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Effective elution of RDX and TNT from particles of Comp B in surface soil

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Abstract

During live fire training exercises, large amounts of explosives are consumed. Low order detonations of high explosive payloads result in the patchy dispersal of particles of high explosive formulations over large areas of firing range soils. Dissolution of explosives from explosive formulation particles into soil pore water is a controlling factor for transport, fate, and effects of explosive compounds. We developed an empirical method to evaluate soils based on functionally defined effective dissolution rates. An automated Accelerated Solvent Extractor was used to determine the effective elution rates under controlled conditions of RDX and TNT from soil columns containing particles of Comp B. Contrived soils containing selected soil geosorbants and reactive surfaces were used to quantitatively determine the importance of these materials. Natural soils from training ranges of various soil types were also evaluated. The effects of geosorbants on effective elution rates were compound- and sorbent-specific. TNT elution was less than that of RDX and was greatly slowed by humic acid. Iron and iron-bearing clays reduced the effective elution rates of both RDX and TNT. This empirical method is a useful tool for directly generating data on the potential for explosives to leach from firing range soils, to identify general bulk soil characteristics that can be used to predict the potential, and to identify means to engineer soil treatments to mitigate potential transport. Published by Elsevier Ltd.

Keywords: Particle; Dissolution; Explosive; Transport

1. Introduction

Live fire training exercises are essential for maintaining the readiness of military forces (U.S. Army Training Support Center, 2003). During these exercises large amounts of explosives are consumed. For example the 155 mm M107 howitzer high explosive (HE) round contains 12 kg hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2.7 kg 2,4,6-trinitrotoluene (TNT) and 0.7 kg wax (MIDAS, 2005). High explosive detonation reactions are typically very complete, and the levels of chemical by-products produced are minimal. Duds, complete detonation failures, are usually detonated in place using plastic explosives by range safety teams. Additionally, low order detonations of the high explosive payloads result in the patchy dispersal of particles of high explosive formulation over large areas of firing range soils (Radtke et al., 2002). Where present the median size of HE particles on firing range soils is of order 1 mm (Jenkins et al., 1998; Taylor et al., 2004).

The United States Environmental Protection Agency (EPA) has estimated that the Department of Defense (DOD) has between 5000 and 8000 firing ranges containing explosive contaminants (Williams, 2000). Two hundred of these are large ranges that contain explosive contaminants that potentially threaten the environment. Today military training ranges present an interesting paradox. While their primary mission remains troop training, commanders must also manage bases as important biological habitat islands. Population growth and urban sprawl at the perimeters of previously remote bases has concentrated threatened and endangered species into firing ranges and the actively

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secured buffer zones around these ranges. These natural resource islands are viewed as highly prized national assets by conservation organizations that would like to use them as seed populations for their habitat restoration efforts (Nature Conservancy, 2006). In this context the ecological importance of mitigation of chemical contaminants generated by military training exercises is clear. Striking the appropriate balance between the need to train troops and environmental stewardship requires accurate information on the ecological and environmental risks posed by these particles of explosive formulations on firing ranges.

These environmental issues have focused attention and concern on the sustainability of military training ranges. Initial models of environmental transport and fate (Parkhurst and Appelo, 1999) have been used to assess environmental risk. Dissolution of explosives from formulation particles into soil water is a critical step in this process. It determines explosive toxicological exposure, binding to geosorbants, and extent of biodegradation that in turn determines surface and subsurface transport. Actual rates of dissolution continue to be a large source of uncertainty in these models.

The relatively high surface to volume ratio of small (1 mm) explosive particles favors rapid dissolution. The initial mathematical descriptions of the soil source terms for these models are based on idealized dissolution rates (Lynch et al., 2002). These descriptions are based on the dissolution of pure solid materials and require much information, such as the area of water-wettable surface. The wettability of a particle depends upon many factors (Ellerbrock et al., 2005), including hydrophobicity. However, it is very difficult to determine even the fraction of the particle surface area that can be in contact with soil pore water. Other factors also make it very difficult to apply classical dissolution kinetics to the description of a particle of explosive formulation sitting in a surface soil. Explosive formulations are comprised of at least two explosive chemicals, most often as particles coated with binders such as wax or as polyvinyl chloride. For example, the commonly used formulation Comp B is comprised of RDX (60%), TNT (39%) and wax (1%), while plastic explosive (C4) is comprised of RDX (91%) and non-explosive plasticizer (9%) (Pennington et al., 2005).

