FINAL REPORT

Dissolution of NTO, DNAN, and Insensitive Munitions Formulations and Their Fates in Soils

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New explosive compounds that are less sensitive to shock and high temperatures are being used as replacements for TNT and RDX. Two of these explosives, DNAN (2,4-dinitroanisole) and NTO (3-nitro-1,2,4-triazol-5-one), were shown to have good detonation characteristics and are used as the main ingredients in several new explosive formulations. Both compounds, however, are more soluble than either TNT or RDX and have been shown to have some human and environmental toxicity. This project measured the dissolution, photodegradation, and soil adsorption properties of DNAN, NTO, and insensitive munitions formulations that contain them (IMX-101, IMX-104, and PAX-21).
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1 Abstract

1.1 Objective

New explosive compounds that are less sensitive to shock and high temperatures are being used as replacements for TNT and RDX. Two of these explosives, DNAN (2,4-dinitroanisole) and NTO (3-nitro-1,2,4-triazol-5-one), were shown to have good detonation characteristics and are used as the main ingredients in several new explosive formulations. Both compounds, however, are more soluble than either TNT or RDX and have been shown to have some human and environmental toxicity. Data on their fate and transport is needed to determine if DNAN and NTO have the potential to reach groundwater and be transported off military training bases. The objective of this project was to measure the dissolution, photodegradation, and soil adsorption properties of DNAN, NTO, and insensitive munitions formulations that contain them (IMX-101, IMX-104, and PAX-21).

1.2 Technical Approach

Detonation residues of IM formulations, IMX-101, IMX-104, and PAX-21 were characterized using light and electron microscopy, as well as X-ray tomography and Raman spectroscopy and exposed to either simulated rainfall in the lab or to natural rainfall and sunshine outside on a location in New Hampshire. Indoor particles were again examined using X-ray tomography following exposure to water to quantify changes to their 3-D structure as they dissolve. Solution concentrations of NTO, NQ (nitroguanidine), DNAN, RDX 1,3,5-hexahydro-1,3,5-trinitro-1,3,5-triazine, HMX (1,3,5,7-octahydro-1,3,5,7-tetranitrotetrazocine, an impurity in RDX), and ammonium perchlorate (AP) were also measured to calculate the amount of IM constituents dissolved into solution. The photo-degradation of DNAN and NTO in solid (outdoors) and aqueous (in the lab) form was measured to determine if these compounds degrade in sunlight either before or after dissolution. Adsorption and transport behavior of IM compounds in a range of soils collected on training facilities was also studied. Results were used to determine how DNAN and NTO interact with the soils and to correlate transport and fate
parameters to soil properties. Together, obtained dissolution and transport parameters were used in HYDRUS-1D, a software package for simulating water, heat and solute movement in one-dimensional variably-saturated media, to predict the environmental fate of IM explosives for several locations.

1.3 Results

Both outdoor and indoor dissolution experiments indicated that IM constituents dissolve sequentially as predicted by solubility, NTO, followed by NQ and DNAN in IMX-101 and DNAN and RDX in IMX-104. Fast dissolution of most soluble components resulted in porous particles that broke easily. High initial concentrations of NTO caused significant decrease of pH for rainwater in contact with IM formulations. Photo-transformation of outdoor IM was evident; but its relative contribution is smaller than for traditional explosives due to faster dissolution of IM compounds. Solution-phase NTO photo-transformation was influenced by pH and enhanced in the presence of dissolved organic matter, while DNAN photo-transformation rates increased with temperature.

NTO adsorption in soils was very low and further decreased with increasing soil pH, while DNAN was adsorbed and its adsorption positively correlated with soil organic matter and clay. Both NTO and DNAN were transformed in soils and products of DNAN transformation, 2-ANAN (2-amino-4-nitroanisole) and 4-ANAN (4-amino-2-nitroanisole) were observed. Exposing explosive residues to water resulted in initial high peak in concentration for NTO and NQ followed by lower concentrations, and for fairly constants and lower concentration of DNAN. High release of NTO and its low adsorption in soils indicate higher risk of its transport to the ground and surface waters, while DNAN slower dissolution and TNT-like behavior in soils indicates lower potential for off-site transport. However, numerical simulations indicate that both NTO and DNAN would be transformed in soils preventing them from reaching ground water.

1.4 Benefits

The U.S. military is interested in replacing TNT and RDX with DNAN and NTO, which have similar explosive characteristics but are less likely to detonate
unintentionally. Although these replacements are good explosives, basic information about their fate and transport was needed to evaluate their environmental impact and life-cycle management. This project measured their dissolution, photo-degradation, and how aqueous solutions interact with soils, data critical to determining exposure potential and, consequently, risk.
Chapter 1. Outdoor dissolution and photodegradation tests of IM formulations

Susan Taylor, Julie Becher, Marianne Walsh and Dave Ringelberg

Outdoor Experimental tests

These experiments were conducted in Hanover NH where the yearly temperature varies between -12 °C and 28 °C. We placed 5 chunks of IMX-101, 5 chunks of IMX-104 and 2 chunks of PAX-21 on glass frits in dedicated 4 cm diameter Buchner funnels (Figure 1.1). The funnels were attached to 1-L bottles, which fit snugly into an insulated wooden box to insulate and keep the bottles upright. Rainwater or snowmelt that interacted with the chunks was collected in the bottles. About every month, except during the winter when the experiment was snow covered, we exchanged the bottles for clean ones and measured the volume and explosive concentrations in the water samples. Each time we collected samples, we also photographed the pieces of IM in situ to document changes in their appearance and size (Figure 1.1). Our experiment was set up in an area enclosed with a locked chain link fence and next to a dedicated rain gauge and are like those conducted for high explosives (Taylor et al. 2009, 2010).

Figure 1.1. Appearance of a piece of IMX-101, IMX-104 and PAX-21 set outdoor to weather and dissolve. Top row shows particles at 17 days and the bottom row shows the same particles at 363 days.
Our tests allowed us to collect and analyze the dissolved constituents and monitor changes in the appearance of the chunks while at the same time exposing the IM formulations to conditions similar to those experienced on a range—where rain, snow, sun and freeze thaw cycles weather the IM. These tests ran between June 2013 and October 2015 during which time we collected 19 sets of water samples for each IM chunk. The average volume of precipitation interacting with these chunks was 3.7±0.27 L.

**Analytical methods**

We analyzed by HPLC all solutions from the outdoor tests and, using an ion selective probe, analyzed solutions from PAX-21 particles for perchlorate. Two different columns, *NovaPak C8* and *Hypercarb* and stationary phases were used for chromatographic separation of the IM components and transformation products.

**High performance Chromatography**

*NovaPak C8*: Determinations of DNAN were made on a modular system from ThermoScientific composed of a Spectra-System Model P4000 pump, a Spectra-System UV2000 dual wavelength UV/VS absorbance detector (cell path 1 cm) set at 295 nm for DNAN, and a SpectraSYSTEM AS3000 autosampler. Samples were introduced with a 100 µL sample loop. Additional determinations were made for select samples on an Agilent 1200 Series HPLC equipped with a Diode Array Detector (Model G1315B). The spectrum range was 200 to 800 nm. Separations were achieved on a 15 cm x 3.9 mm (4 µm) *NovaPak C8* column (Waters Chromatography Division, Milford, Massachusetts) at 28°C and eluted with 1.4 mL/min of 15/85 (v/v) isopropanol/water. All samples were introduced to the HPLC in a matrix of 1/3 v/v acetonitrile/water. This matrix provides excellent chromatographic peak shapes. Calibration standards, which were acetonitrile solutions, were prepared by mixing 1.00 mL of each standard with 3.00 mL with Type I reagent grade water (MilliQ). To maintain the same proportions volumetrically as the calibration standards, aqueous solutions were prepared by mixing 1.00 mL of each sample with 2.00 mL of MilliQ water and 1.00 mL acetonitrile. Each sample was filtered prior to injection using a PTFE (0.45µm) 25-mm filter unit (Millipore Millex-FH).
**Hypercarb (100% Porous Graphitic Carbon):** NTO, NQ and DNAN were determined following the Standard Operating Procedure DLS810 obtained from M. Hable (personal communication), based on the methods of Le Campion et al. (1997). Samples were injected using a matrix of 3/1 acetonitrile/water. Determinations were made using the same modular systems above except that the column was a 15 cm x 4.6 mm (5 µm) Hypercarb (ThermoScientific) eluted with 1.5 mL/min of 3/1 (v/v) acetonitrile/water with 0.1% trifluoroacetic acid (Fisher HB9813-4) at 28°C. The UV detector was set at 315 nm for NTO, 263 nm for NQ, and 295 for DNAN. Additional determinations of select samples were made on an Agilent 1200 Series HPLC equipped with a Diode Array Detector (Model G4212B). The spectrum range was 200 to 600 nm. The chromatographic separation on the Hypercarb stationary phase uses an eluent composed of 3/1 acetonitrile/water v/v. Thus 3.00 mL of acetonitrile was added to each 1.00 mL aqueous sample. To maintain the same volumetric proportions, 1.00 mL of each calibration standard was mixed with 2.00 mL of acetonitrile and 1.00 mL MilliQ water. Solutions were filtered as for the NovaPak C8 separation.

**Mass Spectrometry (GC-MS)**

Mass spectra were obtained using an Agilent 5973 Mass Selective Detector (MSD). The ionization voltage was 70 eV. The MSD was operated in scan mode (m/z = 29 to 400) and in Selective Ion Monitoring (SIM) for masses 169, 182, and 30. The GC column was a Restek-RTx-5MS (Crossbond® 5% diphenyl/95% dimethyl polysiloxane) (15 m x 0.25 mm, df (film thickness) 1.00 micron). The carrier gas was helium at constant flow (1.4 mL/min) with a linear velocity of 62 cm/s. The oven temperature was 75°C for 2 min, then ramped at 20°C per minute to 220°C and held for 10 minutes. The injection port temperature was 200°C; split-less 1-microL injections with a deactivated liner were used.

Standards of known compounds and matrix samples were introduced to the GC as solutions in acetonitrile that were filtered through PTFE (0.45 µm) filter units (Millipore Millex-FH) into 2-mL amber auto-sampler vials just prior to injection. Analytes from the aqueous samples from the outdoor dissolution experiments were transferred to
acetonitrile using two procedures. The first procedure was solid phase extraction where each PoraPak RDX Sep-Pak Vac (Waters) cartridge was preconditioned with acetonitrile and reagent-grade water according to manufacturer’s instructions. Then 5.00 mL of each aqueous sample was passed through using gravity flow. Each cartridge was placed under vacuum for 1 hour to remove residual water, then eluted with 5.00 mL acetonitrile, of which approximately 4.5 mL were recovered. The second procedure involved evaporating aqueous samples, followed by dissolution of the dried residue in acetonitrile and filtration through a PTFE (0.45µm) 25-mm filter unit (Millipore Millex-FH).

Other analytical methods

An ion-selective electrode (Cole Parmer) was used to quantify the AP. To generate a standard line from which we could determine the AP concentration of the samples, we prepared and analyzed a series of concentrations from a perchlorate standard. Using a Mettler Toledo SevenEasy meter and a pH probe, we measured the pH of the water samples; and we completed a three-point calibration by using pH 4, 7, and 10 solutions.

Micro computed tomography (µCT) images were taken using a SkyScan 1172 X-ray micro tomograph, run at a 40 kV voltage with a 250µA source current. Radiographs (X-ray images) were taken of one chunk of each formulation before being set outside and again near the end of the tests. The images were taken with a 1.3 Megapixel X-ray camera and the cross-sections reconstructed using a modified Feldkamp cone-beam algorithm. For more information on how IM particles were imaged see Taylor et al. (2015).

UV-Vis spectra were acquired of the outdoor samples using a Jasco V-630 spectrophotometer and quartz cuvettes that are UV transparent to 200nm (YeHui Instruments). UV-Vis spectra for the samples were obtained in the wavelength range of 200-800nm. The data interval was set to 1nm, the UV/Vis bandwidth was set to 1.5nm, the response was set to fast, and the scan speed was set to 200nm/min. The D2/WI light source changed at 340nm with a continuous filter exchange. A Spectra Measurement program on the instrument was used to collect each sample’s UV-Vis spectrum. Before
analyzing samples we ran the quartz cuvette filled with DI water as a background, which was used to remove the water signal from the aqueous samples. Between each sample, the cuvette was rinsed with DI water three times and then dried with a lint-free cloth.

**Results**

**Appearance of explosive pieces**

The three formulations were initially white (IMX-101), cream colored (IMX-104) and yellow (PAX-21) but their surfaces turned yellow after two weeks (Figure 1.1) and orange to brick red after a year of exposure to sunlight (Figure 1.2). Microscopic examination of the surfaces of particles exposed to light in a windowsill showed that of the IM constituents only DNAN changed color. Photo-transformation of the other constituents may also be occurring but to colorless products.

During the 16-month long dissolution test all of the IM chunks split and all shed mm-sized particles (Figure 1.2), a faster splitting rate than observed for TNT, Comp B and Tritonal (TNT + aluminum) (Figure 1.3) where only three of 29 chunks split during a three-year test (Taylor et al. 2010). The friability of the IM formulations may be due to the large, ~300µm, crystals they contain, to the voids left when the crystals dissolve, or to fractures produced during detonation (Figure 1.4a, Taylor et al. 2013). Note that the fractures predominantly follow the crystal boundaries and in some cases surround the crystal. We think these fractures de-bond crystals from the matrix (Taylor et al. 2013) and explain why AP, NTO and NQ are found after ‘high order’ detonations when all of the DNAN is consumed (Walsh et al. 2013, 2014): the de-bonded crystals are scattered instead of being detonated. The µCT images of IMX-101-2, IMX-104-4 and PAX-21-2 taken before, part way through, and at the end of the outdoor tests (Figure 1.4b, c, d) show that IMX-101 has lost crystals in its interior and periphery but less so than IMX-104 where all the NTO crystals have dissolved. The ammonium perchlorate in PAX-21 dissolves in the first rainfall leaving voids throughout.
**Figure 1.2.** a) IMX-101-1 set outside to weather and dissolve. The images show how the surface of the piece changed over the 864 days of the experiment.

**Figure 1.3.** We found that IM formulations are very friable compared to traditional explosives.
Dissolution of explosive pieces

Figure 1.5 shows the percent cumulative mass dissolved for each constituent in the IM formulation plotted against the cumulative volume of water collected. The percent cumulative mass was calculated by dividing the mass of each constituent measured in the water samples by the putative starting mass of each constituent. The latter value was obtained by multiplying the initial mass of the chunk by the fraction of each constituent in the formulation. The plots help to highlight compositional variations among the pieces.

Figure 1.5a plots the mass loss data for the five IMX-101 pieces. We see that NTO dissolves first, followed by NQ and finally DNAN. The dissolution rates of NTO and NQ are higher at the start of the test and decrease during the test. The shape of the NTO mass loss with water volume is more clearly seen for IMX-104, which contains no
NQ (Figure 1.5b). In Figure 1.5c we see that the AP in PAX-21 dissolved in the first water sample, leaving DNAN and RDX as the only constituents. As was found for laboratory experiments (Taylor et al. 2013; Richard and Weidhaas 2014), the constituents of the formulations dissolve in the order of their solubility. None of these pieces had completely dissolved after 16 months.

Any increases or decreases in the temperature of rain or surface water, due to changes in the ambient temperature, will affect the dissolution rate of the individual compounds and of the formulations. For example, the solubility of DNAN and NQ increases by a factor of two between 20 and 40 °C and almost doubles for NTO (Appendix A).

Unlike high explosives, IM formulations dissolve throughout their volumes due to their soluble crystals constituents. We cannot, therefore, use dissolution models that assume dissolution from the surface (Lever et al. 2005) to calculate particle life times. For all three formulations, however, the mass loss of DNAN (and RDX) is fairly linear when plotted against water volume (Figure 1.6). The best linear fits to the DNAN data have slopes ranging from 0.0114 to 0.0572 and goodness of fit measures (R^2) between 0.94 and 0.99 (Table 1.1). As DNAN is a main constituent in the matrix, its quasi-linear dissolution allows us to estimate chunk life times. Using the rate of DNAN mass loss versus water volume, the area of the funnel opening and the average yearly precipitation for Hanover NH (~100 cmyr⁻¹, US Climate) we estimate that 3 to 21 years are need to completely dissolve these chunks. Using the average water volume we measured (1.7 L yr⁻¹) the time to dissolution would be 3 to 16 years (Table 1.1).

Quasi-linear dissolution does not occur for the NTO or NQ (Figure 1.7), or for most mm-sizes particles of these formulations (Taylor et al. 2015), or for Comp B and TNT (Lever et al. 2005; Taylor et al. 2009). In all these cases the explosive pieces lose more mass initially when soluble constituents are at or near the surface of the chunk, and then mass loss decreases as constituents are depleted or as water has a harder time contacting the constituents. For DNAN, its low solubility coupled with increases in its surface area explains the linear mass loss. When the IM chunks split the numerous fragments that result, increase the DNAN surface area and dissolution. This idea is supported by the fact that more fragments result in a better linear fit to the mass loss
versus water volume data (Table 1.1). Although fragmentation also affects the dissolution of NTO, NQ and AP none of these show quasi-linear dissolution because the time scales over which these compounds dissolve are shorter than the fragmentation rate.

**Figure 1.5.** Dissolved mass versus precipitation volume for, five IMX-101 (a), five IMX-104 (b) and two PAX-21 (c) chunks placed outside, NTO (blue), NQ (orange), DNAN (green), RDX (red), AP (purple).
**Figure 1.6.** Dissolved DNAN plotted against water volume for outdoor samples of IMX-101, IMX-104 and PAX-21.

**Figure 1.7.** Dissolved NTO (a) and NQ (b) plotted against water volume for outdoor samples of IMX-101, IMX-104 and PAX-21.
Table 1.1. Parameters measured or calculated (life spans) for the 12 pieces of IM explosives set outdoors to weather and dissolve.

<table>
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<th></th>
<th>Initial Mass (mg)</th>
<th>Cum. Dissolved Exp. (mg)</th>
<th>% Mass Loss</th>
<th>Cum. Water Vol. (mL)</th>
<th>Max. # pieces</th>
<th>Exp. Initial DNAN (mg)</th>
<th>Slope Line DNAN</th>
<th>R²</th>
<th>Liters to dissolve chunk</th>
<th>Life span of Chunk* 1.3 L yr⁻¹</th>
<th>Life span of Chunk* 1.7 L yr⁻¹</th>
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Mass Balance for the outdoor tests

We stopped the outdoor experiment after 864 days both to calculate a mass balance for the individual particles (Table 1.2) and to scrap off or dissolve their surfaces to analyze for photo-transformation products. Table 1.2 lists the initial and final masses for the IM pieces. Also shown are initial and final masses of HE particles for comparison. For IM, the difference between the initial and ending masses averaged 0.8±0.6g and about 80% of this value was recovered in the water samples. This suggests that about 20% was lost via photo-degradation.

The conventional explosives (TNT, Comp B, Tritonal and C4) were found to lose less mass (Taylor et al. 2011). The difference between the initial and ending mass averaged 0.2 ± 0.08g (constituents less soluble and particle less friable) but only about 20% of this value was recovered in the water samples. This suggests that ~ 80% was photo-transformed into compounds not analyzed for in the effluent samples (Taylor et al. 2010). Unlike the HE, the percent mass loss of the IM formulations is not inversely related to the mass of the chunks.

UV-Vis

The UV-Vis spectra of the IM constituents are quite distinct and have absorption features in the UV portion of the spectrum (Figure 1.8). DNAN has a very distinctive spectrum with absorbance features at 214, 260 and 299nm. NQ has a peak at 264nm and NTO at 345nm. RDX’s spectrum decreases between 200 and 300nm and is featureless except for a small shoulder at 235nm. Ammonium perchlorate, another constituent of PAX-21, has a flat UV-Vis spectrum.

We also made UV-Vis measurements of some of the known degradation products of DNAN: 2,4-diaminoanisole; 4-methoxy-3-nitrophenol (4-MeO-3-NP); 2,4-dinitrophenol; 2-methoxy-5-nitrophenol (2-MeO-5-NP); 2-methoxy-5-nitroaniline (MENA, or 2-MeO-5-NA, also called 2-amino-4-nitroanisole, or 4-ANAN); and 4-methoxy-3-nitroaniline (4-MeO-3-NA, also called 4-amino-2-nitroanisole, or 2-ANAN) (Figure 1.9). The 2,4-diaminoanisole has a spectrum with peaks at 307 nm and 204 nm with a slight shoulder at 240 nm. The UV-Vis spectrum for 4-methoxy-3-nitrophenol exhibits strong absorption peaks at 374nm and 218nm, and two shoulders at 275nm and 245nm. The 2-methoxy-5-nitrophenol spectrum is weak with a broad peak centered around ~350nm.
Table 1.2. List showing the initial mass of the outdoor samples and the percentage not recovered. The recovered mass is the final mass of the particle added to the mass analyzed from the effluent via HPLC. Data are given for both IM and HE formulations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>IM Formulations</th>
<th>HE Formulations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M&lt;sub&gt;i&lt;/sub&gt;</td>
<td>M&lt;sub&gt;f&lt;/sub&gt;</td>
</tr>
<tr>
<td>IMX-101-1</td>
<td>3.55</td>
<td>1.43</td>
</tr>
<tr>
<td>IMX-101-2</td>
<td>1.39</td>
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</tr>
<tr>
<td>IMX-101-3</td>
<td>0.63</td>
<td>0.02</td>
</tr>
<tr>
<td>IMX-101-4</td>
<td>0.53</td>
<td>0.04</td>
</tr>
<tr>
<td>IMX-101-5</td>
<td>0.31</td>
<td>0.05</td>
</tr>
<tr>
<td>IMX-104-1</td>
<td>2.00</td>
<td>0.70</td>
</tr>
<tr>
<td>IMX-104-2</td>
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<td>0.13</td>
</tr>
<tr>
<td>IMX-104-3</td>
<td>0.99</td>
<td>0.23</td>
</tr>
<tr>
<td>IMX-104-4</td>
<td>0.49</td>
<td>0.13</td>
</tr>
<tr>
<td>IMX-104-5</td>
<td>0.22</td>
<td>0.01</td>
</tr>
<tr>
<td>PAX-21-1</td>
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<td>0.41</td>
</tr>
<tr>
<td>PAX-21-2</td>
<td>0.25</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Initial (M<sub>i</sub>) and final (M<sub>f</sub>) masses of the particles.
Diff= M<sub>i</sub>-M<sub>f</sub>
M<sub>diss</sub>= Mass determined from effluent samples via HPLC
M<sub>miss</sub>= Mass missing= M<sub>i</sub>-(M<sub>f</sub>+M<sub>diss</sub>)
HPLC mass/ mass not recovered= (M<sub>diss</sub>)/(M<sub>i</sub>-(M<sub>f</sub>+M<sub>diss</sub>)}
The 2,4-Dinitrophenol spectrum has a large absorption peak at 366nm and smaller ones at 235 and 268nm. The 2-methoxy-5-aniline had strong absorption peaks at 368nm, 318nm, 258nm, and 224nm. Its overall shape resembled that of the 2,4-dinitrophenol spectrum, but shifted to shorter wavelengths. The 4-methoxy-3-nitroaniline also had a strong absorption peaks with a large peak at 386nm and a sharp peak at 231nm. Its overall shape was quite similar to that of 2,4-diaminoanisole, just shifted towards longer wavelengths.
Figure 1.9. UV-Vis spectra of known transformation products of DNAN.

