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Aims and Scope

The main purpose for this journal is to promote scientific investigation, technical advancements, and information exchange in the two closely related areas of energetic materials (EM) and chemical propulsion (CP). Numerous energetic materials have been developed recently for various chemical propulsion applications. Significant advancements in energetic material synthesis, characterization, and model simulation have also been made in recent years. It is expected that this trend will continue even at a greater pace in the future. Nano-sized ingredients and certain novel components offer specific advantages for both military and commercial applications in the chemical propulsion field. The ignition and combustion behavior of various new materials have shown special characteristics based upon experimental, theoretical, and computational research efforts. With the current emphasis on environmental impact, safety, and efficiency, efforts will be made in future development by considering green, insensitive, and high-performance energetic materials. In the chemical propulsion area, there have been numerous advancements in solid, liquid, and hybrid rockets. Similarly, energetic fuels and oxidizers have been formulated and processed for solid-fuel ramjets, ducted rockets, pulse detonation engines, etc. Many challenging problems, such as erosion of nozzle and high-temperature insulation materials, are topics of today's research. In spite of notable advances, many technological gaps have been identified in the combustion of energetic materials for propulsion purposes. This journal is intended to provide a valuable source of technical information associated with the energetic material development related to the advancements in chemical propulsion systems.

The journal is aimed to: 1) promote communication between researchers, designers, and manufacturers regarding state-of-the-art approaches in the combustion field of propellants, explosives, and pyrotechnics; 2) address new and advanced propulsion systems associated with solid, liquid, and gel energetic materials; 3) enhance the safety techniques in the utilization of energetic materials; and 4) encourage the development of highly reliable propulsion systems. The journal also addresses several pressing global issues in the combustion/propulsion area such as: a) environmental concerns; b) enhanced safety operation; and c) economical utilization.

The scope of this journal covers the following 18 areas:

- Nano Technology and Innovative Methods in EM Development;
- Synthesis & Characterization of EMs;
- Formulation, Processing, and Manufacturing of EMs;
- Insensitive Munitions;
- Hazard Reduction and Safety Aspects;
- Theoretical Modeling and Numerical Simulation for CP and EM;
- Performance Evaluation of EMs;
- Aging, Stability, and Compatibility;
- Recycling, Disposal, and Environmental Aspects;
- Test Methods and Diagnostic Techniques in CP and/or Combustion of EMs;
- Ignition and Initiation Processes;
- Detonation and/or Deflagration Processes;
- Thermobarics and Thermites;
- Innovative Rocket Propulsion Techniques;
- Rocket Thermal Protection Materials;
- Environmentally-Friendly "Green" Propellants;
- Commercial Applications of EMs; and
- Performance of Advanced Propulsion Systems.

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IGNITION AND COMBUSTION OF NICKEL COATED AND UNCOATED ALUMINUM PARTICLES IN HOT POST-FLAME ENVIRONMENT

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It is well known that aluminum particles require a high temperature to achieve ignition, often in excess of 1900 K. Lowering the ignition temperature of Al particles can increase the efficiency of solid propellant-based propulsion systems and aluminized explosives. Current methods to reduce the ignition temperature include both reducing the particle size to the nanoscale and/or applying coatings that aid ignition. In this work, an experimental study of ignition and combustion of isolated 5 wt.% Ni-coated and uncoated aluminum particles was conducted. Two particle sizes (nominally, 32 and 9 μm in diameter) were examined. The ignition and combustion properties of these aluminum particles were observed in the post-flame zone of a multidiffusion flat-flame burner at atmospheric pressure. The results showed that the applied nickel coating decreased the ignition temperature of the Al particles by an average of 750 K for 32-μm diameter particles and between 200 and 300 K for the 9-μm diameter particles. Measurements of particle burning times indicated that the application of the nickel coating does not affect the overall burning time of the particles. Thus, the application of nickel coatings on Al particles significantly decreases the ignition temperature while not affecting the overall combustion behavior.

KEY WORDS: *energetic materials, aluminum combustion, nickel-coated aluminum*

1. INTRODUCTION

Aluminum particles are widely employed in solid propellant applications as an energetic fuel additive (Kuo et al., 2004). In addition to propulsion, aluminum particles have also been utilized in explosive applications (Kim et al., 2007). When used in explosive applications, Al particles need to ignite rapidly at relatively low temperatures due to the relatively short time scales of a blast compared to a propulsion system.

Ignition temperature data compiled by Trunov et al. (2005) indicates that the ignition temperature for Al particles with a diameter of 10 μm or less can be as low as 1200 K. For Al particles with a diameter of 100 μm or larger, the ignition temperature is around 2300 K, which is near the melting point of alumina. Parr et al. (2003) also observed a similar trend of decreasing ignition temperatures for small Al particle sizes.

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Beckstead (2005) performed a comprehensive summary on the combustion of larger, diffusion-limited, aluminum particles from a wide range of sources. A D^n burning-time, t_b, law with very weak dependence on ambient pressure and temperature was found to applicable for larger, diffusion-limited, particle sizes. When the size of Al particles was decreased to 10 μm diameter, Bazyn et al. (2005) found pressure exponents of –0.9, 0.2, and 0.3, for O_2, H_2O, and CO_2 respectively, (i.e., $t_b \propto p_i^n$) where p_i is the partial pressure of the ith species). The burning times of 80-nm diameter Al particles were found to decrease Arrheniusly with increasing ambient temperature and were also found to be a strong function of pressure (Bazyn et al., 2006). Temperature and pressure dependence on t_b is a strong indication that the Al particle burning mechanism transitions from a diffusion-limited to a chemical kinetic-limited regime when the particles are on the order of 10 μm diameter or smaller.

Applying nickel coatings on Al particles has gained recent attention due to several advantages. First, the nickel coating can protect aluminum particles from slow oxidation during storage (Foley et al., 2005). Second, Ni can react with Al to form NiAl via exothermic intermetallic reactions, which aids ignition by supplying additional sensible energy ($\Delta h^0_{f,\mathrm{NiAl}} = -188$ KJ/mol) to the Al particle and reduces ignition temperature and delay time (Andrzejak et al., 2007; Rosenband and Gany, 2009; Shafirovich et al., 2002). Ni-clad Al particles can even react in inert environments (Shafirovich et al., 2002). Small piles of uncoated Al particles were found to be unignitable when heated by an electrical tape, while 5 wt.% Ni-coated particles readily ignited (Rosenband and Gany, 2009). Third, nickel coatings have also been shown to reduce Al particle agglomeration in propellants (Babuk et al., 2001; Bocanegra et al., 2007; Breiter et al., 1990).

Andrzejak et al. (2007) and Rosenband and Gany (2009) proposed similar ignition mechanisms for Ni-coated Al particles involving a series of intermetallic Ni-Al reactions while the particle is being heated. At 660°C, a solid layer of $NiAl_3$ begins to form at the interface. On reaching the melting point of $NiAl_3$ at 854°C, solid Ni_2Al_3 begins to form at the interface. At 1133°C, the Ni_2Al_3 subsequently melts and begins to form NiAl. Crack formation and liquid Al spill mechanisms have also been proposed for Ni-coated Al particle ignition (Yagodnikov and Voronetskii, 1997) and Muksayan et al. (2001). Exothermic reactions occur between the liquid Al core and the solid Ni shell as the particle absorbs heat and the aluminum core begins to melt. The Ni shell eventually cracks due to the difference in thermal expansion coefficients between Ni and Al, spilling molten Al on the outer surface of the Ni coating. The spilling effect exposes liquid Al directly to the oxidizing environment and greatly increases Ni/Al interfacial area and, consequently, the net rate of chemical energy release from intermetallic reactions. Note that the crack and spill Ni-coated Al particle ignition mechanism is only active if there is a discernible and continuous Ni-layer on the surface.

Most of the previous studies on ignition and combustion of Ni-coated Al particles have focused on either very large particles (on the order of 1 mm or larger) or very slow heating conditions. It is unclear whether applying nickel coatings will have similar advantages if the particle size is reduced to a diameter used in practical propulsion and explosive devices or if the heating rate is increased to a value typical of a flame. Thus, this paper focuses on the ignition and combustion of practically-sized Ni-coated Al particles under rapid heating situations in the post-flame zone of a flat-flame burner.

2. METHOD OF APPROACH

The Al particles used in this study were supplied by Alon Gany and Valery Rosenband of Technion of Israel and consist of two sizes that were nominally 9- and 32-μm diameter and coated with a 5 wt.% layer of Ni. Uncoated Al particles of the same lot were also obtained from the same source for comparison purposes. The size distributions—provided by the supplier—of the particles used in this study before the nickel coating are shown in Fig. 1. These two particle sizes were selected because 9-μm particles are in the transitional regime between chemical kinetic-controlled and diffusion-controlled combustion, while 32-μm particles are diffusion limited. Scanning electron microscopy (SEM) images shown in Fig. 2 demonstrate that the coating consists of very small nanosized spheres, revealed by energy dispersive spectroscopy to be primarily nickel. The SEM images indicate that the coating is fairly uniform on some particles while others exhibit large uncoated portions. It is likely that the nanosized Ni spheres were simply damaged or rubbed off during handling. Evidence of nanosized Ni spheres removed from the particles is shown in Fig. 2(b) directly below the particle in the center of the image. Because the Ni-coating is nonuniform, the passivating effect reported by Foley et al. (2005) is not expected to occur for these samples. Auger electron spectroscopy

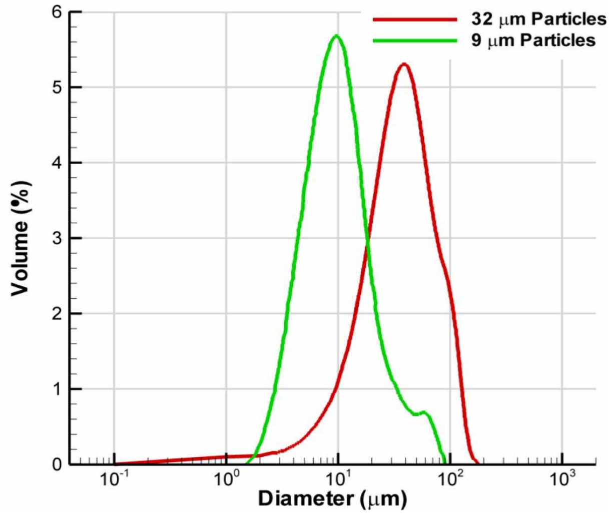


FIG. 1: Size distribution of the uncoated Al particles used in this work supplied by Gany and Rosenband.

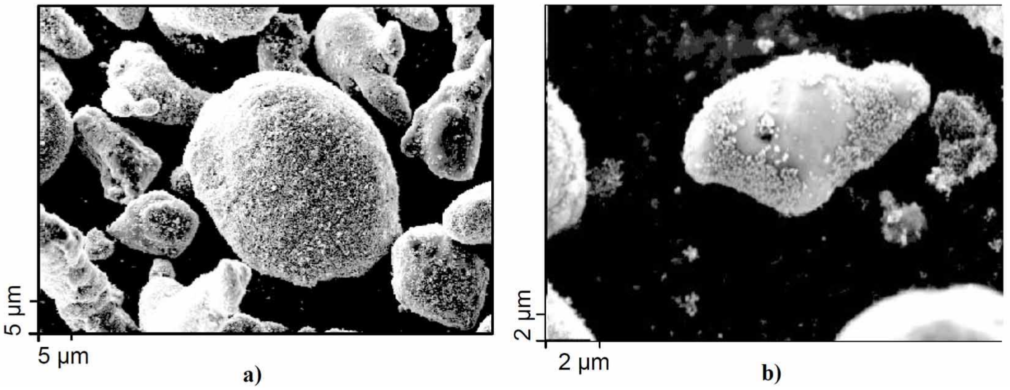
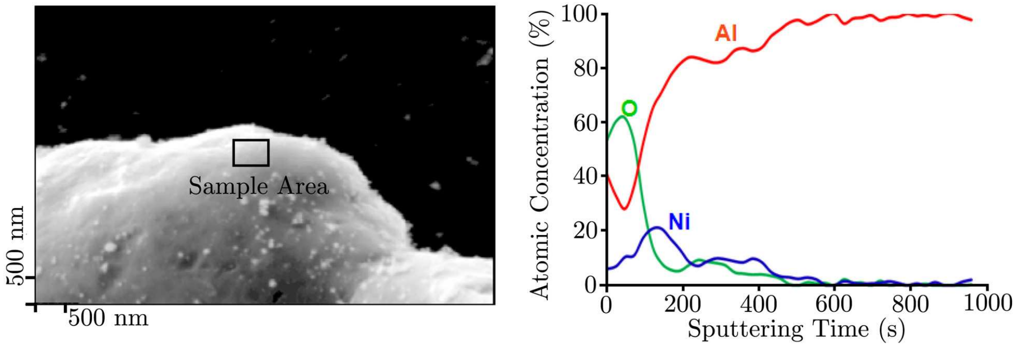


FIG. 2: SEM images of the 32-µm Ni-coated Al particles showing: (a) uniformly coated particles and (b) particles with bare, uncoated spots.

(AES) with 5 keV argon ions was used on a bare spot of a 9-µm particle (shown in Fig. 3). The results indicate that the surface is primarily aluminum oxide—which has an O to Al atom ratio of 1.5—with very little nickel. Interestingly, the peak of the nickel atom concentration of a bare spot is inside the particle rather than on the surface and a distince Ni layer cannot be found. Note that due to the irregularity of the Al particles it is impossible to know the orientation of the surface with respect to the argon ion beam. Thus, sputtering time cannot be converted into depth from the surface with any degree of certainty. AES on a bare spot of a 32-µm particle (see Fig. 4) yielded similar results for the atomic concentration of Ni. The main difference between the AES results is that a 30% carbon impurity is present on the surface of the larger particles, which slowly decays to zero concentration inside the particle along with O and Ni.



a) Sample Area **b)** Element Concentration

FIG. 3: Auger electron spectroscopy results on a bare region of a 9-µm Ni-coated Al particle: (a) SEM of sample area and (b) atomic concentration as a function of sputtering time.

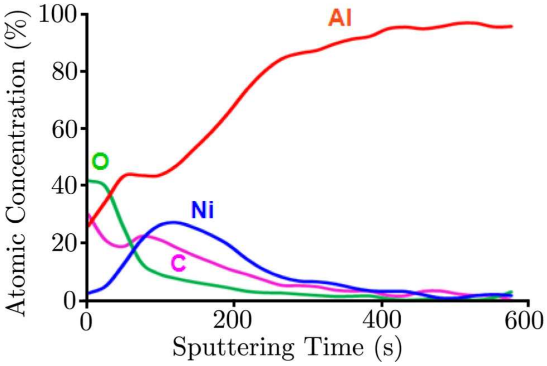


FIG. 4: Atomic concentration as a function of sputtering time using AES on a bare region of a 32-μm Ni-coated Al particle.

A modified multidiffusion flat-flame (or Hencken) burner was used to ignite the coated and uncoated Al particles. The burner has a core region with multiple diffusion flamelets that simulate a single flatflame. A multidiffusion flat-flame burner allows much higher burned gas temperatures needed to study Al particle ignition and combustion, which are not obtainable using a standard premixed flat-flame burner. The fuels of the Hencken burner were selected to be a mixture of carbon monoxide and hydrogen, which were controlled by individual flow meters on a control panel adjacent to the burner. Thus, allowing the relative product concentrations of H_2O and CO_2 to be systematically varied. Oxygen was used as the oxidizer and nitrogen was used as a diluent, which was mixed into the same stream as O_2. A 14 inch long quartz tube was placed around the multidiffusion flame burner to prevent the diffusion of ambient air into the products. The tube also provides well-defined boundary conditions for performing detailed simulations of the post-flame zone of the reactor. The Al particles are entrained with the fuel mixture and introduced into the center of the post-flame zone using a fluidized bed feeder. A 400-mesh sieve was placed at the exit of the fluidized bed feeder to prevent any large Al agglomerates from entering the post-flame zone. Houim et al. (2008) have shown that this relatively simple technique works well in mitigating agglomeration of aluminum flakes in the same apparatus. Figure 5 shows a schematic diagram of the experimental setup that was used in this investigation.