Climate and soil types are also important variables in determining dissolution, transport, and fate of explosives in soil. The Fort Irwin National Training Center is located approximately 37 miles northeast of Barstow, California in the High Mojave Desert, midway between Las Vegas, Nevada and San Bernardino, California. The primary soil material is sand. Precipitation ranges from 50 to 100 mm a year. In contrast, the clayey sand of Fort Polk, Louisiana, located in the Lower West Gulf Coastal Plain eco-region, has an average annual rainfall of 1270 mm, whereas at the former Nebraska Ordnance Plant, located approximately 35 miles northeast of Lincoln, Nebraska, the soil is silty and the annual rainfall is 700 mm. Geosorbants and reactive minerals in these different soils are known to greatly affect the fate of explosives in soils (Szecsody et al., 2004).

In soil matrices the effects on dissolution of contact area and wettability cannot be separated from the effects of pore size and water transport. When combined, these effects yield the effective elution rate of particles in surface soil measured using the procedures described. In this approach the particles and the soils in which the particles are lodged modify the dissolution source terms to be used in models.

The theory of dissolution kinetics is highly developed (Cussler, 1997; Dali and Carstensen, 1998) but simple models do not capture the complexity of dissolution in soil, and detailed models have an unwieldy number of parameters. For instance, the effective specific area of each size fraction can be further described in terms of geometrical factors, roughness factors, and wettability factors. All of these parameters are variable initially, and change rather dramatically with time in realistic situations (Fig. 1).

Phelan et al. (2003) simulated larger soil columns with glass beads and larger amounts of explosives in low flow conditions. Hewitt and Bigl (2005) also used larger columns and low flow, similar to expected flow in groundwater after dissolution. However, the flow during actual dissolution at the higher rates in fully saturated wet surface conditions during rain fall can be quite different than such leisurely seepage. Our ultimate objective is to understand the factors controlling the dissolution of actual residues of high explosive formulations and their transport through real soils. Once the contaminant is fully dissolved, many

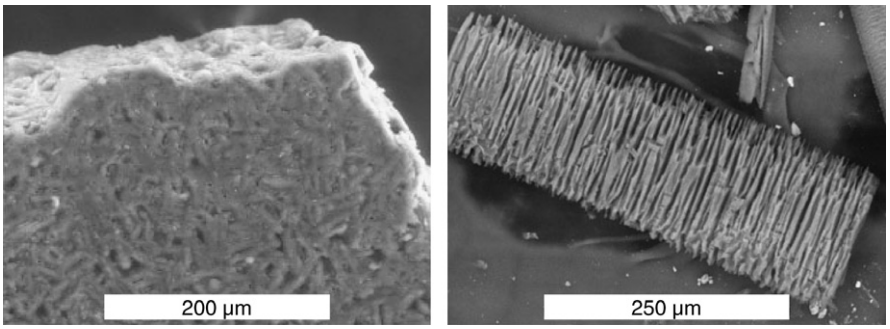

Fig. 1. Illustrating the complex initial and evolving surface areas in explosive particle 2 dissolution. Left: Comp B particle freshly cleaved. Right: TNT particle after 10 min 3 dissolution in water and sand.

water transport models can adequately model transport through any given soil. However, in longer soil columns that are operated for many days at low flow rates the effects of absorption, transformation, and biological and chemical degradation can mask the effects of the soil matrices on dissolution.

An accelerated solvent extractor (ASE; Dionex, Sunnyvale, CA) was used to determine the overall effective elution of the explosive particles. Such overall effective rates of dissolution and leaching are most important for determining the effective availability of contaminants (Crundwell, 2001; Szolar et al., 2004). The short soil columns used in the ASE cells was suggested to provide quick relative comparisons on effective elution rates of different particles in and on different soils.

