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Solubility and Dissolution Kinetics of Composition B Explosive in Water

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Abstract

High order detonation of military ordnance can deposit trace residues of explosive chemical constituents on or in surface soil. Low order detonations can disperse distinct solid phase energetic material as fine particulates to large masses. Mass transfer of solid phase energetics to soil pore water is being evaluated to assess environmental impacts to soil and groundwater. This report documents measurements of solubility and dissolution kinetics of Composition B (60% RDX/40% TNT) in water. The solubility of RDX and TNT were determined at environmentally relevant temperatures (7 to 40 °C) in both deionized and tap water. Demilitarized Composition B explosive was cracked and sieved to produce discrete size fractions simulating low order detonation debris for use in dissolution kinetics experiments. The kinetics of dissolution were determined in an unconstrained dissolution process where the solution concentrations were below solubility maxima. Dissolution rates were derived from solution concentration and calculated particle surface area changes over time.

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Contents

1.0 Introduction 6

2.0 Composition B Preparation 7
2.1 Source Material 7
2.2 Size Separates 7
2.3 BET Surface Area 8

3.0 Solubility vs. Temperature 10
3.1 Background 10
3.2 Methods and Materials 10
3.3 Results and Discussion 11

4.0 Solubility Kinetics 15
4.1 Methods and Materials 15
4.2 Results and Discussion 15
4.2.1 Dissolution Results 15
4.2.2 Derived Dissolution Flux 16

5.0 Summary 20

References 21

List of Figures

Figure 1. Composition B Starting Material 7
Figure 2. SEM Photograph of 500 to 600 µm Size Fraction 9
Figure 3. RDX Solubility – Tap Water and Deionized Water 13
Figure 4. Compiled RDX and TNT Solubility Data 12
Figure 5. Early Time Solubility Kinetics 16
Figure 6. Full Duration Solubility Kinetics 16
Figure 7. Derived Dissolution Flux for Composition B Particles in Water 18

List of Tables

Table 1. Sieve Series 7
Table 2. Specific Surface Area of Composition B Size Separates 8
Table 3. RDX and TNT Mass Fraction in Each Size Separate 8
Table 4. Historic RDX Solubility Data (Army, 1971) 10
Table 5. Historic RDX Solubility Data (Sikka et al, 1980) 10
Table 6. Historic RDX Solubility Data (Bier et al, 1999) 10
Table 7. Solubility of RDX in Deionized Water 12
Table 8. Solubility of RDX in Tap Water 12
Table 9. TNT Solubility in Tap Water from Composition B 13
Table 10. RDX Solubility in Tap Water from Composition B 13
Table 11. Aqueous Solubility Empirical Correlation 14
Table 12. Average Dissolution Flux for Each Particle Size 18

1.0 Introduction

Detonation of military ordnance produces residues of explosive chemical constituents on or in surface soil. The residue left from a high order detonation is typically very small and may be analogous to a sorbed surface layer on soil particles. Low order detonations occur infrequently, but may disperse distinct solid phase energetic material as fine particulates to large masses. A low order detonation is a very ill defined process where the energetic material burns rather than detonates. The rate of burning, pressure buildup in the ordnance, and fracture of the ordnance case determines the dispersal of the energetic material.

The nature of the explosive residue deposited by low order detonations is poorly understood, however, the initial mass of explosive material dispersed onto the surface soil is expected to be much greater than for the deposits from a high order detonation. Results from high order detonation of mortars and landmines have shown very trace quantities of explosive residues indicating near complete consumption of the main charge (Jenkins et al, 2002; Phelan et al, 2001).

Mass transfer of the chemicals from solid phase energetic materials to soil pore water is a critical process that influences the risk of groundwater contamination. To begin to understand the mass transfer process, tests were performed to determine the maximum solubility of military grade RDX and Composition B (60% RDX/40% TNT) in tap and deionized water. The Composition B was broken and sieved into three particle size groups to simulate low order detonation debris and initial screening tests were performed to assess dissolution rates into water.

2.0 Composition B Preparation

2.1 Source Material

The Composition B material was obtained from the demilitarization line at McAlester Army Depot, Oklahoma. Military ordnance was heated until the main explosive charge melted. The melt was poured onto a conveyor belt and allowed to solidify to produce a thin sheet (~ 5 mm). The thin sheet was broken into pieces for packaging and shipment to Sandia. Figure 1 shows the Composition B material as received.