Particle ignition temperatures were determined using a “go” or “no-go” ignition criteria based on the observed luminosity of the injected particles. During each ignition test, the diluent portion of oxidizer stream was slowly increased while holding the fuel and oxygen flow rates constant until the particles would no longer ignite. Increasing the nitrogen flow rate in the oxidizer supply line lowers both the effective oxidizer concentration for the Al particle and temperature of the burner product gases. The fuel and oxidizing gaseous mixture used for the flat-flame burner at the onset of particle ignition were utilized to determine the adiabatic flame temperature and effective oxidizer

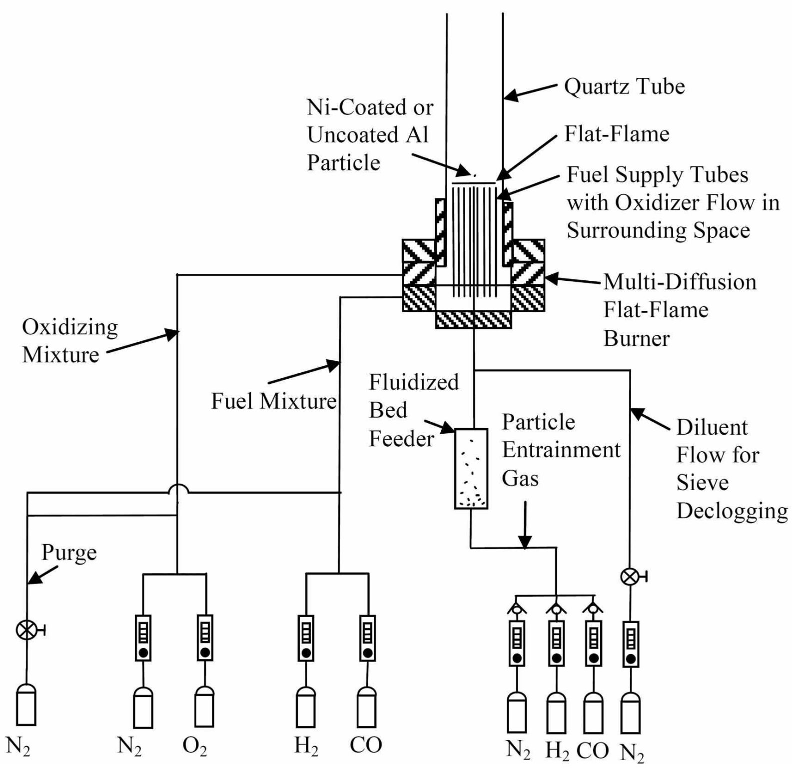


FIG. 5: A schematic process flow diagram of experimental test setup, including the flow control to the burner and fluidized-bed particle feeder.

concentration, which characterized the ignition criterion for the injected particles. Because video images were used to determine the status of ignition, tests were conducted to ensure the Al particles were burning and not just emitting visible radiation without igniting. In these tests, the fluidized bed feeder was loaded with a mixture of 10- and 200-μm diameter aluminum oxide particles. The aluminum oxide particles were not visible to the naked eye or the camera even at the highest temperature conditions, while burning particles were. Therefore, in regular tests, the Al particles were determined to be undergoing combustion when they were emitting visible light. If a particle is detected as a bright streak on the video images, then the particle is considered to be ignited (see Fig. 6).

Although the primary objective of this study was to determine if the nickel coating reduced the ignition temperature of Al particles, it was also important to measure the burning duration to determine if the Ni coating has any influence the post-ignition processes. The combustion times were measured in two ways. In the first method, a photomultiplier tube (PMT), focused on the centerline of the post-flame zone with a two-inch cylindrical lens, was used to measure the emission intensity of the burning Al

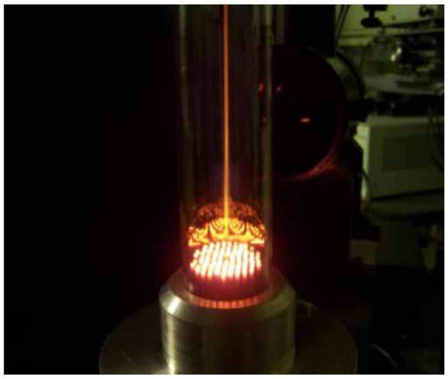
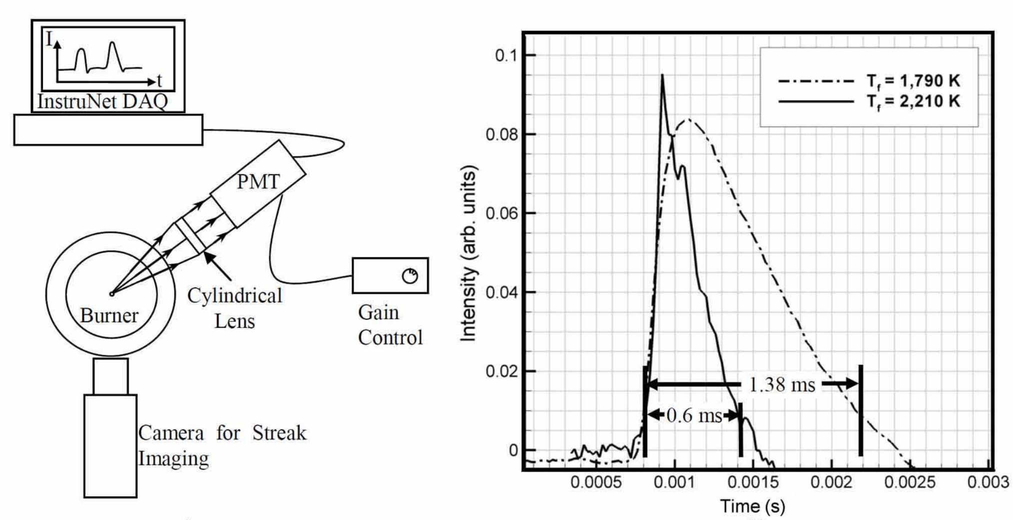


FIG. 6: Image of the multidiffusion flat-flame burner and visible Al particle streak.

particles. The overall burning time of the particles was determined based on a rise and fall of the intensity-time trace. The combustion duration was defined to be time between the first discernible rise above the background noise and the subsequent decay to that same intensity level. A sketch of the PMT diagnostic system, typical outputs from the PMT, and the burning time definition are illustrated in Fig. 7. Particles may travel out of the viewing range of the cylindrical lens in poor oxidizing environments. In these instances, a second method using streak-like video images were used to deduce the particle combustion time, t_b, of the particles



a) b)

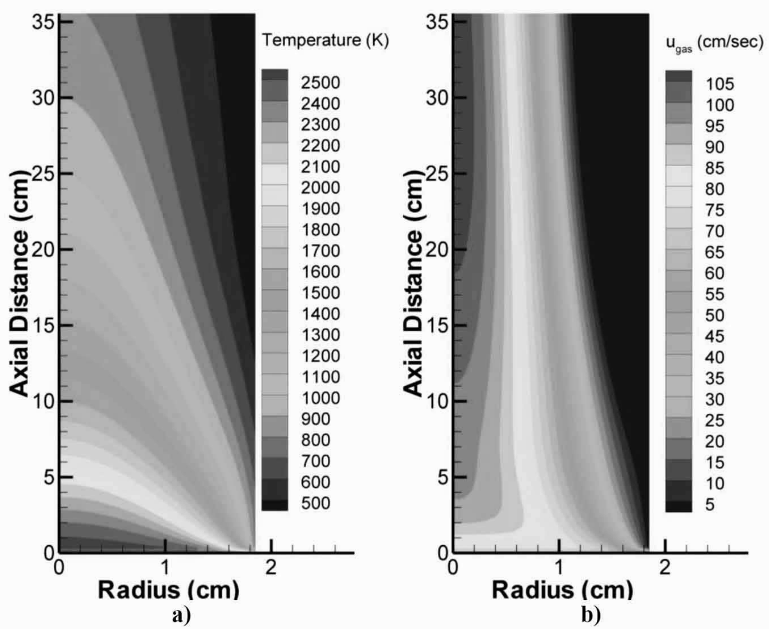
FIG. 7: (a) Schematic of the PMT and camera diagnostic systems for measuring the burning times of the aluminum particles and (b) typical PMT measured intensity-time traces of Al flakes at two test conditions using 100% H_2 fuel.

$$t_b = \frac{L_{\text{streak}}}{u_{\text{gas}}} \tag{1}$$

where L_{streak} is the distance the particle travels while it is burning and u_{gas} is the average gas velocity from the beginning to the end of the burning streak.

The average gas velocity needed for Eq. (1) was calculated using CHEMKIN's cylindrical channel shear-layer flow reactor (Kee et al., 2007) with the GRI-MECH 3.0 reaction mechanism (Smith et al., 2009). The inlet boundary condition for the reactor was radially uniform with a mass flow rate and gaseous species mixture set at the constant pressure equilibrium condition. For each flow-rate setting used, the temperature on the outer wall of the quartz tube was measured at four axial locations. Taking natural convection and thermal resistance of the quartz tube into account, the temperature profile along the inside of the quartz tube was estimated and used as a Dirichlet temperature boundary condition. Typical results from the CHEMKIN simulations are shown in Fig. 8. To validate the reactor calculations, the temperature of the burner gases at the exit of the quartz tube was measured and compared to calculations. The majority of the reactor simulations exhibited errors between 50 and 100 K, which is within the uncertainties of the flow rate and temperature measurements.

To ensure that the measured burning times between PMT and photographic methods were consistent, burning times of the particles were measured using both methods when



a) b)

FIG. 8: Typical calculated post-flame zone: (a) gas temperature and (b) gas velocity distributions in the quartz tube with 100% H_2 fuel an overall burner equivalence ratio of unity. Note that the axial distance is measured from the burner surface.

applicable. In all test cases conducted, the measured burning time difference between the PMT and photographic methods were statistically insignificant.

3. RESULTS AND DISCUSSION

The flow rate for each of the burner reactant species were varied to determine the ignition temperature of the Ni-coated and uncoated Al particles as a function of effective oxidizer concentration. It has been well documented that the oxidizing species vary in their level of effectiveness in oxidizing aluminum particles. In this work, the effective oxidizer mole fraction, $X_{\text{OX,eff}}$, defined by Beckstead (2005) is used

$$X_{\text{OX,eff}} = X_{\text{O}_2} + 0.5X_{\text{H}_2\text{O}} + 0.22X_{\text{CO}_2}, \tag{2}$$

where X_i is the mole fraction of chemical species i. The concentrations of the three major oxidizers were determined using equilibrium calculations based on the relative flow rates of the fuel, oxidizer, and diluent species at each of the onset-of-ignition conditions.

The ignition temperatures for Ni-coated and uncoated 9-μm particles as functions of effective oxidizer mole fraction are shown in Fig. 9(a). Curve fits of the ignition threshold criterion for the 9-μm coated and uncoated Al particles are given by:

$$T_{\text{ign, 9μm Ni}} \geq 956(X_{\text{OX, eff}})^{-0.266};\;\; 0.065 < X_{\text{OX, eff}} < 0.28, \tag{3}$$

and

$$T_{\text{ign, 9μm bare}} \geq 1078(X_{\text{OX, eff}})^{-0.313};\;\; 0.077 < X_{\text{OX, eff}} < 0.32, \tag{4}$$

respectively. Note that the average reduction in ignition temperature is around 300 K for the 9-μm particles.

The ignition criterion for the coated and uncoated 32-μm Al particles are given by

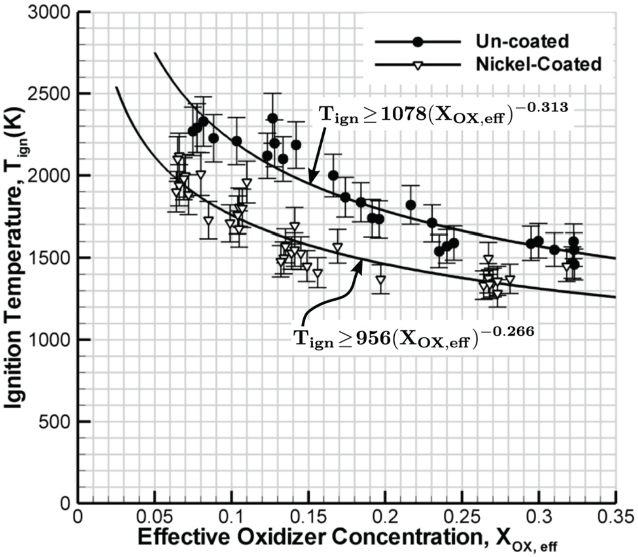
$$T_{\text{ign, 32μm Ni}} \geq 969(X_{\text{OX, eff}})^{-0.190};\;\; 0.048 < X_{\text{OX, eff}} < 0.24, \tag{5}$$

and

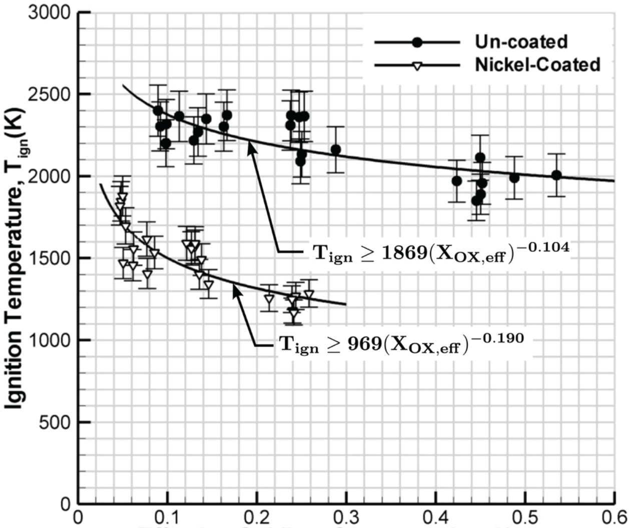
$$T_{\text{ign, 32μm bare}} \geq 1869(X_{\text{OX, eff}})^{-0.104};\;\; 0.091 < X_{\text{OX, eff}} < 0.54, \tag{6}$$

respectively. These correlations and the measured data are shown in Fig. 9(b). The application of nickel coatings on larger particles is even more substantial for 32-μm particles, the average reduction of ignition temperature is around 750 K. The validity of the correlations developed for uncoated and Ni-coated 9- and 32-μm diameter particles are shown in Fig. 10. These graphs indicated that most of the data are within ±10% of the correlation.

The ignition temperature of the uncoated 9-μm particles lies between 1450 and 2350 K while the ignition temperature 32-μm uncoated particles is typically higher and lies between 1850 and 2400 K. The trend of increasing ignition temperature with Al particle



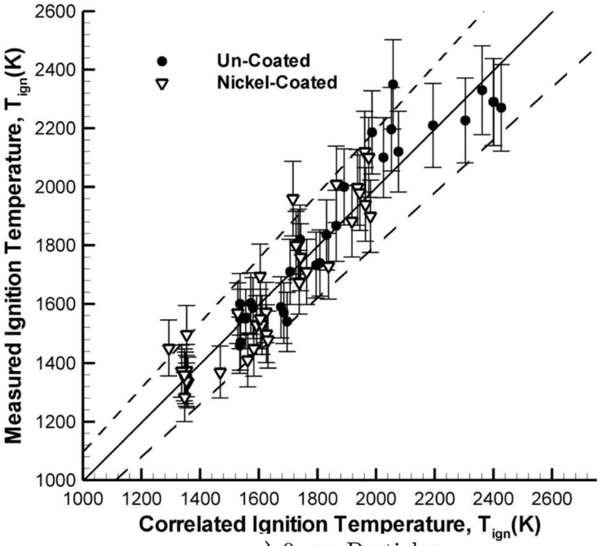
a) 9-μm Particles



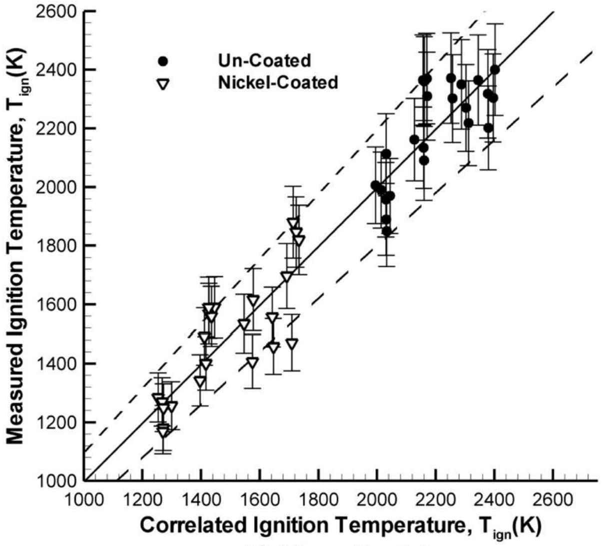
b) 32-μm Particles

FIG. 9: Measured ignition temperature of (a) 9- and (b) 32-µm Ni-coated and uncoated aluminum particles as a function of the effective oxidizer mole fraction, $X_{\mathrm{OX,eff}}$.

diameter is an agreement with the data compiled by Trunov et al. (2005). The ignition temperature of the 9-µm Ni-coated particles lies between 1280 and 2120 K, while the ignition temperature 32-µm Ni-coated particles was actually lower and lie between 1170 and 1869 K. It is clear that the Ni coating substantially reduces the ignition temperature



a) 9-μm Particles



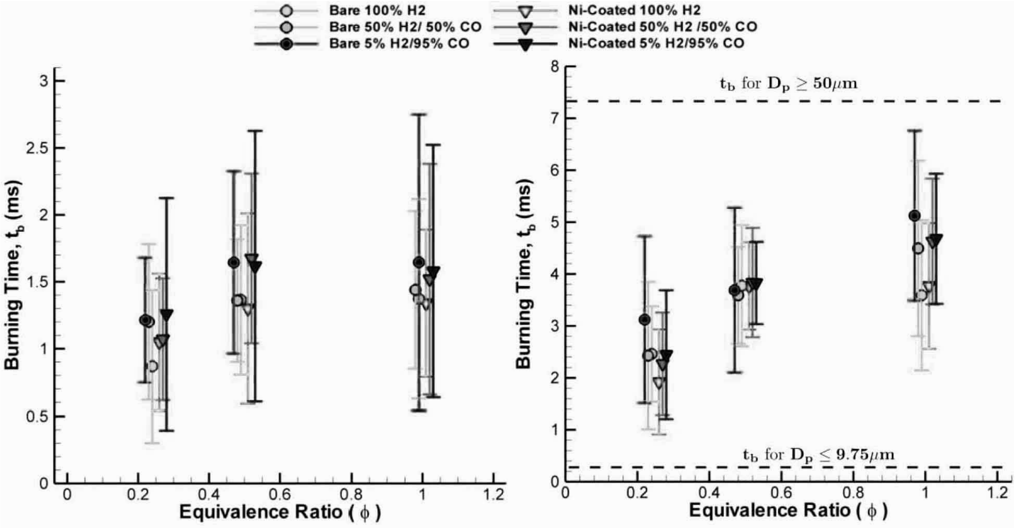
b) 32-μm Particles

FIG. 10: Correlated ignition temperature versus the measured ignition temperature for (a) 9- and (b) 32-µm diameter Ni-coated and uncoated Al particles with 10% uncertainty boundaries.

of larger Al particles. However, it is not quite as effective at reducing the ignition temperature of the 9-µm particles. The reason for the reduced performance is simply that the smaller uncoated Al particles already ignite at fairly low temperatures and do not need too much assistance from the Ni-Al alloying reactions. The smaller particles would ignite at temperatures as low as 750 K if the Ni-coating were to reduce their ignition temperature the same amount for the larger particles, which is clearly unreasonable. For larger particles ($D_p > 32$ μm), the nickel coating substantially reduces Al particle ignition temperature by about 750 K at all effective oxidizer concentrations considered in this study.