2. Materials and methods

2.1. Soils

Surface soils were obtained from Fort Irwin, CA (March 2004), the Nebraska Ordnance Plant (June 2002), and Ft. Polk, LA (July 2003). Surface soils were passed dry through a 2 mm sieve. All soils were stored at 4 °C and homogenized before use. Soils were physically mixed until the levels of explosives in subsamples produced a standard error of less than 5%. Characteristics of these are given in Table 1, where C.E.C is cation exchange capacity in milliequivalents per 100 g. Fort Irwin soil was collected from the center of a mortar crater and next to a low-order detonation. The Nebraska Ordnance Plant soil is from an area of the plant historically used for disposal and testing. Ft. Polk is located 100 km north of Lake Charles, LA, and the soil sampled was from a grenade range with primary explosive contaminant Comp B. Biologically active garden soil (50/50 vol/vol sand with MiracleGro All Purpose Potting Mix) was added in some experiments. Soil characterization analyses were performed by A&L Analytical Laboratories Inc. (Memphis, TN).

Table 1
Characteristics of training range soils

Soil Characteristic	Ft. Irwin	NOP	Ft. Polk
Soil pH	4.6	5.3	8.0
Clay %	<0.1	27.5	14.3
Sand %	100	40.0	82.9
Silt %	<0.1	32.5	2.9
TOC %	0.2	1.1	0.4
C.E.C. (meq per 100 g)	0.2	33.2	<0.1
Mean (standard deviation)			
Explosives (mg kg^{-1})	Ft. Irwin	NOP	Ft. Polk
TNT	446 (53)	19(1)	287(21)
RDX	<1 (<1)	223 (39)	454 (42)

The Ft. Irwin soil was from a months-old TNT mortar crater. The Nebraska Ordnance Plant (NOP) soil was from a decades old Comp B site, and the Ft. Polk soil was from a historically used grenade range.

2.2. Chemicals

Water used in this study was distilled deionized water and subsequently run through a Milli-Q (Waters) purification system. Methanol was GC quality and purchased from Burdick and Jackson (Muskegon, MI). TNT and RDX analytical standards were purchased from Ultra Scientific (North Kingstown, RI). Military grade Comp B was obtained from the Picatinny Arsenal (NJ). Clays were obtained from the Clay Minerals Society (Purdue University, West Lafayette, IN). Activated carbon (60/80 mesh) was obtained from Calgon Carbon Corporation (Pittsburgh, PA). Humic acid, manganese (IV) oxide, and iron (II, III) oxide powders (60/80 mesh) were obtained from Sigma–Aldrich (St. Louis, MO). Ottawa sand (20/30 mesh) from Fisher Scientific (Fairlawn, NJ) was further prepared by rinsing with water and autoclaving. Purified TNT linear crystals (99% purity) with sizes from 100 μm to over 1 mm were obtained by recrystallization from saturated acetone solution. Purified oblong RDX crystals (99% purity) with sizes of order 100 μm were obtained by recrystallization from saturated ethanol solution. Comp B particles were obtained by cleaving larger chunks at room temperature and hand-picking fragments with a size of order 1 mm.

2.3. Determination of dissolution rates

Triplicate dissolution rate measurements were carried out using test tubes containing 10 ml Milli-Q water. The explosive particles were weighed and placed into the test tube containing the 10 ml water and immediately mixed on a vortex mixer for 1 min. The solution was centrifuged for 70 s at 2000 rpm. A sample of 1 ml was pipetted out of the center of the test tube 3 min after being mixed with a vortex mixer and filtered through a 0.45 μm syringe filter from Lab Source into a 2.0 ml amber HPLC vial. The solution was immediately diluted with an equal volume of methanol and capped for analysis. As soon as the 1 ml sample was withdrawn from the test tube, a stopwatch was started and for one run the sampling procedure was repeated to yield six time points of 1, 3, 6, 10, 20, and 30 min. The rates were calculated assuming first order kinetics (Cussler, 1997). The larger undissolved TNT and Comp B particles were retrieved after these experiments and reused.

