

Short Communication

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Deposition of PETN Following the Detonation of Seismoplast Plastic Explosive

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Abstract: Many nation's armed forces are undertaking efforts to minimize the environmental impacts of live-fire military training. Based on this, the Canadian Department of National Defence has undertaken a project to examine potential alternatives to the use of Composition C4, an RDX-based plastic explosive. Plastic explosives are widely used by all armed forces for both military engineering tasks and explosive ordnance disposal and their use may lead to the deposition of explosives in the environment, namely RDX, in the case of C4. RDX is very stable in the environment, water soluble, and moves relatively rapidly towards surface and groundwater bodies. One option identified as a potential RDX-free formulation is a pentaerythritol tetranitrate (PETN) based plastic explosive, commercially available in Germany and referred to as Seismoplast. In order to measure the environmental impacts of this formulation, a deposition rate study was conducted. These tests consist

of evaluating the detonation efficiencies of munitions during detonation scenarios representative of military training. Data generated from these tests are the deposition masses of the energetic components in the explosive filler, which in this case is PETN. To achieve this objective, seven blocks of Seismoplast were open detonated over a surface of pristine snow, and post-detonation surface samples were collected to measure residual PETN. The trial demonstrated that less than 1×10^{-7} % of PETN is deposited upon detonation of Seismoplast. The energetic material deposition rates obtained in this trial are much lower than rates obtained for the RDX-based C4 currently in-service within Canada. Switching from a RDX-based plastic explosive to one based on PETN may be an interesting option through which the Department of National Defence can reduce the environmental impact of its activities.

Keywords: PETN · Deposition · Environmental impact · RDX · Contaminant

1 Introduction

Plastic explosives are widely used by military units, most notably by engineers for demolition activities and by explosive ordnance disposal (EOD) teams for the blow-in-place destruction of unexploded ordnance (UXO). The well-known plastic explosive formulation Composition C4, based on hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), is used by many nations. RDX is very stable in the environment, water soluble and moves relatively rapidly towards surface and groundwater bodies in Ranges and Training Areas (RTA). Such properties contribute to the adverse environmental impacts of RDX which have been discovered recently [1–3]. The US Environmental Protection Agency has designated RDX as a possible human carcinogen that also targets the nervous system and can cause seizures in humans and animals when large amounts are inhaled or ingested [4]. RDX ecotoxicity was also extensively studied in Canada and showed toxicity to various receptors [5,6]. Therefore, North-American RDX thresholds in water bodies are low, in the order of parts per billion [7].

The Canadian Department of National Defence, like many defence organizations, are undertaking efforts to

minimize the environmental impacts of their activities to ensure that RTAs remain sustainable for the completion of mandated training activities. The physicochemical properties of RDX, along with the impacts of RDX on human health and the environment raised an interest for studying alternatives to RDX-based explosives. In order to better understand the deposition of contaminants from the functioning of various munitions, deposition rate (DR) studies have recently been designed. DR studies are an effective tool to determine the masses of explosive constituents dispersed in representative detonation scenarios. A method for the precise and reliable determination of constituent DR was developed by the Cold Regions and Engineering Laboratory and involves the detonation of munitions items over a surface of pristine snow [8]. RDX DRs following the detonation of C4 blocks were tested using this protocol on different occasions and showed that 12 mg to 19 mg of RDX were

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deposited per C4 block, out of an original mass of 516 g of RDX [9,10]. Recent studies have also been conducted to determine the DR of new insensitive formulations using this method [11,12].

Based on the RDX DR measured from C4, options for the potential replacement of RDX-based plastic explosives were reviewed and considered. One option under consideration involves a German plastic explosive based on the explosive pentaerythritol tetranitrate (PETN). This formulation is referred to as Seismoplast and is composed of 85% PETN in an inert binder. From an environmental fate point of view, PETN's half-life is 2.4 d, meaning it will degrade very rapidly once dispersed in the environment [13]. Fate studies recently conducted showed that it mainly degrades into dinitrated PETN products and ultimately into nitrate and pentaerythritol [14]. PETN was also recently identified as the least toxic explosive in a literature review [15]. To the best of our knowledge, there are presently no published environmental criteria or guidelines for PETN. Studies to date reported very low solubility of PETN in water with values of 1.9 mg L^{-1} at 25°C [16], 1.5 mg L^{-1} at 20°C [17], and 1.55 mg L^{-1} at 25°C [14]. In comparison, RDX solubility is 56.4 mg L^{-1} at 25°C [3]. Based on these facts, it appears that PETN is less soluble and persistent than RDX. In order to compare Seismoplast with C4 and assess how much PETN would be released by the detonation of PETN-based plastic explosive blocks, a DR study was conducted. This short communication presents the results from the Seismoplast deposition trial and presents original data on the efficiency of detonation of a PETN-based plastic explosive.