We made UV-Vis measurements of the 218 effluent samples and plot the spectra of the first (1st), tenth (10th) and eighteenth (18th) water samples collected from the outdoor tests (Figure 1.10). The results show temporal changes in the UV-Vis
spectra of each IM formulation but these are due to changes in the composition of the effluent and not to degradation products. For example, IMX-101 initially has absorption features consistent with the presence of NTO and NQ. The 10th sample shows an absorption peak dominated by NQ while the 18th sample is starting to show a DNAN signature. Similarly, IMX-104 initially has a spectrum that matches that of NTO, but the spectrum becomes more like that of DNAN and RDX in latter samples. PAX-21 has a spectrum that matches that of DNAN, there being no NTO of NQ in this formulation.

The absence of DNAN peaks in IMX-101 and IMX-104 is due to the presence of the much more soluble constituents, NTO and NQ. As the NTO is dissolved and depleted from IMX-101 particles, NQ dominates the UV-Vis spectrum. Once NQ is depleted the spectrum of the much less soluble DNAN appears. For IMX-104 as the NTO is depleted the spectrum of DNAN starts to emerge. This transition can be tracked by a shift to shorter wavelengths of NTO’s main absorption peak (Figure 1.11). The NTO peak position holds steady at 340 nm until the NTO concentration in the sample drops below 500mg/L, at which point the peak position decreases to 300nm. For PAX-21, as AP completely dissolves in the first sample, only the spectra of DNAN and RDX are present. We can see the absorption features corresponding to DNAN but they are superimposed on a steep slope characteristic of RDX. The spectra of the IM formulations are consistent with the compositional change occurring in the individual particles as constituents of the particles dissolve.

None of the UV-Vis spectra had absorbance features near 600nm, features we would expect from degradation products responsible for the color change on the explosive samples and in the effluent from those samples (Figure 1.10). The samples, however, were all diluted to between 3 and 6 mg/L to obtain absorption values between 0 and 2 absorbance units. To check if small amounts of other compounds were being diluted to near 0 absorption units, we also analyzed some undiluted samples. Here most of the absorption features were out of the linear range (>2) but we still saw no features in the visible portion of the spectrum, suggesting the colored compounds occur at very low concentrations.
Figure 1.10. Plots showing the UV-Vis spectra for the first (black), tenth (green) and eighteenth (orange) water sample collected from IM pieces placed outside to weather.
**Figure 1.11.** Plot of NTO concentration in effluent collected from IMX-104 outdoor chunks versus the UV-Vis Peak position (nm) for NTO.

**Photo-degradation of explosive pieces**

Similar to light induced changes on the surfaces of high explosives (Taylor et al. 2010) we think that photo-transformation of the IM particle surfaces is also occurring. Evidence of photo-transformation includes color changes of the outdoor IM pieces (Figure 1.2, 1.3), the presence of unknown peaks in their HPLC chromatographs (Figure 1.12), large pre-solvent peaks in the HPLC chromatograms where polar substances elute, and the absence of unknown peaks and good mass balances (100±5%) in samples from laboratory tests not exposed to sunlight (Taylor et al. 2015). Some of these photo-produced compounds are soluble as they color the water samples.
Figure 1.12. Chromatograms from a NovaPak C8 column plotting absorption units at 230 nm versus minutes for a water sample collected from an IMX-104 indoor dissolution test (top, no sunlight exposure, Taylor et al. 2015a) and an outdoor test (bottom). DNAN, RDX and HMX peaks are well defined but there are many unknown peaks as well as a large pre-solvent peak (arrow) in the outdoor sample.

We focused on the degradation of DNAN because microscopic observation of IM formulations showed that only DNAN changed color. DNAN transformation pathways and products have been reported for several matrices including cell cultures, soil microcosms, sludge bioassays, treated wastewater (alkaline hydrolysis, zero-valent iron, fluidized-bed bioreactors), toxicity test organisms, irradiated aqueous solutions, and oxic aqueous solutions (Appendix B). No studies have reported on the photo-transformation products that form on the surface of solid pieces of DNAN or DNAN in IM formulations.
Most of the studies listed in Appendix B focused on biological transformation products (see Olivares et al. 2016 for a review). The physical, chemical, and toxicological properties of some of DNAN’s transformation products are known because the products are used in dyes or as reagents for chemical synthesis (Appendix C). The most commonly reported transformation product is 2-methoxy-5-nitroaniline, which is abbreviated as MENA. MENA forms by reducing the ortho nitro group of DNAN, reported to be favored over reduction of the para nitro group. Under anaerobic conditions, reduction of both nitro groups forms 2,4-diaminoanisole (Olivares et al. 2016).

There are fewer studies of photo-transformation products of DNAN in aqueous solutions. Both Hawari et al. (2015) and Rao et al. (2013) found 2-methoxy-5-nitroanilalaniline and 2,4-dinitrophenol intermediates, not end products. Hawari et al. (2015) also reported formamide derivatives, from amino-nitro-anisole and amino-nitro-phenol, as intermediates. The final products of a DNAN aqueous solution photolyzed over 21 days were, nitrate anion (0.7 mole), ammonium (1 mole), and formaldehyde/formic acid (0.9 mole), per mole of DNAN degraded (Hawari et al. 2015). Using FTIR, Rao et al. (2013) found -COOH or -C=O in aqueous DNAN samples after 5 days of irradiation.

To help identify the photo-degradation compounds in our samples, we purchased standards of six compounds known to form from DNAN (2,4-diaminoanisole; 4-methoxy-3-nitrophenol; 2,4-dinitrophenol; 2-methoxy-5-nitrophenol; 2-methoxy-5-nitroaniline (MENA); and 4-methoxy-3-nitroaniline) and analyzed them along side the aqueous samples from our outdoor tests. We used a suite of instruments including UV-Vis, HPLC (two columns and a diode array detector), and GC Mass spectrometry. Determining any photo-transformation products of IM constituents is important because these could be toxic, soluble and a threat to groundwater (Appendix C).

**HPLC and GC-MS Analyses**

The HPLC and GC-MS retention times for some of DNAN’s transformation products are shown in Table 1.3. Unknowns could sometimes be identified by matching their GC-MS chromatograms with those in the NIST library (Appendix D).
Table 1.3. Retention times and peak absorbance wavelengths for standards, for identified and for unknown compounds. We found that the HPLC retention times shifted depending on what other compounds were present in the sample. Here we listed the times for the pure standards, when available.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>GC-MS Retention time (min.)</th>
<th>NovaPak Retention time (min.)</th>
<th>Hypercarb Retention time (min.)</th>
<th>MW</th>
<th>(\lambda_{\text{max}}) (nm)</th>
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<td>1,2,4-benzenetriol#</td>
<td>7.8, 8.2</td>
<td>0.7</td>
<td>2.7, 6.0, 13.3</td>
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<td>254, 374</td>
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<td>4.9**</td>
<td>33.8</td>
<td>184</td>
<td>212, 257, 294</td>
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<td></td>
<td></td>
<td></td>
<td>182</td>
</tr>
<tr>
<td>Unknown 1</td>
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<td>37.1</td>
<td></td>
<td>215, 270, 400</td>
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<td>4-nitroaniline</td>
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<td>2.56</td>
<td>35.58</td>
<td>138</td>
<td>240, hump 380</td>
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<td>2-methoxy-5-nitrophenol#</td>
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<td>4.5</td>
<td>19.7</td>
<td>169</td>
<td>212, 242, 304, 344</td>
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<td>Unknown C</td>
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<td></td>
<td></td>
<td></td>
<td>214</td>
</tr>
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<td>Unknown 3</td>
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<td></td>
<td>222, 314</td>
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<td>216, 241, 273, 372</td>
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<td>NTO#</td>
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<td>0.67*</td>
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<td>214, 312</td>
</tr>
<tr>
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<td>MNA</td>
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<td>13.56</td>
<td>152</td>
<td>Broad peak 228 and 372</td>
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<td>Unknown B</td>
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<td></td>
<td>198</td>
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<tr>
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<td>12.2</td>
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<td>220, 275, 330</td>
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<td>4.0</td>
<td>24</td>
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<td>0.76*</td>
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<td>HMX</td>
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</tr>
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<td>RDX#</td>
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<td>2.2</td>
<td>222</td>
<td>231- shoulder</td>
</tr>
<tr>
<td>2,4-Dinitroaniline</td>
<td>11.2</td>
<td>3.88</td>
<td>24.46</td>
<td>183</td>
<td>226, 260, 306, 378</td>
</tr>
</tbody>
</table>

# Pure standard; * Elutes close to the solvent peak; ** To retain 2,4-DNP on the C8 column, we lowered the pH of the mobile phase (acetic acid added to 85/15 water/isopropanol) below the pK\(_a\) of 2,4-DNP (4.09), to ensure that the compound was in the non-dissociated form. Above the pK\(_a\), the very polar phenolate ion forms and elutes with the solvent peak; ***Not compatible with high temperature of the GC and elutes as a broad, asymmetrical peak. Italized values highlight uncertain matches between compounds identified by HPLC and GC-MS.

After analyzing the standards, we analyzed: (1) water samples for IMX-101, IMX-104 and PAX-21 collected from the beginning (T=1, 17 days), middle (T=10, 360 days) and end (T=18, 800 days) of the outdoor dissolution experiment; (2) the acetonitrile used to extract frits for IMX-101-1, IMX-104-1 and PAX-21-1; (3) DNAN thin films that were exposed to sunlight and some also to UV-radiation and (4) a saturated DNAN solution. We were interested in determining if the photo-degradation products formed on these various samples were different.
Compounds detected in the effluent and on the frits of the outdoor IM formulations

We analyzed the solid products dried onto the frits holding the IM samples as well as the effluent derived from the IM surfaces (Table 1.4). Below we focus on the degradation compounds but NQ and NTO where also present in all IMX-101 sample, NTO, RDX and HMX in all IMX-104 samples and AP, RDX and HMX in the PAX-21 (T=1) sample and RDX and HMX in the other PAX-21 samples. We also detected unknowns (UK). The most prominent were labeled using numbers for HPLC unknowns and letter for those detected by GC-MS. Note that for most of these samples the quantities of degradation products were small relative to DNAN, and as the DNAN concentration decreased, the concentrations of the products were undetectable.

Effluent Samples

All the effluent samples had 4-MeO-3-NP and most had 2-MeO-5-NA. The concentrations of 4-MeO-3-NA, 2-MeO-5-NP and UK-1 were lower and consequently not always detected by all three analytical methods. Trace quantities of DNP were observed by GC-MS only and 2-MeO-5-NP could only be detected using selective ion monitoring at m/z = 169 whereas the higher concentrations of 4-MeO-3-NP were also detected in full scan mode.

PAX-21 T=1 was unusual in having a high concentration of 2-MeO-5NA (10% of the DNAN), and a microbial biofilm (Figure 1.13). This is the only sample we analyzed that contained ammonium perchlorate and we think that the latter promoted the microbial growth that transformed DNAN into 2-MeO-5NA. PAX-21 also contained small amounts of 4-MeO-3-NP and 4-MeO-3-NA and three compounds that we identified by matching their mass spectra to ones in the NIST database. They are N-methyl-p-nitroaniline (MNA), 2,4-dinitroaniline and 4-nitroaniline (Figure 1.13).

MNA is added to DNAN during the production of PAX-21 to reduce DNAN’s the melting temperature (Doll et al. 2006). The structure of 4-nitroaniline suggests it formed from MNA and we think that the 2,4-dinitroaniline was an impurity in the DNAN. PAX-21 was one of the first insensitive explosive produced and contained DNAN purchased from China that was of lower purity than the DNAN produced at Holston Army Ammunition Plant (Fung et al. 2010). DNAN at Holston is produced by
direct nitration of para-nitroanisole (Fung et al. 2010) or by the reaction of 4-chloro-1,3-dinitrobenzene (Fedoroff et al. 1960). Our GC-MS analysis of DNAN from Holston showed trace amounts of chloronitrobenzenes and 1-Ethoxy-2,4-dinitrobenzene and we occasionally detected these compounds in our DNAN crystal samples (Appendix D).

The T=10 and T=18 effluent samples still contained small amounts of 4-nitroaniline but MNA and 2,4-dinitroaniline were not detected. The GC-MS chromatograms for these samples showed a sharp DNAN peak superimposed on two broad peaks; the one at 10.3 is RDX and the one at 9.9 is thought to be HMX. Both RDX and HMX degrade in the GC-MS column (Appendix D). Except for PAX-21 T=1, the effluent samples were similar to one another.

Compositional changes of effluent samples with time.

Two effluent samples IMX-101-18 and IMX-104-18 were analyzed immediately after collection and then re-analyzed after being refrigerated for six months. The HPLC Hypercarb analyses for the initial IMX-101 sample shows that it contained an unknown peak at 1.1, NQ, NTO, 4-MeO-3-NA, 4-MeO-3-NP, two unknown peaks at 21.3 and 24 min. and DNAN. After 6 months the sample contained NQ, NTO, an unknown peak at 2.4 min, 4-MeO-3-NA, 4-MeO-3-NP, unknown peaks
at 15.5, 19.6 and 22.2 min, 2-MeO-5-NA, DNAN and UK-1. These comparisons suggest that 2-MeO-5-NA, the peak at 2.4 min and UK-1 developed in the solution.

Hypercarb analyses done on IMX-104 show that initially the effluent sample contained some small peaks in the pre-solvent peak area, NTO, RDX, HMX, 4-MeO-3-NA, 4-MeO-3-NP, two small peaks at 21.3 and 23.4 min. and DNAN. After six months the sample contained NTO, RDX, an unknown peak at 2.4, HMX, 4-MeO-3-NP, DNAN and UK-1. Again the peak at 2.4 min and UK-1 developed in the solution.

Frit Samples

The frit samples appear to have a more compounds that the effluent samples including an unknown (UK-3), unique to these samples. HPLC Hypercarb analyses of the IMX-101 frit samples show DNP, the methoxy phenols and anilines, UK-1, -2, and -3 (Figure 1.14), and an unknown at 18.5 min. GC-MS for this sample found both methoxy phenol and aniline isomers and UKs -A, -B and –C.

The IMX-104 frit samples contained 4-MeO-3-NP, 2-MeO-5-NP, 2-MeO-5-NA, and 4-MeO-3-NA and UK-1, -2, and -3. Similar to the frit analyses for the other formulations, the PAX-21 frit sample also contained small amounts of 4-MeO-3-NP, 2-MeO-5-NA, and 4-MeO-3-NA, UKs 1, 2 and 3 (Table 1.4). The greater number of compounds detected is likely attributable to sample concentration, which was greater for the solid material extracted off the frit than for the effluent samples.

DNAN crystals and aqueous DNAN solutions

Products formed on solid DNAN may be different from those formed in on IM formulations or in aqueous DNAN solutions. To find out, we dissolved DNAN crystals and evaporated the solution into thin films, thus maximizing the surface area exposed to sunlight.
Table 1.4. Results from the GC-MS and NovaPak8 (NP) HPLC columns for samples analyzed.

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<thead>
<tr>
<th>Compound</th>
<th>2,4-DNP</th>
<th>UK-A</th>
<th>2-MeO-5-NP</th>
<th>UK-C</th>
<th>4-MeO-3-NP</th>
<th>4-MeO-3-NA</th>
<th>UK-B</th>
<th>2-MeO-5-NA</th>
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<tr>
<td>MW</td>
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<td>182</td>
<td>169</td>
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<td>169</td>
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<td>184</td>
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</tr>
<tr>
<td></td>
<td>HPLC</td>
<td>HPLC-UK-1</td>
<td>HPLC-UK-3</td>
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<td>HPLC-UK-3</td>
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<tr>
<td>Retention Time (min)</td>
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<td>8.67</td>
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<td>9.03</td>
<td>20</td>
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<td>IM Outdoor</td>
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<td></td>
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IMX101 Frit: Acetonitrile rinse of IMX101 particle supporting glass frit from the outdoor dissolution studies.
SS Film: DNAN film on a glass surface that was formed from a volume of a stock solution of DNAN in acetonitrile.
Crystals: DNAN crystal thin films exposed to ambient light and UV light (312 nm) from a FOTO/Photronics Transilluminator (FOTODYNE Incorporated, Hartland, WI).
Aqueous Evap: Saturated aqueous solution of DNAN set in the window sill.
For GC-MS, all effluent samples were solid-phase extracts analyzed by Single Ion Monitoring at mass 169. We exposed crystal 7 to both sunlight and to 18 hrs of UV irradiation.

- All three techniques found the compound
- Not detected
- na - not analyzed
Figure 1.14. Hypercarb analyses of effluent from frit samples showing elution times of the methoxy aniline and phenol compounds (red arrows) and the elution time of three unknown compounds.
HPLC analyses of the DNAN thin films contained 4-MeO-3-NA, 4-MeO-3-NP, 2-MeO-5-NA, UK-1 and UK-2. Interestingly, we found what appear to be two isomers of DNAN, one that eluted at ~12 min. and the other at ~20 min. Using the GC-MS we identified small amounts of 4-MeO-3-NA, 4-MeO-3-NP, 2-MeO-5-NA, UK-B, and larger amounts of UK-A. We also found small amounts DNAN manufacturing impurities: chloronitrobenzenes eluting at 6.05 and 6.9 min., 2-propanol, 1-chloro-, phosphate (3:1) eluting at 9.73 and 1-ethoxy-2,4-dinitrobenzene eluting at 9.85. Compounds were identified if their GC-MS chromatograms matched chromatograms in the NIST database > 90%.

Initially the DNAN saturated solution contained only DNAN and UK-2. With time the DNAN solution developed 4-MeO-3-NA, 4-MeO-3-NP, 2-MeO-5-NA, UK-1, a peak at 9.8 and the UK-2 disappeared. We think UK-2 is an isomer of DNAN and that the other compounds derive from the photo-transformation of DNAN.

In summary, the effluent samples tend to have fewer compounds than the frit samples or the irradiated thin films. As the effluent samples were collected about every two to three weeks, compounds washed off the IM formulations had time to interact with one another in solution, albeit in the dark. Such interaction might explain results from irradiation studies of DNAN aqueous solutions that appear to reach a stable end state after three weeks (Hawari et al. 2015).

**Unknowns-HPLC**

We used the UV-Vis spectra from the diode array detectors on the HPLC to pair unknown peaks seen using the two HPLC methods. Figure 1.15 shows examples of three unknown peaks that we were able to pair. UK-1 was found in most of the samples we analyzed, UK-2 appears to be a DNAN isomer, and UK-3 is unique to the frits.

*Unknown 1:* The first panel shows the HPLC chromatograms for an IMX-104 effluent sample (T=18) collected on day 800 of the test. Below the chromatograms are the UV-Vis spectra of the compound producing the peaks. The compound eluting at 5.5 min. on the NovaPak has a very similar UV-Vis spectrum to that eluting at 37 min. on the Hypercarb.
Figure 1.15. Effluent collected from IMX-104 (T=18) and UV-Vis spectrum of the peak at 5.5 min. on the Novapak and at 37 min. on the Hypercarb column. Unknown peaks and their UV-Vis spectra from the IMX-101#1 frit extracts.
**Unknown 2:** The second set of chromatograms is from the IMX-101-1frit extract. One compound (red arrows) eluted at 10.2 min. on the *NovaPak* and 12.2 and occasionally at 20.5 min. on the Hypercarb column (UK-2). Their UV-Vis spectra resemble that of DNAN but the wavelengths at which the major absorption peaks occur are shifted to longer wavelengths. For example, DNAN has absorption peaks at 214, 260 and 299 nm, whereas this compound has absorption peaks at 220, 276 and 330 nm. We think this compound is 2,6-DNAN.

**Unknown 3:** The IMX-101-1frit extract had another unknown compound (UK-3) unique to these samples. This compound (blue arrows in Figure 1.15) eluted at 12 min. on the *NovaPak* and at 14.6 min. on Hypercarb column.

We saw many transient peaks in the HPLC chromatograms. The UV-Vis spectra of some of these resemble those of the known degradation products suggesting similar structures.