2.4. Determination of effective elution rates

An Accelerated Solvent Extractor (ASE; Dionex, Sunnyvale, CA) was used to determine the effective elution of the explosive particles. Triplicate experiments were performed at room temperature with no heating of the sample, pressure equaling 500 psi, with a 1 min ASE static and purge time, involving 1 cycle, and 100% Milli-Q water only (no organic solvent). Baseline conditions were established using ASE cells filled with 100% Ottawa sand.

Each clean ASE cell was assembled and bottom-fitted with a 2.0 cm circular glass microfiber filter from Whatman. The cell was filled with 5 g sand on bottom, and 3 g of sample material and any explosive particles were weighed and placed atop the homogenized sample material. An additional 3 g of sand was added on top. The cell was then placed onto the ASE and a sequence was run involving the above-described method with a water rinse before and after each cycle. The sequence was carried out using several 40 ml clear collection vials for each single cell. The times were recorded as the time at which the ASE needle withdrew from the collection vial.

As soon as the needle withdrew from one collection vial, the stopwatch for the next sample was started. In all cases, as soon as the needle left the collection vial the vial was removed, the volume of the extract measured, a 1.0 ml aliquot was taken from the vial, filtered through a 0.45 μm syringe filter, and 0.5 ml of the filtrate was cut 50/50 with methanol for HPLC analysis. The rates were calculated assuming first order kinetics.

2.5. Explosives analysis

Explosives were analyzed using a high pressure liquid chromatography (HPLC) by modified EPA Method 8330 (U.S.E.P.A., 2000). The instrument was an Agilent 1100 Series HPLC (Palo Alto, CA) equipped with a quaternary pump, autosampler with a 200 μl loop injector, diode array UV absorbance detector, and a column oven. An Agilent LC-18 reverse-phase HPLC column (100 cm × 4.6 mm × 5 μm) was used as the primary column, along with a Hypersil ODS C-18 pre-column. The system was operated at 39 °C and at a flow rate of 1.5 ml min^{-1} with 68% of the mobile phase consisting of 20 mM NH_4CL and 32% consisting of a methanol/butanol mixture (98:2 v/v). Peaks were measured at 254 nm. The calibration curves of all explosives were linear between 0.1 and 50 mg l^{-1}, with limits of detection 0.05 mg l^{-1} for RDX and 0.04 mg l^{-1} for TNT. Each sample of triplicate experiments was measured singly.

2.6. Surface area analysis

The low-temperature nitrogen adsorption surface areas of aliquots of 0.2 g of explosive particles were determined in triplicate via N_2 adsorption Brunauer, Emmett, and Teller (BET) isotherms using a Quantachrome NOVA 4000e high speed surface analyzer. The particles were placed in a desiccator at room temperature for 1 day. Then they were exposed to vacuum at room temperature overnight, prior to nitrogen adsorption measurements as per manufacturer's instructions. (It should be noted that water-wettable surface areas are not obtainable through conventional surface area measurements.) Confirmatory Kr adsorption BET isotherms on one 0.2 g aliquot each of TNT and RDX were performed by Porous Materials Inc. (Ithaca, NY).

3. Results

The results of our most controlled studies are presented first, followed by experiments on increasingly complex, more environmentally-relevant systems and mixtures. Rates of dissolution of pure compounds in idealized systems are followed by those of explosive formulations in increasingly complex soil and water systems. The effects of successively more complex systems on measured effective elution rates provides a means to determine which physical and chemical environmental variables have the largest impacts on the transport of explosives through soils.

The rates of TNT and RDX dissolution in water at 27 °C under idealized conditions were predicted using Lynch et al. (2002) from N_2 exposed surface areas and compared to those we measured in continuously mixed, simple test tube systems (Table 2). The predicted rate of pure TNT dissolution was 3.4 times faster than the measured rate, and the predicted rate for pure RDX was 4.2 times faster than the measured rate.