2 Experimental Section

2.1 Trial Set-up

The deposition trial was conducted at the Defence Research and Development Canada (DRDC) Valcartier test site located in the Valcartier RTA. The trial was conducted in February 2014 by DRDC in collaboration with the Munitions Experimental Test Center Valcartier. It involved EOD personnel responsible for the explosive initiations and detonations. Weather conditions were average for the time of year and considered ideal for a DR trial. There was a 1.2 meter deep snowpack on site, temperatures varied between -18°C and -10°C throughout the day, and there were sporadic light winds. Prior to detonations, three field blanks were collected in the area where the detonations would later be performed in order to assess the explosive background contamination. Seven locations were selected using sufficient distances between the detonation points (DP) to avoid plume cross-contamination. Walking trails were done using snowshoes to reach the DP to ensure EOD safety and ice blocks were placed to minimize the penetration of the detonation in the soil profile, thus avoiding cross-contamination (Figure 1). Seismoplast blocks were placed on the ice blocks and detonators were placed in the center of the

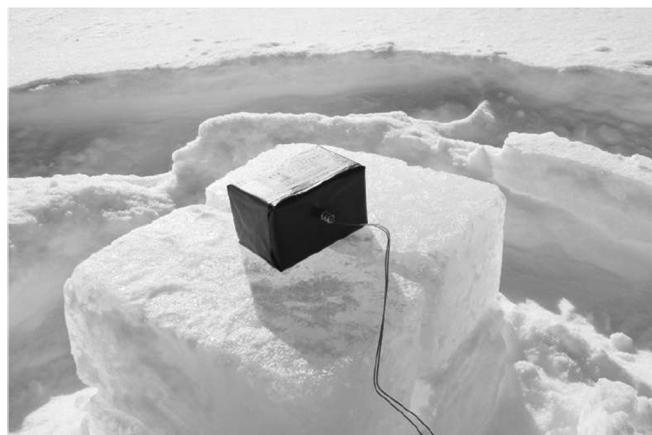


Figure 1. Detonation point set-up with ice block.

Seismoplast block. The seven blocks were detonated in two series, four blocks were placed, wired, and detonated in a sequence in the morning and three blocks in the afternoon.

2.2 Sample Collection, Processing, and Analytical Methods

After detonation, as soon as the site was cleared by the EOD team, the sampling teams delineated the plume area (Figure 2) and collected the snow samples within and around the detonation areas using snowshoes. Precautions were taken to avoid bringing cross-contamination between the plumes by washing the snowshoes and the sampling gear using clean snow and wipes.

Once the areas were delineated, two-person teams sampled the inside of the plumes, by collecting three replicates of composite samples using the method described by Walsh [8]. One person collected the area just outside of the plume from an annulus 0–3 m outside the demarcated plume. Surface snow samples ($10 \times 10 \times 2.5$ -cm deep) were collected using specifically designed spoons. Around 100



Figure 2. Detonation area delineated after walking around the visible plume.

increments were collected using a random systematic approach to statistically represent the whole deposition area and large composite snow samples were built using this strategy. The exact amount of increments was recorded to determine the sampled surface leading to the calculation of the deposition rate. Snow samples were brought back to the laboratory and kept frozen at -20°C until processing. Samples were processed by melting the snow overnight at room temperature, and the melted water was filtered using $45\ \mu\text{m}$ glass microfiber filters to remove the solid soot residues. The volumes of water were recorded, and a fraction of 500 mL of water was concentrated over a SEP-Pack cartridge following method EPA-8330b [18], then re-extracted using acetonitrile. The residues obtained from the glass microfiber filters were also extracted using 40 mL of acetonitrile overnight. All glassware used in the process was carefully washed with water and soap, and then rinsed three times using de-ionized Type-1 reagent grade water ($18\ \text{M}\Omega\text{-cm}$). Laboratory blanks were included in the process to ensure its effectiveness. A series of laboratory control samples, consisting of Type-1 reagent grade water ($18\ \text{M}\Omega\text{-cm}$) spiked at various concentrations within the calibration curves were run to determine the recovery of PETN using our extraction method. Analyses on the solvent extracts were conducted using two analytical chromatographic methods. The extracts were analyzed by High Pressure Liquid Chromatography (HPLC) with a photodiode array detector (PDA), on a Supelcosil LC-18, $250\times 3\ \text{mm}\times 5\ \mu\text{m}$ column and a mixture of water and methanol (50%) as the eluent and an external calibration curve between 0.05 and $10\ \text{mgL}^{-1}$. Calibration standards were purchased from Accustandard. No PETN was detected using this method and extracts were re-analyzed using a gas chromatographic (GC) method on a DB-1 column of 7.4 m, with a nominal diameter of $530\ \mu\text{m}$ and a nominal film thickness of $1\ \mu\text{m}$ and also using a secondary column as a DB-200 of 5.9 m, with nominal diameter of $530\ \mu\text{m}$ and a nominal film thickness of $1\ \mu\text{m}$. The inlet was a cool-on column injector used with hydrogen in a constant flow mode. The columns were coupled to electron capture detectors (μECD) and an external calibration curve was used between $0.1\ \text{ng mL}^{-1}$ and $20\ \text{ng mL}^{-1}$. When taking into account the concentration factor from the pre-concentration step, the method led to a PETN detection limit of $0.01\ \text{ng mL}^{-1}$.