Figure 1. Composition B Starting Material

2.2 Size Separates

The Composition B was further reduced in size by first freezing in liquid nitrogen and then by placement into a ball mill which was rotated for 1 hour at ~ 60 revolutions per minute. The material from the ball mill was placed into a sieve shaker, including the zirconium oxide balls, with the sieves as shown in Table 1 and shaken for 1 hour. Size fractions were collected and the shaker operated for another three cycles.

Table 1. Sieve Series

Sieve Number	Opening (μm)
16	1180
18	1000
30	600
35	500
140	106
170	90
635	20

Approximately 500 g of Composition B was processed. Size fractions containing 1000 to 1180 μm, 500 to 600 μm and 90 to 106 μm were collected. There was very little in the less than 20 μm fraction. To quantify the fraction of RDX and TNT in each Composition B size separate, ca. 0.010 g (± 0.0001 g) was dissolved into 10 mL of acetonitrile, diluted 1:1 with water and quantified using the RP-HPLC as described below. The results of the mass fraction of RDX and TNT in each size separate are shown in Table 2.

Table 2. RDX and TNT Mass Fraction in Each Size Separate

Component	90 to 106 μm	500 to 600 μm	1000 to 1180 μm
RDX	0.546	0.598	0.579
TNT	0.454	0.402	0.421

These results indicate that the Composition B size separates stayed near the typical 60/40-blend ratio, with slightly lower ratio for the 90 to 106 μm size separate.

2.3 BET Surface Area

The specific surface area of each size separate was measured using a Micromeritics Accelerated Surface Area and Porosimetry 2405 Instrument that measures BET surface area with Kr gas. The results for the BET specific surface area measurements are shown in Table 3 along with estimates based on the geometry of a spherical particle.

Table 3. Specific Surface Area of Composition B Size Separates

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

This data indicates that the measured BET surface areas are much greater than that estimated from uniform spherical particles by a factor of 13 to 70. This may be due to the non-spherical nature of the size separates and that there were many smaller size particles found on the surface of the larger particles when observed with scanning electron microscopy (SEM). Figure 2 shows a SEM photograph of the 500 to 600 μm size fraction showing many smaller particles present on the surface of the principal particles.

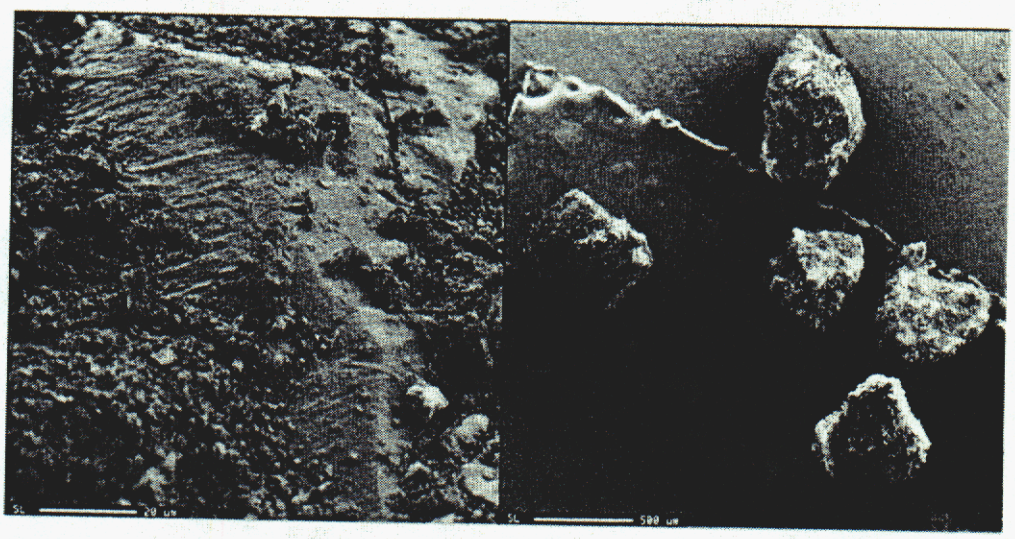

Figure 2. SEM Photograph of 500 to 600 μm size fraction

3.0 Solubility vs. Temperature

3.1 Background

Water solubility of RDX has been reported by several reference handbooks with data mostly at room temperature (McGrath, 1995; Rosenblatt, 1991; Stephen and Stephen, 1963; Urbanski, 1964; Verschueren, 1983). Temperature dependent water solubility data has been reported by Army, 1971 (Table 4), Sikka, 1980 (Table 5) and Bier, 1999 (Table 6). In this work, water solubility measurements were completed for RDX from military grade RDX and for RDX and TNT from Composition B in the temperature range expected in near surface soils.