**Unknwons GC-MS**

The GC-MS analyses provide the molecular weight and information about the structure of unknown compounds. We have labeled the unknowns found by GC-MS using letters as we are still trying to match them to the unknown compounds found by HPLC.

**Unknown A:** In the GC-MS chromatograms of the most samples, we saw a peak with a retention time of 8.45 minutes and a base peak of m/z = 182 (SM6). The unknown compound has the characteristics of a nitroaromatic that include an ion (m/z = 136) resulting from loss of 46 (NO₂) and the presence of m/z = 30 (NO). The ion m/z = 106 corresponds to a loss of 76 (CH₂ONO₂).

The mass spectrum did not produce a high quality match in the NIST database. Hawari (2011) reported a compound with a molecular weight of 182 that he suggested was 4-nitrophenol with a -NH-CHO group in the ortho position, C₇H₆N₂O₄ (Appendix D). An alternative structure is the nitroso compound, 1-methoxy-4-nitro-2-nitrosobenzene (Appendix D). The photodecomposition of nitrobenzene to nitrosobenzene has been reported by Hastings and Matsen (1948) and our data support either structure. Regardless of its structure, the compound must be fairly stable or continually produced or both as it is seen in most samples. We think this compound is the same as UK-1 found by HPLC because the latter is present in the same samples and has a UV-Vis spectrum consistent with that of a nitroaromatic compound.
Unknown B (DNAN isomer): A peak with a retention time of 9.34 minutes and a mass spectrum consistent with DNAN (probably, 2,6-DNAN) was present in the DNAN samples that were analyzed within the first few days of exposure to sunlight or UV light (312 nm) (Figure 1.16) and in the Frit samples. The compound was only detected in one of the effluent samples (IMX-101-1, T=1). If this compound is 2,6-DNAN it is likely a manufacturing impurity of 2,4-DNAN, analogous to the presence of 2,6-DNT in military grade 2,4-DNT. We think this compound corresponds to UK-2 seen in the HPLC chromatograms because both unknowns are found in the same samples and because the UV-Vis spectrum of UK-2 is very similar to that of DNAN.

Unknown C: A peak with a retention time of 9.03 minutes and a mass spectrum of 214 was found only in the frit samples. We think this may be the same compound as UK-3 found by HPLC because it too was only found only in these samples. Although we have a mass and possibly a UV-Vis spectrum for this compound its identity is not known.

Unknown D: A small peak at 9.8 min (just after the 2,4-DNAN peak) had a base peak at m/z = 184. Assuming this base peak corresponds to the molecular ion, a molecular weight of 184 is consistent with 2-hydroxylamino-4-nitroanisole that is a precursor to 2-methoxy-5-nitroaniline (2-MeO-5-NA). As described by McCormick et al. (1976) for TNT and other nitroaromatics, a nitro (-NO₂) group is reduced to an amino (NH₂) group via a nitroso (-NO), followed by hydroxylamino (-NHOH) intermediates. Given that we detected 2-MeO-5-NA in most of our samples and possibly a nitroso (UK-A), detection of this intermediate is plausible.
Figure 1.16. (a) Mass spectrum of an unknown compound having a slightly shorter retention time than that of 2,4-DNAN and a similar pattern of mass fragments; tentatively identified as 2,6-DNAN; (b) Mass spectrum of 2,4-DNAN; (c) DNAN solution before and after exposure to sunlight. Note the peak we think corresponds to 2,6-DNAN disappears after sunlight exposure while 4-Methoxy-3-Nitrophenol, the methoxy nitoaniline isomers and unknown A are formed.
Conclusion

Insensitive formulations differ from conventional explosives in that they: deposit more of their fill onto range soils during high order and blow-in-place detonations; contain crystalline components that have widely different aqueous solubility, and that are orders-of-magnitude more soluble than TNT or RDX; and have a DNAN matrix that is less soluble than the crystal constituents. Our work shows that for the same mass deposited, IM formulations will dissolve more quickly than HE formulations. Not only are their components more soluble, but IM formulations are more friable than TNT and Comp B and crumble into many pieces, thereby increasing the surface area available to dissolve.

As was found for laboratory tests on mm-size particles, the outdoor tests show that the constituents of these formulations dissolve in the order of their solubility. Unlike the laboratory tests, the outdoor results reveal that DNAN dissolves quasi-linearly as a function of precipitation. We think fragmentation of these cm-sized particles is responsible for this quasi-linear dissolution and use this relationship to estimate decadal particle life spans for cm-sized particles.

DNAN (2,4-dinitroanisole) is one of the main ingredients in insensitive munitions formulations and one of the least soluble of the multiple constituents of the IMX-101, IMX-104 and PAX-21, studied here. Its low solubility suggests that solid DNAN persists on range soils and can be photodegraded. To determine what products formed on pieces of IM formulations we analyzed precipitation that had wetted chunks of three IM formulations set outdoors and analyzed the glass frits holding these samples. We also exposed DNAN films and a DNAN solution to sunlight in the laboratory.

In most cases, the peaks of transformation products detected by HPLC and GC-MS were small, <1%, compared to the peak for 2,4-DNAN, suggesting that DNAN will be the main compound entering the soil. Many peaks appeared in the chromatograms, most associated with transient compounds that were only found in a couple of samples. The exception was Unknown 1, possibly a nitrosobenzene, which was found in the majority of the samples. It, along with the methoxy phenols and methoxy anilines, are the most common DNAN degradation products found in our samples. Microbes are likely responsible for producing the methoxy-nitroanilines in our non-sterile samples and PAX-21-1 (T=1) had high concentrations of 2-MeO-5-NA and a
microbial biofilm. We think the ammonium perchlorate present in this sample stimulated microbial growth. DNP is occasionally present in small quantities but it does not appear to be a persistent photo-transformation product of DNAN under the conditions tested here.

Our results differ from those found for aqueous DNAN samples irradiated in solution possibly because during these tests the compounds in solution interacted and continued to be irradiated a process that produced a few end products. We studied photo-transformation products formed explosive surfaces that were dissolved by precipitation. Once dissolved the compounds were no longer exposed to sunlight similar to what would occur in the field where explosive aqueous solutions would enter the soil quickly. DNAN and small quantities of the compounds identified here are likely entering training range soils.

Acknowledgements

The Strategic Environmental Research and Development Program (SERDP) funded this work under their environmental restoration program and we thank Dr. Andrea Leeson, our program manager, for her continued support. The Engineer Research and Development Center’s (ERDC) 6.1 Basic Research program funded a portion of the DNAN photo degradation work and we thank them for their support.

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US Climate http://www.usclimatedata.com/climate/hanover/new-hampshire/united-states/usnh0102


Chapter 2. Outdoor dissolution studies in Arizona

Katerina Dontsova, Edward Hunt, Susan Taylor

Introduction

In order to determine if climatic conditions affect dissolution of insensitive munitions we conducted experiments in Oracle, AZ complementary to ones previously performed in New Hampshire by Dr. Taylor for traditional and insensitive munitions. She conducted outdoor weathering and dissolution tests for four high explosives (2,4,6-trinitrotoluene, TNT, Comp B, Tritonal (TNT + aluminum) and C4) and three IM formulations (IMX-101, IMX-104 and PAX-21) (Taylor et al., 2009; Taylor et al., 2015a). Less dissolution should occur in Arizona than New Hampshire given the lower rainfall rate (60 cm yr⁻¹ versus 100 cm yr⁻¹) (Table 2.1). The pattern of rainfall distribution is also different between New Hampshire and Arizona with two monsoon seasons in Arizona (larger in the summer and smaller in the winter) when several high intensity rainstorms can happen per week and little rainfall between monsoons, and lack of snow cover. Mean solar radiation is higher in Arizona than in New Hampshire (approximately 3.5 kWh/m²/day in NH and 7.2 kWh/m²/day in AZ). However, we also expect that phototransformation on the surface could shield the underlying explosives so that the weathering rind will develop slowing further transformation under conditions when rainfall does not remove products from the surfaces.

Table 2.1. Temperature and rainfall conditions in Hanover, NH, where original dissolution experiments were conducted, and Oracle, AZ, location of current study.

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Methods

We performed outdoor dissolution and phototransformation experiments under natural rainfall and sunlight and determined amount of IM constituents that that was dissolved relative to
total deposited on the soils and contribution of phototransformation. We employed methodology developed by Dr. Taylor for outdoor dissolution experiments in New Hampshire. Three different formulations were tested IMX-101 (43% DNAN, 20% NTO, 37% NQ), a TNT replacement, IMX-104 (32% DNAN, 53% NTO, 15% RDX), Comp B replacement, and PAX-21 (DNAN 34%, AP 30%, RDX 36%), formulation that has been discontinued but provides valuable insight into patterns of IM dissolution (Figure 2.1). Some of the explosive particles used for these experiments were obtained from blow in place studies (Walsh et al., 2013; Walsh et al., 2014; Walsh et al., 2015), while others were obtained from the manufacturer. Particles were previously characterized using micro-computed tomography (μCT) (Taylor et al., 2013a) to determine their internal structure.

![Composition of IM formulations IMX-101, IMX-104 and PAX-21](image)

**Figure 2.1.** Composition of IM formulations IMX-101, IMX-104 and PAX-21 (modified from Taylor et al., 2013b).

Individual pieces of explosives were placed in Buchner funnels with glass frits (4-cm-diameter with 145–175 μm openings) attached to 0.5 L bottles (Figure 2.2). Particles in the funnels were exposed to sunlight and rainfall. When it rained, precipitation wetted the particles, dissolved energetic ingredients in the formulations and products of their phototransformation, and traveled through the funnels to the bottles shielded from sunlight and temperature extremes by the isolated box. In the sample box we also placed solutions of NTO, DNAN, and NQ at 1 and 10 mg L⁻¹ concentrations as well as solutions of IMX-101 and 104 that were sampled regularly to control for degradation in solution. The bottles were exchanged after rainfall, and the explosive pieces photographed *in situ* and weighed. Since the IM particles tend to become fragile after initial exposure to rainfall due to NTO dissolution we placed them in PTFE mesh cradles, which allowed removal of particle for weighing without disturbing it. We also measured precipitation volumes and determined concentrations of explosives (NTO, DNAN, RDX, AP and NQ) and their known
transformation products (2-ANAN, 2-amino-4-nitroanisole, also known as 2-methoxy-5-nitroaniline or MENA and its isomer 4-ANAN, 4-amino-2-nitroanisole, products of DNAN transformation) and impurities (HMX in RDX) of the water samples. An adjacent LP02 pyranometer provided solar radiation data, while collected solution volumes were used to estimate amount of rainfall that the particles were exposed to during the period of study.

**Figure 2.2.** Experimental setup to examine dissolution and phototransformation of insensitive munitions: a) a bottle for collection of solution with a funnel attached and unweathered particle of IMX-104; b) a particle of IMX-104 from low-order detonation on a glass frit and PTFE mesh in the funnel after one month of exposure to sunlight (no rain); c) a light-protected container with bottles and funnels with the particles exposed to sun and rainfall. Container is equipped with temperature sensors and the LP02 pyranometer to measure solar radiation.

Solution was analyzed for energetic compounds and their transformation products and impurities using Dionex Ultimate 3000 high performance liquid chromatograph (HPLC) equipped with a diode array detector (ThermoFisher, MA) and Dionex ICS 5000 ion chromatography system (IC) with conductivity detectors (ThermoFisher, MA). The method for NTO adapted from Le Campion et al. (1999) employed 75:25 acetonitrile (ACN): deionized water mobile phase acidified with 0.1% trifluoroacetic acid (TFA) ran isocractically at 1 mL min⁻¹. NTO and its transformation product (5-amino-1,2,4-triazol-3-one, ATO) were separated using a Thermo Scientific Hypercarb column at 32°C. NTO was detected at approximately 2.8 minutes using 315 nm wavelength, while 220 nm wavelength was monitored for ATO (Le Campion et al., 1999). DNAN, RDX, NQ, HMX and DNAN transformation products 2-ANAN and 4-ANAN, were analyzed using the Thermo Scientific Acclaim reversed phase column C-18
with 5-µm particle size, mobile phase ratio of 43:57 methanol and water and a flow rate of 1 mL min⁻¹ (Olivares et al., 2013). The wavelengths used for detection and quantification were 300 nm for DNAN, NQ, 254 nm for 2-ANAN, 4-ANAN, RDX, HMX, and 210 nm for DAAN. The retention times for each compound on HPLC were for DNAN approximately 21 minutes, 11 minutes for 2-ANAN, 6 minutes for 4-ANAN, 8 minutes for RDX, 5 minutes for HMX, and 3 minutes for NQ. Detection limits were 0.015 mg L⁻¹ for DNAN, 2-ANAN, 4-ANAN, NQ, RDX, HMX, and 0.020 mg L⁻¹ for NTO.

Perchlorate ion (ClO₄⁻) was analyzed using Ion Chromatography: Dionex™ IonPac™ AS20 capillary IC Column and AG20 guard column with 22 minute run at 0.012 mL min⁻¹ and 35mM KOH isocratic eluent. Concentrations of ammonium (NH₄⁺) and nitrate (NO₃⁻), known products of NTO transformation (Krzmarzick et al., 2015; Madeira et al., 2017) as well as phototransformation of DNAN (Hawari et al., 2015), were also determined using Ion Chromatography (Thermo Scientific Dionex™ ICS-5000+ Ion Chromatography System). For nitrates we incorporate the capillary IC using Ion Swift MAX-100 0.25 mm x 250 mm column with flow rate of 0.012 mL/min. Ammonium method used an analytical microbore column (2 mm x 250 mm IonPac 12A column) with flow rate of 0.25 mL min⁻¹.

**Results**

**Weather conditions during experiment**

Experiment was started on February 4th 2016 when six particles each of IMX-101, IMX-104 and PAX-21, three from manufacturer (MA, MB, and MC) and three resulting from low order detonations (FA, FB, and FC) (Walsh et al., 2013; Walsh et al., 2014; Taylor et al., 2015a; Walsh et al., 2015), were put outside to dissolve. Particle weight varied between 0.1718 and 2.6151 g. Experiment still continues with particles exposed, but results here are presented through 390 days of the experiment. Figures 2.3 and 2.4 show global radiation measured close to the particles and average rainfall in mm (determined from weight of solution collected in each bottle) as a function of time from the beginning of experiment. Both annual (Figure 2.3a) and daily (Figure 2.3b) variation can be observed in the amount of light particles were exposed to over during of experiment. There was little rainfall in the 1st 150 days of the experiment followed by
summer and winter monsoons with more frequent rains after that (Figure 2.4).

**Figure 2.3.** Global radiation, expressed as average irradiance per 15 minutes, W m$^{-2}$, measured next to the experimental setup over the course of the experiment (a) and a close up for shorter period of time to show daily variation.

**Figure 2.4.** Rainfall amount and distribution during experiment, mean across all samples, mm.
### Particle appearance

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<td>13 May 2016 Day 99</td>
<td>12 December 2016 Day 312</td>
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<tr>
<td>IMX-104 MB</td>
<td></td>
<td></td>
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<td>PAX-21 FB</td>
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**Figure 2.5.** Images of particles of IMX-101, IMX-104 and PAX-21 over time as they were exposed to sunlight and rainfall in Oracle, AZ.

Particles exposed to sun and rainfall changed their appearance over time (Figure 2.5). They changed color from cream-colored or yellowish to brick red indicative of the phototransformation products of DNAN. The color intensity generally increased over time, except for PAX-21 which initially became brighter but later developed a paler greyish cover on the surface as a result of armoring of the surface with undissolved crystals of RDX. Color intensity also was higher before the rainfall periods and lower after. Particles of all studied formulations developed pits on the surface where crystals of more soluble constituents, such as NTO and NQ in IMX-
101, NTO in IMX-104, and AP in PAX-21 were originally present. Several particles also broke apart.

**Dissolution of IM constituents**

As observed in previous indoor and outdoor experiments (Taylor et al., 2015a; Taylor et al., 2015b) energetic components dissolved in order of their solubility, with NTO and NQ in IMX-101, NTO in IMX-104, and AP in PAX-21 dissolving 1st followed by DNAN and RDX (Figure 2.6). There were distinct steps in the dissolution plots corresponding to dry periods between the periods of frequent rainfall. In general, plots appeared less gradual than ones obtained for insensitive munitions in New Hampshire under wetter conditions (Taylor et al., 2015a).

Perchlorate dissolved the fastest and reached plateau for several particles indicating that all perchlorate in the particle was dissolved. Calculated percent dissolved was not necessarily 100% when this happened due to deviation from ideal mixture composition in the particle. There was difference in behavior of fired and unfired particles of PAX-21 with quick initial dissolution of perchlorate in manufactured particles (Figure 2.6c) and more gradual release in detonated particles (Figure 2.6d). This is better seen in the plots of IM dissolution as a function of cumulative rainfall (Figure 2.9). The pattern was attributed to the difference in shape between two groups of particles: detonated and not detonated. While detonated particles were chunky, manufactured particles were slivers, with higher specific surface area and majority of perchlorate accessible to water from the surface.

Dissolution of NTO and NQ was also quicker initially followed by slower dissolution over time (Figure 2.7 and 2.8). It is explained by higher solubility and consequently fast dissolution of these compounds as they are exposed on the surface as particle is 1st deposited followed by slower dissolution later due to access to these compounds being restricted by DNAN matrix.

RDX and DNAN dissolved much slower and patterns of their dissolution were similar (Figure 2.7, 2.8, 2.9) and linearly related to cumulative rainfall. The plots of DNAN and RDX concentration vs. cumulative rainfall did not overlap though as size and surface area of each particle was different, but was similar for similarly sized particles.
For most constituents there was a negative non-linear relationship between amount of rainfall and solution concentrations (not shown), possibly due to kinetic limitation on dissolution during high intensity rainfall. This would indicate that climates where high intensity rains predominate would have less explosives dissolved per rainfall amount. This is supported by data so far collected in Arizona.

**Figure 2.6.** Dissolution of NTO, NQ and DNAN from IMX-101 (a), NTO, RDX, and DNAN from IMX-104 (b), and perchlorate, RDX, and DNAN from PAX-21 (c and d) as a function of time.
Figure 2.7. Dissolution of NTO, NQ and DNAN, as a function of rainfall amount from six IMX-101 particles. NTO is indicated in green, NQ in burgundy and DNAN in blue.

Figure 2.8. Dissolution of NTO, RDX, and DNAN as a function of rainfall amount from six IMX-104 particles. NTO is indicated in green, NQ in burgundy and DNAN in blue.
**Figure 2.9.** Dissolution of ClO$_4^-$, RDX, and DNAN as a function of rainfall amount from six PAX-21 particles. NTO is indicated in green, NQ in burgundy and DNAN in blue.

**Table 2.2.** Removal of munitions constituents in solution as percent of original mass in the particle.

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<tr>
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<th>IMX-101 (NQ)</th>
<th>IMX-104 (DNAN)</th>
<th>IMX-104 (RDX)</th>
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<td>2.75</td>
<td>4.38</td>
<td>39.85</td>
<td>1.67</td>
</tr>
<tr>
<td>FA</td>
<td>2.43</td>
<td>15.05</td>
<td>40.81</td>
<td>5.26</td>
<td>4.64</td>
<td>47.42</td>
<td>0.53</td>
</tr>
<tr>
<td>FB</td>
<td>1.26</td>
<td>9.10</td>
<td>39.17</td>
<td>2.21</td>
<td>2.84</td>
<td>34.70</td>
<td>1.45</td>
</tr>
<tr>
<td>FC</td>
<td>2.71</td>
<td>16.98</td>
<td>53.27</td>
<td>2.77</td>
<td>4.07</td>
<td>20.90</td>
<td>2.79</td>
</tr>
<tr>
<td>Average</td>
<td>2.58</td>
<td>19.83</td>
<td>53.78</td>
<td>4.23</td>
<td>4.39</td>
<td>43.85</td>
<td>1.69</td>
</tr>
<tr>
<td>SE</td>
<td>0.33</td>
<td>3.57</td>
<td>5.53</td>
<td>1.35</td>
<td>0.78</td>
<td>10.30</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Over 390 days of the experiment 53.8 ± 5.5% of NTO dissolved from IMX-101 particles and 43.9 ± 10.3 from IMX-104 (Table 2.2) likely due to presence of 6% of less than 20-µm crystals of NTO mixed in with 360 µm crystals in IMX-101, while in IMX-104 larger (300 µm)
with smaller specific surface area crystals of NTO are used (Figure 2.1). Similarly, more RDX was removed from IMX-104 then PAX-21 (4.39 ± 0.78% vs 1.66 ± 0.30% because crystal size of RDX in IMX-104 is smaller (4 µm), while in PAX-21 31% of RDX is coarser 100-µm crystals and only 5% are 8 µm (Figure 2.1).

In IMX-101, less NQ (19.8 ± 3.6%) is dissolved than NTO (53.8 ± 5.5%) consistent with an order of magnitude higher solubility of NTO and with presence of smaller NTO crystals in the mixture when NQ crystal size was 300 µm. However, in IMX-104 and PAX-21, similar percentage of RDX and DNAN was recovered in solutions despite higher water solubility of DNAN. Comparisons between different IM constituents described above are based on dissolution values normalized to the content of each compound in the formulation, un-normalized concentrations had similar relationship between compounds to normalized ones for IMX-101 and PAX-21 and higher concentrations of DNAN than RDX in IMX-104. There was no significant effect of whether particles were new or resulted from low order detonations on recovery of IM constituents dissolution.

**Figure 2.10.** Correlation between concentrations of HMX and RDX in solutions resulting from dissolution of IMX-101 and PAX-21 particles.