The rates of dissolution of TNT and RDX from Comp B formulation in the completely mixed test tube systems were generally comparable to those of the pure compounds in the same system (Table 2). Little effect of the binding material was observed on these initial dissolution rates.

We then compared the rates of TNT and RDX dissolution from Comp B particles in completely mixed test tube systems to those measured when Comp B was placed in simple Ottawa sand ASE elution columns (Fig. 2). By reusing larger particles of sizes 1–3 mm, the actual rates of dissolution in pure water of multiple individual particles with various surface areas can be compared to the rates of dis-

Table 2
Surface areas of explosive particles as measured by the N_2 adsorption method (mean and standard deviation; $n = 3$) and measured water solubility of TNT and RDX at 27 °C ($n = 3$)

	TNT	RDX	Comp B	
Nitrogen surface area ($cm^2\ g^{-1}$)	690 (380)	4100 (1200)	220 (40)	
Aqueous solubility (mg l^{-1})	210 (4)	56 (2)		
Dissolution rate (mg $cm^{-2}\ s^{-1}$)	TNT	RDX	Comp B TNT	Comp B RDX
Predicted[a]	2.3E−04	5.0E−05	–	–
Measured mean	6.8E−05	1.2E−05	4.3E−05	3.6E−05
Standard deviation	1.4E−05	1.5E−06	2.0E−05	2.0E−05

[a] Lynch et al. (2002).

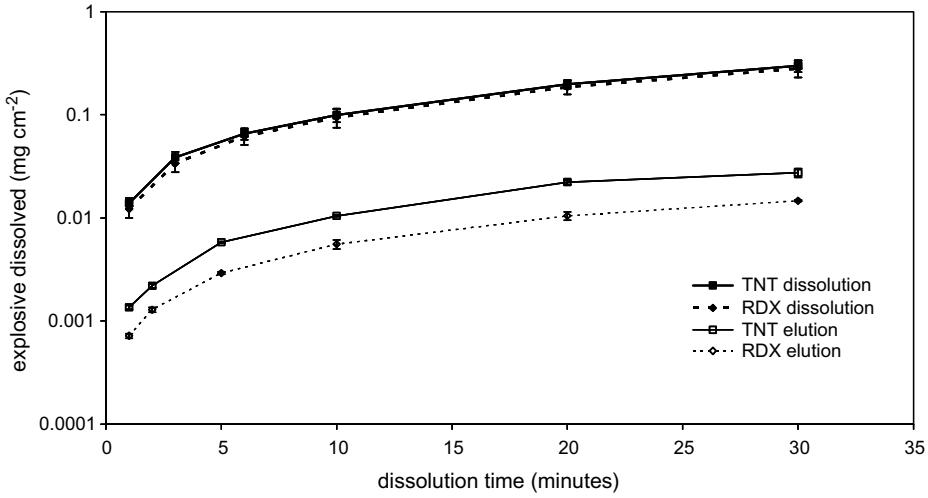

Fig. 2. Effects of ASE elution in saturated sand compared to dissolution in water, for 2 single runs of one set of Comp B particles, reusing the same particles for the elution as 3 for the dissolution. The measured concentrations in the aqueous solutions are normalized 4 by aqueous volume and initial particle area.

solution when in contact with soil particles. The fastest rates of TNT and RDX dissolution were measured in completely mixed, water-only systems (top curves in Fig. 2) after dissolving for several lengths of time. Placing these same Comp B particles in Ottawa sand and eluting with water at corresponding lengths of time slowed the measured rates of TNT and RDX dissolution (hereafter referred to as effective elution rates) by one or more orders of magnitude compared to water-only systems. Less than 10% of the mass of the smallest of these particles was dissolved during these experiments. In only these experiments the ASE static time varied from 1 min up to 30 min; in all other ASE elutions the static time was 1 min.