Table 4. Historic RDX Solubility Data (Army, 1971)

Temperature (°C)	Solubility (gm/100 gm water)
30	0.005
50	0.025
70	0.076
90	0.19
100	0.28

Table 5. Historic RDX Solubility Data (Sikka et al, 1980)

Temperature (°C)	Solubility (mg/L) (mean, std dev)	Number of samples
10	28.9 ± 1.0	6
20	42.3 ± 0.6	9
26.5	59.9 ± 1.4	6
30	75.7 ± 1.1	7

determined spectrophotometrically

Table 6. Historic RDX Solubility Data (Bier et al, 1999)

Temperature (°C)	Solubility (mg/L)
20	27.2
25	34.5
30	43.8
35	55.6
40	70.7
45	89.7
50	113.9

Calculated from given formula: $y(mM/L)=0.047e^{(0.0478*T/°C)}$

3.2 Methods And Materials

The aqueous solubility of RDX was measured by direct sampling of a suspension of crystalline material in both deionized water and tap water. The aqueous solubility of RDX and TNT in Composition

B was measured in tap water only. For each sample, the suspension was allowed to settle to prevent collection of crystalline material. Sample filtration was not performed due to concerns of analyte loss on filter media. Two separate 125mL Erlenmeyer flasks were filled with 100mL of either deionized water or tap water and placed into a constant temperature bath. The water was stirred using a Teflon-coated magnetic stir bar. The water temperature was controlled by a constant-temperature water bath (Neslab, Model RTE-101) recirculated through a copper coil in the water bath. Approximately 100mg of RDX (Military Grade containing 90% RDX and 10% HMX) was placed into the water and allowed to mix for 1 week to ensure complete equilibration.

All sample aliquots were determined gravimetrically (+/- 0.00001g) then converted to volumetric values using the density values at 22.8°C. Water samples (~1mL) were collected by disposable pipette and placed into a 10mL vial containing about 6mL of deionized water to limit precipitation from higher temperature conditions. To determine if any chemical residue remained in the pipette, 1.5mL of acetonitrile (CH_3CN) was imbibed then placed into a 2mL autosampler vial for quantitation. Four water and four acetonitrile wash samples were obtained at each temperature. Sample data were collected at both rising to temperature and falling to temperature. Temperature was measured with a mercury thermometer (+/- 0.1 °C). The solution remained at the desired temperature for 2 to 7 days before samples were taken. Each sample was analyzed in duplicate.

The water samples were analyzed by RP-HPLC using a Waters 600 System Controller, Waters 715 Ultra Wisp Autosampler, and a Waters 996 Photodiode Array Detector. Samples were injected (20μL) into either a Water Xterra RP-18 5μm 4.6x250 mm column or a Waters Symmetry R C18 5μm 4.6x250 mm column and eluted with a 55:45 acetonitrile and water eluant run in isocratic mode. The photodiode array detector was run in scan mode accumulating all peaks found from 210 to 400nm for the elution time of RDX. The 254 nm wavelength was used for calibration and quantification of RDX and TNT.

The acetonitrile wash sample was quantified with a 1μL injection into a HP 6890 Gas Chromatograph equipped with a micro electron capture detector and a 0.53 mm x 7 m RTX 5 0.1μm film thickness column. The parameters used for the HP 6890 Gas Chromatograph were as follows: the split/splitless injector was programmed for a 220°C inlet temperature, starting column temperature of 70°C for 2 minutes, and then increased to 200°C at 10°C/min, then held for 3 minutes.

3.3 Results and Discussion

Tables 7 and 8 summarize the solubility data for RDX from military grade RDX in deionized water and tap water, respectively. While the total (sum of water sample and acetonitrile wash) appears to

be larger for each temperature, the difference is not statistically different. The acetonitrile rinse detects some analyte because there is a small amount of water/analyte remaining in the pipette after discharge. A large amount of analyte in the acetonitrile rinse could indicate crystalline material was imbibed – invalidating the sample; however, this was not the case. In addition, the standard deviations of the mean were also very small, indicating the samples were obtained from a homogeneous solution.