We detected HMX in solutions resulting from dissolution of formulations containing RDX, IMX-104 and PAX-21, consistent with presence of HMX in technical grade RDX. While released HMX concentrations were different due to different amount of RDX present in each formulation (15% in IMX-104 and 36% in PAX-21), they were highly correlated to RDX
concentrations (P equal to 2.50*10^{-72} and 2.64*10^{-64} for IMX-104 and PAX-21 respectively) for both formulations and slopes of the lines were not statistically different (0.094 ± 0.005 for IMX-104 and 0.094 ± 0.006 for PAX-21) and agreed with known percent HMX in RDX (Figure 2.10). Since differences in formulation total composition and particle size of RDX crystals did not affect ratio of HMX to RDX in solution we think that both compounds dissolve from the formulations together and are not affected by differences in their solubilities.

We also observed products of DNAN transformation, 2-ANAN and its isomer 4-ANAN in collected solutions, possibly due to contamination of the particles with microbial communities as a result of dust deposition. Greater concentrations of 2-ANAN than 4-ANAN were measured indicating regioselectivity of transformation reaction (Hawari et al., 2015; Arthur et al., 2017). A sum of these products in solution averaged 1.27 ± 0.16% of DNAN concentrations in IMX-101, 1.12 ± 0.12% in IMX-104, and 3.50 ± 0.33% in PAX-21 but varied in time. Samples collected in the 1st 150 days of exposure, when there was little rain (Figure 2.3), accumulated larger percentage of DNAN transformation products. No change in concentration of constituents was observed in the control vessels that were left outside but protected from sun (and potentially bacteria-carrying dust) within the experimental box and no products of DNAN transformation were detected in these solutions indicating that transformation was happening on explosives particles.

We also detected ammonium and nitrate, products of NTO biotransformation (Krzmarzick et al., 2015; Madeira et al., 2017), in solutions resulting from dissolution of IMX-101 and 104. Both nitrate and ammonium have also been shown to result from DNAN photolysis in solution (Hawari et al., 2015) and nitrate was detected during RDX photolysis (Bedford et al., 1996; Taylor et al., 2010). However, we cannot definitely attribute them to transformation of IM constituents in these experiments due to concurrent detection of these ions in blank samples without the particles, as well. After removal of several outliers with ammonium concentrations above 30 mg L^{-1} (1/27 in blank, 5/162 in IMX-101 and 3/162 in IMX-104) average concentration over 390 days of the experiment for blank samples was 4.0 ± 1.9 mg L^{-1} (mean ± confidence interval) for ammonium and 2.2 ± 0.9 mg L^{-1} for nitrate, while results for IMX-101 were 2.99 ± 0.43 mg L^{-1} for ammonium and 3.24 ± 1.75 mg L^{-1} for nitrate, and for IMX-104 it was 3.09 ± 0.39 mg L^{-1} for ammonium and 3.35 ± 0.72 mg L^{-1} for nitrate, not significantly different from blank without explosives for both ions. We explain presence of these ions in blank samples by
atmospheric deposition in natural rainfall and dust, and since they were not different from IM samples have to conclude that transformation of IM constituents was not the source of N-containing inorganic ions. However, ratio of nitrate to ammonium was different between blank and IMX samples. There was a strong relationship between ammonium and nitrate concentrations for blank, IMX-101 and IMX-104 samples (P value of $1.98 \times 10^{-6}$ and $2.30 \times 10^{-47}$, and $1.43 \times 10^{-55}$, respectively) and while slopes of these relationships were not statistically different between IMX-101 and IMX-104, they were significantly lower for blank samples (Figure 2.11).
Figure 2.11. Relationship between ammonium and nitrate concentrations in solutions of IMX-101, IMX-104 and blank samples without explosives.
It was observed that pH of solutions resulting from dissolution of IMX-101 and IMX-104 particles was related to their NTO concentrations (Figure 2.12) consistent with previous observations in lab and outdoor dissolution experiments for IM formulations (Taylor et al., 2015a). The relationship was similar across the two studied formulations that contain NTO, IMX-101 and IMX-104. However, there was a considerable scatter in the data likely due to contamination with high pH dust that is prevalent in the Southwest.

![Figure 2.12](image.png)

**Figure 2.12.** Relationship between pH and NTO concentration for solutions resulting from dissolution of IMX-101 and IMX-104 particles. Data was combined for all studied particles.

**Mass balance**

Weight of IM formulation particles decreased with time and rainfall. Lab dissolution studies for traditional munitions (Taylor et al., 2009) and IMX-101, IMX-104 and PAX-21 (Taylor et al., 2015a) showed good mass balance with all mass loss for the particles recovered in solution. However, in outdoor experiments in New Hampshire for both traditional and insensitive munitions while there was linear relationship between mass loss in the particles and recovery in solution, the slope was less than one, indicating that there was some amount of energetics that was lost from the particle but not recovered in solution by HPLC analysis (Chapter 1). This mass loss was attributed to phototransformation of energetics and formation of volatile and unknown products of phototransformation. In New Hampshire for the traditional munitions on
average $83.5 \pm 4.4\%$ original mass lost from the particle was not recovered in solution (Chapter 1), while for IM munitions percent was lower ($18.7 \pm 3.7\%$) due to higher solubility and faster dissolution of IM components, such as NTO, NQ and AP (Chapter 1). In Arizona, percent of IM explosives not recovered was higher, but not significantly different from New Hampshire with $22.8 \pm 17.8\%$ (Table 2.3). In addition, in New Hampshire there was no difference between formulations in amount of IM components that were not recovered.

**Table 2.3.** Removal of IM constituents in solution, percent of original present in the particle, after 390 days of exposure to sunlight and rainfall outdoors.

<table>
<thead>
<tr>
<th></th>
<th>Initial mass, g</th>
<th>Final mass, g</th>
<th>Difference, g</th>
<th>Dissolved mass, g</th>
<th>Missing mass, g</th>
<th>Dissolved mass/ Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMX 101 MA</td>
<td>0.7764</td>
<td>0.3190</td>
<td>0.4574</td>
<td>0.1808</td>
<td>0.2766</td>
<td>0.40</td>
</tr>
<tr>
<td>IMX 101 MB</td>
<td>0.4783</td>
<td>0.3237</td>
<td>0.1546</td>
<td>0.1305</td>
<td>0.0241</td>
<td>0.84</td>
</tr>
<tr>
<td>IMX 101 MC</td>
<td>0.3985</td>
<td>0.2983</td>
<td>0.1002</td>
<td>0.0808</td>
<td>0.0194</td>
<td>0.81</td>
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<tr>
<td>IMX 101 FA</td>
<td>0.6943</td>
<td>0.5028</td>
<td>0.1915</td>
<td>0.1039</td>
<td>0.0876</td>
<td>0.54</td>
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<tr>
<td>IMX 101 FB</td>
<td>2.6151</td>
<td>2.2553</td>
<td>0.3598</td>
<td>0.3079</td>
<td>0.0519</td>
<td>0.86</td>
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<td>IMX 101 FC</td>
<td>0.6396</td>
<td>0.4903</td>
<td>0.1493</td>
<td>0.1159</td>
<td>0.0334</td>
<td>0.78</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.70</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>IMX 104 MA$^a$</td>
<td>0.2036</td>
<td>0.1214</td>
<td>0.0822</td>
<td>0.0741</td>
<td>0.0081</td>
<td>0.90</td>
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<tr>
<td>IMX 104 MB</td>
<td>0.7192</td>
<td>0.5639</td>
<td>0.1553</td>
<td>0.1157</td>
<td>0.0396</td>
<td>0.74</td>
</tr>
<tr>
<td>IMX 104 MC</td>
<td>0.1718</td>
<td>0.1200</td>
<td>0.0518</td>
<td>0.0391</td>
<td>0.0127</td>
<td>0.75</td>
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<td>IMX 104 FA</td>
<td>0.8688</td>
<td>0.4544</td>
<td>0.4144</td>
<td>0.2398</td>
<td>0.1746</td>
<td>0.58</td>
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<td>IMX 104 FB</td>
<td>0.9744</td>
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<td>0.6600</td>
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<td>IMX 104 FC</td>
<td>0.8604</td>
<td>0.4858</td>
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<td></td>
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<td>PAX 21 MA</td>
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<td>PAX 21 MB</td>
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<td>0.2520</td>
<td>0.0569</td>
<td>0.0925</td>
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<td>PAX 21 MC</td>
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<td>0.0795</td>
<td>0.1284</td>
<td>-0.0489</td>
<td>1.61</td>
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<tr>
<td>PAX 21 FA$^b$</td>
<td>1.1052</td>
<td>0.6808</td>
<td>0.4244</td>
<td>0.1845</td>
<td>0.2399</td>
<td>0.43</td>
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<tr>
<td>PAX 21 FB</td>
<td>2.2643</td>
<td>1.4603</td>
<td>0.8040</td>
<td>0.6624</td>
<td>0.1416</td>
<td>0.82</td>
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<td>PAX 21 FC</td>
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<td>0.5633</td>
<td>0.3637</td>
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<tr>
<td>CI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.40</td>
</tr>
</tbody>
</table>

$^a$ Sample was damaged and last weight measurement was taken on day 223.

$^b$ Sample was damaged and last weight measurement was taken on day 148.

Taylor et al. (2010) demonstrated for the traditional formulations that largest particles loose the most mass, but small chunks lose a larger percentage of their initial mass due to a
larger ratio of surface area to mass. Using data collected by Dr. Taylor we observed a significant linear relationship between mass loss and initial particle mass ($P = 0.00238$) and significant negative correlation between mass loss as a fraction of the original (normalized mass loss) and original mass ($P = 0.00444$), though power function better described the second trend (Figure 2.13a and b). Linear relationship between mass loss and original mass was also observed for insensitive munition in New Hampshire (Taylor et al., 2015a) and Arizona ($P$ equal $3.89 \times 10^{-10}$ and $2.71 \times 10^{-7}$ for NH and AZ respectively) (Figure 2.13c and f). However, the slopes were 9 to 20 times larger than for traditional munitions, indicating larger mass loss (faster dissolution and transformation). The relationship between normalized mass loss and original mass was weaker for IMs (Figure 2.13d and g): there was a significant negative correlation for NH data ($P=0.0430$) but relationship was not significant for AZ data ($P=0.948$). The patterns were similar across all three IM formulations studied in AZ. The slope for mass loss vs. original mass was significantly higher for NH ($0.67 \pm 0.06$) than AZ ($0.30 \pm 0.07$) indicating greater amount of mass loss. The difference can be probably explained by the shorter duration of the experiment (13 vs 29 month), as ratios between time of exposure and slopes between two locations are almost identical ($29 \text{ months} / 13 \text{ months} = 2.23$ and $0.67 / 0.30 = 2.23$).

In experiments conducted in Arizona, it was also observed that there was a linear relationship between particle mass loss and energetics concentrations in solutions for each particle (Figure 2.14) as demonstrated by Taylor et al. (2010) for traditional munitions in New Hampshire. It was not possible to develop the same relationship for IMs in NH due to fragility of the particles. However, by placing particles in the mesh cradles in AZ experiments we were able to weight them without disturbing. Results showed that the slope of this relationship between particle mass loss and energetics recovery in solutions was smaller than one, $0.70 \pm 0.16$ for IMX-101, $0.79 \pm 0.12$ for IMX-104 and $0.86 \pm 0.28$ for PAX-21, much higher than for traditional munitions which varied between 0.16 and 0.40. There was not significant difference between IM formulations.
Figure 2.13. Relationship between particle size and mass loss of the particles for outdoor dissolution of traditional and insensitive munitions in New Hampshire and Arizona. Data for traditional munitions from Taylor at al. (2010) and for IMs from Taylor et al. (2015a).
Figure 2.14. Relationship between mass loss during particle dissolution and phototransformation and recovery of products of dissolution and phototransformation in solution analyzed by HPLC, using IMX-101 FB, IMX-104 MB, and PAX-21 MA particles as examples.
Conclusions

We conducted outdoor dissolution and phototransformation experiments for particles (as manufactured and resulting from low-order detonations) of IMX-101, IMX-104 and PAX-21 formulations. We observed release of formulation constituents in solution and mass loss of the particles as a result of dissolution and phototransformation. IM constituents dissolved in order of their solubility, with most soluble compounds dissolving first. NTO dissolved 1st from IMX-101 followed by NQ and DNAN, while in IMX-104 NTO was followed by DNAN and RDX and in PAX-21 AP was followed by DNAN and RDX in about the same concentrations. Comparison between different formulations and compounds indicated that in addition to solubility a factor that apparently influenced dissolution was crystal size of the constituents. Presence of smaller crystals with larger specific surface area resulted in greater dissolution relative to amount in the formulation. Constituents with high solubility, NTO, NQ and AP, exhibited non-linear increase with cumulative rainfall that particles were exposed to, with faster initial dissolution when crystals on the particle surface are dissolving. Over time as surface crystals were removed and crystals deeper within the particle were dissolving, release of these compounds into solution slowed down due to time needed for these constituents to diffuse to the particle surface. This trend is different from what was previously observed for the traditional munitions and more similar to behavior of propellants because of the large difference in solubilities of DNAN matrix and NTO, NQ and AP explosive fill. DNAN and RDX exhibited linear dissolution with rainfall. There was a trend for decrease in concentration of dissolving compounds in solution with increase in rainfall intensity. That would indicate that small intensity rains spread over time would dissolve more of IM constituents compared to few large rainfall events of the same total volume.

The mass of the particles decreased with time, but mass loss was not recovered completely in collected solution when analyzed by HPLC. Larger particles lost more mass but unlike traditional munitions when normalized to original mass amount lost was not inversely related to particle size. More mass relative to the original was lost in experiment conducted in New Hampshire than in current experiment, but difference was consistent with shorter duration of Arizona experiment. There was also a significant positive correlation between amount lost and recovery of constituents and their known transformation products in solution. The slope was larger (higher recovery) than was measured for traditional explosives likely due to faster
dissolution of IM compounds. There was no difference in this relationship between three studied formulations.

We recovered products of DNAN transformation, 2-ANAN and 4-ANAN. Their percentage relative to DNAN changed over time but was between one and two percent of DNAN concentrations on average for all three formulations. We also detected HMX present in IMX-104 and PAX-21 formulations as admixture in RDX. HMX recovery was similar for the two formulations and consistent with known content of HMX in technical grade RDX. We also measured inorganic N ions, nitrate and ammonium, possible products of NTO and DNAN transformation, but could not attribute them positively to explosives transformation due to their presence in blank solutions without any explosives, as well.

This study further examined dissolution and transformation of IM munitions when exposed to rainfall and sunlight outdoors, simulating behavior of IM residues during use on training grounds. Obtained data and established relationships between measured parameters help predict release of IM energetics and impact of IM deposition on contamination of the environment.

Acknowledgements

This work was funded by the Strategic Environmental Research and Development Program, SERDP, project ER-2220. We are grateful to Anthony Di Stasio and Erika Rivera, US Army Armament Research, Development and Engineering Center (ARDEC), Picatinny Arsenal for providing IMX-101 and IMX-104.

References


Chapter 3. Dissolution and Transport ofInsensitive Munitions Formulations IMX-101 andIMX-104 in Saturated Soil Columns


This material is a part of the dissertation defended by Jenifer Arthur as one of the requirementsfor her PhD degree.

Abstract

Military training exercises can result in deposition of energetic residues on militarytraining ranges and potentially groundwater contamination with munition constituents. Toevaluate dissolution and transport of energetic constituents from the new insensitive munitions(IM) formulations we conducted saturated column experiments with particles of IMX-101, whichcontains 19.7% 3-nitro-1,2,4-triazol-5-one (NTO), 36.8% nitroguanidine (NQ), and 43.5% 2, 4-dinitroanisole (DNAN) and IMX-104, which has 53.0% NTO, 15.3% 1,3,5-hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 31.7% DNAN. NTO and DNAN are emerging munitionscontaminants. The two soils used were Camp Swift (Bergstrom sandy clay loam, mixed,superactive, thermic Cumulic Haplustolls) from Camp Swift, TX and Camp Guernsey (Keeline-Turnercrest loam, mixed, superactive, calcareous, mesic Ustic Torriorthents) from CampGuernsey, WY. Flow interruption experiments were conducted to investigate sorption non-equilibrium between soil and solution phases. We used HYDRUS-1D to determine dissolutionand fate and transport parameters from the breakthrough curves and compared them with onesdetermined from lab and outdoor dissolution studies without soils and with batch and columntransport studies conducted previously with the same soils. The results indicated that insensitivemunition compounds dissolved in order of aqueous solubility as indicated by earlier dissolutionstudies. Estimated dissolution rates were higher for explosive compound with higher aqueoussolubilities. Initial elution of the high concentration pulse of highly soluble NTO and NQ wasfollowed by lower concentrations later, while DNAN had generally lower and more constantconcentrations. The sorption of NTO and NQ was low, while RDX, HMX, and DNAN all
adsorbed to the soils. We observed that DNAN transformed in soils with formation of amino-reduction products, 2-ANAN (2-amino-4-nitroanisole) and 4-ANAN (4-amino-2-nitroanisole). Adsorption parameters determined by HYDRUS-1D generally agreed with batch and column study adsorption coefficients for pure NTO and DNAN. Even in the low organic matter soils selected in this study DNAN experienced significant retardation indicating potential for its natural attenuation.

Introduction

The United States Army and BAE systems (Arlington, VA) have developed safer insensitive munitions (IM) formulations to replace 2,4,6-trinitrotoluene (TNT) and Composition B which contains 1,3,5-trinitro-1,3,5-triazine (RDX) and TNT. TNT can be vulnerable to temperature and shock causing it to detonate. Two explosive compounds, 3-nitro-1,2,4-triazol-5-one (NTO) and 2, 4-dinitroanisole (DNAN) are being tested to determine whether they will be suitable replacements. The IM formulations that have been developed using NTO and DNAN are IMX-101, composed of 19.7% NTO, 36.8% nitroguanidine (NQ), and 43.5% DNAN; and IMX-104 (53.0% NTO, 15.3% RDX, and 31.7% DNAN). NTO is used as a filler whereas DNAN is being used as a binder in these melt-cast explosive formulations.

When munitions do not completely detonate, a low-order detonation, a significant mass of the explosive compounds originally present in a round can become deposited on the ground. Training ranges are a particular concern due to the great number of rounds fired in the same location, resulting in some cases in contamination of the groundwater with munition constituents (Jenkins et al., 2001). The likelihood of IM rounds having incomplete detonation is higher than that for traditional explosives (Walsh et al., 2013) therefore resulting in more munition constituents on the ground. When explosives are exposed to rainfall, they gradually dissolve, and laboratory and outdoor studies have demonstrated that NTO and DNAN readily dissolve from IM formulations (Taylor et al., 2013; Taylor et al., 2015a; Taylor et al., 2015b). Explosive residues being transported off military ranges can result in closure of the ranges or limit training.

Exposure to explosive compounds have been found to have adverse health effects. The toxicity of the chemical compounds in IMX-101 and 104 is used to quantify the threat to the environment and human health. Health and environmental effects associated with exposure to explosive compounds vary by the explosive. Toxicological reports of NTO showed that it not
toxic to rats and mice when given orally ($LD_{50} > 5 \text{ g kg}^{-1}$), however, during skin application studies with rabbits it was found to be mildly irritating (London and Smith, 1985). Microbial degradation studies of NTO in soils show nitroreduction followed by the cleavage of the primary amine, 5-amino-1,2,4-triazol-3-one (ATO) (Le Campion et al., 1999b). Metabolic intermediates produced during the process of nitroreduction of nitro-compounds displayed cytotoxicity and neurotoxicity (Koch et al., 1979; Walton and Workman, 1987; Le Campion et al., 1999b). The oral $LD_{50}$ for NQ is 3.9 g kg$^{-1}$ in mice and 10.2 g kg$^{-1}$ in rats. Direct contact with NQ may cause irritation to the eyes and burning of the skin. Exposure to sublethal doses of NQ in rodents has caused gastrointestinal, respiratory, and central nervous system effects. Chronic exposure may result in slight hematological and liver function changes (Deeter, 2000). NQ also has low acute and chronic toxicity to a range of aquatic organisms; however, products of NQ photolysis are 100-fold more toxic (Burton et al., 1993; Sunahara, 2009). Information on the health effects of HMX is limited. It does have low toxicity to aquatic organisms. No deaths of humans and animals have resulted from inhalation exposure (Sunahara, 2009; Pichtel, 2012). RDX’s reported $LD_{50}$ in literature ranges from 44 to 300 mg kg$^{-1}$ in rats. The major toxic effects of RDX include anemia with secondary splenic lesions, hepatotoxicity, possible central nervous system involvement, and urogenital lesions. In humans and animals RDX is slowly absorbed from inhalation and from the stomach after ingestion. Chronic exposure to humans via inhalation of fine particles causes epileptiform seizures and unconsciousness. RDX is poorly adsorbed through the skin (Etnier, 1986; Deeter, 2000). Toxicological reports for DNAN indicate that it is toxic to bacteria *Vibrio fischeri* and freshwater green algae *Pseudokirchneriella subcapitata* in the mg L$^{-1}$ range and to earthworm *Eisenia andrei* and perennial ryegrass *Lolium perenne* in the mg kg$^{-1}$ range (Dodard et al., 2013). It can be metabolized in the body to 2,4-dinitrophenol, which is a chemical with a high acute and chronic toxicity. It is a slight skin irritant and mild irritant to the eyes (Davies and Provatas, 2006). Amino derivatives of DNAN, 2-ANAN (2-amino-4-nitroanisole) and 4-ANAN (4-amino-2-nitroanisole) has been shown to have both lower (Liang et al., 2013) and higher (Olivares et al., 2016) microbial toxicity than DNAN, so it has not been definitely established.

The two major processes that influence potential transport of explosive compounds off-site once they dissolved from IM particles are adsorption and transformation in soils. Knowing the physical and chemical properties of the explosive compounds can aid in analyzing the
Environmental fate and transport (Table 3.1). High aqueous solubility of NTO and NQ indicates that both compounds will be expected to readily dissolve in water, while lower solubilities of DNAN and RDX indicate that their dissolution would be slower.