The lower ignition temperature of the coated 32-μm particles in comparison to the coated 9-μm particles is quite surprising. This counterintuitive result cannot be explained by any bias error from more radiation being emitted from larger particles, since a similar trend was not observed for the uncoated particles. The cracking and spilling ignition mechanism proposed by Muksayan et al. (2001) is not applicable and cannot be used for explanation because the Ni coating has bare spots, which do not have a discernible Ni layer (see Figs. 2–4). It remains unclear what the reason is for this result. A detailed microstructural analysis of the Ni-coated particles during the ignition process may provide some insight into the physical reason for this result, but is beyond the scope of this paper.

The combustion times of the particles were measured and shown as a function of overall equivalence ratio, ϕ, in Fig. 11. Error bars correspond to one standard deviation above and below the mean burning time of the particles. Each point is a mean value of 20 data points, with 10 data points collected using the PMT method when applicable and other 10 using the photographic technique. Because of the relatively large scatter of burning time data, it is impossible to develop a statistical correlation for the particle



a) 9-μm Particles b) 32-μm Particles

FIG. 11: Measured burning times of (a) 9- and (b) 32-μm nickel-coated and uncoated aluminum particles with comparison to expected burning times for particles with diameters of 9.75 and 50 μm using the simplified correlation of Beckstead (2005).

burning times as a function of burner operating conditions. The main reason for such a scatter in burning time measurements is due to the broad particle size distributions shown in Fig. 1. The simplified burning time correlation of Beckstead (2005) was applied to the nominally 32-μm diameter particles at the 10% (9.75 μm) and 90% (50 μm) levels of the cumulative distribution function. These burning time boundaries can be seen as two dashed lines in Fig. 11. Thus, it is clear that the large variation in particle size distribution is responsible for most of the data scatter in measured particle burning time.

Figure 12 shows the Al particle burning time data compiled by Beckstead (2005) along with the results from the current study. The combustion times for 32-μm particles match reasonably well with the correlation developed by Beckstead. However, the smaller 9-μm particles seem to have combustion times that are longer than those predicted by correlation of Beckstead (2005). As observed by Bazyn et al. (2005) and Lynch et al. (2009), the particle combustion times for particles approaching 10 μm and below are in the transition regime between kinetic-limited and diffusion-limited combustion. Thus, the burning times of the smaller particles are expected to deviate from a D^2 correlation. Applying the transitional-regime correlation of Lynch et al. (2009) to a test condition where the 9-μm Al particles were burning in one mole of H_2O and roughly five moles of N_2 predicts a burning time of 1.1 ms. This correlated value is inside the range of measurements shown in Figs. 11 and 12 and substantially higher than the correlation of Beckstead (2005).

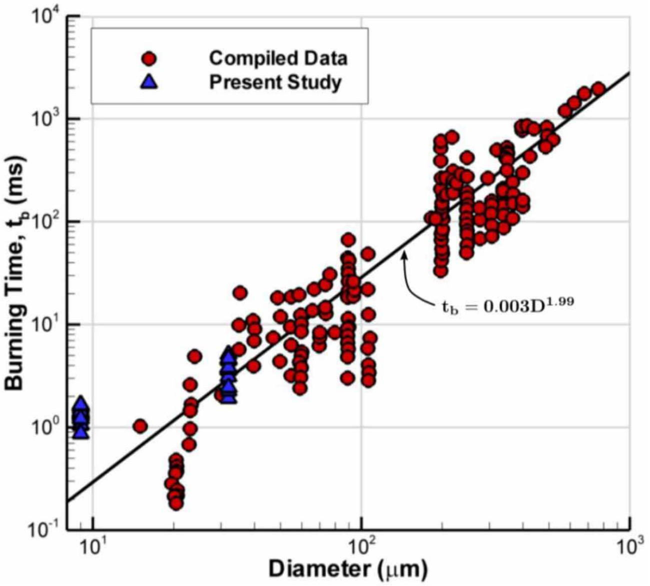


FIG. 12: Correlation of many sources of experimental burning time data compiled by Beckstead (2005).

Despite the inability to produce a statistically significant burning time correlation, these results confirm that the nickel coating does not have an appreciable effect on the combustion time of the Al particles. Even though the cool down period of the particles was not subtracted from the burning time measurements, it is expected that the 5 wt.% Ni coating will have a very small influence on the radiative and thermal properties of the burnt oxide particles. Thus, regardless of whether or not the cool down period is taken into account, the overall observation that the 5 wt.% Ni coating has a negligible effect on the combustion time of the coated particles is valid.

4. CONCLUSIONS

In this work, a study on the ignition and combustion of uncoated and Ni-coated particles were performed in the post-flame zone of a flat-flame burner. The results indicate that application of Ni-coatings to 32-μm Al particles in the diffusion-limited regime can substantially reduce the ignition temperature by 750 K. However, unless agglomeration is a concern for a particular application, it is questionable whether or not Ni-coating are actually needed for smaller Al particles ($D_p < 9$ μm), because the Ni coating is much less effective at reducing the ignition temperature. The measured burning times of the Al particles were not statistically affected by the Ni coating. The burning times of the larger particles fit well with a D^n law typical of diffusion-limited combustion, while the measured burning times of the smaller, 9 μm, particles match quite well with correlations developed for Al particles in the transition regime between the diffusion- and kinetic-controlled combustion.

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REFERENCES

Andrzejak, T. A., Shafirovich, E., and Varma, A., Ignition mechanism of nickel-coated aluminum particles, *Combust. Flame*, vol. **150**, pp. 60–70, 2007.

Babuk, V., Vassiliev, V., and Sviridov, V., Propellant formulation factors and metal agglomeration in combustion of aluminized solid rocket propellant, *Combust. Sci. Technol.*, vol. **163**, pp. 261–289, 2001.

Bazyn, T., Krier, H., and Glumac, N., Oxidizer and pressure effects on the combustion of 10-μm aluminum particles, *J. Propul. Power*, vol. **21**, pp. 577–582, 2005.

Bazyn, T., Krier, H., and Glumac, N., Combustion of nanoaluminum at elevated pressure and temperature behind reflected shock waves, *Combust. Flame*, vol. **145**, pp. 703–713, 2006.

Beckstead, M., Correlating aluminum burning times, *Combust. Explos. Shock Waves*, vol. **41**, pp. 533–546, 2005.

Bocanegra, P. E., Chauveau, C., and Gökalp, I., Experimental studies on the burning of coated and uncoated micro and nano-sized aluminium particles, *Aerospace Sci. Technol.*, vol. **11**, pp. 33–38, 2007.

Breiter, A. L., Mal'tsev, V. M., and Popov, E. I., Means of modifying metallic fuel in condensed systems, *Combust. Explos. Shock Waves*, vol. **26**, pp. 86–92, 1990.

Foley, T. J., Johnson, C. E., and Higa, K. T., Inhibition of oxide formation on aluminum nanoparticles by transition metal coating, *Chem. Mater.*, vol. **17**, pp. 4086–4091, 2005.

Houim, R., Boyd, E., and Kuo, K. K., Combution of aluminum flakes in the post-flame zone of a hencken burner, *Int. J. Energet. Mater. Chem. Propul.*, vol. **7**, pp. 55–71, 2008.

Kee, R. J., Rupley, F. M., Miller, J. A., Coltrin, M. E., Grcar, J. F., Meeks, E., Moffat, H. K., Lutz, A. E., Dixon-Lewis, G., Smooke, M. D., Warnatz, J., Evans, G. H., Larson, R. S., Mitchell, R. E., Petzold, L. R., Reynolds, W. C., Caracotsios, M., Stewart, W. E., Glarborg, P., Wang, C., McLellan, C. L., Adigun, O., Houf, W. G., Chou, C. P., Miller, S. F., Ho, P., Young, P. D., Young, D. J., Hodgson, D. W., Petrova, M. V., and Puduppakkam, K. V., *Chemkin 4.1.1*, Reaction Design, San Diego, 2007.

Kim, K., Wilson, W., Peiris, S., Needham, C., Watry, C., Ortley, D., and Zhang, F., Effects of particle damage during detonation of thermobarics on subsequent reactions, *21st International Colloquium on the Dynamics of Explosives and Reactive Systems (ICDERS 21)*, Poitiers, France, 2007.

Kuo, K., Risha, G., Evans, B., and Boyer, E., Potential Usage of Energetic Nano-sized Powders for Combustion and Rocket Propulsion, *Materials Research Society Symposium Proceedings*, Vol. 800, Materials Research Society, Warrendale, PA, pp. 3–14, 2004.

Lynch, P., Krier, H., and Glumac, N., A correlation for burn time of aluminum particles in the transition regime, *Proceedings of the Combustion Institute*, vol. **32**, pp. 1887–1893, 2009.

Muksayan, A., Lau, C., and Varma, A., Gasless combustion of aluminum particles clad by nickel, *Combust. Sci. Technol.*, vol. **170**, pp. 67–85, 2001.

Parr, T., Johnson, C., Hanson-Parr, D., Higa, K., and Wilson, K., Evaluation of advanced fuels for underwater propulsion, *39th JANNAF Combustion Subcommittee Meeting*, December 2003.

Rosenband, V. and Gany, A., Activated metal powders as potential energetic materials, *Int. J. Energetic Mater. Chem. Propul.*, vol. **8**, pp. 291–307, 2009.

Shafirovich, E., Mukasyan, A., Thiers, L., Varma, A., Legrand, B., Chauveau, C., and Gkalp, I., Ignition and combustion of al particles clad by ni, *Combust. Sci. Technol.*, vol. **174**, no. 3, pp. 125–140, 2002.

Smith, G. P., Golden, D. M., Frenklach, M., Moriarty, N. W., Eiteneer, B., Goldenberg, M., Bowman, C. T., Hanson, R. K., Song, S., Gardiner, W. C., Lissianski, V. V., and Qin, Z., aviable at 2009, Gri-mech 3.0, http://www.me.berkeley.edu/gri_mech/

Trunov, M. A., Schoenitz, M., and Dreizin, E. L., Ignition of aluminum powders under different experimental conditions, *Propell. Explos. Pyrotech.*, vol. **30**, pp. 36–43, 2005.

Yagodnikov, D. and Voronetskii, A., Experimental and theoretical study of the ignition and combustion of an aerosol of encapsulated aluminum particles, *Combust. Explos. Shock Waves*, vol. **33**, pp. 49–55, 1997.

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ENVIRONMENTAL CHARACTERIZATION OF MILITARY TRAINING RANGES FOR MUNITIONS-RELATED CONTAMINANTS: UNDERSTANDING AND MINIMIZING THE ENVIRONMENTAL IMPACTS OF LIVE-FIRE TRAINING

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An important R&D effort was dedicated to the characterization of ranges and training areas and to the study of the environmental fate and the ecotoxicological impacts of munitions constituents in the last 20 years in Canada and the United States. Major environmental issues were identified, and the sources of munitions constituents in training ranges are better understood. Protocols were developed for collecting representative soil samples and their effective processing. In the last years, a large effort was dedicated to the measurement of the mass of munitions constituents deposited both at target impact areas and at firing positions, which led to a good estimation of source terms of contaminants. In Canadian ranges and training areas, efforts were also dedicated to characterize both surface and subsurface aquifers and geology, and detailed hydrogeological and geological mapping. All the data acquired over the last years have been used to build hazards and vulnerability maps, which can be combined to draw risk maps that represent great assets from a risk-management perspective. The next step is the development of environmentally sound solutions that will sustain military training and maintain force readiness. In order to achieve that goal, efforts are committed to the modification of actual live-firing activities to minimize their environmental adverse impacts. Finally, Canada is aiming at developing greener and insensitive munitions that will ease the environmental pressure. This paper is a summary of what has been done in North America toward understanding and minimizing the environmental footprint of munitions.

KEY WORDS: *characterization, munitions, unexploded ordnances, live fire, training ranges, environmental impact, deposition rate, munitions constituents, fate, ecotoxicology, hydrogeology, explosives, propellants*

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1. INTRODUCTION

The readiness of the armed forces is predicated on well-trained troops and continuous enhancement of their munitions arsenal. Sustained live-fire training is critical to preparedness for missions abroad. Military live-fire training activities generate source zones of munitions constituents (MCs) in the environment, which threaten range sustainment. A source zone may be defined as an area where chemicals are deposited, usually on the surface soils, which poses a threat to ecological or human receptors. The Canadian Sustainable Training R&D program is aimed at maintaining both military readiness and environmentally friendly defense activities in order to ensure the long-term usage of military ranges and training areas (RTAs). In order to understand the various aspects related to the dispersion and fate of MCs, multidisciplinary collaborations were established with national and international research centers. In Canada, our main collaborators are the Institut National de la Recherche Scientifique—Centre Eau, Terre et Environnement (INRS-ETE) as well as the Biotechnology Research Institute of the National Research Council of Canada (BRI-NRC). In the United States, our collaborators are from the Engineering Research and Development Center, Cold Regions Research and Engineering Laboratory (ERDC-CRREL). Over the years, various aspects of research were supported by many stakeholders, including Defence R&D Canada (DRDC), R&D thrusts (Munitions and Firepower and Sustain thrusts), Director General Environment (DGE), Director Land Environment (DLE), and an U.S. peer-reviewed funding program, the Strategic Environmental Research and Development Program (SERDP, Arlington, VA). In order to better understand the extent of the problem, DRDC initiated a research program for the environmental assessment of the Army's RTAs. The RTA characterization work was conducted both in Canada and the United States and was done in collaboration with U.S. scientists from ERDC-CRREL to better understand the nature and extent of contamination.

Extensive surface soil characterization of most of the Canadian RTAs was done in conjunction with hydrogeological studies performed by INRS-ETE. Moreover, the study of the environmental fate of energetic materials (EMs) was conducted in close collaboration with BRI-NRC scientists. The strategy of sampling, sample treatment, and the analytical chemistry of soil and water samples and the RTA characterization work was done in collaboration with U.S. scientists from ERDC-CRREL (Ampleman et al., 1998, 2000, 2003a,b, 2004, 2008a, 2009; Brochu et al., 2008; Clausen et al., 2007; Dubé et al., 1999; Diaz et al., 2007; Jenkins et al., 1997a,b, 1998, 1999, 2001, 2004, 2005; Hewitt et al., 2003, 2007a,b, 2009; Thiboutot et al., 1997, 1998, 2000, 2001a,b, 2002, 2003a,b,c, 2004, 2008a; Marois et al., 2003, 2004; U.S. EPA, 2006; Walsh et al., 2002, 2004). Protocols were published both in Canada and the United States to effectively characterize the huge tracks of military live-fire lands (Hewitt et al., 2009; Jenkins et al., 2005a; Thiboutot et al., 2012). Through DRDC's participation in the North Atlantic Treaty Organization (NATO), the authors are aware that very few countries have published such protocols up to now. The only country other than Canada or the United States that has reported a similar document is Norway (Voie et al., 2010). Figure 1 illustrates the numerous RTAs characterized for MCs deposition across North America by the DRDC and CRREL teams. The RTAs characterized over the years are spread out all over North America, which allowed the study of the effects of various geological formations and various climates.