Table 7. Solubility of RDX (mg/L) in Deionized Water

Temp (°C)	Water plus CH_3CN Rinse		Water Sample Only		
	Mean	S.D.	Mean	S.D.	Approach
11.4	31.6	2.4	31.2	2.2	Rising
11.6	33.4	0.7	33.1	0.8	Rising
13.8	32.8	0.6	32.7	0.6	Falling
20.4	44.7	0.3	44.5	0.3	Rising
20.6	45.3	0.4	45.1	0.4	Rising
20.6	43.7	0.4	43.6	0.4	Rising
20.9	44.4	0.3	44.3	0.3	Falling
29.8	66.8	0.4	66.6	0.4	Rising
30.0	68.6	0.4	68.4	0.4	Falling
38.8	105.4	0.5	105.3	0.5	Rising
39.2	110.4	1.8	110.0	1.8	Rising

Table 8. Solubility of RDX (mg/L) in Tap Water

Temp (° C)	Water plus CH_3CN Rinse		Water Sample Only		
	Mean	S.D.	Mean	S.D.	Approach
11.4	25.1	0.1	25.0	0.1	Falling
11.6	24.6	0.3	24.5	0.3	Falling
20.4	40.6	0.0	40.3	0.1	Falling
20.4	40.1	0.2	39.9	0.2	Falling
20.6	39.3	0.6	39.1	0.5	Rising
29.4	65.8	0.8	65.5	0.8	Falling
30.0	66.5	0.5	66.1	0.4	Rising
39.3	96.3	0.4	96.0	0.4	Rising
39.4	97.7	0.5	97.2	0.4	Rising

Figure 3 shows the total solubility of RDX in deionized water compared to the total solubility of RDX in tap water. The solubility values in tap water and in deionized water appear very similar and the data was repeatable when comparing rising to temperature and falling to temperature conditions.

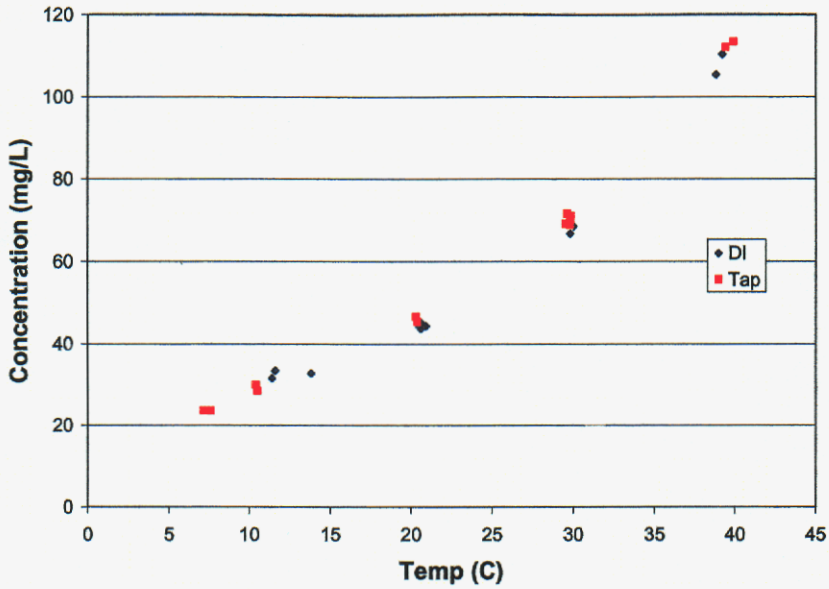

Figure 3. RDX Solubility – Tap Water and Deionized Water.

The results for the solubility of TNT and RDX from Composition B are shown in Table 9 and 10, respectively. Since the solubility of RDX in tap water was comparable to that in deionized water, all RDX data and all TNT data (including triple recrystalized [3X] TNT, Phelan and Barnett, 2001) were compiled and plotted. Figure 4 shows this data and a curve fit line each for TNT and RDX.