3 Results and Discussion

The detonation set-up was relevant to capture the residues. The seven plume areas ranged between 222 and $306\ \text{m}^2$ and no cross-contamination between the plumes was observed. In comparison, C4 blocks plume areas varied between 138 and $214\ \text{m}^2$ [8,9]. All quality assurance procedures indicate that the data are robust. The field blank results came back with no detection of any explosive residues, indicating a pristine snow cover which is relevant for

the trial. The laboratory blanks also came back non-detected, indicating an efficient cleaning process. Recoveries of the PETN from the PETN spiked samples were within normal range ($\pm 10\%$) with no apparent loss of PETN. The resulting samples from the seven plumes analyzed by HPLC-PDA came back with non-detectable concentrations of PETN. Further analysis of the extracts by GC-ECD revealed no traces of PETN either, with a much lower detection limit (DL) of $0.01\ \text{ng mL}^{-1}$. Using half of this DL ($0.005\ \text{ng mL}^{-1}$) in the calculations for the whole plume, deposition rate of PETN from the detonation of Seismoplast blocks revealed to be smaller than $1\times 10^{-7}\%$. This is considered a very low DR, and it is four orders of magnitude smaller than the RDX DR from C4, which is $4\times 10^{-3}\%$ [9]. This very low DR is favorable to its use, as its environmental footprint is extremely small. Moreover, the forensic traces deposited will be rapidly degraded and shall not reach any sensitive receptors. Further study of PETN's degradation pathway is needed to ensure that no toxic compounds are produced.

4 Conclusions

RDX is now recognized as a problematic and bioavailable explosive that has the tendency to move towards RTAs water bodies. Two options are available to mitigate RDX dispersion in RTA: to enclose RDX in a contained environment by designing ranges with barriers (membranes, roofs, reactive barriers), or to eliminate RDX from the formulations. While it is not practical to eliminate all RDX-based munitions in the military inventories, replacing C4 with a non-RDX containing plastic explosive is an option that is under consideration at this time to reduce the spreading of RDX in RTAs. The first replacement candidate studied was the German PETN based Seismoplast plastic explosive. The deposition rate trial conducted on this plastic explosive demonstrated that very low, non-detectable levels of PETN are deposited at the detonation point. The PETN deposition rate is four orders of magnitude less when compared to the RDX deposition rate from C4. Furthermore, preliminary results and a review of the literature indicated that PETN is much less soluble, persistent, and toxic than RDX. Based on these results, PETN based plastic explosives appear to be a good replacement choice for use for both engineering and EOD needs. However, further study is required before the Department of National Defence changes its current in-service plastic explosive for a plastic explosive based on PETN.

Symbols and Abbreviations

DL	– Detection limit
DR	– Deposition rate
DP	– Detonation point

DRDC – Defence Research and Development Canada
 ECD – Electron capture detector
 EOD – Explosive ordnance disposal
 GC – Gas chromatography
 HPLC – High pressure liquid chromatography
 PDA – Photodiode array detector
 PETN – Pentaerythritol tetranitrate
 RDX – Hexahydro-1,3,5-trinitro-1,3,5-triazine
 RTAs – Ranges and training areas