Table 3.1. Environmentally relevant chemical and physical properties of DNAN, NTO, NQ, and RDX, including solubility at 25°C, octanol-water partition coefficient (K_{ow}), soil organic carbon adsorption coefficient (K_{OC}).

<table>
<thead>
<tr>
<th>Property</th>
<th>DNAN</th>
<th>NTO</th>
<th>NQ</th>
<th>RDX</th>
<th>HMX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility, mg L^{-1}</td>
<td>276.2^{a1}</td>
<td>16642.0^{c2}</td>
<td>2600 -5000^{b3}</td>
<td>59.9^{a4}</td>
<td>5^{5}</td>
</tr>
<tr>
<td>Log K_{ow}</td>
<td>1.7-1.92^{b}, 1.62^{a6}, 1.58^{7}</td>
<td>0.37-1.03^{b6}</td>
<td>-0.83^{b8}</td>
<td>0.81-0.87^{b3}</td>
<td>0.19^{a9}</td>
</tr>
<tr>
<td>Log K_{OC}</td>
<td>3.11^{a10}, 2.2^{b11}</td>
<td>3.03^{a10}, 2.1^{b11}</td>
<td>0.356^{b12}, 1.41^{b13}</td>
<td>0.88-2.4^{b4}</td>
<td>0.54-2.8^{a14}</td>
</tr>
</tbody>
</table>

^a measured; ^b estimated; ^c interpolated from measured values.

1 (Boddu et al., 2008); ^2 (Spear et al., 1989); ^3 (Mirecki et al., 2006); ^4 (Brannon and Pennington, 2002); ^5 (Glover and Hoffsommer, 1973); ^6 (Sokkalingam et al., 2008); ^7 (Hawari et al., 2015); ^8 (Dave et al., 2000); ^9 (Yoon et al., 2002); ^10 (Pesce-Rodriguez, unpublished); ^11 (Chen, 1977); ^12 (Burrows et al., 1989); ^13 (Rugge et al., 1998); ^14 (Boyer et al., 2007).

Taylor et al. (2013; 2015a; 2015b) conducted a series of experiments evaluating dissolution of IM compositions. Laboratory drip tests under controlled conditions mimicking conditions found on military training ranges indicated that IMX formulations dissolution is controlled by the aqueous solubility of the explosive compounds, with NTO dissolving 1st followed by NQ, and DNAN in IMX-101 and by RDX and DNAN in IMX-104 (Taylor et al., 2013; Taylor et al., 2015b). Dissolution of most soluble components removed them from the outer layers of the particle and created a porous structure (Taylor et al., 2013). These patterns were also observed in the outdoor dissolution studies, where in addition phototransformation of IM compounds was observed (Taylor et al., 2015a). While dissolution of NTO and NQ was high initially and then decreased over time, as these compounds were removed from the outer shell of IM particles, DNAN dissolution tended to be more constant over time.

Sorption coefficients in soil such as K_{d}, K_{OC}, as well as octanol-water partition coefficient, K_{ow}, have been reported for the traditional components of these formulations, NQ, RDX and NTO, however, for NTO and DNAN information is more sparse. NQ and NTO are both very mobile and have low K_{d}, K_{OC}, and K_{ow} values (Mirecki et al., 2006; Mark et al., 2016).
Mark et al. (2016) examined NTO interactions with a number of soils and concluded that adsorption was low and not related to amount of organic carbon in the soil, but was strongly influenced by soil’s pH due to the ionic character of NTO molecule. NQ is not adsorbed or transformed in soils (Dontsova et al., 2007; Dontsova et al., 2008; Taylor et al., 2012) in agreements with its low $K_{ow}$ values (Burrows et al., 1989; Dave et al., 2000). Log $K_{ow}$ values have been reported for DNAN and its transformation products by Hawari et al. (2015). DNAN has a higher $K_{ow}$ value indicating that it would be less mobile than NQ, NTO and RDX in soil. Batch and column soil adsorption study experiments were conducted to determine fate and transport parameters DNAN in soil (Arthur et al., 2017). It was observed that DNAN strongly adsorbed to soils with linear adsorption coefficients ranging between 0.6 and 6.3 L kg$^{-1}$, and Freundlich coefficients between 1.3 and 34 mg$^{1-n}$ L$^n$ kg$^{-1}$. Both linear and Freundlich adsorption coefficients positively correlated with cation exchange capacity and the amount of organic carbon in the soil. The column studies confirmed the impact of sorption on retardation of DNAN during transport. It was also shown that DNAN readily transforms to amino transformation products, 2-ANAN and 4-ANAN. RDX has intermediate behavior with higher $K_{ow}$, and $K_{OC}$ values than NTO and NQ, but lower than for DNAN. Low $K_d$, $K_{OC}$, and $K_{ow}$ values have been reported for RDX indicating that RDX will be mobile (Haderlein et al., 1996; Singh et al., 1998).

Richard et al. (2014) conducted dissolution and sorption experiments with IMX-101 and then examined leaching of IM compounds in effluent produced as a result of simulated rainfall. They found that IMX-101 particles dissolved slowly under simulated rainfall conditions with NQ and NTO dissolving first, leaving DNAN crystals. The results of the sorption experiments showed that DNAN and NTO sorption to soils fit the Freundlich isotherm best and desorption was limited.

The objective of this study was to examine the dissolution and fate (adsorption and mass loss) of IMX-101 and IMX-104 in two soils collected from military training ranges in Camp Swift, TX and Camp Guernsey, WY. The results are assessed and compared to the individual compounds which are part of the insensitive munitions formulations. Implications of correlations between dissolution, fate and transport parameters and soil properties for IMX-101 and IMX-104 are discussed.
Materials and Method

Soils

Camp Swift (Bergstrom sandy clay loam, mixed, superactive, thermic Cumulic Haplustolls) and Camp Guernsey (Keeline-Turnercrest loam, mixed, superactive, calcareous, mesic Ustic Torriorthents) were the soils used for this experiment. These two soils were previously used in batch and column transport experiments conducted with NTO and DNAN (Dontsova et al., 2014; Mark et al., 2016; Arthur et al., 2017; Mark et al., 2017). These soils were selected for their low organic matter content to provide conservative estimate of soil attenuation of IM compounds. Soil samples were collected to a depth of 30 cm. Camp Swift soil samples were collected at Camp Swift, TX, while Camp Guernsey soil samples were collected in Camp Guernsey, WY. Soils were air-dried and sieved (<2 mm) prior to being analyzed for pH, electrical conductivity (EC), cation exchange capacity (CEC), organic carbon content (OC), and clay mineralogy (Mark et al., 2016) (Table 3.2). Both soils had high pH and low OC content, but differed in their particle size. Camp Swift has high clay content and Camp Guernsey is a sandy soil.

Table 3.2. Measured physical and chemical properties of soils used in dissolution and transport studies with IMX-101 and IMX-104 (Mark et al., 2016).

<table>
<thead>
<tr>
<th>Soil</th>
<th>Texture</th>
<th>Clay</th>
<th>Silt</th>
<th>Sand</th>
<th>pH</th>
<th>ECb</th>
<th>SSAc</th>
<th>OCd</th>
<th>CEC8.2e</th>
<th>Mineralogy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Camp Swift</td>
<td>sandy clay loam</td>
<td>23.7</td>
<td>20.8</td>
<td>55.6</td>
<td>7.83</td>
<td>203</td>
<td>15.1</td>
<td>0.34</td>
<td>6.5</td>
<td>K,M,S,Q</td>
</tr>
<tr>
<td>Camp Guernsey</td>
<td>loam</td>
<td>4.1</td>
<td>12.5</td>
<td>83.4</td>
<td>8.21</td>
<td>477</td>
<td>3.9</td>
<td>0.77</td>
<td>2.9</td>
<td>S,M,K,C,Q</td>
</tr>
</tbody>
</table>

a In 1:1 soil:water;
b EC = Electrical conductivity;
c SSA = specific surface area;
d OC = organic carbon;
e CEC8.2 = cation exchange capacity at pH 8.2
f Mineralogy is listed in order of decreasing content: C = chlorite, HIV = hydroxyl-interlayered vermiculite, K = kaolinite, M = mica, Q = quartz, S = smectite, V = vermiculite.
Column Experiments

To measure dissolution and transport behavior of IMX-101 and IMX-104, saturated flux-controlled flow column experiments were conducted under steady-state and transient conditions. Supelco (Belfonte, PA) glass columns with internal diameter of 1.18 cm and 7-cm length were used in this study. Columns were packed with Camp Guernsey and Camp Swift soils. Small increments of soil were added to each column during packing to ensure even distribution and to minimize preferential flow. Glass wool was placed on the top and bottom of the soil profile to prevent soil movement. The average packed bulk density ($\rho_b$) was 1.61 ± 0.05 g cm$^{-3}$ for Camp Guernsey soil and 1.51 ± 0.04 g cm$^{-3}$ for Camp Swift soil. The bulk density was determined by the dry mass of the soil used to pack the glass columns of known volume.

Columns were saturated from bottom to top with 0.005 M CaCl$_2$ background solution for 1 hour to avoid air entrapment. Pore volume of the columns was determined by the volume of solution necessary to fill the packed column. After this, about 50 mg of undetonated and detonated IMX-101 and IMX-104 was placed on top of the column on a layer of glass wool (Figure E1). Technical grade IMX-101 and IMX-104 used in the experiments (undetonated samples) were provided by US Army Armament Research, Development and Engineering Center (ARDEC), Picatinny Arsenal, while detonated samples were residues of low order detonations.

PTFE caps were used to seal the tops of the columns. Tygon microbore tubing connected PTFE caps with the Cole-Parmer (Vernon Hills, IL) Master flex peristaltic pump which supplied solution. Columns were connected to the pump on the top and flow was started. Pump flow rate was calibrated for target flow rate of 0.01 mL min$^{-1}$ or 0.55 cm h$^{-1}$ before the start of the experiments. Measured average flow rate was 0.008 ± 0.001 mL min$^{-1}$ with Darcy flux of 0.42 ± 0.05 cm h$^{-1}$. After three to five pore volumes (PVs) for IMX-101 (five to eight PVs for IMX-104) depending on the soil, IM particles were removed and flow was switched to background solution (0.005 M CaCl$_2$) that was applied for another three to five pore volumes to monitor the elution of the explosives from soil. In addition, flow interruption studies were conducted, where flow was stopped for 24 hours to allow the explosives to equilibrate with the soil. This technique is used to differentiate between different mechanisms responsible for sorption non-equilibrium (Brusseau et al., 1989; Brusseau et al., 1997).

Effluent samples were collected continuously into 4-mL amber vials using a Teledyne ISCO (Lincoln, NE) Foxy 200 Fraction collector with a 200-vial capacity. Conservative tracer,
Br⁻, in the effluent was analyzed using Ion Chromatography (Dionex ICS 5000 with diode array) to determine the longitudinal dispersivity (\( \lambda \)) and observe for preferential flow for each soil, while high performance liquid chromatography was used to quantify eluting IM components as described below. Once experiments ended, columns were subdivided into thirds (top, middle, bottom) and soil extractions were performed using acetonitrile. A 1:2 soil to acetonitrile suspensions were agitated for 24 hours, centrifuged and filtered using 0.45 μm Millex-HV PVDF filter (EMD Millipore Darmstadt, Germany) (U. S. Environmental Protection Agency, 1994) followed by HPLC analysis.

Eight columns were used for each continuous flow dissolution study experiments with two replicate experiments for each explosive treatment. A total of twenty-four columns were packed with either Camp Swift or Camp Guernsey soil.

**Analytical Method**

Column effluent was analyzed for energetic compounds and their transformation products using Dionex Ultimate 3000 high performance liquid chromatograph (HPLC) equipped with a diode array detector (ThermoFisher, MA). The running method for NTO was adapted from Le Campion et al. (Le Campion et al., 1999a). The parameters used for analyzing NTO samples were the following: mobile phase ratio of acetonitrile (ACN): deionized water (75:25) with 0.1 % TFA, was run isocratically at 1 mL min⁻¹. Oven temperature was set at 32°C. NTO and its transformation products were separated using a Thermo Scientific Hypercarb Column. NTO was detected at approximately 2.8 minutes using 315 nm wavelength. The UV detector was set at 220 nm to monitor for presence of ATO (Le Campion et al., 1999a). No ATO was detected. The operational method for DNAN, RDX, NQ, HMX and DNAN transformation products was adapted from Olivares et al. (2013). The following parameters were used to analyze these samples: a mobile phase ratio of 43:57 methanol and water; the Thermo Scientific Acclaim reversed phase column C-18 with 5-μm particle size; and a flow rate of 1 mL min⁻¹. The wavelengths used for detection and quantification were 300 nm for DNAN, NQ, 254 nm for 2-ANAN, 4-ANAN, RDX, HMX, and 210 nm for DAAN. The retention times for each compound on HPLC were for DNAN approximately 21 minutes, 11 minutes for 2-ANAN, 6 minutes for 4-ANAN, 8 minutes for RDX, 5 minutes for HMX, and 3 minutes for NQ. Detection limits were 0.015 mg L⁻¹ for DNAN, 2-ANAN, 4-ANAN, NQ, RDX, HMX, and 0.020 mg L⁻¹ for NTO.
Numerical Analysis

All experiments were analyzed using the HYDRUS-1D code for simulating the one-dimensional movement of water, heat and multiple solutes in variably saturated porous media (Šimůnek et al., 2008; Šimůnek and van Genuchten, 2008). The software was used in the inverse mode to analyze breakthrough curves (BTC) obtained in the column experiments. HYDRUS-1D was modified to also estimate dissolution rate of explosive materials in solid form. This modification has been used in previous studies (Dontsova et al., 2006; Dontsova et al., 2008; Dontsova et al., 2009; Taylor et al., 2012) to estimate the dissolution rates of energetic materials, explosives and propellants. The following models were used in analysis of BTC: the advection-dispersion equation for the Br⁻ tracer and equilibrium sorption model (with decay) for explosives and their transformation products.

Nonreactive Solute

The advection-dispersion equation can best describe the transport behavior of the bromide tracer. The equation describes the constant water content, dispersion coefficient and flux density:

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - \frac{\partial qC}{\partial z} \quad Eq. 3.1 \]

where \( C \) is the concentration of the solution [ML⁻³], \( z \) represents the spatial coordinate [L], \( D \) is the dispersion coefficients which accounts for both hydrodynamic and molecular dispersion [L²T⁻¹] which is represented in equation 3.2.

\[ D = \lambda v + D^* \quad Eq. 3.2 \]

\( q \) is the volumetric fluid flux density [LT⁻¹] evaluated by Darcy–Buckingham law. \( v \) is the average linear velocity [LT⁻¹], \( \lambda \) is the longitudinal dispersivity [L], and \( D^* \) represents the effective diffusion coefficient [L²T⁻¹].

Dissolution

For explosive materials in this study, the DNAN, NTO, NQ, HMX, and RDX dissolution rate, \( Y \), was defined as:

\[ Y = \max (\xi e^{-\chi t}, a\xi) \quad Eq. 3.3 \]

where \( \xi \) is the initial dissolution rate (mg L⁻¹ h⁻¹), \( \chi \) is the decay constant (T⁻¹), \( a \) is the dimensionless constant that defines the minimum dissolution rate or steady state dissolution rate \((a\xi)\) as a fraction of the initial maximum dissolution rate \((\xi)\), and \( t \) is time (T). If \( \xi e^{-\chi t} > a\xi \) then \( \xi e^{-\chi t} \) is used in the equation. If \( \xi e^{-\chi t} < a\xi \) then \( a\xi \) is used in the equation. Results of the dissolution
rates are calculated relative to the mass of the IMX-101 or 104 added to the column (Taylor et al., 2012).

**Reactive Transport**

The transport of explosives was best described by equilibrium sorption with decay. Sorption, $S$, (MM$^{-1}$) is assumed to be instantaneous and is defined as:

$$S = K_d C$$  \hspace{1cm} \text{Eq. 3.4}

where $K_d$ is the linear adsorption coefficient (L$^3$M$^{-1}$). The transport equation is then as follows for flux density, constant water content, dispersion coefficient, bulk density, and distribution coefficient:

$$\frac{\partial \Theta C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - \frac{\partial q C}{\partial z} - \rho_b \frac{\partial S}{\partial t} - \varphi + \gamma$$  \hspace{1cm} \text{Eq. 3.5}

where $\varphi$ is the sink/source term which accounts for zero, first order and other reactions [ML$^{-3}$T$^{-1}$]. In this model $\varphi$ is the first-order rate constant for the solution only [ML$^{-3}$T$^{-1}$]:

$$\varphi = k \Theta C$$  \hspace{1cm} \text{Eq. 3.6}

$k$ represents the mass-loss rate coefficient due to transformation and/or irreversible adsorption (T$^{-1}$), $\Theta$ represents the volumetric water content [LL$^{-3}$], $C$ was defined previously, and $\gamma$ is the dissolution rate as described in equation 3.2 (mg L$^{-1}$ h$^{-1}$), and $\rho_b$ is the bulk density (g cm$^{-3}$).

**Parameter Estimation**

Numerical analysis of the experimental data was performed by first using the nonreactive tracer bromide to estimate the longitudinal dispersivity, $\lambda$ (cm). The equilibrium sorption with decay model was used to analyze explosive BTC. The dispersivity was then a fixed value determined for the tracer. The following parameters were estimated for explosives; $K_d$ (L kg$^{-1}$) and dissolution parameters, $\zeta$, $\chi$, and constant $\alpha$, which multiplied by $\zeta$ gives the steady-state dissolution rate (mg L$^{-1}$ h$^{-1}$). The mass-loss rate coefficient for dissolved phase, $k$ (h$^{-1}$) (degradation rate) was set to be equal to one determined from batch studies for DNAN (Arthur et al., 2017) and NTO (Mark et al., 2016), and derived from literature for NQ, RDX, and HMX. It was estimated by HYDRUS-1D for 2-ANAN and 4-ANAN. The 95% confidence intervals and $R^2$ values for fitted parameters were obtained by analyzing the observed and predicted breakthrough concentrations. Parameter estimates were considered significant if they were different than zero. Mass balance calculations were performed for all IM components by integration of each BTC, performing soil extractions, and extractions of remaining IM particles.
Results and Discussion

Measured bromide BTC were all symmetrical and well described using the advection-dispersion transport model (Figures 3.1, 3.2, 3.4, and 3.5). Longitudinal dispersivity was slightly larger for the coarser soil Camp Guernsey (0.57 ± 0.57 cm) than for the finer soil Camp Swift (0.20 ± 0.23) but differences were not significant (Tables 3.3 and 3.4). Breakthrough curves for the conservative tracer occurred at one pore volume (~420 min) which indicates a lack of preferential flow or air entrapment within the column.

All IMX-101 components, NTO, NQ, and DNAN, as well as 2-ANAN and 4-ANAN, transformation products of DNAN, were observed in the effluent from both detonated and undetonated IMX-101 (Figure 3.1). 2-ANAN and 4-ANAN, that were not detected in batch experiments, were observed before in DNAN column experiments (Arthur et al., 2017). Behavior of NTO, NQ, and DNAN was consistent with previously determined NQ (Haag et al., 1990; Dontsova et al., 2007; Taylor et al., 2012) and DNAN (Arthur et al., 2017) and NTO (Mark et al., 2016) fate and transport parameters; and agreed with patterns of IMX dissolution observed in laboratory drip studies (Taylor et al., 2013; Taylor et al., 2015b). The IM constituents BTCs followed a general pattern of high initial peak in effluent concentration followed by fast decrease and relatively steady-state (though still decreasing) concentrations after that. This pattern was very pronounced for NTO and NQ, while for DNAN effluent concentrations were relatively constant once breakthrough occurred.

For NTO, breakthrough with the tracer was observed for all IMX-101 experiments, detonated and undetonated, with and without flow interruption (Figures 3.1 and 3.2). NTO also had the highest maximum outflow concentrations in all experiments despite only representing 19.7% of the total mass of IMX-101. The high concentrations of NTO seen in the effluent are consistent with its high solubility and with laboratory drip studies (Taylor et al., 2013; Taylor et al., 2015b). The arrival of NTO on the breakthrough curve was at the same time as the nonreactive tracer Br– (Figures 3.1, 3.2, 3.4, and 3.5). This indicated that NTO was not adsorbing to the soil. In solution NTO is in its deprotonated form and negatively charged at environmentally relevant pHs (Smith and Cliff, 1999). Previous research conducted on soil adsorption of NTO showed high mobility and low sorption (Braida et al., 2012; Hawari et al., 2012; Richard and Weidhaas, 2014; Mark et al., 2016). NTO $K_d$’s were not significantly
different from zero in HYDRUS-1D simulations for IMX-101 and therefore were set to zero (Table 3.3).

NQ was the second compound to break through (Figure 3.1). It is similar to NTO in that it is a relatively inert compound in soil environments. NQ also arrived with the nonreactive tracer Br⁻ on the breakthrough curve (Figure 3.2) indicating NQ was not adsorbing to the soil. Previous research has indicated limited adsorption of NQ to soil and little degradation/transformation (Haag et al., 1990; Dontsova et al., 2007; Dontsova et al., 2008; Taylor et al., 2012). IMX-101 is comprised of 36.8% NQ, however, the initial peak concentrations of NQ were lower than those of NTO. The solubility of NTO is 4 times higher than NQ (Table 3.1), explaining higher concentrations of NTO over NQ. Kₜ’s were very low compared to the range of 0.15 to 0.43 L kg⁻¹ reported by Pennington et al., (1996) and 0.14 to 0.61 L kg⁻¹ reported by Taylor et al. (2012), but were consistent with Haag et al. (1990) value which was less than 0.1 L kg⁻¹.