Next, we examined the composition of contrived soils placed in the ASE column on the effective elution rates of TNT and RDX. The effective elution rates of TNT and RDX from Comp B particles that were allowed to stand in water-saturated sand for 1 min between column purges were compared to the rates of elution of the same particles in sand mixed with various amendments. The relative effective elution rates of TNT and RDX from soil columns containing sorptive and potentially reactive amendments are shown in Fig. 3. These effective elution rates are normalized to those from pure Ottawa sand columns.

The effect of the additions of organic and inorganic sorptive amendments to the Ottawa sand columns varied greatly. The addition of 10% (vol/vol) activated carbon to Ottawa sand reduced the effective elution rate of RDX by 80%, and that of TNT by 90% relative to pure Ottawa sand. The addition of 10% humic acid (vol/vol) to Ottawa sand did not affect significantly the elution of RDX from the column but almost completely prevented TNT from eluting. The high surface area of the non-swelling kaolin clay could be expected to adsorb explosives and thus retard explosive elution from the Ottawa sand columns. However, 10% (vol/vol) kaolin clay had no effect on the mean relative

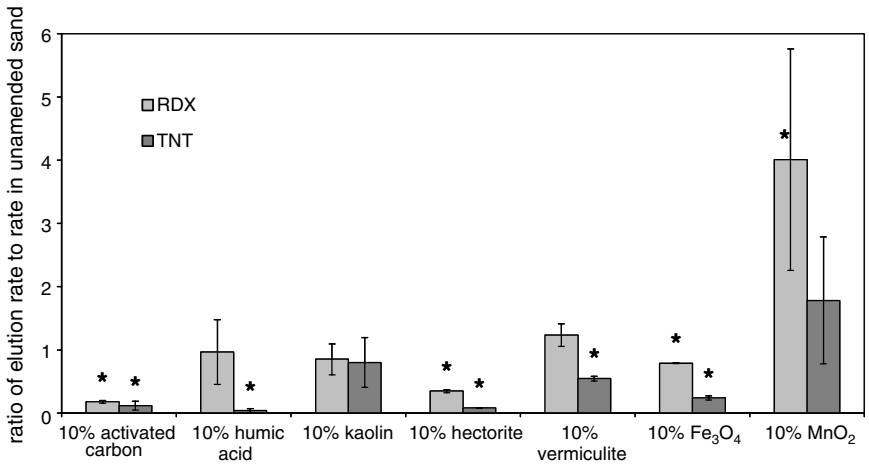

Fig. 3. Effects of geosorbants and reactive minerals on the elution of RDX and TNT 2 derived from solid Comp B particles through contrived soils in ASE cells. The 3 comparison is made to the same particles in Ottawa sand. Error bars shown are ±1 4 standard deviation, with $n = 3$.

elution of either TNT or RDX in the short soil columns used. Hectorite clay at 10% (vol/vol) reduced the effective elution of RDX by approximately 60% and TNT by approximately 90%. Vermiculite at 10% by volume reduced TNT elution by approximately 50%, with no mean effect on RDX elution.

Two common soil metal minerals had very different effects on effective elution rates of TNT and RDX. Iron oxide at 10% by volume reduced the effective elution rate of RDX by approximately 25%, and reduced TNT by 80%. In contrast, manganese oxide at 10% by volume increased the mean effective elution rate of RDX by approximately 400%, with no statistically significant effect on TNT elution. The iron oxide had highly reproducible effects. Although the effect of iron oxide may be related to adsorption of explosive compounds from the soil pore water, it is difficult to ascribe the effect of the manganese oxide to compounds already dissolved: the manganese oxide must be directly affecting the particles of Comp B (Table 3).