Table 9. TNT Solubility in Tap Water from Comp B

Temp (°C)	Concentration (mg/L)
7.2	69.2
7.6	69.5
10.4	77.2
10.5	78.0
20.3	113.1
20.4	112.8
29.6	151.2
29.8	151.8
39	238.0
39.6	237.2

Table 10. RDX Solubility in Tap Water from Comp B

Temp (°C)	Concentration (mg/L)
7.2	23.6
7.6	23.5
10.4	29.9
10.5	28.4
20.4	45.4
20.3	46.6
29.5	69.1
29.8	68.9
29.8	71.0
29.6	71.5
39.9	113.3
39.4	112.0

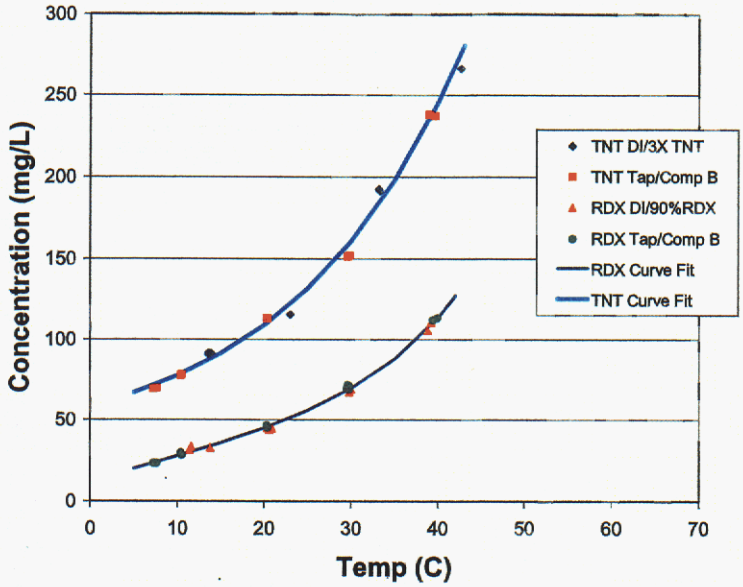

Figure 4. Compiled RDX and TNT Solubility Data

Curve fitting routines can provide numerous possible equations, all with very good correlation coefficients. Equations were chosen that represented the data well, but also fit the low temperature data exceptionally well. While some equations may show a higher correlation coefficient (r^2), there can be too much deviation from the low temperature data. Table 11 shows the equations and coefficients for both the RDX and TNT compiled data.

Table 11. Aqueous Solubility Empirical Correlation

	Equation	a	b	c	r^2
TNT	$y = a+b\exp(-x/c)$	20.176	36.295	-22.061	0.994
RDX	$y^{-1} = a+b\ln x$	0.0804	-0.0194		0.997

4.0 Dissolution Kinetics

4.1 Methods and Materials

The dissolution kinetics test was designed to be non-limiting - such that neither the RDX nor TNT would reach saturation conditions (RDX C_{sat} = ~ 40 mg/L; TNT C_{sat} = ~ 120 mg/L). The test was initiated by placing ca. 0.002 g (± 0.0001 g) of each size fraction into a 125 mL Erlenmeyer flask and adding 0.050 L (± 0.000125 L) of deionized water via volumetric pipette. The flasks were mixed on an oscillating table at 225 revolutions per minute at normal laboratory temperature of ~22 - 23°C. Each size fraction was completed in triplicate.

Water samples (~ 2 mL) were collected with disposable pipette and placed directly into an autosampler vial. Samples were collected at 20, 60, 120, 240, 360, 1440, 1920, 2880 and 3360 minutes. The water samples were analyzed by RP-HPLC using a Waters 600E System Controller, Waters 717 plus Autosampler, and Waters 996 Photodiode Array. Samples were injected (10 µl) into Brownlee Spheri-5 RP-18 5 µm 4.6x250 mm column and eluted with a 65:35 methanol+water run in isocratic mode. The photodiode array was run in scan mode accumulating all peaks found from 230 to 400 nm for the elution time of TNT or RDX. Calibration and quantification used the 254 nm wavelength for both RDX and TNT.

4.2 Results and Discussion

4.2.1 Dissolution Results

Using the quantity of Comp B and the RDX/TNT ratio from Table 2, an estimate of the maximum solubility (C_{max}) of each component was made for reference in the dissolution kinetics time series test. Figure 5 shows the dissolution rate data up to 500 minutes. For each size fraction, the TNT reaches greater C/C_{max} values faster than the RDX and the smaller size fractions dissolve faster than the larger size fractions. Figure 6 shows the complete dissolution time series results. For the 90 to 106 µm size separate, the solutions equilibrated at C/C_{max} = 0.90 to 0.93 within about 500 minutes. The 500 to 600 µm size separate reached C/C_{max} = 0.96 to 1.04 and the 1000 to 1180 µm reached C/C_{max} = 0.99 to 1.03. All of the C/C_{max} values are essentially at unity given measurement uncertainties.

