Attend SERDP/ESTCP annual meetings
- Submit results of microscopic analysis of MC-colloids to peer-reviewed journal
  - This effort appears to be unsuccessful and we have changed scope to pursue FTIR and other methods with new collaborators (US ACE ERDC)
- Begin unsaturated flow experiments, Site 1 (no unsaturated experiments on Ottawa sand)
- Disassemble columns, analyze soil for particle transport, and complete transport modeling of column experiments, Site 1
  - Note, first round of experiments used Ottawa sand rather than Site 1
- Realistic simulations of MC transport through the subsurface, Site 1
- Collect uncontaminated intact soil samples, Sites 2-4
- Batch experiments and preliminary geochemical modeling, Sites 2-4
- Begin saturated flow experiments, Sites 2-4

Year 3

- Monthly Financial Reports (MFR)
- Quarterly Progress Report (QPR)
- Attend SERDP/ESTCP annual meeting
- Final Technical Report
- Unsaturated flow experiments, Sites 2-4
- Disassemble columns, analyze soil for particle transport, and complete transport modeling of column experiments, Sites 2-4
- Realistic simulations of MC transport through the subsurface, Sites 2-4
- Submit results of column experiments and hydrological modeling to peer-reviewed journal
  - First paper on test column experiments was submitted May 2011

PUBLICATIONS

Journal Submissions (in review, in press and published)

Lavoie, B., Mayes, M.A., and McKay, L.D. Transport of explosive residue surrogates in saturated porous media. In review with Water, Air, and Soil Pollution, May 2011. Revision in progress, August 2011.

Presentations

Sharma, P., Mayes, M.A., and Tang, G. 2011. Geochemical controls on sorption and transport of nitroaromatic compounds (TNT and RDX) in soils from Massachusetts Military Range. American Geophysical Union Fall Meeting, December 1-5, San Francisco, CA.

Sharma, P., Mayes, M.A., and Tang, G. 2011. Geochemical controls on sorption and transport of nitroaromatic compounds (TNT and RDX) in soils from Massachusetts Military Range. Partners in Environmental Technology Technical Symposium and Workshop, November 29-December 1, Washington, D.C.

Tang, G., Mayes, M.A., Sharma, P., Lavoie, B., and McKay, L.D. 2010. Modeling coupled dissolution, solute, and particle transport of explosive residue in saturated porous media. Partners in Environmental Technology Technical Symposium and Workshop, November 29-December 1, Washington, D.C.

Lavoie, B., Mayes, M.A., and McKay, L.D. 2011. Mobility of Particulate and Dissolved Munitions Constituents in the Vadose Zone at Operational Ranges. Tennessee Water Resources Symposium, April 11-13, Burns, TN.

Mayes, M.A., McKay, L.D., and Lavoie, B. 2010. Mobility of particulate and dissolved munitions constituents in the vadose zone at operational ranges. Partners in Environmental Technology Technical Symposium and Workshop, November 29 - December 1, Washington, D.C.

Lavoie, B., Minkin, Jr., S., Mayes, M.A., Biggerstaff, J., McKay, L.D., and Perfect, E. 2010. Transport of dissolved and particulate explosives compounds in saturated flow column experiments. Joint Meeting of the Southeastern and Northeastern Sections of the Geological Society of America, March 14-16, Baltimore, MD.

Mayes, M.A., McKay, L.D., Biggerstaff, J.B., Zhang, F., Minkin, S., Lavoie, B., and Koehn, K. 2009. Mobility of particulate and dissolved munitions constituents in the vadose zone at operational ranges. Partners in Environmental Technology Technical Symposium and Workshop, December 1-3, Washington, D.C.

Journal Submissions (in preparation)

Sharma, P., Mayes, M.A., Tang, G. Geochemical controls on fate of dissolved MCs in soils from operational ranges. To be submitted to Env. Science and Technology by the end of Oct 2011.

Tang, G., Mayes. M. A., Sharma, P, and Lavoie B. 2011 Modeling dissolution, particle, and solute transport of explosive residue in saturated porous media. Advances in Water Resources. To be submitted by Dec. 1, 2011.

Sharma, P., Tang, G., Mayes, M.A. Geochemical controls on transport of Composition B residues in soils from operational ranges. To be submitted by end of February 2012.

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