The understanding and evaluation of the source terms for most weapons, both at impact areas and firing positions (FPs), were needed to better assess the actual source term of contaminants generated by the live-firing activities. Various trials were dedicated to estimating the deposition rates of most weapon platforms and characterizing the accumulation at target areas. In 2000, a six-year research project (SERDP ER-1155) was initiated by DRDC and CRREL, cosponsored by Canadian stakeholders and SERDP to study the deposition, accumulation, and fate of explosives at live-fire training ranges. SERDP project ER-1155 focused on impact areas where explosives such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) were deposited, and where the potential for groundwater contamination was thus the highest. This project allowed the development of transport processes descriptors for the current explosives and their main transformation products and contributed to the understanding of the various sources of explosive contamination in target impacts areas (Jenkins et al., 2005a; Pennington et al., 2001, 2002, 2003, 2004, 2005, 2006a,b).

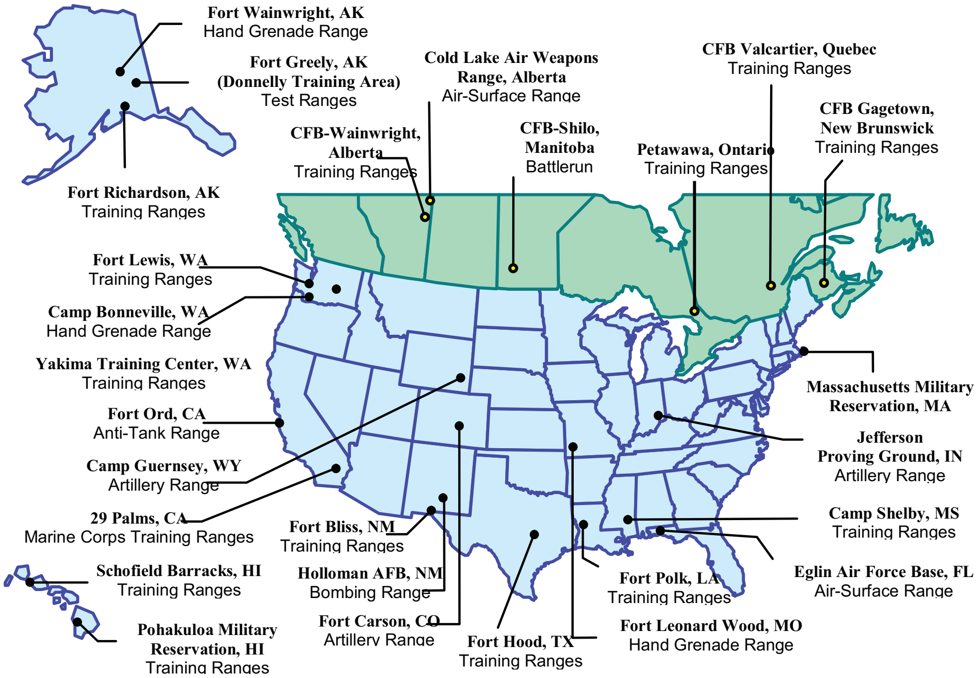

FIG. 1: RTAs characterized in North America.

In 2006, SERDP project ER-1481 was initiated and cosponsored by SERDP and DLE to study the distribution, fate, and transport of propellant residues at firing points associated with live-fire training with munitions (Ampleman et al., 2008b, 2010; Jenkins et al., 2007, 2008; Poulin et al., 2008a,b; Poulin and Diaz, 2008; Quémerais et al., 2007a,b; Thiboutot et al., 2008b,c, 2009, 2010; Walsh et al., 2006, 2008, 2009). This allowed a better understanding of the contamination pattern at the firing positions. Several studies have also been performed on the wider fate of munitions constituents, mostly in collaboration with INRS-ETE and BRI-NRC (Bordeleau et al., 2007, 2008a,b; Halasz et al., 2002; Hawari et al., 2000a,b, 2001; Lewis et al., 2009; Mailloux et al., 2008a; Martel et al., 2007, 2009; Monteil-Rivera et al., 2004; Robertson et al., 2007; Zhao et al., 2004). A large effort was also dedicated in Canada on the study of the ecotoxicological impacts of MCs (Doddard et al., 2005; Lachance et al., 2008; Sarrazin et al., 2009; Robidoux et al., 2000, 2001, 2005, 2006; Rocheleau et al., 2008; Sunahara et al., 2001, 2009).

On the basis of these studies, environmental issues were identified and solutions to these problems are under development. Efforts are dedicated to modifying live-firing activities to minimize their environmental footprints. A few of the efforts presently conducted to minimize the deposition of MCs in Canadian RTAs will be presented. This paper describes the North American approach toward understanding and minimizing the environmental footprint of munitions in a live-fire context.

2. CONTAMINANTS OF CONCERN

Accurately detecting the type and quantity of contamination from MCs and their breakdown products in water, soil, and sediments is vital for assessing the extent of contamination and ultimately the risk to human and ecological receptors. This paper focuses on specific munitions-related contaminants and methods specific to RTAs and unexploded ordnances (UXOs) contaminated sites. The contaminants of concern that might be dispersed in the environment following live-fire training are mainly EMs and metals. Conventional weapons for live-fire training use EMs in the form of propellants (propulsion) and main charge explosive (detonation).

The explosives that are most frequently detected in RTAs are: RDX, 2,4,6-trinitrotoluene (TNT) and its main degradation products 2-amino-4,6-dinitrotoluene (2-A-DNT) and 4-amino-2,6-dinitrotoluene (4-A-DNT), high-melting explosive or octrahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and rarely 2,4,6-trinitro-phenylmethylnitramine (tetryl) (Jenkins et al, 2005a). Propellants include both rocket and gun propellants. Most rocket propellants consist of a rubbery binder filled with ammonium perchlorate (AP) oxidizer and may contain powdered aluminum as fuel. Propellants may also be based on nitrate esters, usually nitroglycerine (NG), nitrocellulose (NC), or a nitramine such as RDX or HMX. Gun propellants are usually referred to as single base (composed of NC), double base (composed of NC and NG), or triple base [composed of NC, NG and nitroguanidine (NQ)]. Single-base propellants may also contain

2,4-dinitrotoluene (2,4-DNT) with traces of 2,6-dinitrotoluene (2,6-DNT). The vast majority of gun propellant formulations in Canada are either single- or-double base propellants and include lead as a decoppering agent, which represents another adverse environmental contaminant. Propellant formulations contain several other minor components such as stabilizers, plasticizers, and burn rate modifiers, but they represent $<2\%$ by weight of the propellants and have never been detected as MCs in soil surfaces. The major classes of EM used by the Department of National Defence (DND) are presented in Fig. 2. Tables 1 and 2 present the most commonly used explosive and propellant formulations in North American RTAs. In summary, the main EMs of concern in RTAs are: RDX, HMX, TNT, 2-A-DNT, 4-A-DNT, 2,4-DNT, 2,6-DNT, NG, NQ, and AP. NC is not included in this list because it is a polymer of very low toxicity and bioavailability and complex to analyze in environmental matrixes.

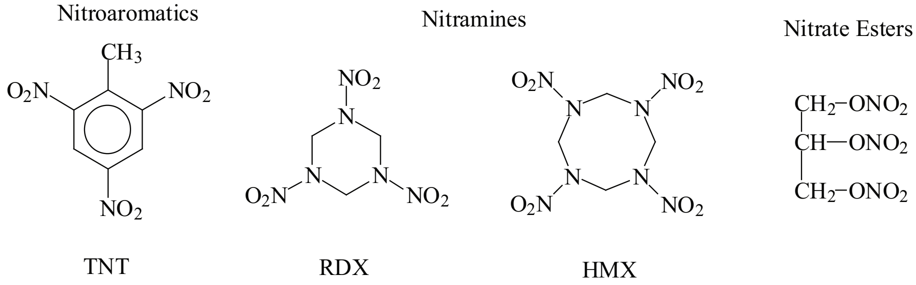

FIG. 2: Major classes of explosives.

TABLE 1: Explosives formulations

Military appellation	**Usage**	**Ingredients**
Composition B	Artillery, mortar, grenade	60% RDX (contains 10% HMX) 39% TNT (1% TNT isomers and DNT)
C-4	Demolition explosive	91% RDX and wax
Tritonal	Air force bombs	80% TNT, 20% aluminium
TNT	Artillery	TNT
Octol	Antitank rockets	70% HMX (contains 10% RDX), 30% TNT
A4	40-mm grenade	RDX (contains 10% HMX)

TABLE 2: Propellant formulations

Military appellation	**Usage**	**Main ingredients**
Single base	Small arms to 155 mm	NC, 2,4-DNT
Double base	Antitank rockets	NC, NG
Triple base	Large caliber guns	NC, NG, NQ
Composite	Rockets and missiles	Polymeric binder, AP

Live firing of munitions also spreads inorganic contaminants in the environment. Metals are deposited onto range soils by a variety of processes. High-order detonations generally disperse very fine metal particles, with the exception of prefragmented rounds, which might produce large fragments even in high-order scenarios. Much larger fragments are generally produced by low-order detonations. Metals can be transformed in other metallic compounds not originally present in the munitions. This transformation can occur either during the detonation process or during weathering of the metallic particles deposited on the range. For example, during a detonation event, the temperatures and pressures reach extremely high values that exceed the melting temperatures of some of the metallic compounds present in the munitions. These molten species are then free to react with other compounds to form new alloys, metallic complexes, or salts, which will all have their own environmental fate. After dispersion in the surface soil, both chemical and physical weathering of the metallic particles of fragments will take place. All the metals originally present in munitions are dispersed in RTAs after detonation, either in their original state, or as other metallic compounds. The list of metal analytes of concern will be presented later on in this paper.

3. SOURCES OF MUNITIONS CONSTITUENTS IN RANGE AND TRAINING AREAS

An understanding of the source of MCs in RTAs will facilitate the delineation of the source zones of EMs and metals in RTAs. This will help in establishing the localization, size, and shape of the decision units (DUs), or areas where sampling should be conducted.

3.1 Sources of EMs

The study of the sources of EMs is divided into two main groups: the firing positions (FPs) and the target impact areas. In the case of the FPs, several environmental assessment studies have shown that residues coming from the incomplete combustion of gun propellant accumulate as solid fibrous particulates in front of the FPs of guns, from small arms to large calibers (Ampleman et al., 2008b, 2010; Jenkins et al., 2007, 2008; Poulin et al., 2008a,b; Poulin and Diaz, 2008; Quémerais et al., 2007a,b; Thiboutot et al., 2008b,c, 2009, 2010; Walsh et al., 2006, 2008, 2009). Figures 3 and 4 show trials conducted to measure the masses of propellant deposited from the live firing of artillery and tank munitions. Constituents of concern at FPs are mostly 2,4-DNT and NG. Concentrations up to 140 mg/kg were observed at the FPs of small arms ranges (Walsh et al., 2007a), while concentrations as high as 6100 mg/kg of NG were detected behind antitank firing positions (Thiboutot et al., 2004).

The measurements of the mass of propellant residues deposited from various platforms have resulted in a good estimation of the source term of each type of firing, and

FIG. 3: Major classes of explosives.

FIG. 4: Propellant deposition trial, 105 mm artillery.

global results obtained are presented in Table 3. This table represents the most comprehensive database on propellant accumulation at this time.

Accumulation of NG and 2,4-DNT in the environment is cumulative over the years, since the NC matrix protects MCs from degradation and dissolution processes. A study on the fate of propellant residues was conducted on a former antitank FP that had been inactive for more than 35 years (Thiboutot et al., 2010). This study demonstrated that

TABLE 3: Deposition of propellant residues from live firing of various platforms

Weapon system	**Weapon size**	**Munition tested**	**EM**	**Residues / round (mg)**	**Deposition rates (%)**
Small cal. (U.S.)	9 mm pistol	M882	NG	2.1	5.32
	5.56 mm rifle	M855	NG	1.8	1.10
	5.56 mm MG	M27	NG	1.3	0.71
	7.62 mm MG	M80	NG	1.5	0.56
			DNT	0.0018	0.05
	12.7 mm MG	M9	NG	11	0.74
Small cal. Canada	9 mm pistol	MK1 Ball	NG	0.74	1.39
	9 mm pistol	Frangible	NG	0.95	1.97
	9 mm pistol	115 FMJ Ball	NG	2.03	3.90
	5.56 mm C7 rifle	Frangible	NG	1.06	0.62
	5.56 mm C7 rifle	C77 ball clip	NG	0.30	0.19
	5.56 mm C7 rifle	C79A1 blank clip	NG	0.02	0.05
	5.56 mm C8 AC	C77 ball clip	NG	0.07	0.04
	5.56 mm C8 AC	C79A1 blank clip	NG	0.02	0.06
	5.56 mm C9 MG	C77/C78 link	NG	0.05	0.03
	5.56 mm C9 MG	C79A1 blank clip	NG	0.01	0.01
	7.62 mm C6 MG	C21/C19 ball link	NG	0.98	1.36
	7.62 mm C6 MG	C24 blank	NG	0.16	na
	0.338 Cal rifle	Match B406	NG	0.03	0.001
	0.5 Cal MG	M2/M17 link	NG	0.25	0.02
	0.5 Cal rifle	AAA750	NG	0.27	0.02
Med cal.	40 mm	Mk281 Mod 0	NG	2.2	0.59
		M430	NG	76	8.44

TABLE 3: Continued

Weapon system	**Weapon size**	**Munition tested**	**EM**	**Residues / round (mg)**	**Deposition rates (%)**
Mortars	60 mm	M888 / M702	NG	0.088	0.0065
	81 mm	M301A3 / M185	NG	1,000	3.3
	120 mm	M933 / M230	NG	350	1.4
Rockets	84 mm	M136 (AT4)	NG	95,000	73
	84 mm	Carl Gustav	NG	20,000	14
	66 mm	M72 LAW	NG	42	0.19
	204 mm	GMLRS	AP	< 1.6	< 0.000003
	203 mm	MK-58 AIM-7	AP	2.000	0.000000425
Howitzers	105 mm	M1 / M67	DNT	34	0.081
	105 mm	M1 charge 5	DNT	29	0.050
	105 mm	M1 charge 4	DNT	135	0.290
	105 mm	M1 charge 6	DNT	193	0.230
	155 mm	M107 / M3	DNT	1.2	0.0000480
British L131	155 mm	L8 charge 3	NQ	0.066	0.00000870
		L8 charge 5	NQ	0.857	0.0000442
		L10 charge 8	NQ	0.415	0.0000062
		L8 charge 3	NG	0.015	0.00000579
		L8 charge 5	NG	0.200	0.0000304
		L10 charge 8	NG	0	0
Tank	105 mm	C109A1(Canada)	DNT	7.9	0.00263

levels as high as 4000 mg/kg of NG are still detected in the surface soils, showing that the residence time of propellant residues was long, consistent with work conducted by Dontsova et al. (2009a). Using Table 3 and data from range firing logbooks, it is now possible to estimate the quantity of propellant residues that is deposited over a determined period at a specific range. As an example, if 100 rounds of 84 mm Carl Gustav are fired on a range, it means that around 200 g of NG will be deposited behind the firing position. A comprehensive review paper on propellant deposition rates for various munitions has been presented at a NATO RTO symposium (Ampleman et al., 2011).

Another source of propellant residues identified in RTAs comes from the burning of excess artillery propellant charges. Artillery guns use a propelling charge system composed of multiple charge bags to fire projectiles at required distances. Following a gun firing operation, discarded propelling charge increments were open burned near the gun position on the soil surface or on snow/ice in the winter (Figs. 5 and 6). Sampling of the surface soils demonstrated that burning residues built up and represented a threat to the environment and human health. A recent fate study conducted by INRS-ETE demonstrated that 500 g of burning residues spread over 1 m^2 of surface soil may lead to the contamination of more than 7.5 million liters of groundwater in the first infiltration (Martel et al., 2010). Contrary to the particles deposited at the gun mouth, which led to a very slow dissolution rate of 2,4-DNT or NG, open burning led to a highly leachable fraction of 2,4-DNT, which is rapidly brought to the groundwater (Martel et al., 2010). This situation mandated the development of a safe and environmental alternative destruction method for the excess propelling charges. This will be covered in Section 8 on mitigation methods.

Overall, the following areas can be considered potentially contaminated by propellant residues in RTAs' FP:

FIG. 5: Field expedient burning of excess artillery propellants.

FIG. 6: Leftover residues after burning on snow.

- In front of gun FPs, from small arms to 155 mm calibers
- Behind and in front of antitank rocket FPs
- At former excess propellant field expedient burning sites

At the other end of the range, target areas were highly suspected of being contaminated by explosive residues. Many trials were dedicated to better understanding the deposition pattern of explosive residues from various scenarios (Jenkins et al., 2005a; Pennington et al., 2001, 2002, 2003, 2004, 2005, 2006a,b, 2008a,b; Walsh et al., 2005b). The conclusions drawn from this work are presented in this subsection. The following sources of explosives have been studied: high-order detonations, low-order detonations, UXO blow in place (BIP), UXO shell cracking, and UXO corrosion.