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References

- [1] T. W. Sheremata, A. Halasz, L. Paquet, S. Thiboutot, G. Ampleman, J. Hawari, The Fate of the Cyclic Nitramine Explosive RDX in Natural Soil, *Environ. Sci. Technol.* **2001**, *35*, 1037–1040.
- [2] K. M. Dontsova, S. L. Yost, J. Simunek, J. C. Pennington, C. W. Williford, Dissolution and Transport of TNT, RDX, and Composition B in Saturated Soil Columns, *J. Environ. Qual.* **2006**, *35*, 2043–2054.
- [3] J. Pichel, Distribution and Fate of Military Explosives and Propellants in Soils: A Review, *Appl. Environ. Soil Sci.* **2012**, *2012*.
- [4] Agency for Toxic Substances and Disease Registry, *Toxicological Profile for RDX*, CAS#: 121-82-4, U.S. Department of Health and Human Services, Public Health Service, ATSDR, Atlanta, GA, USA, **2012**, <http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=412&tid=72> (Accessed 25 February 2015).
- [5] G. Sunahara, G. Lotufo, R. Kuperman, J. Hawari, S. Thiboutot, G. Ampleman, *Ecotoxicology of Explosives*, Taylor and Francis, Boca Raton, **2009**.
- [6] P. Y. Robidoux, J. Hawari, G. Bardai, L. Paquet, G. Ampleman, S. Thiboutot, G. I. Sunahara, TNT, RDX and HMX Decrease Earthworm (*Eisenia Andrei*) Life-Cycle Responses in a Spiked Natural Forest Soil, *Archives Environ. Contamin. Toxicol.* **2002**, *43*, 379–388.
- [7] *Environmental Protection Agency Technical Fact Sheet Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)*, Environmental Protection Agency, Washington, D.C., USA, **2014**. http://www2.epa.gov/sites/production/files/2014-03/documents/ffrrofactsheet_contaminant_rdx_january2014_final.pdf, (Accessed 25 February 2015).
- [8] M. R. Walsh, M. E. Walsh, C. E. Ramsey, *Measuring Energetic Residues on Snow*, ERDC/CRREL Report TR-07-19, Engineer Research and Development Center/Cold Regions Research and Engineering Laboratory, Hanover, NH, USA, **2007**.
- [9] M. R. Walsh, M. E. Walsh, I. Poulin, S. Taylor, T. A. Douglas, Energetic Residues from the Detonation of Common US Ordnance, *Int. J. Energ. Mater. Chem. Propul.* **2011**, *10*, 169–186.
- [10] A. D. Hewitt, T. F. Jenkins, T. A. Ranney, J. A. Stark, M. E. Walsh, S. Taylor, M. R. Walsh, D. L. Lambert, *Estimates for Explosives Residue from the Detonation of Army Munitions*, ERDC/CRREL Report TR-03-16, Engineer Research and Development Center/Cold Regions Research and Engineering Laboratory, Hanover, NH, USA, **2003**.
- [11] M. R. Walsh, M. E. Walsh, S. Taylor, C. A. Ramsey, D. B. Ringelberg, S. Thiboutot, G. Ampleman, E. Diaz, Characterization of PAX-21 Insensitive Munition Detonation Residues, *Propellants Explos. Pyrotech.* **2013**, *38*, 399–409.
- [12] M. R. Walsh, M. E. Walsh, C. A. Ramsey, J. Zufelt, S. Thiboutot, G. Ampleman, L. Zunino, Energetic Residues from the Detonation of IMX-104 Insensitive Munitions, *Propellants Explos. Pyrotech.* **2014**, *39*, 243–250.
- [13] T. F. Jenkins, C. Bartolini, T. A. Ranney, *Stability of CL-20, TNAZ, HMX, RDX, NG, and PETN in Moist, Unsaturated Soil*, ERDC/CRREL Report TR-03-7, Engineer Research and Development Center/Cold Regions Research and Engineering Laboratory, Hanover, NH, USA, **2003**.
- [14] J. Hawari, G. I. Sunahara, N. Perreault, A. Halasz, L. Paquet, S. Dodard, M. Sarrazin, K. Savard, *Environmental Fate and Ecological Impact of Emerging Energetic Chemicals (ADN, DNAN and its Amino-Derivatives, PETN, NTO, NQ, FOX-7, and FOX-12) and an Insensitive Formulation*, DRDC-RDDC-2014-C178, National Research Council, Energy Mine and Environment, Ottawa, Ontario, Canada, **2014**, http://cradpdf.drdc-rddc.gc.ca/PDFS/unc156/p800385_A1b.pdf, (Accessed 25 February 2015).
- [15] N. Čenas, A. Nemeikaite-Čeniene, J. Marozien, V. Šarlauskas, J. V. Baublys, *Explosives as Toxic Environmental Pollutants: the Level of Contamination, Toxicity, and its Mechanisms*, EUExcert (Certifying Expertise in European Explosives Sector), Karlskoga, Sweden, **2014**, http://www.euexcert.org/pdf/Explosives_hazards_for_humanhealth_and_livingorganisms-toxicityreview_Vilnius-LT.pdf, (Accessed 25 February 2015).
- [16] E. J. Merrill, Solubility of Pentaerythritol Tetranitrate in Water and Saline, *J. Pharm. Sci.* **1965**, *54*, 1670–1671.
- [17] The Merck Index: *An Encyclopedia of Chemicals, Drugs, and Biologicals*, (Ed.: S. Budavari) Merck, Rahway, **1989**, p. 7068.
- [18] *USEPA Nitroaromatics and Nitramines by High-Pressure Liquid Chromatography*, USEPA SW846 Method 8330B, Environmental Protection Agency, Washington, D.C., USA, **2006**, <http://www.epa.gov/osw/hazard/testmethods/pdfs/8330b.pdf>, (Accessed 25 June 2014).

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