Additional kinetics experiments were conducted to compare rates of dissolution under two different environmentally relevant water transport regimes in the soil columns. We assume one rate of dissolution, K, occurred when an explosive particle is at rest in moist but unsaturated soil and chemical transport from the particle is diffusion limited. A second rate of dissolution, k, occurred during the 1 min ASE static time when water was being flushed into and through the saturated soil column and dissolved explosives were being advectively mixed. For a first order process starting from mass m_1, the mass m_2 remaining after both the diffusive (T) and advective (Δt) mixing periods is given by the two parameter model

$$m_2 = m_1 \cdot \exp(-KT - k\Delta t)$$

The results of a two parameter fit for a Ft. Polk run and for runs of TNT particles in sand and garden soil mix are presented in Table 4. The calculated explosives dissolution rates during unsaturated periods of diffusive mixing are smaller by orders of magnitude than explosives dissolution rates during saturated periods of advective mixing, for both larger TNT particles and smaller Comp B particles. The frequency and duration of rain storms and the hydraulic conductivity of a soil will significantly affect source terms for explosives transport through training range soils.

Table 3
The relative rates of elution of TNT and RDX from range soils

	Ft. Irwin	NOP	Ft. Polk
Initial elution rate (pg per minute)			
Mean TNT	14.7	1.0	71.5
Standard deviation TNT	8.2	0.5	23.3
Mean RDX		35.5	53.1
Standard deviation RDX	–	24.7	34.5
Fractional elution rate (% per minute)			
Mean TNT	1.1	1.8	8.3
Standard deviation TNT	0.4	0.7	2.0
Mean RDX		5.3	3.9
Standard deviation RDX		2.2	1.8

The initial elution rate is the first time point. The % results are reported relative to the remaining concentrations in the soils, continued for the series of time points.

Table 4
The results of a 2 parameter fit for ASE runs of TNT particles in sand and garden soil mix, and for a Ft. Polk ASE run

	Sand TNT	Soil TNT	Ft. Polk TNT	Ft. Polk RDX
k (% per minute)	0.92	0.55	8.1	2.5
K (% per minute)	0.0081	0.0012	0.0	0.0
r^2	0.994	0.992	0.989	0.993

The r^2 is the usual correlation fit factor. The Ft. Polk soil was fit well by a one-parameter model.

4. Discussion

Source terms used for current explosives transport and fate models are based on idealized dissolution kinetics. In accord with Phelan et al. (2003), Hewitt and Bigl (2005), and Jenkins et al. (2005), we found that source terms based on idealized dissolution models can grossly overestimate transport of explosive contaminants through soils. This bias occurs even though the concentrations in the soil water were much below the solubility limit. These models can overestimate by orders of magnitude the dose of explosives likely to be experienced by an ecological receptor as well as underestimate the time scales of the residual pool of explosive contaminants accumulating on active training ranges.

Military training ranges are located in different ecoregions and exercises are conducted on soils of diverse compositions. The three soils reported here reflect some of this diversity. As expected the levels of high explosives in these soils was highly variable and depended on the locations from which the samples were collected. Of these explosives the Ft. Irwin soil contained only TNT, the NOP soil contained mainly RDX and the Ft. Polk soil contained both TNT and RDX.

We measured the elution of explosives from particles in ASE cells under varying flow conditions, and found that the major dissolution occurred during saturated conditions. We did not find that disturbance of the soil made an initial burst of dissolution, although sampling and handling may have enabled more explosives to be transported. Homogenization in particular may have made more explosives uniformly accessible to water. In accord with Dann et al. (2006), we found that site-specific characteristics are important in determining explosives elution behavior and no current single particle mathematical model can predict this behavior with sufficient accuracy.

The measured BET adsorption isotherm specific surface areas of the explosive particles given in Table 2 are orders of magnitude larger than the geometric areas visually estimated by Lynch et al. (2002). Dissolution models based upon those smaller estimated results have not been shown

to extrapolate several orders of magnitude. The surface area of interest for dissolution is the water-wettable surface. The BET specific surface area can be expected to be larger than the water-wettable specific surface area, but even for cleanly prepared Comp B the actual surface area is much greater than the visually estimated geometric area. Thus, neither the BET area nor the visual geometric area is a valid estimator of the area to be used in particle dissolution modeling, and the effective use of particle dissolution models requires source terms that depend on other factors including soil properties.

Thus, the idealized rates of dissolution measured by Lynch et al. (2002) can only be applied in soil models with caution.

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