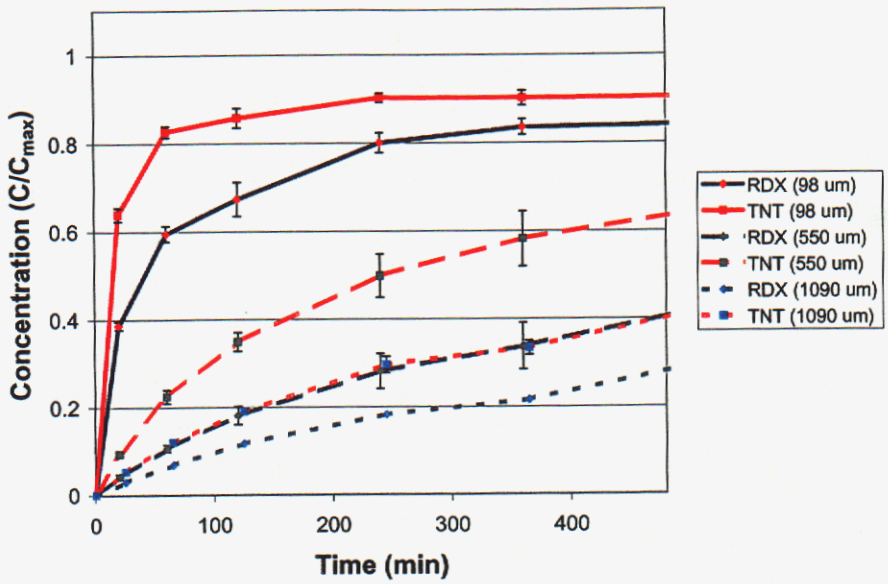

Figure 5. Early Time Dissolution Results

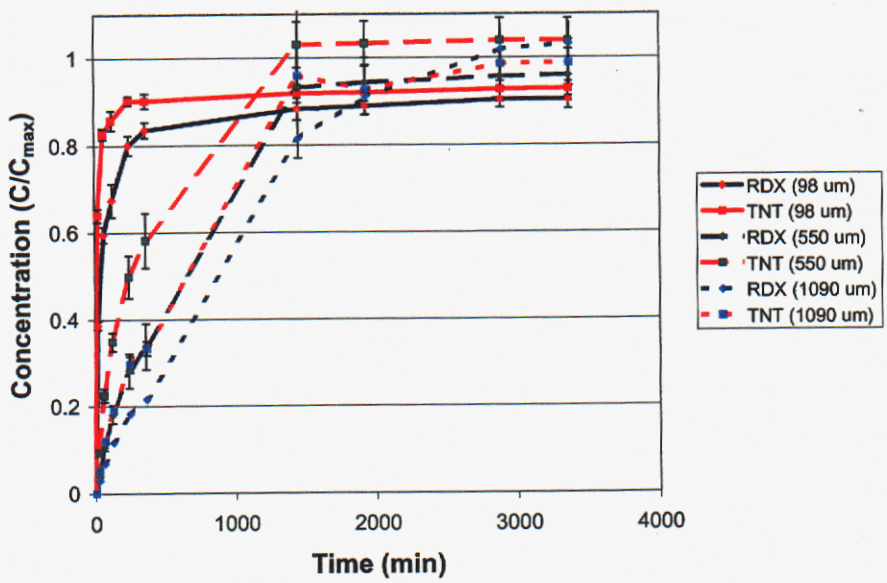

Figure 6. Full Duration Dissolution Results

4.2.2 Derived Dissolution Flux

Dissolution flux estimates were calculated for each sampling time interval. The calculation was not straightforward because the particle mass and surface area both decrease over time. For this analysis, several assumptions were necessary to develop a solution: 1) all particles have the 'mean diameter', 2) all particles decrease in mass and diameter equally, 3) the total number of particles is constant, 4) the particle density is constant, 5) the particles are rigid, spherical, and smooth.