DNAN was the last compound to break through (Figure 3.1). The curve was symmetrical and indicated retardation. DNAN also had the lowest effluent concentrations. Previous research conducted has shown that DNAN adsors to soil (Hawari et al., 2015; Arthur et al., 2017). The adsorption of DNAN to soil is heavily influenced by the organic carbon and clay content in the soil and DNAN forms transformation products 2-ANAN and 4-ANAN (Arthur et al., 2017). Kₜ values estimated by HYDRUS-1D (Table 3.3) were closer to batch experiment Kₜ’s (0.60 ± 0.20 L kg⁻¹) for Camp Swift soil then estimated column experiment Kₜ values (1.2 ± 0.08 L kg⁻¹) (Arthur et al., 2017). 2-ANAN and 4-ANAN were detected in column effluent and also exhibited retardation (Figure 3.1). They both appeared at the same time as DNAN on the BTC for detonated and undetonated IMX-101. 2-ANAN concentrations in the effluent were about an order of magnitude lower than DNAN concentrations and 4-ANAN concentrations were smaller than 2-ANAN concentrations indicating regioselectivity of DNAN amino-transformation (Hawari et al., 2015). Tailing occurred at the end of the experiments for 2-ANAN and 4-ANAN. Kₜ values estimated for 2-ANAN were similar to the values determined in column transport study of pure DNAN (0.43-1.93 L kg⁻¹) (Arthur et al., 2017). Estimated mass loss rates for 2-ANAN were similar to the estimated mass loss rate determined for 2-ANAN in Camp Swift soil in column transport studies (0.03 ± 0.04 h⁻¹) (Arthur et al., 2017).

Flow interruption experiments were conducted for detonated IMX-101 only. After resuming flow after 24 hours, effluent NTO and NQ concentrations increased in both soils and
then returned to steady state values consistent with continuing dissolution of IM particles while flow is interrupted (Figure 3.2). For DNAN no clear decrease or increase in concentration was observed after flow interruption but concentrations of its transformation products, 2-ANAN and 4-ANAN, increased immediately after flow was resumed indicating continued transformation. Absence of corresponding decrease in DNAN concentration was explained by low transformation rate relatively to error of the measurement. DNAN also did not experience increase in concentration following flow resumption like NTO and NQ due to relatively slow dissolution rate of DNAN. 2-ANAN exhibited tailing on the elution curve however, 4-ANAN decreased in concentration (Figure 3.2). There were no significant differences between undetonated and detonated IMX-101 $K_d$ values for all constituents. Furthermore, there were no significant differences between $K_d$ values in the two soils. Transformation rates of DNAN were fixed in HYDRUS-1D simulations at the values determined in batch studies (Arthur et al., 2017) and not allowed to change. However, good agreement between simulated and measured BTCs for IF experiments indicates that these values described observed patterns well.

Suggested mechanism explaining the shape of the BTCs is ready dissolution of the IM constituents on the external surfaces of the IM particles, faster for more soluble components, and slower for less soluble ones, followed by slower dissolution of constituents within the matrix, where it is limited by diffusion from the particle interior, as described for propellant constituents due to insoluble nitrocellulose matrix (Dontsova et al., 2009; Taylor et al., 2011; Taylor et al., 2012), but not previously observed for explosive formulations (Dontsova et al., 2006). While constituent concentrations in solution and estimated dissolution parameters differed between individual columns (Table 3.3), HYDRUS-1D simulated $Y_{max}$ dissolution rates had a highly signification correlation between individual propellants in the IMX-101 formulation, NTO and DNAN (Figure 3.3, $P=0.000423$) indicating a link between dissolution of constituents from the IM particles. The Thompson tau method was used to determine outliers within the data set. $Y_{max}$, $Y_{min}$, and $\chi$ for NTO and NQ undetonated were higher than detonated (Table 3.3) but differences were not significant. The $\chi$ and $Y_{max}$ for DNAN were higher but the $Y_{min}$ lower in undetonated IMX-101 than detonated. However, in undetonated versus detonated IMX-101(Table 3.3). Parameter estimates for IMX-101 from Taylor et al., 2015b, underestimated the dissolution parameters in this study, possibly due to larger size, and therefore lower specific surface area, of the particles they used (Table E1).
Figure 3.1: Breakthrough curves for individual propellants for detonated IMX-101 in Camp Swift soil. NTO, 3-nitro-1, 2, 4-triazol-5-one; NQ, nitroguanidine; DNAN, 2, 4-dinitroanisole; 2-ANAN, 2-amino-4-nitroanisole; 4-ANAN, 4-amaino-2- nitroanisole. Vertical grey solid line indicates switch to background solution.
Figure 3.2: Breakthrough curves for individual propellants for detonated IMX-101 flow interruption in Camp Swift soil. NTO, 3-nitro-1, 2, 4-triazol-5-one; NQ, nitroguanidine; DNAN, 2, 4-dinitroanisole; 2-ANAN, 2-amino-4-nitroanisole; 4-ANAN, 4-amino-2- nitroanisole. Vertical dashed line indicates start of 24-hr flow interruption. Vertical grey solid grey line indicates switch to background solution.
Table 3.3: Dissolution and transport parameters obtained by HYDRUS-1D for saturated column experiments involving Br⁻ tracer and IMX-101 (19.7% NTO, 36.8% NQ and 43.5% DNAN) in Camp Swift and Camp Guernsey soils. λ was estimated from Br⁻ breakthrough, whereas $K_d$, $\chi$, $Y_{\text{max}}$, $Y_{\text{min}}$, mass-loss rate coefficient, $k$, from explosives. D = detonated, UD = undetonated, and NA= $K_d$ fixed to zero.

<table>
<thead>
<tr>
<th>Soils, Treatment</th>
<th>Bromide</th>
<th>NTO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda$</td>
<td>95% CI</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Camp Swift D</td>
<td>0.20</td>
<td>0.28</td>
</tr>
<tr>
<td>Camp Swift D</td>
<td>0.13</td>
<td>0.08</td>
</tr>
<tr>
<td>Camp Guernsey D</td>
<td>0.21</td>
<td>0.13</td>
</tr>
<tr>
<td>Camp Guernsey D</td>
<td>0.42</td>
<td>0.34</td>
</tr>
<tr>
<td>Mean and Std. dev</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Camp Swift UD</td>
<td>0.28</td>
<td>0.26</td>
</tr>
<tr>
<td>Camp Swift UD</td>
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<td>0.11</td>
</tr>
<tr>
<td>Camp Guernsey UD</td>
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<td>0.10</td>
</tr>
<tr>
<td>Camp Guernsey UD</td>
<td>0.16</td>
<td>0.15</td>
</tr>
<tr>
<td>Mean and Std. dev</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Camp Swift D FI</td>
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</tr>
<tr>
<td>Camp Swift D FI</td>
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</tr>
<tr>
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<td>1.83</td>
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</tr>
<tr>
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<td>Mean and Std dev</td>
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<td></td>
</tr>
<tr>
<td>Soils, Treatment</td>
<td>$K_a$</td>
<td>95% CI</td>
</tr>
<tr>
<td>----------------------</td>
<td>-------</td>
<td>---------</td>
</tr>
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<td>Camp Swift D</td>
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</tr>
<tr>
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<td>0.09</td>
</tr>
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IMX-104 contains 53.0% NTO, 15.3% RDX, and 31.7% DNAN, 33.3% more NTO and 11.8% less DNAN than IMX-101. The behavior of NTO was similar to that of NTO in IMX-101, however it was retarded slightly more in both Camp Swift and Camp Guernsey soils. Similarly, to patterns observed for IMX-101, NTO arrived before all other IM constituents in the IMX-104 and had the highest peak and steady-state concentrations (Figure 3.4). NTO $K_d$’s ranged from 0 to 0.23 L kg$^{-1}$ (Table 3.4) which in some cases was higher than $K_d$ values obtained for NTO in the IMX-101 dissolution studies and $K_d$ values obtained in batch study experiments performed by Mark et al. (2016). RDX was the second IM compound to break through (Figure 3.4). RDX exhibited retardation due to sorption, as demonstrated by the delay in RDX breakthrough relative to the conservative tracer. $K_d$ values obtained for RDX ranged between 0.20 to 0.85 L kg$^{-1}$ (Table 3.4). These values fell within the range of 0 to 8.2 L kg$^{-1}$ RDX $K_d$ values reported by Brannon et al. (2002) but were higher than the reported $K_d$ values by Dontsova et al. (2006). Another propellant in the effluent was HMX. HMX is present in original formulation as a contaminant in RDX (about 10% of RDX amount). Concentrations of HMX in solution were smaller than those of RDX. HMX $K_d$’s ranged from 0.36 to 1.27 L kg$^{-1}$ (Table 3.4). These values were consistent with HMX $K_d$ values reported by Brannon et al. (2002) (< 1 L kg$^{-1}$) and Dontsova et al. (2006) (0.22-0.36 L kg$^{-1}$). HMX is more strongly adsorbed by soils than RDX, DNAN, 2-ANAN, and 4-
ANAN (Figure 3.4). Breakthrough for DNAN, 2-ANAN, and 4-ANAN occurred at about 3 pore volumes (Figure 3.4). All curves were asymmetrical. The arrival curve of DNAN, 2-ANAN, and 4-ANAN appeared at the same time however as DNAN decreased on elution, 2-ANAN exhibited tailing and 4-ANAN increased then decreased. DNAN $K_d$ values ranged from 0.58 to 1.47 L kg$^{-1}$ (Table 3.4) and were similar to results of batch kinetic and column transport studies of DNAN. DNAN $K_d$ values in Camp Swift and Camp Guernsey soils were 0.60 ± 0.20 L kg$^{-1}$ and 0.90 ± 0.10 L kg$^{-1}$, respectively, and 1.2 ± 0.08 L kg$^{-1}$ in column studies for Camp Swift soil (Arthur et al., 2017). 2-ANAN $K_d$ values ranged from 0.40 to 4.88 L kg$^{-1}$ (Table 3.4).

Flow interruption experiments were conducted with detonated IMX-104. Flow interruption had no effect on NTO in Camp Swift soil (Figure 3.5). RDX and HMX exhibited greater attenuation to the soil than NTO. The breakthrough for RDX occurred around 2 pore volumes whereas HMX was 4 pore volumes (Figure 3.5). HMX concentrations were lower than RDX concentrations. RDX and HMX concentrations first decreased and then increased after flow resumption. Predicted BTC showed smaller range of both decrease and increase, indicating that used RDX transformation rate (Brannon and Pennington, 2002), as well as dissolution rate calculated using it were lower than observed. DNAN, 2-ANAN and 4-ANAN also adsorbed to the soil as indicated by the delay in the BTC (Figure 3.6). Before flow interruption DNAN and 2-ANAN concentrations decreased with time on the arrival wave. After resuming flow DNAN concentrations slightly decreased and 2-ANAN and 4-ANAN concentrations increased indicating transformation in Camp Swift soil. Concentrations of NTO, RDX, HMX, DNAN and 2-ANAN all increased after follow interruption in Camp Guernsey soil (Figure E2). There were no significant correlations of $K_d$ values between undetonated and detonated IMX-104 nor were there differences in $K_d$ values between the two soils used in the experiments. A significant or highly significant correlations existed between HYDRUS-1D estimated values for $Y_{min}$ NTO and $Y_{min}$ RDX ($P = 0.0061$), $Y_{max}$ NTO and $Y_{max}$ DNAN ($P = 0.010$); and $Y_{min}$ HMX and $Y_{min}$ DNAN ($P = 0.018$) (Figure 3.6). The $Y_{max}$ NTO and $Y_{max}$ DNAN correlation was also seen in the IMX-101 studies. When comparing estimated dissolution parameters between treatments, we found that minimum dissolution rates and decay constants of NTO were lower for detonated IMX-104 than in undetonated IMX-104. The maximum dissolution rate was higher for NTO in detonated IMX-104. All three estimated parameters were higher in undetonated IMX-104 than detonated IMX-104 for RDX. The estimated minimum dissolution rate and decay constant were higher for HMX.
in detonated IMX-104. The maximum dissolution rate was higher in undetonated IMX-104. Lastly, DNAN’s maximum and minimum dissolution rates were high for detonated IMX-104 and the decay constants were similar for both treatments (Table 3.4).

The dissolution parameters were compared to dissolution parameter estimates obtained by Taylor et al. (2015). Their parameter estimates were lower than the estimates obtained from this study (Table E1). This may be due to the size of the particle dissolved during analysis.

**Figure 3.4:** Breakthrough curves for individual propellants for detonated IMX-104 particle in Camp Swift soil. NTO, 3-nitro-1, 2, 4-triazol-5-one; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; DNAN, 2, 4- dinitroanisole; 2-ANAN, 2-amino-4-nitroanisole; 4-ANAN, 4-amino-2-nitroanisole. Vertical grey solid line indicates switch to background solution.
Figure 3.5: Flow interruption breakthrough curves for individual propellants for detonated IMX-104 particle in Camp Swift soil. NTO, 3-nitro-1, 2, 4-triazol-5-one; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; DNAN, 2, 4-dinitroanisole; 2-ANAN, 2-amino-4-nitroanisole; 4-ANAN, 4-amino-2-nitroanisole. Vertical dashed grey line indicates start of 24-hr flow interruption. Vertical solid grey line indicates switch to background solution.
Table 3.4: Solute transport and dissolution parameters obtained by HYDRUS-1D for column saturated experiments involving bromide and IMX-104 (53.0 % NTO, 15.3% RDX, and 31.7% DNAN) in Camp Swift and Camp Guernsey soils. $\lambda$ was estimated from bromide BTCs, whereas $K_d$, a, maximum dissolution rate coefficient, minimum dissolution rate coefficient, mass-loss rate coefficient, $k$, from explosives. D = detonated, UD = undetonated. NA = $K_d$ fixed to zero.

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**Figure 3.6:** Correlations between simulated $Y_{\text{max}}$ and $Y_{\text{min}}$ of individual propellants in IMX-104 formulation from continuous flow experiments. NTO, 3-nitro-1, 2, 4-triazol-5-one; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; DNAN, 2, 4- dinitroanisole.

For both IMX-101 and IMX-104 maximum and minimum dissolution rates between some individual compounds within the IMX formulations have shown to be related. Dissolution rates are affected by the solubility of the compound, temperature, particle size and surface area, and agitation. During these experiments, constant temperature was maintained, thus it was not a factor influencing the dissolution rate and the solid IMX particle was stationary on top of the soil profile. For this study, the dissolution rate may have been affected by the particle size surface area and the solubility of the compounds. The solubility of each compound is listed in Table 3.1. NTO is highly soluble followed by NQ, DNAN, and RDX.

IMX-101 and IMX-104 are made by meltcasting. During production NTO, NQ, and RDX crystals are added to the molten DNAN. Two different studies conducted by Taylor at al.
(Taylor et al., 2013; Taylor et al., 2015a; 2015b) on the dissolution of IMX-101 and IMX-104 demonstrated that the compounds dissolved in order of their solubilities. They found that in IMX-101, NTO and NQ dissolved faster than DNAN and that more NTO dissolved from each particle than NQ. These findings were also supported by Richard et al. (2014). They found that IMX-101 particles dissolved slowly under simulated rainfall with NTO and NQ dissolving first, followed by DNAN. For IMX-104, dissolution of the explosives compounds also followed the order of the most soluble compound NTO dissolving first followed by DNAN and RDX. Tables 3.3 and 3.4 list the dissolution parameters estimated by HYDRUS-1D. In our studies, NTO has the highest maximum and minimum dissolution rates followed by NQ, and DNAN for IMX-101 and for IMX-104, NTO again has the highest maximum dissolution rate followed by DNAN, RDX, and HMX. The maximum dissolution rates followed the pattern that the compounds dissolve in order of their solubilities observed by Taylor et al. (2013; 2015a; 2015b). IMX-101 and IMX-104 both contain NTO and DNAN in their formulations. IMX-104 contains 2.6 times more NTO than IMX-101 and 1.4 times less DNAN. The maximum and minimum dissolution rates are higher for NTO in IMX-101 than IMX-104. NTO could be shielded by DNAN, RDX, and HMX which are less soluble resulting in lower dissolution rates of NTO in IMX-104. When comparing the maximum and minimum dissolution for DNAN, we found that the dissolution rates of DNAN in IMX-101, when normalized for its percent in the formulation are lower than the rates in IMX-104. This could be the result of how accessible DNAN is to the simulated rainfall. The small particle could have NTO and NQ on the outside and DNAN on the inside. The compounds would need to dissolve before the water could access DNAN, resulting in lower dissolution rates. The shrinking core model gives a good description of the dissolution behavior of the IMX particles. It describes how reactions occur first on the outer skin of the particle. The zone of the reaction then moves into the solid, leaving behind inert (in our case, less soluble) materials as well as exposing another layer of the reactant (e.g. Levenspiel, 1999, pages 569-570). NTO has the highest solubility. When NTO dissolves from the outside of the particle reaction front moves deeper. This process continues and thus the unreacted core of the particle, where NTO remains, shrinks. Taylor et al. (2015) examined the physical changes undergone by insensitive munitions particles during dissolution. They confirmed that for IMX-101, NTO and NQ dissolved from the outside of the particles leaving behind thin bridges of DNAN which
dissolves slower. The resulting IMX porous material allowed access of water to NTO and NQ in particle interior promoting their dissolution, followed by diffusion to particle exterior.

**pH of the Insensitive Munitions solutions**

The pH of effluent solutions of IMX-101 and IMX-104 was measured after the water interacted with the explosives and soil column. In solution, NTO is acidic and has a pKa of 3.67-3.76 (Lee et al., 1987; Smith and Cliff, 1999). NTO acts as a weak acid as a result of the N-H bond dissociation. Taylor et al. (2015a) showed that pH of NTO solutions is inversely related to their concentrations and can reach pH values as low as 2-3. During transport NTO solutions are buffered by reactions with the soil and the average pH of IMX-101 the outflow effluent solution was 8.44 ± 0.19 and the average pH of IMX-104 outflow effluent solution was 8.27 ± 0.26. However, for several pore volumes collected (Figure E3) when NTO concentrations are the highest also had lower pH values.

The deprotonated form of NTO would be predominately present in the outflow effluent solutions of IMX-101 and IMX-104, in agreement with findings by Smith and Cliff (1999). Most of NTO for these studies was recovered in solution and remaining particles (Table 3.5).

Measuring the pH of the solutions can help indicate which form of NTO is likely to be present in the field. Mark et al. (2016) found a highly significant inverse relationship between NTO soil adsorption coefficients and soil pH.

**Mass balance**

IMX-101 (NTO, NQ, DNAN) and IMX-104 (NTO, RDX, DNAN) constituents were recovered in column effluent, soil extracts, and residual particle extracts. In addition to parent compounds recoveries, DNAN transformation products 2-ANAN and 4-ANAN were recovered. HMX was also recovered in IMX-104 studies. Mass balance calculations (Table 3.5) indicate the majority of the individual compounds were recovered in effluent solution as well as in the residual particle. There were no significant differences in solution recoveries of individual compounds in detonated versus undetonated IMX-101 nor between continuous flow versus flow interruption experiments for detonated samples except for NQ (P = 0.0048). In soil recoveries, there was only a significant difference between continuous flow vs flow interruption detonated for NTO (P = 0.031) and 2-ANAN (P = 0.012). NTO had the highest recoveries in solution
followed by NQ, DNAN, 2-ANAN and 4-ANAN (Table 3.5). DNAN had the highest recovery in soil followed by NTO and NQ, 2-ANAN, and 4-ANAN.

For IMX-104, there were no significant differences in undetonated versus detonated IMX-104 in soil recoveries nor in continuous flow versus flow interruption soil recoveries of individual IM components. There was a significant difference between the solution recoveries of 2-ANAN in undetonated versus detonated samples (P = 0.028), as well as, a significant difference between continuous and flow interruption detonated solution recoveries of 2-ANAN (P = 0.015). NTO also had the highest recoveries in effluent solution followed by DNAN, RDX, 2-ANAN, 4-ANAN, and HMX (Table 3.5). DNAN had the highest recovery in soil followed by RDX, NTO, 4-ANAN, 2-ANAN, and HMX. DNAN, RDX, and HMX recoveries in solution were lower than NTO (Table 3.5). DNAN, 2-ANAN, 4-ANAN, RDX, and HMX all adsorbed to the soil as shown by the delay in their BTC (Figure 3.5).

Recoveries of the explosive compounds from the soil were small (Table 3.5). The way experiments were designed, majority of munitions constituents should be desorbed from the soils and eluted by the time experiment was finished and soils extracted with acetonitrile. However, it is possible that some of the energetics were strongly adsorbed where they would not be desorbed with water. Previous research has shown limited desorption of NTO and DNAN from soil with water and with acetonitrile (Richard and Weidhaas, 2014; Mark et al., 2016; Arthur et al., 2017). NQ has also shown limited desorption from soil. Previous research of recoveries of NQ from soil were found to be directly dependent on the amount of organic matter present in the soil, as the organic matter increased the percent recovery decreased (Williams et al., 1989). For our studies the amount of organic matter present in the soils was <1 % (Table 3.2). However, a minimal amount of NQ was extracted from the soil. Acetonitrile has been found to be a good solvent for extracting RDX and HMX from soil (Jenkins and Grant, 1987), however, in our study we had poor recoveries of RDX and HMX using acetonitrile (Table 3.5), possibly as a result of irreversible adsorption and/or transformation (Yaron et al., 2012). Transformation products were not detected for NTO, RDX, HMX or NQ. However, the transformation products of DNAN, 2-ANAN and 4-ANAN were detected and recovered in solution and soil extractions for DNAN which Arthur et al. (2017) also reported. Higher recoveries of explosive compound in solution over residual mass of IMX-101 is likely the result of the particle not getting simulated
rainfall/water on top of it, resulting in minimal recovery of the compounds in solution and soil recoveries.
Table 3.5: Mass recoveries of IMX-101 and IMX-104 constituents in effluent, soil and extractions of remaining IM particles during dissolution column transport studies. FI= flow interruption for 24 hours. D = detonated, UD = undetonated.