High-order detonations are defined as detonations that reach the desired pressure and detonation velocity. The evaluation of explosives deposition following high-order detonations is not a simple task. The detonation process involves high pressure and temperature, and the deposition pattern can be very complex to assess. Various trials were conducted and led to the development of a setup involving detonation on pristine snow cover, which allowed an easier delineation of the deposition plume (Jenkins et al., 2002; Walsh et al., 2007b). Table 4 presents representative high-order results obtained with mortars, hand grenades, and artillery rounds. As illustrated in Table 4, the quantities of explosive deposited from high-order detonations are very small, almost at forensic

TABLE 4: Mass of explosive deposited from high-order detonations

Weapons system	Explosive	Number of rounds fired	Percent of unburned explosive deposited (%)	Mass deposited per round (μg)
Mortar 60 mm	RDX	11	3×10^{-5}	94
Mortar 81 mm	RDX	5	2×10^{-3}	8500
Mortar 81 mm	TNT	5	3×10^{-4}	1100
M67 Hand grenade	RDX	7	2×10^{-5}	25
Howitzer 105 mm	RDX	9	7×10^{-6}	95
Howitzer 105 mm	TNT	9	2×10^{-5}	170
Howitzer 155 mm	RDX	7	5×10^{-6}	310

levels. The quantities are spread over large areas, and do not lead to the buildup of concentrations of concern of explosives. Low-order detonations might happen in various scenarios in live-firing events. A large percentage of the fired munitions function as designed and generate high-order detonations. A fraction varying from 1 to 50% of rounds might generate low-order detonations or UXO. The failure rate of munitions depends on the type of round, and in general, artillery rounds have a malfunctioning rate around 1–5%, whereas antitank rockets have a malfunction rate as high as 50%. A low-order detonation is defined as a detonation that does not reach the maximum detonation pressure and temperature, and is sometimes referred to as a deflagration. Low-order detonations were achieved on purpose by using a weak detonation trigger (Pennington et al., 2001, 2002, 2003, 2004, 2008a,b), and it was found that while high-order detonations deposit micrograms of fine explosive dust, low-order detonations deposit gram quantities of explosives from fine dust to large chunks. Table 5 presents deposition results measured from low-order detonations of mortar and artillery shells. When sampling RTAs, low-order detonation sites were encountered where the presence of high concentrations of explosives was always detected. Figure 7 presents a representative low-order detonation crater sampled in Canadian Force Base (CFB) Cold Lake RTA (Ampleman et al., 2004). The reddish color of the pond indicated the presence of TNT photodegradation by-products.

TABLE 5: Mass of explosive deposited from low-order detonations

Item	Explosive fill	Percent of unburned explosive deposited (%)	Mass deposited (g)
Mortar 60 mm	Composition B	35	67
Mortar 81 mm	Composition B	42	300
Howitzer 105 mm	Composition B	27	620
Howitzer 155 mm	TNT	29	2000

FIG. 7: Low-order detonation crater in Cold Lake RTA.

In order to solve the safety risk that a surface UXO represents in our RTAs, explosive ordnances disposal (EOD) teams regularly proceed to an UXO BIP operation that consists of detonating C-4 blocks nearby the UXO (without moving it). The impacts of disposal operations conducted on RTAs when encountering UXO by detonating them with C-4 is now better understood. The use of unconfined C-4 blocks generates the dispersion of RDX in the surrounding of the detonation point (Pennington et al., 2002, 2003, 2004, 2005, 2006,a,b, 2008,a,b). Moreover, the probability of leading to low-order detonations when doing BIP is higher than in a live-firing context, since the UXO can be partially buried or in a configuration that does not allow a high-order event when initiating it with C-4. Therefore, locations where intense BIP has been conducted might present measurable concentrations of RDX from the C-4 and also of other explosives from the UXOs.

Finally, an important source of explosive in RTAs was identified through the quest for understanding the explosive contamination pattern. Surface UXOs in impact areas are susceptible of being hit by razor sharp flying fragments from close-proximity high-order detonations. Designed experiments using 81 mm mortar shells demonstrated that this phenomenon is very easy to achieve and led to gram to kilogram quantities of explosives in the surrounding environment (Lewis et al., 2009; Walsh et al., 2011a). This indicates that the surface to near-surface UXOs that are exposed to other rounds that explode nearby represent an important source of explosive in the surface soils. The broken shells can release as much as the totality of their explosive content in the environment. This source of explosive residues stresses the importance for regular clearance of surface UXOs in RTAs. EOD teams normally take care of the UXOs by BIP as soon as they identify one. The regular elimination of surface UXOs from highly used impact areas such as an artillery impact central area might not be always feasible and, therefore, cracked UXOs shall be looked for when sampling for explosive residues in target impact areas, and the surrounding area must be sampled. If feasible, remains of the cracked UXO shall be eliminated either by detonation or else by collecting the large chunks of explosives that may remain on site. A detailed review paper on explosive deposition rates for various munitions has been presented at a NATO RTO symposium (Walsh et al., 2011a).

On a longer-term perspective, corrosion of the munitions casings also represents a source of explosives in the environment and a related risk to the underlying groundwater. The corrosion rate is a complex phenomenon, which depends on soil conditions, on heating/cooling and wet/dry cycles, on soil physicochemical characteristics, and many other parameters. It is assumed that corrosion represents a long-term source term that is still undefined and that most of the risk is not related to surface soils but to groundwater.

The major conclusions from RTAs characterization and explosive deposition studies are as follows:

- A forensic amount of explosives is deposited when a round is functioning as designed.
- BIP detonations deposit a greater percentage of residues than live-fire high order and deposit RDX from the C-4 donor charge.
- By far, the largest explosive residues deposition is from low-order detonations and particles deposited that range from micrometers to centimeters in diameter.
- As a rule of thumb: it takes 10,000 to 100,000 high-order detonations to deposit the same amount of explosive as one low-order detonation.
- Surface UXO cracking may expose as much as 100% of the explosive filler to the environment and also represents an important source of contamination.

3.2 Sources of Metals

The precise knowledge of the metallic composition of munitions is generally unknown, because this kind of information is proprietary to the manufacturer. Nevertheless, the following subsection provides an overview of the main known sources of metals in RTAs as well as their deposition processes.

As for EMs, the studies of metal deposition in RTAs are divided in two parts: the metals at the FP and at the impact areas. In the case of the FP, metals generally come from the detonation of the primer, from the combustion of the gun propellant, from the erosion of munitions or weapon during the firing event, or from large metallic parts ejected from the weapon during the firing, such as small arms cartridge cases. The metals that could be expected would mostly be copper, zinc, lead, and mercury. Firing positions are generally small areas on which contaminants could potentially accumulate very fast.

However, metallic species are seldom detected at firing positions in concentrations above guidelines. Large metallic parts, such as casings, are recovered by the users after the training activity. The screening for metals at an FP is therefore not mandatory.

In the case of impact areas, the metals come from the projectiles. In general, medium- and large-caliber munitions projectiles are made of steel [an alloy of iron (Fe) and carbon (C)] or aluminum (Al). Small-caliber bullets mainly contain lead (Pb), antimony (Sb), arsenic (As), copper (Cu), and zinc (Zn), and grenade bodies are generally made of brass, a Cu-Zn alloy. Fe and Al are ubiquitous in the environment and of little concern, but Pb, Sb, Cu, and Zn are regulated in Canada. In addition, a wide variety of metals are also present in the other parts of the munitions (e.g., fuse, booster and primer cups, cartridge, tail, stabilizing fins, primer tube, connecting elements, percussion pin, etc.), albeit in smaller quantities. For example, the 60 mm mortar contains Fe in the shell, aluminum, Zn, magnesium (Mg), and Cu in the tail and the stabilizing fins, and Al, Cu, bismuth (Bi), and Pb in the cartridge. Primary explosives also constitute another source, albeit small, of heavy metals such as Pb or mercury (Hg). A comprehensive guide has been published by ITRC (2005) and includes the list of contaminants targeted for analysis in small arms ranges, as shown in Table 6. Most of the metallic debris deposited in the impact areas of RTAs come from the munitions' casings and are located in the vicinity of targets. However, an important source of metals in RTAs that is often overlooked is the target itself (e.g., old tanks, cars, trucks, etc.) that can be partly disintegrated by the detonation of munitions into metallic debris of various particle size and compositions. This metallic debris also has an environmental impact and should not be neglected when performing an environmental risk assessment.

4. SAMPLING STRATEGY FOR MUNITIONS CONSTITUENTS IN SURFACE SOILS

The primary objectives in RTAs characterization are as follows:

- To measure the surface soil contaminants that may pose a threat to the health of military users that may come in contact with the contaminants (human exposure)
- To measure the surface soil contaminants that may further be dissolved and brought to the surface water bodies
- To measure the surface soil contaminants that may further be dissolved and reach the groundwater
- To measure the surface soil concentrations that may pose a threat to local ecological receptors (ecotoxicity)
- A combination of some or all of the above

TABLE 6: Constituents of small arms munitions

Constituent	Symbol	Source
Lead	Pb	Primary constituent of most projectiles
Lead styphnate/lead azide		Primary constituent of most primers
Antimony	Sb	Hardening agent
Antimony Sulfide		From 5% to 30% is used in most primer compounds
Arsenic	As	Lead shot constituent (used in the production of small shot since it increases the surface tension of dropped lead, thereby improving lead shot roundness)
Copper	Cu	● Sometimes a primary alloy in center-fire ammunition and some small-caliber rifle bullets ● also used in frangible pistol ammunition ● Jacket alloy metal (Increases hardness)
Bismuth	Bi	Lead shot replacement
Tin	Sn	Primary metal for center-fire ammunition and shot (increases hardness)
Zinc	Zn	Jacket alloy metal
Iron	Fe	Iron tips on penetrator rounds and steel shot (has been used successfully to remediate high levels of lead and arsenic in some soils)
Tungsten	W	Alternative projectile material to lead (recent research indicates there may be some adverse environmental and human health concerns regarding tungsten)
Nickel	Ni	Coating to improve shot performance
Cobalt and chromium	Co and Cr	Alloys in some ammunition rounds

There are numerous challenges in obtaining representative results of the level of contamination by MCs over military live-firing ranges that cover many square kilometers and where a multitude of activities involving munitions are conducted. First of all, the nature of explosive and propellant dispersion comprises both compositional and distributional heterogeneity. The compositional heterogeneity is due to the intrinsic nature of the explosives and propellants: the formulations are complex and are inhomogeneous in nature from their conceptions. In other words, compositional heterogeneity is described as the variability of contaminant concentrations between the particles that make the population, which leads to a fundamental error. The fundamental error is managed by collecting and analyzing sufficient sample mass to address the compositional heterogeneity.

There is also a very high distributional heterogeneity in the dispersion of MCs. Taylor et al. (2006) and Jenkins et al. (1999, 2004, 2005b), have studied extensively the high heterogeneous pattern associated with explosive and propellant distribution. Solid particles may vary from very fine dust to large chunks of explosives, up to centimeter size. This heterogeneity results in a segregation error. In order to minimize the fundamental error and compensate for compositional heterogeneity, a greater sample mass must be collected, and in order to minimize the segregation error and compensate for the distributional heterogeneity, multiple subsamples must be collected. To achieve that, it is recommended to use a composite sampling strategy with a judgmental systematic random sampling design to characterize the average concentration of MCs within a chosen area or DU.

This approach is different from the collection of discrete samples and the commonly used practice of field splitting or laboratory subsampling by removing only a portion of the sample received from the field for further processing. Composite sampling is not a new concept and has been well documented (Esbensen, 2004; Hathaway, 2005; Jent et al., 2006; Keith, 1991). While composite sampling was not new, there was a very high resistance in the United States from the U.S. Environmental Protection Agency (EPA) to accept the application of compositing in RTAs characterization. The assumption was that this led to sample dilution and that discrete sampling was more appropriate. Composite sampling is done by collecting a minimum of 50 small increments of soil from a specified DU and combining these into a single sample. A DU can be defined as an area where a decision is to be made regarding the extent and magnitude of contamination with respect to the potential environmental or human health hazards posed by the exposure to munitions contaminants. Table 7 presents a general guidance as to the minimum number of increments to use, depending on the size of the DU. A minimum of 50 subsamples is recommended to form a sample that weights between 1 and 2 kg. The size and location of the DUs is planned using knowledge sufficient to delineate areas that are likely to be contaminated. The DU is walked in a serpentine manner and increments are collected at each three to four steps, in the same area of the subunit. When all the surface of the DU is covered, the same process is repeated after a rotation of the sampling path by 90 deg, as illustrated in Fig. 8. Where practical, a rectangular shape DU is recommended for ease of sampling. DUs of 100 to 200 m^2 and larger have successfully been used to map

TABLE 7: Minimum number of increments recommended in function of the size of the DU

Size of the DU	Number of increments
0–10 m^2	50
10–50 m^2	75
50–100 m^2	100

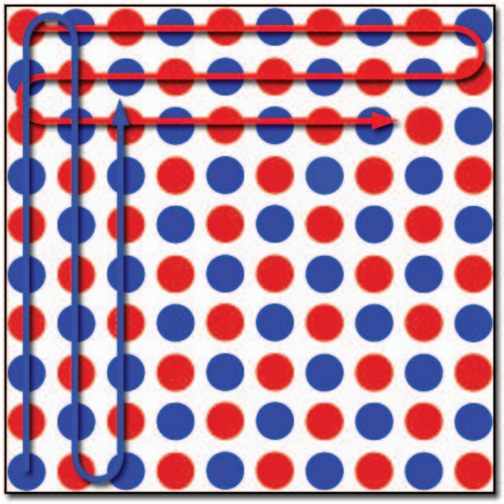

FIG. 8: Systematic sampling approach in a square DU.

explosive residues on active ranges. For larger DUs, the sample mass collected needs to be larger than 2 kg, such as up to 5–7 kg.

Using composite sampling, reliable estimates of mean concentrations for the specified area of virtually any size are obtained. Properly collected replicate samples should lead to a relative standard deviation lower than 30% between replicates.

Sampling in RTAs represents a high safety risk since the RTAs are in general heavily impacted with UXOs. All the personnel involved in the sampling campaign need a mandatory safety briefing given by the range control office. When entering a UXO contaminated range, the sampling team must always be accompanied by an experienced EOD specialist, who will indicate the safe path for walking and driving. In very high–density UXO areas or in antitank impact areas where piezoelectric fuses might be triggered only by the shadow of a person, access might be either denied or restricted to the EOD specialist only, who could perform the sampling after precise sampling instructions.

With the exception of ranges where the surface is regularly physically moved, the highest concentrations of MCs are always present in the top 2.5 cm of surface soil. A variety of sampling tools are available to collect soil samples. They range from a spade to hydraulic powered coring equipment. Representative soil samples can best be obtained by using a core-sampling tool. Indeed, CRREL has developed a coring device that is handy and most helpful in RTAs. It involves a soil plunger, which can be adapted to vary the sampling depth, and the corer diameter can also be varied, depending on the sampling goals. The choice of collection tools often depends on the cohesiveness, coarseness, and moisture content of the soil. Scoops and spoons are necessary for non-cohesive soils and heavily cobbled surfaces. Coring tools are recommended for cohesive surface soils with and without vegetation. Samples should be stored in a polyethylene bag, tightly closed. Splitting the sample in the field to reduce the volume sent for laboratory analysis is not recommended. The whole samples are stored in the cold and dark and sent to the laboratory for homogenization and analysis.

5. SAMPLE PROCESSING

Sample processing is as important as the sampling itself because it will ensure whole sample representativeness. The heterogeneous nature of MC mandates that care be taken in the careful homogenization of the sample. Air drying of the soil samples must be conducted in the dark to avoid the alteration of the contaminants of concern. Once the samples are dried, they need to be homogenized to ensure that the subsample is representative of the whole sample. There are two methods for homogenizing: the acetone slurry method, and the mechanical grinding method. The first method uses acetone to dissolve the EM compounds and redistribute them evenly on the soil particles, while the second method relies on mechanical grinding to reduce the size of the EM particles and fibers to the same size as the soil particles to ensure uniform dispersion (EPA SW846 Method 8330b). The two methods for sample homogenization will not be described in detail in this paper, but can be found in Thiboutot et al. (2012). After thorough homogenization, a 10 g sample is extracted with acetonitrile and analyzed following the EPA 8330b method (U.S. EPA, 2006).

Energetic-spiked samples are not recommended on a routine basis, because 1–2 kg samples would need a relatively large amount of standard. However, a 10 g subsample after homogenization should be fortified with a known concentration of nitroaromatics and nitramines for every batch of samples collected in a specific geological formation. Background samples (10% of the total number of samples) need to be collected at a site of the same representative geology as the DU samples. Table 8 highlights the EMs that were most frequently encountered in specific ranges.