The following method describes an analytical solution that solves for the dissolution flux rate and specific surface area as a function of time. Particle density, initial diameter and initial mass are fixed parameters; and, the solution concentration was the only time dependent parameter. Dissolution flux rates were estimated for each time interval. The dissolution flux rate is defined as the change in mass per unit area and time.

$$\Phi_i = \frac{\Delta M_i}{\Delta t \cdot A_{s_i}} \qquad [1]$$

Where, Φ_i is the dissolution flux rate, ΔM_i is the change in total mass at the end of time interval i, Δt is the difference in time for the interval, and A_{si} is the total surface area. To solve Equation 1 the mass and surface area at each interval must be determined.

The change in mass (ΔM_i) over a specific time interval is determined from

$$\Delta M_i = \Delta C_i \cdot V_s \qquad [2]$$

Where, ΔC_i is the change in concentration over the interval and V_s is the total volume of the solution, both quantities experimentally measured.

Thus, the total mass M_{ti} at each time interval is

$$M_{t_i} = M_{t_{i-1}} - \Delta M_i \qquad [3]$$

The constant number of particles in each size fraction is determined by

$$x = \frac{M_{t=0}}{\rho_p \cdot V_{p=0}} \qquad [4]$$

And the constant density is

$$\rho_p = \frac{M_p}{V_p} = \frac{M_t}{x \cdot V_p} \qquad [5]$$

With

$$V_p = \frac{\pi}{6} d^3 \qquad [6]$$

Where, M_p is the mass/particle, M_t is the total initial mass of Composition B (g), ρ_p is the density of a Composition B particle (1.65 g/cm^3), V_p is the volume of a particle (cm^3/particle), and d is the mean particle diameter (cm). The initial number of particles for the 90–106 μm size fraction was about 1200 to 1400, the 500–600 μm was about 6 to 8, and for the 1000–1180 μm was only one particle.

Using Eq [5] and [6], the time dependent diameter is derived as:

$$d_i = \left(\frac{M_{ti}}{M_{t(i-1)}} \right)^{\frac{1}{3}} \cdot d_{(i-1)} \qquad [7]$$

The total surface area, A_{si}, is defined as the specific surface area, A_{spi} (cm^2/g), multiplied by the total mass, M_{ti}, of Composition B particles at the end of the interval.

$$A_{s_i} = A_{sp_i} \cdot M_{t_i} \qquad [8]$$

The specific surface area is defined as the surface area per particle (πd^2) divided by the mass per particle. The estimated specific surface area at each time interval is obtained by assuming the total number of particles is equal, all particles are spherical with mean diameter, and the density is constant. The specific surface area is found as:

$$A_{sp(i)} = \frac{A_i}{m_i} = \frac{x \cdot A_i}{M_{ti}} \qquad [9]$$

$$A_i = \pi \cdot d_i^2 \qquad [10]$$

Where A_i, and m_i are the surface area and mass per particle of diameter d_i, respectively. The surface area available for mass transfer into solution declines as the Composition B mass and particle diameter declines.

Table 12 and Figure 7 show the derived average and standard deviation flux values for dissolution of the Composition B particles into water. Up to the 360 minute sample the dissolution flux showed continuous declines for all particle sizes. After 360 minutes, the 90-106 μm particle size dissolution flux continued to decline as the material had achieved about 85% of C_{max} at that time. The two larger size fractions showed slight increases in dissolution flux after 360 minutes before declining. The largest size fraction (1000 to 1180 μm) required the entire test period to fully dissolve.

These results are in agreement with previous results, which showed dissolution flux of TNT at 4,164 μg/cm^2-hr (= 1,157 ng/cm^2-sec); but, in contrast with results for RDX at 361μg/cm^2-hr (= 100 ng/cm^2-sec) (Brannon and Pennington, 2002).