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<thead>
<tr>
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<th>Soil Recoveries</th>
<th>IMX Particle Recoveries</th>
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<th>IMX Particle Recoveries</th>
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Conclusion

This study examined the dissolution, fate and transport behavior of IMX-101 and IMX-104 in two soils. We showed that DNAN, RDX, and HMX adsorb to soil. Under flow conditions, NTO and NQ have low potential for natural attenuation and DNAN, RDX, and HMX show potential for natural attenuation in soils. DNAN readily transforms to 2-ANAN and 4-ANAN. Under flow interruption conditions, DNAN transforms to 2-ANAN and 4-ANAN. However, NQ, HMX and DNAN concentrations increase and NTO decreases after flow interruption indicating transport process are controlled by dissolution. Estimated adsorption coefficients from HYDRUS-1D for each explosive compound were similar to those of pure NTO, NQ, DNAN, RDX, and HMX. Therefore, using distribution coefficients from batch studies of pure explosives in solution can estimate transport of the insensitive munitions formulations.

Acknowledgements

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Chapter 4. Predicting Dissolution and Transport of IMX-101 and IMX-104 Constituents using HYDRUS-1D


This material is a part of the dissertation defended by Jenifer Arthur as one of the requirements for her PhD degree.

Methods

HYDRUS-1D including dissolution was used to simulate the dissolution, fate and transport of 3-nitro-1,2,4-triazol-5-one (NTO), nitroguanidine (NQ), and 2,4-dinitroanisole (DNAN) in IMX-101; and NTO, DNAN, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) in IMX-104 in three soils, Plymouth, Camp Swift, and Camp Guernsey. We simulated transport to 20 cm depth over a year and transport to the groundwater level for a 1 year, 10 year and 25 year time periods for a fully saturated soil profile receiving precipitation characteristic of the location of soil collection. Fully saturated conditions present a conservative estimate of the time needed for explosive profile to propagate down, the time would be longer under unsaturated conditions.

Depth to the groundwater was determined for each soil as the lowest value for the well closest to the soil collection location (Lu and Ralph, 1998). Rainfall intensity and distribution through the year for each soil were determined using mean precipitation record for each location (Lu and Pignatello, 2002). We assumed that no precipitation occurred when rainfall amount per day was lower than 1.27 cm (0.5 in) and for the days that the rainfall amount was above this number we assumed that total rainfall for the year was uniformly distributed over the days when it rained. The flow rate was assumed to be equal to precipitation rate.

Dissolution and transport parameters used for forward simulations: maximum dissolution rate ($Y_{max}$), minimum dissolution rate ($Y_{min}$), and decay constant ($\chi$), linear adsorption coefficient ($K_d$), and mass-loss rate coefficient ($k$), were previously determined in this study (Arthur et al., 2017, Chapter 3). NQ $K_d$ and $k$ were determined from Mirecki et al. (2006). RDX and HMX $K_d$
and $k$ were selected from a summary of published parameters using percent clay, percent organic carbon and cation exchange capacity (Brannon and Pennington, 2002). Dissolution rates were calculated for a 50 mg source of IMX-101 or IMX-104 as used in column experiments. While in long simulations energetics in such small particles will soon be completely dissolved, in the field conditions a variety of particle sizes are present and larger particles would continue to dissolve over longer time periods. Here we assumed that dissolution rates for particles of different sizes would be similar and the particles will never dissolve completely (assumed to be a constant source). While this is a simplification, developing a relationship between particle size and dissolution rate and linking it to the participle size distribution during energetic deposition resulting from low-order detonations and frequency of low-order detonations was outside the scope of this project. The assumptions we made provide a conservative estimate for potential groundwater contamination.

The bulk density ($\rho_b$) was obtained from the USDA soil web survey and porosity (n) was calculated from the $\rho_b$. The longitudinal dispersivity ($\lambda$) was determined using soil texture, depth and flow boundary condition (Leeuw et al., 2007). Tables 4.1 and 4.2 lists all input parameters used for forward simulations. Forward simulations for transport of NQ in Camp Swift and Plymouth soil and HMX in Camp Guernsey soil were conducted assuming constant input of these compounds over time at solubility limit because dissolution simulations indicated that their concentrations do not go below solubility under simulated conditions.
Table 4.1: Dissolution and transport parameters used for forward simulation of energetic compounds in IMX-101, 3-nitro-1,2,4-triazol-5-one (NTO), nitroguanidine (NQ), 2,4-dinitroanisole (DNAN), and 2-amino-4-nitroanisole (2-ANAN).

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Table 4.2: Dissolution and transport parameters used for forward simulation of IMX-104 compounds: 3-nitro-1,2,4-triazol-5-one (NTO), 2,4-dinitroanisole (DNAN), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and 2-amino-4-nitroanisole (2-ANAN).

<table>
<thead>
<tr>
<th>Soil</th>
<th>Explosive Compound</th>
<th>Depth to ground water</th>
<th>( \lambda )</th>
<th>( \rho_b )</th>
<th>( n )</th>
<th>flow rate</th>
<th>Total 1 year rainfall</th>
<th>( K_d )</th>
<th>( k )</th>
<th>( \chi )</th>
<th>( Y_{\text{max}} )</th>
<th>( Y_{\text{min}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Camp Guernsey</td>
<td>NTO</td>
<td>2562 cm</td>
<td>21.7</td>
<td>1.30</td>
<td>0.51</td>
<td>0.00927</td>
<td>35.0</td>
<td>0.02</td>
<td>0.007</td>
<td>0.12</td>
<td>49821</td>
<td>0.03</td>
</tr>
<tr>
<td>Camp Guernsey</td>
<td>RDX</td>
<td>2562 cm</td>
<td>21.7</td>
<td>1.30</td>
<td>0.51</td>
<td>0.00927</td>
<td>35.0</td>
<td>0.16</td>
<td>0.000</td>
<td>0.18</td>
<td>305</td>
<td>0.16</td>
</tr>
<tr>
<td>Camp Guernsey</td>
<td>HMX</td>
<td>2562 cm</td>
<td>21.7</td>
<td>1.30</td>
<td>0.51</td>
<td>0.00927</td>
<td>35.0</td>
<td>0.30</td>
<td>0.000</td>
<td>0.19</td>
<td>441.5</td>
<td>0.02</td>
</tr>
<tr>
<td>Camp Guernsey</td>
<td>DNAN</td>
<td>2562 cm</td>
<td>21.7</td>
<td>1.30</td>
<td>0.51</td>
<td>0.00927</td>
<td>35.0</td>
<td>0.90</td>
<td>0.003</td>
<td>0.23</td>
<td>4687.5</td>
<td>0.09</td>
</tr>
<tr>
<td>Camp Guernsey</td>
<td>2-ANAN</td>
<td>2562 cm</td>
<td>21.7</td>
<td>1.30</td>
<td>0.51</td>
<td>0.00927</td>
<td>35.0</td>
<td>1.6</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Results and Discussion

IMX-101 dissolution and transport to 20 cm depth in Camp Guernsey and Plymouth soils

The results of the forward simulations of explosive compounds comprising IMX-101 at a depth of 20 cm in Camp Guernsey soil with 1 year of rainfall, as well as a plot of rainfall are shown in Figure 4.1. NTO and DNAN breakthrough curves (BTC) had the same patterns observed in dissolution and transport laboratory studies: NTO was the first compound to breakthrough at 129 days, followed by DNAN at 141 days and 2-amino-4-nitroanisole (2-ANAN), a product of DNAN transformation, at 174 days; NTO had higher concentrations than DNAN, and DNAN transformed producing a small amount of 2-ANAN. The pattern observed for all BTCs was increase in energetics concentrations over time during flow periods followed by decrease when there is no infiltration due to in situ transformation.

Figure 4.1. Breakthrough curves of NTO, DNAN, and 2-ANAN in Camp Guernsey soil at a 20-cm depth with 1 year of rainfall. Plot of flow rate versus time. Zero flow rate indicates periods of no flow.
IMX-101 dissolution and transport to groundwater in Camp Guernsey soil

Forward simulations of NTO, NQ, and DNAN in Camp Guernsey soil with 1 year, 10 years and 25 years rainfall are shown in Figure 4.2. The depth to groundwater level for Camp Guernsey soils is 2562 cm (25.62 m) and the average flow rate is 0.00927 cm h\(^{-1}\), similar to flow rates used in column experiments. After 1 year of rainfall on a 50-mg particle of IMX-101, NTO breakthrough (depth at \(\frac{1}{2}\) max concentration) was at 51.24 cm (0.51 m) depth, but low concentrations of NTO reached a depth of 358 cm due to dispersion and diffusion. NTO concentrations decreased with depth. The 1 year line shifting to the left indicates that NTO is degrading in the soil. The NTO depth profiles for 10- and 25-year simulations overlapped with 1-year profile indicating that NTO completely degrades in Camp Guernsey soil each year during a prolonged period of no flow. We do not take into account changes in soil temperature and potential freezing, which would decrease transformation rates. However, freezing would also prevent NTO dissolution, so the effects of temperature on dissolution and transformation may counterbalance each other. NTO never reaches groundwater in Camp Guernsey soil over a 25-year period of average rainfall.

Due to lack of transformation and adsorption in soils, NQ was more mobile in Camp Guernsey soil than NTO. After 1 year of rainfall at 0.025 mg L\(^{-1}\), NQ breakthrough occurred at a depth of 77 cm (0.77 m) and some NQ was reaching the depth of 384.86 cm (3.84 m). After 10 years of rainfall, NQ reached a depth of 1384 cm (13.84 m) at a concentration of 0.01 mgL\(^{-1}\), but not groundwater; and after 25 years of rainfall on the particle, NQ reached groundwater level but at a very low concentration (0.05 mg L\(^{-1}\)). The breakthrough of NQ after 10 years and 25 years occurred at a depth of 256.24 cm (2.56 m).

DNAN, the last compound in IMX-101, adsorbs to and degrades in the soil and is not as mobile as NTO and NQ (Figure 4.3). After 1 year of rainfall, it reached a depth of 51.25 cm. All three time periods overlap in Camp Guernsey soil indicating, as was observed for NTO, that a long annual period of no flow removes all DNAN from soil profile each year. 2-ANAN, one of the known transformation products of DNAN, exhibited the same behavior as DNAN in Camp Guernsey soil, except the concentrations were very small. 2-ANAN reached a maximum depth of 77 cm. DNAN and 2-ANAN never reached groundwater level in Camp Guernsey soil.
Figure 4.2: Forward simulations of NTO, NQ, DNAN and 2-ANAN in Camp Guernsey soil with rainfall over 1 year, 10 years and 25 years.

**IMX-101 dissolution and transport to groundwater in Camp Swift Soil**

The next soil used for forward simulation was Camp Swift. The groundwater level in Camp Swift soil is at 6156 cm (61.56 m). We simulated NTO, NQ, and DNAN with the same time periods as Camp Guernsey. The average flow rate in Camp Swift soil was 0.01228 cm h⁻¹. After 1 year of rainfall on a 50-mg particle of IMX-101, NTO surface concentrations were lower than the NTO concentrations in Camp Guernsey soil consistent with the higher flow rate for this
soil (Figure 4.3). The behavior of NTO in Camp Swift soil was similar to NTO behavior in Camp Guernsey soil (Figure 4.2), it had little adsorption but degraded in soil and was relatively mobile. After 1 year of rainfall, NTO breakthrough occurred at a depth of 51 cm (0.51 m) and small concentrations reached a depth of 122 cm. NTO has not reached groundwater level in 25 years or simulation: depth profiles for NTO for all three time periods overlapped.

NQ again was more mobile than NTO in this soil as it was in Camp Guernsey soil. After 1 year of rainfall, NQ breakthrough occurred at a depth of 123.11 cm (1.23 m) and NQ reached a depth of 784 cm (7.83 m) at 0.03 mg L\(^{-1}\). After 10 years, NQ breakthrough occurred at a depth of 1,477 cm (14.77 m). NQ at 0.01 mg L\(^{-1}\), concentration could be detected at 3,201 cm (32.01 m). After 25 years of rainfall, NQ breakthrough occurred at a depth of 3,755 cm (37.55 m), and was observed at groundwater depth (6,156 cm or 61.5 m) at 0.04 mg L\(^{-1}\) concentration.

DNAN initial concentrations were smaller and it was not as mobile as NTO and NQ. DNAN adsorbed and degraded in the soil and reached a depth of 308 cm (3.8 m) with a concentration of 0.01 mg L\(^{-1}\). Profiles over 1, 10, and 25 years overlapped. The same behavior was observed for 2-ANAN. 2-ANAN concentrations were smaller than DNAN concentrations and 2-ANAN reached a depth of 185 cm (1.85 m). DNAN and 2-ANAN never reached groundwater.
IMX-101 dissolution and transport to groundwater in Plymouth soil

Plymouth soil was the last soil used for forward simulation analysis of compounds in IMX-101 (Figure 4.4). The groundwater level in Plymouth soil is at 783 cm (7.83 m) and the average flow rate was 0.01495 cm h\(^{-1}\). NTO adsorbed and degraded in the soil. After 1, 10, and 25 years of rainfall on a 50-mg particle of IMX-101, NTO breakthrough occurred at a depth of 16 cm (0.16 m). NTO travelled to a depth of 125 cm (1.25 m) with concentrations of 0.01mgL\(^{-1}\).
NQ, again, was more mobile in the soil than NTO. It did not reach ground water after 1 year, but after 10 and 25 years of rainfall it reached groundwater at solubility limit concentrations due to lack of adsorption or transformation.

**Figure 4.4:** Forward simulations of NTO, NQ, DNAN and 2-ANAN in Plymouth soil with rainfall over 1 year, 10 years and 25 years.

DNAN was not as mobile as NQ and adsorbed and degraded in the soil. After 1 year of rainfall, DNAN concentrations were less than 0.0001 mg L\(^{-1}\) reaching a depth of 31.36 cm (0.314 m). After 10 and 25 years of rainfall, DNAN concentrations reached a depth of 16 cm (0.16 m) with a concentration of 0.01 mg L\(^{-1}\). DNAN transforms to 2-ANAN and 2-ANAN...
concentrations were predicted to be about 2 orders of magnitude smaller than DNAN concentrations in Plymouth soil. 2-ANAN also was not mobile in the soil and DNAN and 2-ANAN travelled to a depth of only 16 cm (0.16 m) cm never reaching the groundwater.

**IMX-104 dissolution and transport to groundwater in Camp Guernsey soil**

Forward dissolution and transport simulations were also done for Camp Guernsey soil with explosive compounds NTO, RDX, and DNAN that comprise IMX-104 (Figure 4.5). The depth to groundwater level for Camp Guernsey soils is 2562 cm (25.62 m) and the average flow rate is 0.00927 cm h⁻¹. NTO displayed the same behavior observed in the IMX-101 simulations. After 1 year, 10 years and 25 years of rainfall, NTO was slightly mobile traveling to a depth of 256 cm. NTO breakthrough occurred at a depth of 51.24 cm (0.51 m). NTO adsorbed to the soil and degraded in the soil in all three time periods of rainfall observed. NTO never reached groundwater level.

RDX was mobile in this soil (Figure 4.5). After 1 year of rainfall was applied to the 50-mg particle of IMX-104, RDX breakthrough occurred at a depth of 77 cm (0.77 m). RDX adsorbed to the soil and traveled to a depth of 307 cm (3.07 m) with a concentration of 0.01 mg L⁻¹; after 10 years to a depth of 1102 cm (11.02 m) with a concentration of 0.01 mg L⁻¹; and after 25 years of rainfall, to a depth of 1051 cm (10.51 m) with a concentration of 0.03 mg L⁻¹. RDX breakthrough occurred at a depth of 538 cm (5.38 m) after 10 years of rainfall and at a depth of 1281 cm (12.81 m) after 25 years of rainfall. Small concentrations of RDX reached a depth of 2050 cm (20.50 m) but not groundwater level.

A small amount of HMX, an impurity in technical-grade RDX, also appears in IMX-104 formulations. HMX concentrations were smaller than RDX concentrations. After 1 year of rainfall applied to the 50-mg IMX-104 particle, HMX adsorbed to the soil and travelled to a maximum depth of 102 cm (1.02 m) with a concentration of 0.03 mg L⁻¹. HMX breakthrough occurred at a depth of 26 cm (0.26 m). After 10 years of rainfall, higher concentrations of HMX were observed in the soil. HMX traveled to a depth of 436 cm (4.36 m) with a concentration of 0.04 mg L⁻¹; and after 25 years of rainfall, to a depth of 974 cm (9.74 m) with a concentration of 0.01 mg L⁻¹. HMX breakthrough occurred at a depth of 205 cm (2.05 m) after 10 years of rainfall and at 487 (4.87 m) after 25 years of rainfall. However, HMX never reached groundwater level.
Figure 4.5: Forward simulations of NTO, RDX, HMX, DNAN and 2-ANAN in Camp Guernsey soil with rainfall over 1 year, 10 years and 25 years.
Only a small concentration of DNAN (0.21 mg L⁻¹) was observed at a depth of 51 cm (0.51 m) over the three different time periods of rainfall. All three lines overlapped (Figure 4.5). There was no 2-ANAN predicted in the soils after 1 year, 10 years, and 25 years of rainfall. Neither DNAN nor 2-ANAN ever reached groundwater level.

**Conclusions**

NTO, DNAN, and 2-ANAN released during dissolution of insensitive munitions were attenuated in the three soils used in simulations, either adsorbed or degraded or both. They did not reach groundwater in any of the soils systems simulated. While NTO and DNAN will naturally attenuate in soil, NQ, RDX, and HMX were more mobile in the simulated cases as years of rainfall continued. NQ is the most mobile explosive compound of those simulated. Therefore, NQ, RDX, and HMX should be monitored for risk of contaminating groundwater.

**References**


Mirecki, Porter, Weiss, 2006. Environmental transport and fate process descriptors for propellant compounds. U.S. Army Engineer Research and Development Center, Vicksburg, MS.


Appendices

Appendix A. Solubility of DNAN, NQ and NTO as a function of temperature.
### Appendix B. Studies investigating the transformation products of DNAN.

<table>
<thead>
<tr>
<th>Compound [CAS]</th>
<th>Matrix Containing DNAN</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Molecular modeling of alkaline hydrolysis mechanism</td>
<td>Salter-Blanc et al. 2013</td>
</tr>
<tr>
<td></td>
<td>Irradiation of aqueous solutions.</td>
<td>Hawari et al. 2015</td>
</tr>
<tr>
<td>4-methoxy-3-nitrophenol [15174-02-4]</td>
<td>Irradiation of aqueous solutions.</td>
<td>Hawari et al. 2011</td>
</tr>
<tr>
<td>4-methoxy-3-nitroaniline [577-72-0]</td>
<td>Zero-valent iron treatment of PAX-21 wastewater. Intermediate to formation of 2,4-Diaminoanisole.</td>
<td>Ahn et al. 2011</td>
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<td></td>
<td>Rhizobium lichtii cultures</td>
<td>Schroer et al. 2015</td>
</tr>
<tr>
<td></td>
<td>Suspensions of soils under aerobic and anaerobic conditions. (iMENA)</td>
<td>Olivares et al. 2016</td>
</tr>
<tr>
<td></td>
<td>Artificially contaminated soil microcosms (aerobic)</td>
<td>Perreault et al. 2012</td>
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<td>Sludge bioassays under aerobic, microaerophilic, and anaerobic conditions</td>
<td>Olivares et al. 2013</td>
</tr>
<tr>
<td></td>
<td>Reduction with zero valent iron in lab solutions and bacteria in cell cultures</td>
<td>Hawari et al. 2015</td>
</tr>
<tr>
<td></td>
<td>Earthworms and ryegrass shoots exposed to DNAN amended soil</td>
<td>Dodard et al. 2013</td>
</tr>
<tr>
<td></td>
<td>Rhizobium lichtii cultures</td>
<td>Schroer et al. 2015</td>
</tr>
<tr>
<td></td>
<td>Suspensions of soils under aerobic and anaerobic conditions</td>
<td>Olivares et al. 2016</td>
</tr>
<tr>
<td>2,4-Dinitrophenol [51-28-5]</td>
<td>Irradiated aqueous solutions. Minor (&lt;3% of total nitrogen) product with nitrate and nitrite as major products.</td>
<td>Rao et al. 2013</td>
</tr>
<tr>
<td></td>
<td>Rhesus Macaques dosed with DNAN. Found in blood and urine. Concentrations were higher in blood due to presumed nitroreduction to amino-nitrophenols.</td>
<td>Hoyt et al. 2013</td>
</tr>
<tr>
<td></td>
<td>Aerobic cell cultures with bacteria isolated from Holston AAP activated sludge</td>
<td>Fida et al. 2014</td>
</tr>
<tr>
<td></td>
<td>Enriched cell cultures (transient product)</td>
<td>Richard and Weidhaas (2014)</td>
</tr>
<tr>
<td></td>
<td>Irradiation (UV and sunlight) of aqueous DNAN solutions. Unstable product. Formed nitrocatechol (dihydroxy-nitrobenzene).</td>
<td>Hawari et al. 2015</td>
</tr>
<tr>
<td>2,4-Dinitrophenolate [20350-26-9]</td>
<td>Molecular modeling of alkaline hydrolysis mechanism</td>
<td>Salter-Blanc et al. 2013</td>
</tr>
<tr>
<td></td>
<td>Anaerobic fluidized-bed bioreactor</td>
<td>Platten et al. 2010</td>
</tr>
<tr>
<td>Compound [CAS]</td>
<td>Matrix Containing DNAN</td>
<td>Reference</td>
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<td>Sludge bioassays under aerobic, microaerophilic, and anaerobic conditions</td>
<td>Olivares et al. 2013</td>
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<tr>
<td>Reduction with zero valent iron in lab solutions and bacteria in cell cultures</td>
<td>Hawari et al. 2015</td>
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<tr>
<td>Suspensions of soils under anaerobic conditions</td>
<td>Olivares et a. 2016</td>
<td></td>
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<tr>
<td>Azo Dimers from DAAN 2,4-Diaiminoanisole)</td>
<td>Anaerobic fluidized-bed bioreactor</td>
<td>Platten et al. 2010</td>
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<td>Oxic (actively aerated) aqueous solutions of DAAN.</td>
<td>Hawari et al. 2015</td>
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<td>Sludge bioassays under aerobic, microaerophilic, and anaerobic conditions</td>
<td>Olivares et al. 2013</td>
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<tr>
<td>Suspensions of soils under aerobic and anaerobic conditions</td>
<td>Olivares et a. 2016</td>
<td></td>
</tr>
<tr>
<td>Nitrate/Nitrite</td>
<td>Irradiated aqueous solutions. Nitrate and nitrite were major products.</td>
<td>Rao et al. 2013</td>
</tr>
<tr>
<td>Irradiation of aqueous solutions. For each mole of DNAN degraded, nitrate anion (0.7 mole), ammonium (1 mole), formaldehyde/formic acid (0.9 mole) was formed.</td>
<td>Hawari et al. 2015</td>
<td></td>
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</tbody>
</table>
**Appendix C. Properties of DNAN and its transformation products.**