When metals are the analytes of interest, it is also essential to process the soil samples before their analysis. The purpose of sample treatment is to produce a smaller, dry and manageable sample suitable for laboratory-scale analysis while at the same time

TABLE 8: EM commonly observed by range type

Type of Range	RDX	HMX	TNT	2,4-DNT	4ADNT	2ADNT	NG
Hand grenade	✓	✓	✓		✓	✓	
Antitank rocket range	✓	✓	✓	✓	✓	✓	✓
Artillery range	✓	✓	✓	✓			✓
Bombing range	✓		✓				
Demolition range	✓	✓		✓			✓
Small arms ranges							✓

ensuring that the prepared sample is homogeneous and fully representative of the original field material. First, the samples should be dried at temperatures of $<40°C$ to avoid the potential loss of volatile compounds, such as antimony, arsenic, and mercury, and to avoid the oxidation of some heavy metal compounds, especially sulfides. The whole sample should then be sieved using stainless steel screens to remove pebbles, sticks, and bullet fragments larger than 2 mm, and then be ground using a ring pulverizer to decrease the particle size of <75 μm. Care should be exercised to choose a ring pulverizer that will not contaminate the sample with the analytes of interest. Accredited laboratories shall provide detailed information about this operation and the associated contamination. In doubt, a clean sand sample obtained from a local supplier could be sent to the laboratory for analysis with and without the pulverization step.

The analysis of metals should be done using inductively coupled plasma-mass spectrometry (ICP-MS) or inductively coupled plasma-atomic emission spectrometry (ICP-AES) following the general guidelines of EPA methods 6020A or 6010C, respectively (U.S. EPA, 1994, 2007). Generally, ICP-MS is used to determine concentration levels in parts per billion and below while the ICP-AES is used to determine levels in parts per million and higher. Table 9 illustrates the metals commonly detected in concentrations above guidelines in soils of specific ranges.

Field sampling reproducibility of composite sampling should be subject to quality assurance and quality control requirements similar to those traditionally required to demonstrate laboratory analytical reproducibility. Field replicates provide a measure of the total error or variability of the data set. The sampling plan must provide for enough replicate QC sampling to obtain the required precision. As a general rule, it is recommended to collect triplicate composite sampling for at least 10% of all the DUs. Whenever possible, the triplicates should be collected by three teams to validate the absence of bias.

6. FATE AND TRANSPORT OF MC

This section will briefly present the general mechanisms that govern the fate and transport of MCs. In general, explosives and propellants have low vapor pressure. Therefore,

TABLE 9: Metals commonly observed by range type

Type of Range	Pb	Cu	Zn	Sb	Cr	Ni	Cd
Hand grenade		✓	✓				✓
Antitank rocket range	✓	✓	✓		✓	✓	
Artillery range	✓	✓	✓				
Bombing range	✓	✓		✓			✓
Demolition range		✓	✓		✓		
Small arms range berms	✓	✓	✓	✓			

their fate is driven by dissolution/leaching, transformation, and mineralization. NG and 2,4-DNT have higher vapor pressure, but when dispersed in a NC matrix, volatilization is highly limited. The fate and the risk associated with a contaminant are closely related, as illustrated in the conceptual model presented in Fig. 9. The risk is associated to the effect of each MC, their metabolites, and their fate. Their fate is driven through transport and degradation.

Propellant residues have a long-term environmental residence time since they are embedded in a NC matrix that protects them from dissolution and further biotic or abiotic processes (Hewitt and Bigl, 2005; Thiboutot et al., 2010). Therefore, the risk to the groundwater is low and most of the MCs remain at the soil surface in the first 2.5 cm of soil for many years, even decades. One exception is 2,4-DNT liberated by field expedient burning of excess artillery propellants. In this case, there is a fraction of highly leachable 2,4-DNT that is available to dissolution and degradation processes (Martel et al., 2012b). The remaining fraction is embedded in NC and will remain at the soil surface for years and will be immobile except for the nitrate that can leach out from the degradation of NG (Martel et al., 2012b). Composite rocket propellants may lead to the dispersion of AP in the environment. It has been demonstrated that when normal functioning occurs, the combustion in the rocket is very effective and AP is not dispersed in RTA (Jenkins et al., 2007; Thiboutot et al., 2008b). Ammonium perchlorate is also included in a few other weapons such as M72 antitank rocket propellants or smoke formulations.

The explosives mostly used in Canadian munitions are TNT, RDX, and HMX based and many efforts were dedicated to better understand their complex fate and transport mechanisms (Halasz et al., 2002; Hawari et al., 2000a,b, 2001; Lewis et al., 2009; Mailloux et al., 2008; Martel et al., 2007, 2009; Monteil-Rivera et al., 2004; Robertson et al., 2007; Zhao et al., 2004). Overviews of the main process descriptors for explosives has been published by Brannon and Pennington (2002), Halsaz et al. (2002), and more

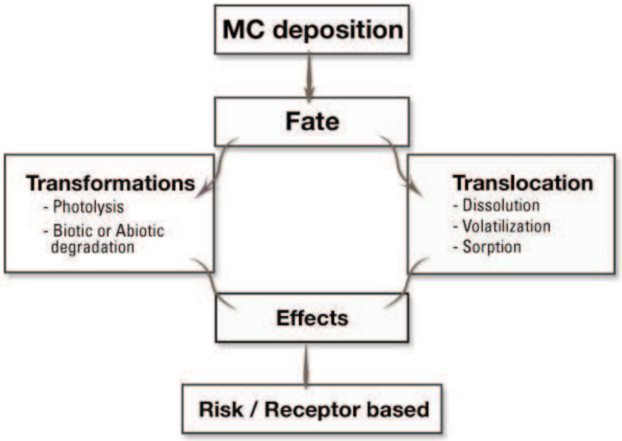

FIG. 9: Conceptual model for the environmental fate of MC.

recently by Monteil-Rivera (2004) and Kaldersi (2011). The environmental fate of explosives can be attributed mostly to their molecular structure and related water solubility, their adsorption to soil particles, and the production of metabolites through biotic and abiotic routes. In other terms, the main processes that control their fate are: solubility and dissolution, adsorption, transformation, biodegradation, photolysis, and volatilization. For instance, TNT is a nitroaromatic and tends to degrade by photolysis, while nitramines such as RDX and HMX can be photodegraded but to a much lower extent. Some photodegradation by-products of TNT are well known, while other species are still to be determined. TNT is also more soluble and dissolves more rapidly in water than RDX or HMX (HMX being the least soluble). TNT can degrade into more than 20 different metabolites with various solubilities and toxicities. For example, the aminodinitrotoluenes (ADNTs) that result from the photolysis or biodegradation of TNT are much more soluble than the parent compound, but they can easily covalently bind to humic acid. Therefore, these metabolites are stabilized by the formation of an amide with the organic content of the soil. Moreover, in soils that contain clay minerals, sorption mechanisms are stronger with TNT and its metabolites than for RDX and HMX (Dontsova, 2009b). Therefore, the relative rates of soil leaching of these three explosives can be explained in terms of the relative water solubilities and adsorption strengths. RDX leaches out faster than TNT, which in turn leaches out faster than HMX. TNT and its metabolites are more soluble than RDX, but their migration is inhibited by strong bonding interactions with soil constituents. On the other hand, HMX has a tendency to remain at the surface of the soil, because it is much less soluble in water. Interactions with the soil are an important factor when characterizing explosives in terms of bioavailability and extractability. TNT is particularly difficult to characterize because it is easily reduced to amino degradation products, namely, 2- and 4-amino-dinitrotoluene (2-and 4-ADNT), 2,4- and 2,6-diamino-nitrotoluene (DANT), and, under anaerobic conditions, 2,4,6-triaminotoluene. All data acquired up to now tend to indicate that most TNT metabolites are rapidly strongly sorbed to soil humic acid, if not irreversibly, which greatly limits their bioavailability. Therefore, even if TNT and its metabolites are considered toxic, they are not readily available for receptors.

The fate and transport of heavy metals in the environment will depend strongly on their solubility in water (which depends of the metal speciation and on the water pH and Eh) and their capacity to bind to the soil constituents. A metal compound with a high solubility and a low binding capacity has a higher mobility and presents a larger potential for leaching in groundwater and/or travel far away from the range. However, a compound having a low solubility will most probably stay on the surface of the soil, and a compound with strong binding affinities will most probably stay either on the surface or in the subsurface, where a specific bonding agent is encountered. In addition, small particles tend to be more mobile, either in solution or as colloids.

The water solubility of heavy metals in their elemental state is generally low. However, heavy metals do not generally remain in their elemental form when they are exposed to weathering and water. They are easily oxidized in their ionic form and will form various salts with soil constituents, all having a different solubility and bioavailability. As a general rule, nitrates, chlorides, bromides, and acetates are readily soluble in water, and sulphides are considered to be insoluble. However, the solubility of hydroxides, sulphates, phosphates, and carbonates will vary depending on the heavy metal counterpart, and on the pH of the water. The lowest solubilities are generally observed in neutral pH water (6.5–7.5). Acidic water ($pH < 6.5$) tends to increase the solubility of most metals salts, while basic water ($pH > 7.5$) will either induce the precipitation and immobilization of an insoluble heavy metal compound, or increase its solubility, depending on the heavy metal. Thus, extreme caution must be exercised when trying to decrease the leaching of soils containing multiple heavy metals by controlling the pH of the soil, because the solubility of some heavy metal compounds may increase when exposed to basic pH.

Key parameters governing the bioavailability of a given heavy metal compound are the composition (organic matter, metallic constituents) and pH of the soil, the particle size distribution, and the contact time between water and the heavy metal compound. These parameters in turn govern measurable, macroscopic parameters, such as the type of soil (sand, silt, clay, etc.), the cation exchange capacity (CEC), and the reduction-oxidation (redox). The binding capacity tends to increase with the decrease of soil particles size. For example, absorption in clay is much higher than in sand, because the groundwater movement in clay is slower, and also because the surface area of soil particles to which a heavy metal compound can bind is higher. In consequence, sandy soils present the highest leaching potential. The contact time between water and the heavy metal compounds is controlled by the amount of annual precipitation, the rainfall intensity, and the hydraulic conductivity of the soils. The absorption of several heavy metal compounds to soil components also tends to increase with the CEC. The redox potential will affect the type of heavy metal compound that is stable in a given area. The mobility of heavy metals is also affected by external physical factors, such as the topographic slope and the intensity of wind.

7. HYDROGEOLOGICAL CHARACTERIZATION OF RTAS

The potential for MCs to travel to water bodies in RTAs varies from quite low probability for NC embedded propellant residues to very high probability for RDX and AP. Therefore, it is imperative to monitor both surface and subsurface water bodies’ quality. In Canada, a large effort was dedicated to the hydrogeological characterization of major RTAs. This approach is carried out as part of a collaborative effort with INRS-ETE. Hydrogeology typically provides detailed information on the quality and flow direction of surface water and groundwater, on the water table depth, and on the various types of soil on which the ranges are built. In Canada, detailed hydrogeological characterization of six Army RTAs has been conducted up to now. The approach is stepwise and, in general, the work is accomplished in sequential phases over a period of three to four years. The number of wells installed per phase is approximately between 15 and 20 and is combined with a detailed surficial and 3D geological survey. This stepwise approach allows the better localization of wells and optimizes the process.

7.1 Well Installation

The major concern for the installation of wells in UXO-contaminated ranges is the possibility of encountering buried UXO during well installation. Another concern is that the wells will be destroyed as gunners use them for target practice. The installation of flush-mounted wells has eliminated this issue, and these types of wells have been installed within impact ranges across Canada (Bordeleau et al., 2008b; Martel et al., 2009). Before any drilling is to be conducted within an area that could have buried UXO present, UXO avoidance activities must have been completed. Qualified personnel (EOD or UXO technicians) will clear pathways to proposed sampling locations, usually done using magnetometers. The pathways must be wide enough for safe passage of drilling equipment and personnel and, in general, a sufficiently large area will be cleared at the sampling location to allow the drilling equipment to maneuver properly. At all drilling locations, down-hole avoidance techniques are required. Each 0.5 m interval needs to be cleared using a magnetometer prior to further advancement of the drilling equipment to insure the safety of the drilling crew.

Mailloux et al. (2008) used a hollow-stem auger to drill wells at the Arnhem antitank rocket range at CFB Valcartier in Canada. In a few wells, split spoon can be used to sample the soil at depth to determine the stratigraphy of the formation. The stratigraphy refers to the layering of the soil strata, and it is important when trying to understand the hydraulic properties of the soil profile. It is critical that wells be installed within the proper aquifer to assess questions of offsite migration. Direct push wells can sometimes be used for groundwater monitoring, depending on the geology and stratigraphy of a given location. More details on well installation can be found in Martel et al. (2012a).

7.2 Water Sampling and Analysis

The collection of groundwater must be representative of the conditions at the site. For groundwater, samples are collected to investigate the water in the aquifer that is migrating through the formation. Installing a well can modify the aquifer’s structure and environment near the well screen, and this may affect the stability of various chemicals in the well and in its vicinity. To minimize this, common practice is to purge three to five well volumes prior to collection of a groundwater sample from the well. This removes the stagnant water that is present in the casing above and below the well screen and water near the screen that might have been affected by the conditions within the well. Studies have shown that explosives are not as readily sorbed by the materials used to sample (Parker et al., 1990; Parker and Ranney, 1994, 1997, 1998). There are several sample collection methods that are commonly used for groundwater sampling. These include the use of bailers, low-flow pumping with a peristaltic pump or a bladder pump, or passive diffusion samplers. The Canadian approach used a low-flow sampling technique with a dedicated system made of a 6 mm Teflon tubing connected to a flexible Viton tubing via a Teflon connector to avoid any cross contamination. The groundwater sample is taken when the groundwater quality parameters are stabilized. Groundwater samples are to be collected in a 1 L amber glass bottle to prevent photodegradation, cooled to 4°C, and shipped by overnight carrier. The stability of energetic compounds can be extended if the water is acidified to pH 2 with sodium bisulfate after collection (Jenkins et al., 1995). Sample analysis is conducted as described in SW846 Method 8330B (U.S. EPA, 2006). Water samples are generally preconcentrated using solid phase extraction to provide adequate detection capability. Most analyses have been conducted using reverse phase high-pressure liquid chromatography (HPLC) using an ultraviolet (UV) detector.

7.3 Thematic Maps

The hydrogeological data collected led to the preparation of several thematic maps such as hydraulic head and surficial geology, as illustrated in Figs. 10 and 11. The following step is the groundwater flow and contaminant transport modeling. This is generally performed using a numerical model such as FEFLOW, which needs to be fed with input

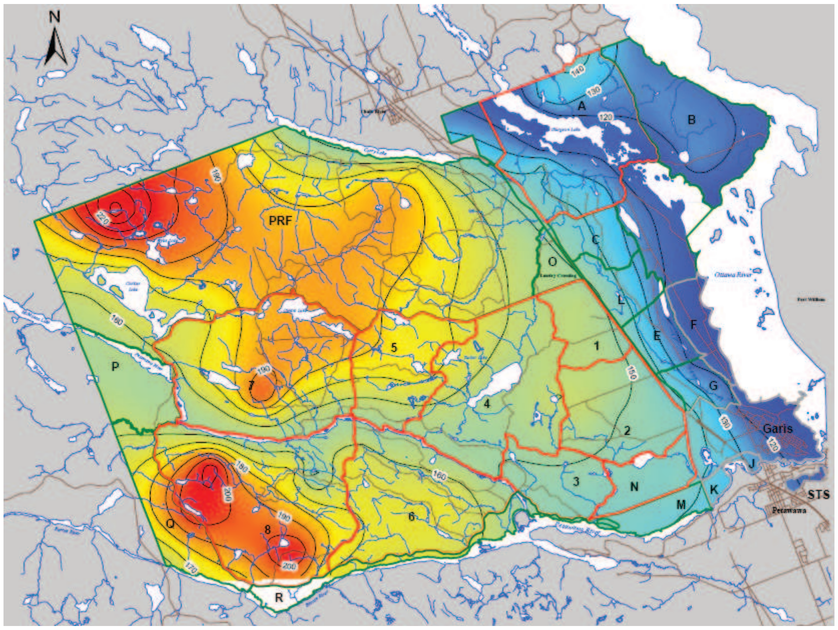

FIG. 10: Piezometric map.