Table 12. Average Dissolution Flux (ng/cm^2-sec) for Each Particle Size

	90-106 um				500-600 um				1000-1180 um			
	RDX		TNT		RDX		TNT		RDX		TNT	
Time (min)	flux	std dev	Flux	std dev	flux	std dev	flux	std dev	flux	std dev	flux	std dev
0	0	0	0	0	0	0	0	0	0	0	0	0
20	1203	40	2837	150	540	75	1263	82	763	46	1372	150
60	428	47	674	31	442	28	981	88	511	115	908	110
120	127	44	88	50	360	67	694	51	436	33	673	20
240	139	16	79	29	265	71	503	165	311	13	559	76
360	44	17	4	7	156	44	320	88	165	37	208	180
1440	8	3	4	3	1051	601	826	213	862	132	1070	360
1920	3	3	2	2	1341	2293	12	11	530	218	370	440
2880	3	0.3	2	1	36	26	20	21	824	566	184	101
3360	1	0.4	1	1	21	24	12	20	375	363	19	17

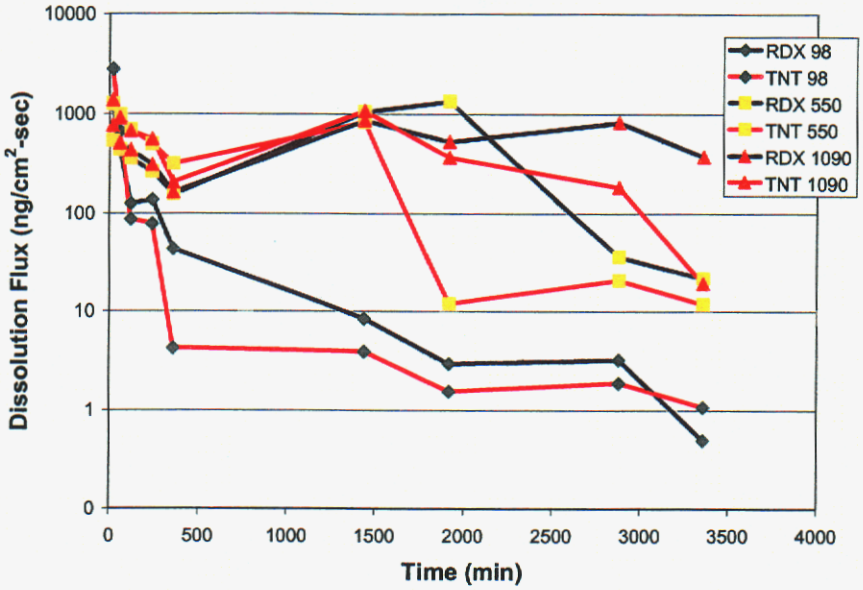

Figure 7. Derived Dissolution Flux for Composition B Particles in Water

5.0 Summary

Military test and training ranges have come under scrutiny as potential sources of groundwater pollution from explosive materials. Live fire operations detonate thousands of ordnance items per year at each facility. While infrequent, low order detonations can leave solid phase energetic material as fine particulates to larger pieces that can dissolve during rainfall events contaminating soil pore water, which can become a source for groundwater pollution. Detonation residues containing RDX are of greatest concern because of the low drinking water advisory limits (McLellan et al., 1988) and the limited degradation rates under typical aerobic vadose zone pore water conditions (Hawari, J., 2000).

This work documented the temperature dependent solubility maxima of RDX from crystalline material in both deionized and tap water, and RDX and TNT from Composition B (~60% RDX/40% TNT) in tap water. There was very little difference in RDX solubility between deionized and tap water. Both RDX and TNT from Composition B showed little difference in solubility values when compared to neat crystalline sources. Data were fit to non-linear equations to allow estimation of solubility values at temperatures intermediate to the observed data.

The rates of dissolution were determined for three Composition B particle size groups: 90 – 100 μm, 500 to 600 μm, and 1000 to 1180 μm. The dissolution tests were designed so that neither the RDX nor the TNT would be solubility limited. The RDX could rise to about 50% of the solubility maxima and the TNT could rise to about 15% of solubility maxima. The smallest particles dissolved very quickly, reaching near C_{max} in about 400 minutes. The largest particles required the full test duration of about 3400 minutes (~2.5 days) to fully dissolve. Estimates of the dissolution rates were derived from the concentration changes over time and an assumed spherical geometry of the Composition B particles. Dissolution rates of 100 to 1000 ng/cm^2-sec were found for all particle sizes and the rates declined as the particles neared complete solubilization.

These results indicate a fairly rapid unconstrained dissolution of Composition B particles into water. On test and training ranges where frequent rainfall occurs, this implies that solid phase energetic materials would be a significant source contributing to groundwater pollution. Additional work is in progress that will evaluate the fundamental processes affecting the mass transfer of solid phase energetic materials to soil pore water using column tests and derive a mass transfer function for use in environmental hydrogeologic simulation models.

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