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Abbreviation</th>
<th>CAS</th>
<th>MW</th>
<th>Formula</th>
<th>Color/Form</th>
<th>Melting Point</th>
<th>Boiling Point</th>
<th>Vapor Pressure (mm Hg, 25 °C)</th>
<th>Log Kow</th>
<th>Hazard Classification from Safety Data Sheet</th>
<th>Other properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-Dinitroanisole [119-27-7] DNAN [MW=198] C₇H₆N₂O₅</td>
<td><img src="image1" alt="Structure" /></td>
<td>DNAN</td>
<td>[119-27-7]</td>
<td>198</td>
<td>C₇H₆N₂O₅</td>
<td>Colorless to pale yellow crystals</td>
<td>88-94 °C Alfa Aesar</td>
<td>207 °C Alfa Aesar</td>
<td>1.15 X 10⁻⁵ (Cuddy et al. 2014)</td>
<td>1.58 (Hawari et al. 2015)</td>
<td>AK Scientific Inc</td>
<td>Sₘ (25 °C) 1.213 g/L Hawari et al. 2015 0.276 g/L at 5 °C Boddu et al. 2008</td>
</tr>
<tr>
<td>2-methoxy-5-nitrophenol [636-93-1] 2-Me-5-NP [MW=169] C₇H₇NO₄</td>
<td><img src="image2" alt="Structure" /></td>
<td>2-Me-5-NP</td>
<td>[636-93-1]</td>
<td>169</td>
<td>C₇H₇NO₄</td>
<td>Yellow powder</td>
<td>104-106 °C Alfa Aesar 96.5 °C ChemSpider (SEPAMiSuite™)</td>
<td>294 °C ChemSpider (SEPAMiSuite™)</td>
<td>1.9 X 10⁻⁴ 1.73 estimated (ChemSpider (SEPAMiSuite™)</td>
<td>Harmful if swallowed. Skin &amp; eye irritant May cause respiratory irritation Harmful to aquatic life with long lasting effects</td>
<td></td>
<td></td>
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<tr>
<td>4-methoxy-3-nitrophenol [15174-02-4] 4-Me-3-NP [MW=169] C₇H₇NO₄</td>
<td><img src="image3" alt="Structure" /></td>
<td>4-Me-3-NP</td>
<td>[15174-02-4]</td>
<td>169</td>
<td>C₇H₇NO₄</td>
<td>Yellow powder AK Scientific Inc</td>
<td>95-103 °C AK Scientific Inc</td>
<td>341 °C ChemNet 294 °C ChemSpider (SEPAMiSuite™)</td>
<td>1.9 X 10⁻⁴ 1.99 estimated (ChemSpider (SEPAMiSuite™)</td>
<td>Skin &amp; eye irritant May cause respiratory irritation</td>
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<td></td>
</tr>
<tr>
<td>Name</td>
<td>Structure</td>
<td>Form</td>
<td>Melting Point</td>
<td>Boiling Point</td>
<td>Vapor Pressure (mm Hg, 25°C)</td>
<td>Log K&lt;sub&gt;ow&lt;/sub&gt;</td>
<td>Hazard Classification from Safety Data Sheet</td>
<td>Other Properties</td>
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<tr>
<td>2,4-Dinitrophenol [51-28-5]</td>
<td><img src="image1" alt="Structural formula" /></td>
<td>yellow crystals</td>
<td>106-108 °C</td>
<td></td>
<td>3.9X10&lt;sup&gt;-4&lt;/sup&gt; mm Hg at 20 deg C</td>
<td>1.7</td>
<td>Toxic if inhaled or contacted by skin.</td>
<td>Damage to organs through prolonged or repeated exposure</td>
<td></td>
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<tr>
<td>4-methoxy-3-nitroaniline [577-72-0] [MW=168] C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;]</td>
<td><img src="image2" alt="Structural formula" /></td>
<td>red powder (ChemSpider NovoChemy Ltd.)</td>
<td>97°C</td>
<td>304°C</td>
<td>3.2 X 10&lt;sup&gt;-4&lt;/sup&gt; (ChemSpider SEPA PISuite&lt;sup&gt;TM&lt;/sup&gt;)</td>
<td>0.92</td>
<td>May cause an allergic skin reaction, or breathing difficulties if inhaled</td>
<td>S&lt;sub&gt;w&lt;/sub&gt; (25°C) 0.43 g/L (Hawari et al. 2015)</td>
<td></td>
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<tr>
<td>2-methoxy-5-nitroaniline [99-59-2] [MW=168] C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;]</td>
<td><img src="image3" alt="Structural formula" /></td>
<td>Orange-red needles or dull orange powder (MP Biomedicals Safety Data Sheet) Orange crystalline powder</td>
<td>117-119 °C</td>
<td>304°C</td>
<td>1.3 x 10&lt;sup&gt;-4&lt;/sup&gt; (est) (MP Biomedicals Safety Data Sheet)</td>
<td>1.51</td>
<td>Toxic if swallowed or in contact with skin, suspected of causing cancer</td>
<td>S&lt;sub&gt;w&lt;/sub&gt; (25°C) 0.252 g/L (Hawari et al. 2015)</td>
<td></td>
<td></td>
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<tr>
<td>Name</td>
<td>Structure</td>
<td>Form</td>
<td>Melting Point</td>
<td>Boiling Point</td>
<td>Vapor Pressure (mm Hg, 25 °C)</td>
<td>Log K&lt;sub&gt;ow&lt;/sub&gt;</td>
<td>Hazard Classification from Safety Data Sheet</td>
<td>Other Properties</td>
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</tr>
<tr>
<td>2,4-diaminoanisole</td>
<td><img src="image" alt="Structure" /></td>
<td>Dark brown crystals (Sigma-Aldrich SDS)</td>
<td>58 °C (Sigma-Aldrich SDS)</td>
<td>0.047 mm Hg at 5 °C (PubChem)</td>
<td>0.5 (PubChem)</td>
<td>Harmful if swallowed, suspected of causing genetic defects, may cause cancer, Toxic to aquatic life with long lasting effects</td>
<td>Sw (25 °C) &gt;40 g/L, Hawari et al. 2015 Miscible with water (PubChem)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[CAS] 615-05-4</td>
<td>[MW] C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>[Abbreviation]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[138.17]</td>
<td>[Formula]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Darkens on exposure to light. Used to prepare dyes, especially hair dyes. Corrosion inhibitor for steel. (Merck) pKa = 5.15 (est) (PubChem)
Max absorption: 635 nm, 587 nm, 545 nm and 511 nm
GCMS 138, 123, 95 m/z
Elutes at 3 mins (with DNAN at 9 mins)
Forms dimers in oxic aqueous solutions
4-Methoxy-m-phenylenediamine, 4-methoxybenzene-1,3-diamine, 1,3-Benzenediamine, 4-methoxy-
Appendix D. GC-MS Retention Times and mass spectra for compounds discussed in this report.

Note that NTO and NQ do not elute as sharp chromatographic peaks. Both compounds are thermally labile and degrade within the hot chromatography column.

<table>
<thead>
<tr>
<th>R. T. (mins)</th>
<th>Compound</th>
<th>Molecular weight, Formula</th>
<th>GC mass spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>1-Chloro-4-nitrobenzene</td>
<td>MW=157.5, C₆H₄ClNO₂</td>
<td><img src="image" alt="Mass Spectrum" /></td>
</tr>
</tbody>
</table>

![Chemical Structure](image)
<table>
<thead>
<tr>
<th></th>
<th>Name</th>
<th>Molecular Weight</th>
<th>Structure</th>
<th>Mass Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.8</td>
<td>1,2,4-Benzenetriol</td>
<td>MW=126, C₆H₆O₃</td>
<td><img src="image" alt="benzenetriol structure" /></td>
<td><img src="image" alt="benzenetriol mass spec" /></td>
</tr>
<tr>
<td>8.02</td>
<td>2,4-Dinitrophenol</td>
<td>MW=184, C₆H₄N₂O₅</td>
<td><img src="image" alt="dinitrophenol structure" /></td>
<td><img src="image" alt="dinitrophenol mass spec" /></td>
</tr>
<tr>
<td>8.45</td>
<td>Unknown A</td>
<td>MW=182, C₇H₆N₂O₄</td>
<td><img src="image" alt="unknown structure" /></td>
<td><img src="image" alt="unknown mass spec" /></td>
</tr>
<tr>
<td>Retention Time (min)</td>
<td>Compound</td>
<td>Molecular Weight (MW)</td>
<td>Molecular Formula</td>
<td>Molecular Ion (m/z)</td>
</tr>
<tr>
<td>---------------------</td>
<td>-------------------</td>
<td>-----------------------</td>
<td>---------------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>8.65</td>
<td>4-Nitroaniline</td>
<td>138</td>
<td>C₆H₆N₂O₂</td>
<td>138 (molecular ion)</td>
</tr>
<tr>
<td></td>
<td><img src="image1" alt="4-Nitroaniline" /></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.67</td>
<td>2-methoxy-5-nitrophenol</td>
<td>169</td>
<td>C₇H₇NO₄</td>
<td>169 (molecular ion)</td>
</tr>
<tr>
<td></td>
<td><img src="image2" alt="2-methoxy-5-nitrophenol" /></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.03</td>
<td>Unknown C</td>
<td>214</td>
<td>C₇H₆N₂O₆</td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image3" alt="Unknown C" /></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
9.06 4-methoxy-3-nitrophenol  
MW=169, C₇H₇NO₄

\[ \text{H}_3\text{CO} \quad \text{OH} \quad \text{NO}_2 \]

169 (molecular ion)  
153 (Loss of O₂=16)  
122 (Loss of NO+OH=47)  
108 (Loss of CH₃NO₂ =61)  
65  
53  
39  
30 (NO)

9.1 NTO  
MW=128, C₂N₄O₃

\[ \text{O}_2\text{N} \quad \text{N} \quad \text{N} \]

130  
83
9.20  4-methoxy-3-nitroaniline  
MW=168, C₇H₈N₂O₃  
\[
\begin{array}{c}
\text{H₂N} \\
\text{NO₂} \\
\text{OCH₃}
\end{array}
\]
168 (molecular ion)  
153 (Loss of CH₃ (-15))  
123  
107 (Loss of CH₃NO₂ (-61))  
92 (Loss of CH₂ONO₂ (-76))  
79  
65  
52  
30 (NO)

9.28  MNA (n-methyl-p-nitroaniline)  
MW=152, C₇H₈N₂O₂  
\[
\begin{array}{c}
\text{NHCH₃} \\
\text{O₂N}
\end{array}
\]
152 (molecular ion)  
122 (Loss of NO (-30))  
77  
65  
50  
39  
30
| 9.37  | Unknown B-DNAN isomer, MW 198 (2,6-DNAN) | 198 (molecular ion)  
|       |                                           | 168 (Loss of NO (-30))  
|       |                                           | 151  
|       |                                           | 76   
|       |                                           | 63   
|       |                                           | 30   |
|       | ![Chemical Structure](image1)              | ![Mass Spectrum](image2) |
| 9.41  | 2-methoxy-5-nitroaniline  
|       | MW=168, C7H8N2O3  
|       |                                           | 168 (molecular ion)  
|       |                                           | 153 (Loss of CH₃ (-15))  
|       |                                           | 122  
|       |                                           | 107 (Loss of CH₃NO₂ (-61))  
|       |                                           | 95 (Loss of NO₂ and HCN (-73))  
|       |                                           | 79   
|       |                                           | 65   
|       |                                           | 52   
|       |                                           | 30 (NO)  
|       | ![Chemical Structure](image3)              | ![Mass Spectrum](image4) |
| 9.6 | NQ  
|     | MW=104, CH₄N₄O₂  
|     | ![NQ structure](image)  
|     | 9.67  
| 2,4-Dinitroanisole (DNAN)  
| MW=198, C₇H₆N₂O₅  
| ![DNAN structure](image)  
| 198 (molecular ion)  
| 168 (Loss of NO (-30))  
| 151 (Loss of HNO₂)  
| 76 (Benzene ring with 4 H)  
| 63 (CH₃ + NO₂ + H₂)  
| 30 (NO)  
| ![DNAN spectrum](image)  
| ![NQ spectrum](image) |
2-propanol, 1-chlorophosphate (3:1)
MW = 328, C₉H₁₈Cl₃O₄
9.81 2-hydroxyl amino-4-nitroanisole
MW=184, C₇H₈N₂O₄
Structure from Hawari et al. 2011.

9.85 1-ethoxy-2,4-dinitrobenzene
MW=212, C₈H₈N₂O₅
10.3  RDX
MW=222, C₃H₆N₆O₆
\[
\text{NO}_2
\]
\[
\text{O}_2\text{N}-\text{N}-\text{N}-\text{NO}_2
\]

11.2  2,4-Dinitrobenzamine
MW=183, C₆H₅N₃O₄
\[
\text{O}_2\text{N}-\text{NO}_2
\]
\[
\text{NH}_2
\]
Appendix E. Dissolution and Transport of Insensitive Munitions Formulations IMX-101 and IMX-104 in Saturated Soil Columns

Figure E1. Image of IMX-101 on top of soil profile during dissolution experiments.

Table E1. $Y_{\text{max}}$, $\chi$ and $Y_{\text{min}}$ estimates obtained from Taylor et al., 2015b for IMX-101 and IMX-104.

<table>
<thead>
<tr>
<th></th>
<th>IMX-101</th>
<th>IMX-101</th>
<th>IMX-101</th>
<th>IMX-104</th>
<th>IMX-104</th>
<th>IMX-104</th>
<th>IMX-104</th>
<th>IMX-104</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NTO</td>
<td>NQ</td>
<td>DNAN</td>
<td>RDX</td>
<td>HMX</td>
<td>DNAN</td>
<td>NTO</td>
<td>NTO</td>
</tr>
<tr>
<td>$Y_{\text{max}}$ (mg L$^{-1}$ h$^{-1}$ mg$^{-1}$)</td>
<td>0.1180</td>
<td>0.0793</td>
<td>0.2973</td>
<td>0.465</td>
<td>0.065</td>
<td>1.121</td>
<td>0.416</td>
<td></td>
</tr>
<tr>
<td>$\chi$ (h$^{-1}$)</td>
<td>0.0001</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>$Y_{\text{min}}$ (mg L$^{-1}$ h$^{-1}$ mg$^{-1}$)</td>
<td>0.0028</td>
<td>0.0048</td>
<td>0.0585</td>
<td>0.131</td>
<td>0.010</td>
<td>0.234</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>
Figure E2. Flow interruption breakthrough curves for individual propellants for detonated IMX-104 particle in Camp Guernsey soil. NTO, 3-nitro-1, 2, 4-triazol-5-one; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; DNAN, 2, 4-dinitroanisole; 2-ANAN, 2-amino-4-nitroanisole. Vertical solid grey line indicates start of 24-hr flow interruption. Vertical grey dashed grey line indicates switch to saturated solution.
Figure E3. pH of samples collected during analysis for IMX-104 Flow interruption experiments. Vertical dashed grey line indicates start of 24-hr flow interruption. Vertical solid grey line indicates switch to saturated solution.
Appendix F. Additional Figures for Dissolution and Transport of Insensitive Munitions Formulations IMX-101 and IMX-104 in Saturated Soil Columns

This appendix includes the results of additional analysis conducted to investigate the dissolution and transport of Insensitive Munitions Formulations IMX-101 and IMX-104 in saturated soil columns.

**Figure F1.** Breakthrough curves for individual explosives for detonated IMX-101 in Camp Guernsey soil. NTO, 3-nitro-1,2,4-triazol-5-one; NQ, nitroguanidine; DNAN, 2,4-dinitroanisole; 2-ANAN, 2-amino-4-nitroanisole; 4-ANAN, 4-amaino-2-nitroanisole.
**Figure F2.** Breakthrough curves for individual explosives for nondetonated IMX-101 in Camp Guernsey soil. NTO, 3-nitro-1, 2, 4-triazol-5-one; NQ, nitroguanidine; DNAN, 2,4-dinitroanisole; 2-ANAN, 2-amino-4-nitroanisole; 4-ANAN, 4-amaino-2- nitroanisole.
**Figure F3.** Breakthrough curves for individual explosives for nondetonated IMX-101 in Camp Swift soil. NTO, 3-nitro-1,2,4-triazol-5-one; NQ, nitroguanidine; DNAN, 2, 4-dinitroanisole; 2-ANAN, 2-amino-4-nitroanisole; 4-ANAN, 4-amaino-2-nitroanisole.
Figure F4: Breakthrough curves for individual explosives for detonated IMX-101 flow interruption in Camp Guernsey soil. NTO, 3-nitro-1,2,4-triazol-5-one; NQ, nitroguanidine; DNAN, 2,4-dinitroanisole; 2-ANAN, 2-amino-4-nitroanisole; 4-ANAN, 4-amino-2-nitroanisole. Start of 24-hr flow interruption = solid vertical line and switch to saturated solution = dashed vertical line.
Figure F5: Breakthrough curves for individual explosives for nondetonated IMX-104 particle in Camp Guernsey soil. NTO, 3-nitro-1,2,4-triazol-5-one; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; DNAN, 2, 4- dinitroanisole; 2-ANAN, 2-amino-4-nitroanisole; 4-ANAN, 4-amino-2-nitroanisole.
Figure F6: Breakthrough curves for individual explosives for nondetonated IMX-104 particle in Camp Swift soil. NTO, 3-nitro-1,2,4-triazol-5-one; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; DNAN, 2, 4- dinitroanisole; 2-ANAN, 2-amino-4-nitroanisole; 4-ANAN, 4-amino-2-nitroanisole.
**Figure F7**: Breakthrough curves for individual explosives for detonated IMX-104 flow interruption in Camp Guernsey soil. NTO, 3-nitro-1,2,4-triazol-5-one; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; DNAN, 2,4-dinitroanisole; 2-ANAN, 2-amino-4-nitroanisole; 4-ANAN, 4-amino-2-nitroanisole. Start of 24hr flow interruption = solid vertical line and switch to saturated solution = dashed vertical line.
Appendix G. Acronyms, Abbreviations, and Symbols

AcN    Acetonitrile
2-ANAN 2-amino-4-nitroanisoile (same as MENA or 2-MeO-5-NA)
4-ANAN 4-amino-2-nitroanisoile (same as 4-MeO-3-NA)
AP     Ammonium Perchlorate
ATO    5-amino-1,2,4-triazol-3-one
C4     Composition 4, a common plastic explosive known as “C4”
Comp B Composition B, a 39:60 mix of TNT and RDX with 1% wax
CRREL  Cold Regions Research and Engineering Laboratory
DNAN   2,4-dinitroanisoile
DNP    Dinitrophenol
DNT    2,4- or 2,6-dinitrotoluene
ERDC   U.S. Army Engineer Research and Development Center
HMX    High Explosive 1,3,5,7-octahydro-1,3,5,7-tetranitrotetrazocine
HPLC   High Precision Liquid Chromatography.
IM     Insensitive Munitions
IMX   Insensitive Munitions eXplosive
k      First-Order Transformation Rate Constant
k_{photo} First-Order Phototransformation Rate Constant
K_{ow} Octanol–Water Partition Coefficient
m/z    Mass/atomic number
MENA   2-methoxy-5-nitroaniline (same as 2-ANAN or 2-MeO-5-NA)
2-MeO-5-NA 2-methoxy-5-nitroaniline (same as MENA and 2-ANAN)
4-MeO-3-NA 4-methoxy-3-nitroaniline (same as 4-ANAN)
2-MeO-5-NP 2-methoxy-5-nitrophenol
4-MeO-3-NP 4-methoxy-3-nitrophenol
MNA    N-methyl-p-nitroaniline
NIST   National Institute of Standards and Technology
NQ     Nitroguanidine
NTO    3-nitro-1,2,4-triazol-5-one
PAX    Picatinny Arsenal eXplosive
pK_a   Acid Dissociation Constant
PTFE   Polytetrafluoroethylene
R^2    Coefficient of Determination
RDX   1,3,5-hexahydro-1,3,5-trinitro-1,3,5-triazine
SERDP Strategic Environmental Research and Development Program
SIM    Selective Ion monitoring
SPE    Solid Phase Extraction
TIC    Total Ion Chromatogram
TNT    2,4,6-trinitrotoluene
UHPLC Ultra High Performance Liquid Chromatography
U.S. EPA United States Environmental Protection Agency
UV-Vis Ultra Violet to Visible spectroscopy