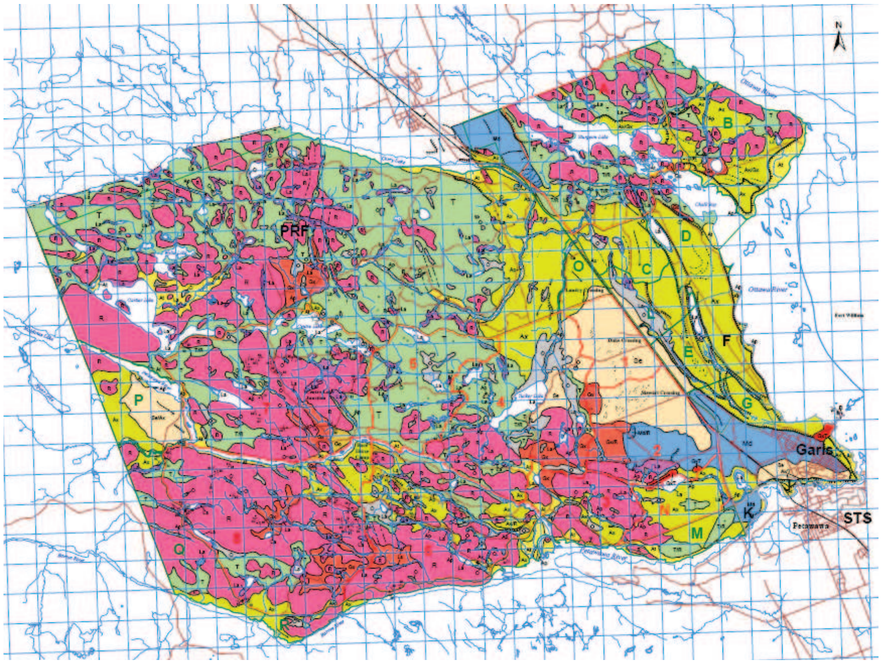

FIG. 11: Surficial geology map.

parameters such as the 3D geological model, the measured hydraulic heads, the measured hydraulic conductivity of the various hydrostratigraphic units, and the recharges. This model allows the reproduction of the behavior of groundwater at regional and local scales, and the prediction of the transport of contaminants, which is extremely important to perform risk analyses of the ecological and human receptors surrounding RTAs. A conceptual model is then built following the geological model and from the knowledge of the environmental fate of EMs. The risk analysis is completed by building hazard, aquifer vulnerability, and risks maps. The vulnerability map reflects the vulnerability of a given aquifer to surface contamination, of which an example is shown in Fig. 12. The hazard for a range is evaluated with an index system specifically developed and based on residue deposition frequency, on the environmental dangerousness of each type of explosive used, and on the surface area of the range where the munitions are used. The environmental dangerousness is based on five criteria, i.e., drinking water toxicity, solubility in water, natural biodegradation, photodegradation, and adsorption on the organic fraction of soil, and is evaluated for each possible EM released in a range. The surface area index is inversely proportional to the surface area of the training area or range. Firing positions have very small deposition areas (order of magnitude 100 m^2) on, behind, or in front of them, whereas impact areas may extend to millions of square meters, which dilute the concentration at the surface and consequently have a lower surface area index. The frequency index, the environmental dangerousness index, and the surface area of

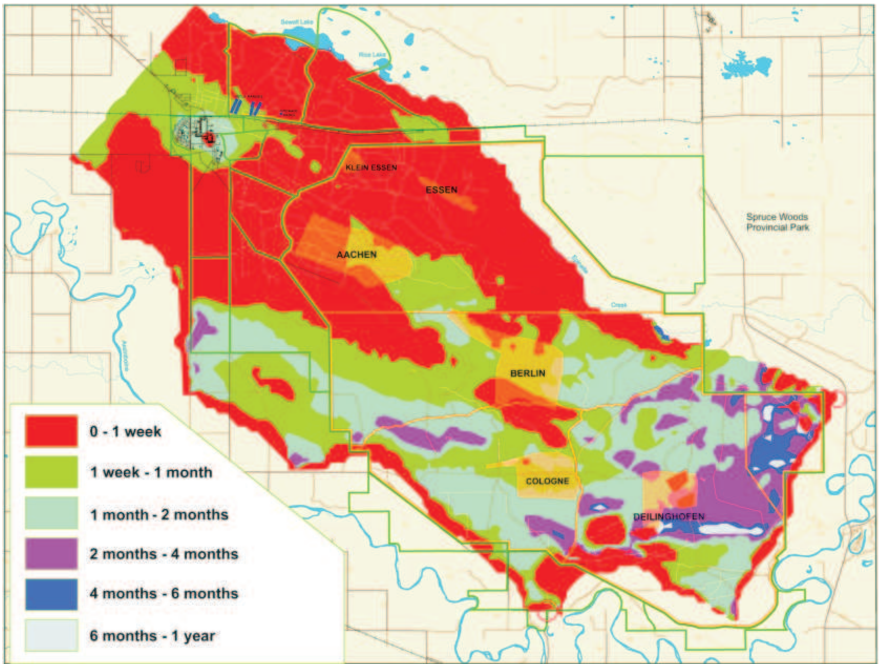

FIG. 12: Vulnerability map.

deposition index are multiplied together to give the hazard value for each of the energetic materials used for a given range. The aquifer vulnerability map and the hazard map are combined to generate the risk map. For more details on aquifer vulnerability, hazard, and risk maps see Martel et al. (2011).

8. RISK MANAGEMENT: MITIGATION METHODS

All the work described above allowed a comprehensive and detailed knowledge of the source of MCs in RTAs. Work was subsequently undertaken to mitigate or eliminate the adverse impacts measured, or else to develop management tools. The vulnerability, hazard, and risk maps represent a good example of highly relevant range management tools. Based on these maps, various decisions, such as range relocation or closure, can be taken to minimize the adverse measured impacts such as reducing the potential for aquifer contamination.

In some instances, tools were developed to completely eliminate the MC from entering the environment. An example of this is the development of a burn table for the destruction of excess artillery and mortar propellants. Various table design iterations and trials have been conducted, and this led to the development of a Canadian table for the burning of the excess artillery and mortar propelling charges (Thiboutot et al., 2011), as illustrated in Fig. 13. Field expedient burning of charges on the surface soils is now

FIG. 13: Canadian burn table.

forbidden in Canada. The table allows the safe destruction of 200 kg of excess charge bags per burn and leads to a 99.5% mass reduction. The design ensures a safe process and burn residues can easily be collected and treated as hazardous materials. The gaseous emissions emitted have been predicted and monitored and are not of concern. The use of the burn table greatly reduces the environmental footprint of artillery live-fire training: the proven accumulation of 2,4-DNT and lead in the environment has been stopped. A standard operating procedure (SOP) for the destruction using the table as well as a procedure for the safe return of the excess charge bags to the ammunition stores have been provided to the military users. Finally, another option is also under study, which is the development of modular charges for 105 mm guns. This would eliminate the requirement for open burning and would increase the sustainability even more.

Another example of a tool under development to minimize MC surface soil deposition is the Canadian small arm bullet catcher. Our characterization work joined with various studies of the fate of metals involving lysimeters have stressed the need to move away from conventional sand backstop butts for small arms ranges. Many prototypes were constructed over the last few years, ending up with a suitable prototype. The new concept uses the slope of the former stop butts, a cell where the water will not penetrate, and a reservoir in case there would be leaks. The goal was to design a cost-efficient bullet trap that could be easily implemented in Canadian small arms training ranges.

Finally, the context of observed environmental impacts from UXO and the study of the energetic formulations from the past highlighted the desired properties to achieve greener munitions. In 2008, Canada initiated a technology demonstration program named RIGHTTRAC for revolutionary insensitive, green and healthier training technology with reduced adverse contamination, aiming at proving that greener and insensitive munitions

(IMs) can decrease the environmental pressure on RTAs and minimize the health hazards the users without decreasing the performance of the munitions (Brochu et al., 2011). The goals of this five-year TDP are to reach a near-zero failure rate, and to eliminate the potential for RDX contamination and the use of toxic and carcinogenic compounds. This will be done by performing significant improvements to the fusing system, the main explosive charge, and the gun propellant.

9. CONCLUSION

The general approach to obtain representative results from the characterization of huge tracks of military RTAs was refined over the years to overcome numerous challenges, including the high compositional and distributional heterogeneity associated with MC dispersion. The research dedicated to munitions deposition and fate led to the development of a detailed protocol for the effective and safe characterization of range and training areas. The sample collection, treatment, and homogenization were carefully studied, and are presently the topic of intense international exchanges for standardization. A protocol covering the main contaminants of concern, i.e., propellants, explosives, and metals, was developed.

The large effort dedicated to the measurement of the deposition rate of MCs both at the target impact areas and at the FP led to a good estimation of the source terms of contaminants generated by various live-firing activities. The research conducted on impact areas demonstrated that normally functioning munitions only spread forensic amounts of their explosive content in the environment. Therefore, most of the contamination comes from UXOs that are cracked open by flying shrapnel coming from the detonation of an incoming round, by incomplete (low order) detonations, or by the BIP destruction of duds. Subsequently, the distribution, fate, and transport of propellant residues at firing points associated with live-fire training with munitions were studied. This allowed for a better understanding of the contamination pattern at the firing positions. The two major sources of propellant residues at the FPs were identified as the deposition of residues from incomplete combustion in the guns and field expedient burning of excess artillery and mortar propellants.

Several studies have also been performed on the fate and behavior of all MCs and their metabolites. This allowed the development of transport process descriptors for current explosives and propellants and their main transformation products. Moreover, the ecotoxicity of munitions constituents was also intensely studied, mostly in collaboration with BRI-NRC. The work conducted on the ecotoxicology of MCs led to international cooperation and publication of soil guidelines and textbook for ensuring military training sustainability.

Major environmental issues were identified and the sources of MCs in training ranges are now better understood. In Canadian Army RTAs, on top of RTAs' surface characterization, large efforts were dedicated to characterize the subsurface, and detailed hydrogeological and geological studies were conducted mainly by INRS-ETE. This led to the acquisition of a large database, and a better understanding of the complex dispersion and fate of munitions-related contaminants toward groundwater. The evaluation of the risk of aquifer contamination associated with military training activities was then allowed, and it produced practical range management tools.

On the basis of the knowledge acquired in the study of the environmental impact of the munitions, our efforts are presently dedicated to the development of environmentally sound solutions that will sustain military training and maintain force readiness. In order to achieve this goal, efforts are committed to the modification of actual live-firing activities. As an example, burn trays were developed and implemented in Canada, and field expedient open burning of excess propellant is now forbidden. Another example is the development of bullet catchers that will retain the heavy metals in enclosed units to avoid their environmental dissemination. In parallel, remediation of sites where levels of concern about munitions-related contaminants were identified will be undertaken.

One important conclusion of this project is that future munitions development must take into consideration the environmental aspects at a very early stage of the development process in order to avoid fielding munitions that would lead to high environmental and liability costs. It is within this context that Canada initiated a project in 2008 to develop greener, insensitive munitions that will ease the environmental pressure on RTAs without decreasing the performance. This represents a holistic approach toward the ultimate objective of totally sustainable military live-firing ranges.

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REFERENCES

Ampleman, G., Thiboutot, S., Gagnon, A., Marois, A., Martel, R., and Lefebvre, R., Study of the Impacts of OB/OD Activity on Soils and Groundwater at the Destruction Area in CFAD Dundurn, DREV R-9827, Defence Research Establishment Valcartier, Val-Bélair, QC, Canada, 1998.

Ampleman, G., Thiboutot, S., Désilets, S., Gagnon, A., and Marois, A., Evaluation of the Soils Contamination by Explosives at CFB Chilliwack and CFAD Rocky Point, DREV TR-2000-103, Defence Research Establishment Valcartier, Val-Bélair, QC, Canada, 2000.

Ampleman, G., Thiboutot, S., Martel, R., Lefebvre, R., Ranney, T., Jenkins, T. F., and Pennington, J., Evaluation of the Impacts of Live Fire Training at CFB Shilo (Final Report), DREV TR 2003-066, Defence Research Establishment Valcartier, Val-Bélair, QC, Canada, 2003a.

Ampleman, G., Thiboutot, S., Lewis, J., Marois, A., Jean, S., Gagnon, A., Bouchard, M., Jenkins, T. F., Hewitt, A. D., Pennington, J. C., and Ranney, T. A., Evaluation of the Contamination by Explosives in Soils, Biomass and Surface Water at Cold Lake Air Weapons Range (CLAWR), Alberta, Phase 1, DRDC Valcartier TR-2003-208, Defence Research and Development Canada–Valcartier, Québec. 2003b.

Ampleman, G., Thiboutot, S., Lewis, J., Marois, A., Gagnon, A., Bouchard, M., Jenkins, T. F., Ranney, T. A., and Pennington, J. C., Evaluation of the Contamination by Explosives and Metals in Soils, Vegetation, Surface Water and Sediment at Cold Lake Air Weapons Range (CLAWR), Alberta, Phase II Final Report, DRDC Valcartier TR 2004-204, Defence Research and Development Canada–Valcartier, Québec, Canada, 2004.

Ampleman, G., Thiboutot, S., Marois, A., and Gagnon, A., Evaluation of Soil Contamination by Explosives and Metals at the Land Force Central Area Training Centre (LFCA TC) Meaford, Ontario (Phase I), DRDC Valcartier TR 2008-390, Defence Research and Development Canada– Valcartier, Québec, 2008a.

Ampleman, G., Thiboutot, S., Marois, A., Gamache, T., Poulin, I., Quémerais, B., and Melanson, L., Analysis of Propellant Residues Emitted During 105-mm Howitzer Live Firing at the Muffler Installation in Nicolet, Lac St-Pierre, Canada, DRDC Valcartier TR 2007-514, Defence Research and Development Canada–Valcartier, Québec, 2008b.

Ampleman, G., Thiboutot, S., Marois, A., and Gagnon, A., Surface Soil Characterization of Explosive and Metals at the Land Force Central Area Training Centre (LFCA TC) Meaford, Ontario (Phase II) Final report, DRDC Valcartier, TR 2009-218, Defence Research and Development Canada–Valcartier, Québec, 2009.

Ampleman, G. Thiboutot, S., Marois, A., Gagnon, A., Woods, P., Walsh, M. R., Walsh, M. E., Ramsey C., and Archambault, P., Evaluation of the Propellant Residues Emitted During the Live Firing of Triple Base Ammunition Using a British 155 mm Howitzer Gun at CFB Suffield, Canada, DRDC TR-10-269, Defence Research and Development Canada–Valcartier, Québec, 2010.

Ampleman, G., Thiboutot, S., Walsh, M. R., Walsh, M. E., Diaz, E., and Brochu, S., Propellant Residue Deposition Rates on Army Ranges; Proceedings of the NATO AVT-177 Symposium on Munition and Propellant Disposal and its Impact on the Environment, pp. 24-1–24-25, Edinburgh, UK, Retrieved 7 March 2012 from http://www.rto.nato.int/abstracts.aspx?RestrictRDP=4, 2011.

Bordeleau, G., Martel, R., Schäfer, D., Ampleman, G., and Thiboutot, S., Groundwater Flow and Contaminant Transport Modeling at an Air Weapon Range, *Environ. Geol.*, vol. **55**, no. 2, pp. 385–396, 2007.

Bordeleau, G., Savard, M., Martel, R., Ampleman, G., and Thiboutot, S., Determination of the Origin of Groundwater Nitrate at an Air Weapons Range Using the Dual Isotope Approach, *J. Contam. Hydrol.*, vol. **98**, no. 3–4, pp. 97–105, 2008a.

Bordeleau, G., Martel, R., Ampleman, G., Thiboutot, S., and Jenkins, T. F., Environmental Impacts of Training Activities at an Air Weapons Range, *J. Environ. Qual.*, vol. **37**, no. 2, pp. 308–317, 2008b.

Brannon, J. and Pennington, J. C., Environmental Fate and Transport Process Descriptors for Explosives, ERDC Report TR-02-10, U.S. Army Engineer Research and Development Center, Vicksburg, MS, 2002.

Brochu, S., Diaz, E., Thiboutot, S., Ampleman, G., Marois, A., Gagnon, A., Hewitt, A. D., Bigl, S. R., Walsh, M. E., Walsh, M. R., Bjella, K., Ramsey, C. A., Taylor, S., Wingfors, H., Qvarfort, U., Karlsson, R.-M., and Ahlberg, M., Environmental Assessment of 100 Years of Military Training at Canadian Forces Base Petawawa: Phase 1—Study of the Presence of Munitions-Related Residues in Soils and Vegetation of Main Ranges and Training Areas, DRDC Valcartier TR 2008-118, Defence Research and Development Canada–Valcartier, Québec, 2008.

Brochu, S., Brassard, M., Ampleman, G., Thiboutot, S., Brousseau, P., Petre, C. F., Côté, F., Poulin, I., Diaz, E., and Lussier, L.-S., Development of High Performance, Greener and Low Vulnerability Munitions—Revolutionary Insensitive, Green and Healthier Training Technology with Reduced Adverse Contamination (RIGHTTRAC), NATO AVT-177, *Proceedings of Munitions and Propellant Disposal and Its Impact on the Environment Symposium*, Edinburgh, October 17–20, DRDC SL 2011-401, 2011.

Clausen, J. L., Scott, C., and Cramer, R. J., Development of Environmental Data for Navy, Air Forces and Marine Munitions, ERDC/CRREL TR-07-7, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, 2007.

Diaz, E., Brochu, S., Thiboutot, S., Ampleman, G., Marois, A., and Gagnon, A., Energetic Materials and Metals Contamination at CFB/ASU Wainwright, Alberta Phase I, DRDC Valcartier TR 2007-385, Defence Research and Development Canada–Valcartier, Québec, 2007.

Doddard, S., Sunahara, G., Kuperman, R. G., Sarrazin, M., Gong, P., Ampleman, G., Thiboutot, S., and Hawari, J., Survival and Reproduction of Enchytraeid Worms, Oligochaeta, in Different Soil Types Amended with Energetic Cyclic Nitramines, *Environ. Toxicol. Chem.*, vol. **24**, no. 10, pp. 2579–2587, 2005.

Dontsova, K. M., Pennington, J. C., Hayes, C., Simunek, J., and Williford, C. W., Dissolution and Transport of 2,4-DNT and 2,6-DNT from M1 Propellant in Soil, *Chemosphere*, vol. **77**, no. 4, pp. 597–603, 2009a.

Dontsova, K. M., Hayes, C., Pennington, J., and Porter, B., Sorption of High Explosives to Water-Dispersible Clay: Influence of Organic Carbon, Aluminosilicate Clay, and Extractable Iron, *J.*

Environ. Qual., vol. **38**, no. 4, pp. 1458–1465, 2009b.

Dubé, P., Ampleman, G., Thiboutot, S., Gagnon, A., and Marois, A., Characterization of Potentially Explosives-Contaminated Sites at CFB Gagetown, 14 Wing Greenwood and CFAD Bedford, DREV TR-1999-137, Defence Research Establishment Valcartier, Val-Bélair, Canada, 1999.

Esbensen, K. H., 50 Years of Pierre Gy's "Theory of Sampling"—WCSB1: A Tribute, *Chemometrics Intell. Lab. Syst.*, vol. **74**, no. 1, pp. 3–6, 2004.

Halasz, A., Groom, C., Zhou, E. Paquet, L., Beaulieu, C., Deschamps, S., Corriveau, A., Thiboutot, S., Ampleman, G., Dubois, C., and Hawari, J., Detection of Explosives and Their Degradation Products in Soil Environments, *J. Chromatog. A*, vol. **963**, no. 1-2, pp. 411–418, 2002.

Hathaway, J. E., Schaalje, G. B., Gilbert, R. O., Pulsipher, B. A., and Matzke, B. D., Determining the Optimum Number of Increments in Composite Sampling, *Environ. Ecol. Stat.*, vol. **15**, pp. 313–327, 2008.

Hawari, J., Beaudet, S., Halasz, A., Thiboutot, S., and Ampleman, G., Microbial Degradation of Explosives: Biotransformation versus Mineralization, *Appl. Microbiol. Biotechnol.*, vol. **54**, no. 5, pp. 605–618, 2000a.

Hawari, J., Halasz, A., Beaudet, S., Groom, C., Paquet, L., Rhofir, C., Ampleman, G., and Thiboutot, S., Characterization of Metabolites During Biodegradation of Hexahydro-1,3,5-Trinitro-1,3,5-Triazine (RDX) with Municipal Sludge, *Appl. Environ. Microbiol.*, vol. **66**, no. 6, pp. 2652–2657, 2000b.

Hawari, J., Halasz, A., Beaudet, S., Paquet, L., Ampleman, G., and Thiboutot, S., Biotransformation Route of Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine by Municipal Anaerobic Sludge, *Environ. Sci. Technol.*, vol. **35**, pp. 70–75, 2001.

Hewitt, A. D. and Walsh, M. E., On-site Processing and Sub-sampling of Surface Soils Samples for the Analysis of Explosives, ERDC TR-03-14, U.S. Army Engineer Research and Development Center, Hanover, NH, 2003.

Hewitt, A. D. and Bigl, S. R., Elution of Energetic Compounds from Propellant and Composition B Residues, ERDC/CRREL TR-05-13, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, 2005.

Hewitt, A., Bigl, S., Walsh, M. E., Brochu, S., Bjella, K., and Lambert D., Processing of Training Range Soils for the Analysis of Energetic Compounds, ERDC/CRREL TR-07-15, U.S. Army Engineer Research and Development Center, Hanover, NH, 2007a.

Hewitt. A. D., Jenkins, T. F., Wash, M. E., Walsh, M. R., Bigl, S. R., and Ramsey, C. A., Protocol for Collection of Surface Soil Samples at Military Training and Testing Ranges for the Characterization of Energetic Munitions Constituents, ERDC/CRREL TR-07-10, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, 2007b.

Hewitt, A. D., Jenkins, T. F., Walsh, M. E., and Brochu, S., Environmental Security Technology Certification Program - Project ER-0628. Validation of Sampling Protocol and the Promulgation of Method Modifications for the Characterization of Energetic Residues on Military Testing and Training Ranges, ERDC/CRREL TR-09-6, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, 2009.

ITRC Small Arms Firing Range Team, Environmental Management at Operating Outdoor Small Arms Firing Range, Interstate Technology and Regulatory Council, Washington DC, 2005. Retrevied March 7, 2012 from http://www.itrcweb.org/gd_smart.asp

Jenkins, T. F., Thorne, P. G., McCormick, E. F., and Myers, K. F., Preservation of Water Samples Containing Nitroaromatics and Nitramines, CRREL Special Report No. 95-16, Cold Regions Research and Engineering Laboratory, Hanover, NH, 1995.

Jenkins, T. F., Walsh, M. E., Thorne, P. G., Thiboutot, S., Ampleman, G., Ranney, T. A., and Grant, C. L., Assessment of Sampling Error Associated with Collection and Analysis of Soil Samples at a Firing Range Contaminated with HMX, CRREL Special Report No. 97-22, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, 1997a.

Jenkins, T. F., Grant, C. L., Brar, G. S., Thorne, P. G., Schumacher, P. W., and Ranney, T. A., Assessment of Sampling Error Associated with the Collection and Analysis of Soil Samples at Explosives Contaminated Sites, *Field Anal. Chem. Technol.*, vol. **1**, no. 3, pp. 151–163, 1997b.

Jenkins, T. F., Walsh, M. E., Thorne, P. G, Miyares, P. H, Ranney, T. A., Grant C. L., and Esparza J., Site Characterization for Explosives Contamination at a Military Firing Range Impact Area, CRREL Special Report No. 98-9, U. S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH, 1998.

Jenkins, T. F., Grant, C. L., Walsh, M. E., Thorne, P. G., Thiboutot, S., Ampleman, G., and Ranney, T. A., Coping with Spatial Heterogeneity Effects on Sampling and Analysis at an HMX - Contaminated Antitank Firing Range, *Field Anal. Chem. Technol.*, vol. **3**, no. 1, pp. 19–28, 1999.

Jenkins, T. F., Pennington, J. C., Ranney, T. A., Berry, Jr., T. E., Miyares, P. H., Walsh, M. E., Hewitt, A. D., Perron, N., Parker, L. V., Hayes, C. A., and Wahlgren, Maj. E., Characterization of Explosives Contamination at Military Firing Ranges, ERDC Technical Report No. TR-01-05, U. S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, 2001.

Jenkins, T. F., Walsh, M. E., Miyares, P. H., Hewitt, A. D., Collins, N. H., and Ranney, T. A., Use of Snow-Covered Ranges to Estimate Explosives Residues from High-Order Detonations of Army Munitions, *Thermochim. Acta*, vol. **384**, pp. 173–185, 2002.

Jenkins, T. F., Ranney, T. A., Hewitt, A. D., Walsh, M. E., and Bjella, K. L., Representative Sampling for Energetic Compounds at an Antitank Firing Range, ERDC/CRREL TR-04-7, U.S. Army Engineer Research and Development Center, Hanover, NH, 2004.

Jenkins, T. F., Thiboutot, S., Ampleman, G., Hewitt, A. D., Walsh, M. E., Ranney, T. A., Ramsey, C. A., Grant, C. L., Collins, C. M., Brochu, S., Bigl, S. R., and Pennington, J. C., Identity and Distribution of Residues of Energetic Compounds at Military Live-Fire Training Ranges, ERDC/CRREL TR-05-10, U.S. Army Engineer Research and Development Center, Hanover, NH, 2005a.

Jenkins, T. F., Hewitt, A. D., Walsh, M. E., Ranney, T. A., Ramsey, C., Grant, C. L., and Bjella, K., Representative Sampling for Energetic Compounds at Military Training Ranges, *Environ.*

Forensics, vol. **6**, no. 1, pp. 45–55, 2005b.

Jenkins, T. F., Pennington, J. C., Ampleman, G., Thiboutot, S., Walsh, M. R., Diaz, E., Dontsova, K., Hewitt, A. D., Walsh, M. E., Bigl, S. R., Taylor, S., MacMillan, D. K., Clausen, J. L., Lambert, D. J., Perron, N. M., Lapointe, M.-C., Brochu, S., Brassard, M., Stowe, R., Farinaccio, R., Gagnon, A., Marois, A., Gilbert, D., Faucher, D., Yost, S., Hayes, C., Ramsey, C. A., Rachow, R. J., Zufelt, J. E., Collins, C. M., Gelvin, A. B., and Saari, S. P., Characterization and Fate of Gun and Rocket Propellant Residues on Testing and Training Ranges: Interim Report 1, ERDC TR-07-1, U.S. Army Engineering Research and Development Center, Vicksburg, MS, 2007.

Jenkins, T. F., Bigl, S. R., Taylor, S., Walsh, M. R., Walsh, M. E., Hewitt, A. D., Fadden, J. L., Perron, N. M., Moors, V., Lambert, D., Bayley, R. N., Dontsova, K. M., Chappel, M. A., Pennington, J. C., Ampleman, G., Thiboutot, S., Faucher, D., Poulin, I., Brochu, S., Diaz, E., Marois, A., Fifield, L. N. R., Gagnon, A., Gamache, T., Gilbert, D., Tanguay, V., Melanson, L., Lapointe, M., Martel, R., Comeau, G., Ramsey, C. A., Quémerais, B., and Simunek, J., Characterization and Fate of Gun and Rocket Propellant Residues on Testing and Training Ranges: Final Report, ERDC TR-08-1, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, 2008.

Jent, P. J., Richard, C., Callahan, C., Levenger, R. S., and Ellis, E. R., How to Take a Truly Representative Environmental Sample, American Society of Civil Engineers, *Proceedings of 2006 GeoCongress*, vol. **187**, no. 13, pp. 1–6, American Cociety of Civil Engineers (ASCE), Atlanta, Georgia, 2006.

Kaldersi, D., Juhasz, A. L., Boopathy, R., and Comfort, S., Soils Contaminated with Explosives: Environmental Fate and Evaluation of State of the art Remediation Processes, *Pure Appl. Chem.*, vol. **83**, no. 7, pp. 1407–1484, 2011.

Keith, L. H., Environmental Sampling and Analysis: A Practical Guide, Lewis Publishers, Boca Raton, Florida, 1991.

Lachance, B., Bergeron, P. M., Bérubé, V., Sunahara, G. I., and Robidoux, P. Y., Validation of Environmental Military Threshold Values for Explosives in Soil, Final, NRC Report No. 49926, National Research Council of Canada, Montréal, 2008.

Lewis, J., Martel, R., Trépanier, L., Ampleman, G., and Thiboutot, S., Quantifying the Transport of Energetic Materials in Unsaturated Sediments from Cracked Unexploded Ordnance, *J. Environ. Qual.*, vol. **38**, no. 6, pp. 2229–2236, 2009.

Mailloux, M., Martel, R., Gabriel, U., Lefebvre, R., Thiboutot, S., and Ampleman, G., Hydrogeological Study of an Antitank Range, *J. Environ. Qual.*, vol. **37**, no. 4, pp. 1468–1476, 2008.

Marois, A., Gagnon, A., Thiboutot, S., and Ampleman, G., Caractérisation des sites de destruction d'explosifs, Base des Forces aériennes de Bagotville, DRDC Valcartier TR 2003-028, Recherche et développement pour la défense Canada–Valcartier, Québec, 2003.

Marois, A., Gagnon, A., Thiboutot, S., and Ampleman, G., Caractérisation des sols de surface dans les secteurs d'entraînement, Base des Forces Canadiennes, Valcartier, DRDC TR 2004-206, Recherche et développement pour la défense Canada–Valcartier, Québec, 2004.

Martel, R., Gabriel, U., and Deschênes-Rancourt, C., Sampling and Characterization Protocol for Groundwater, Surface Water and Water contained in the Unsaturated Zone in the Land Forces

Military Training Areas, INRS-ETE Report No. R-1298, Institut National de la Recherche Scientifique, Québec, 2012a.

Martel, R., Bordeleau, G., and Savard, M., Short- and Long-term Fate and Transport of Nitroglycerin (NG) in the Context of Double-base Propellant Residues at Antitank Firing Positions, INRS-ETE report No. R-1337, Institut National de la Recherche Scientifique, Québec, 2012b.

Martel, R., Boulianne, V., Brochu, S., Parent, G., Francoeur-Leblond, N., Lamarche, L., Ross, M., and Parent, M., Vulnerability, Hazard and Risk Maps as RTAs Management Tools NATO AVT-177 Symposium on Munition and Propellant Disposal and its Impact on the Environment, pp. 27-1–27-22, Edinburgh, 2011, Accessed March 7, 2012 from http://www.rto.nato.int/abstracts.aspx?RestrictRDP=4.

Martel, R., Mailloux, M., Gabriel, U., Lefebvre, R., Thiboutot, S., and Ampleman, G., Behavior of Energetic Materials in Groundwater and an Antitank Range, *J. Environ. Qual.*, vol. **38**, no. 1, pp. 75–92, 2009.

Martel, R., Lange, S., Côté, S., Ampleman, G., and Thiboutot, S., Fate and Behaviour of Energetic Material Residues in the Unsaturated Zone: Sand Columns and Dissolution Tests, INRS-ETE Report No. R-1161, Institut National de la Recherche Scientifique, Québec, 2010.

Monteil-Rivera, F., Halasz, A., Groom, C., Zhao, J. S., Thiboutot, S., Ampleman, G., and Hawari, J., Fate and Transport of Explosives in the Environment: A Chemist's View, Ecotoxicology of Explosives and Unexploded Ordnance, EET Series Textbook, CRC Press, Boca Raton, 2004.

Parker, L. V., Hewitt, A. D., and Jenkins, T. F., Influence of casing materials on trace level chemicals in well water, *Ground Water Monit. Rev.*, vol. **10**, pp. 146–156, 1990.

Parker, L. V. and Ranney, T. A., Effect of concentration on sorption of dissolved organics by well casings, *Ground Water Monit. Rev.*, vol. **14**, pp. 139–149, 1994.

Parker, L. V. and Ranney, T. A., Sampling Trace-Level Organic Solutes with Polymeric Tubing: I. Static Studies, *Ground Water Monit. Rem*., vol. **17**, pp. 115–1124, 1997.

Parker, L. V. and Ranney, T. A., Sampling Trace-Level Organics with Polymeric Tubing: Part 2, Dynamic Studies, *Ground Water Monit. Rem*., vol. **18**, pp. 148–155, 1998.

Pennington, J. C., Jenkins, T. F., Ampleman, G., Thiboutot, S., Branon, J. M., Lynch, J., Ranney, T. A., Stark, J. A., Walsh, M. E., Lewis, J., Hayes, C. A., Mirecki, J. E., Hewitt, A. D., Perron, N., Clausen, J., and Delfino, J. J., Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 2, ERDC TR-02-8, U.S. Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, MS, 2002.

Pennington, J. C., Jenkins, T. F., Ampleman, G., Thiboutot, S., Brannon, J. M., Lewis, J., Delaney, J. E., Clausen, J., Hewitt, A. D., Hollander, M. A., Hayes, C. A., Stark, J. A., Marois, A., Brochu, S., Dinh, H. Q., Lambert, D., Martel, R., Brousseau, P., Perron, N. M., Lefebvre, R., Davis, W., Ranney, T. A., Gauthier, C., Taylor, S., and Ballard, J. M., Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 3, ERDC TR-03-02, U.S. Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, MS, 2003.

Pennington, J. C., Jenkins, T. F., Ampleman, G., Thiboutot, S., Brannon, J., Clausen, J., Hewitt, A. D., Brochu, S., Dubé, P., Lewis, J., Ranney, T., Faucher, D., Gagnon, A., Stark, J., Brousseau, P., Price, C., Lambert, D., Marois, A., Bouchard, M., Walsh, M., Yost, S., Perron, M., Martel, R., Jean, S., Taylor, S., Hayes, C., Ballard, J., Walsh, M.E., Mirecki, J., Downe, S., Collins, N., Porter, B., and Richard, K., Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 4, ERDC/EL TR-04-4, U.S. Army Engineer Research and Development Center, Vicksburg, MS, 2004.

Pennington, J. C., Jenkins, T. F., Thiboutot, S., Ampleman, G., Clausen, J., Hewitt, A. D., Lewis, J., Walsh, M. R., Walsh, M. E., Ranney, T. A., Silverblatt, B., Marois, A., Gagnon, A., Brousseau, P., Zufelt, J. E., Poe, K., Bouchard, M., Martel, R., Walker, D. D., Ramsey, C. A., Hayes, C., Yost, S. L., Bjella, K. L., Trépanier, L., Berry, T. E., Lambert, D., Dubé, P., and Perron, N. M., Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 5, ERDC TR-05-2, U.S. Army Engineer Research and Development Center, Vicksburg, MS, 2005.

Pennington, J. C., Jenkins, T. F., Ampleman, G., Thiboutot, S., Hewitt, A. D., Brochu, S., Robb, J., Diaz, E., Lewis, J., Colby, H., Martel, R., Poe, K., Groff, K., Bjella, K., Ramsey, C. A., Hayes, C. A., Yost, S., Marois, A., Gagnon, A., Silverblatt, B., Crutcher, T., Harriz, K., Heisen, K., Bigl, S. R., Berry, J., Thomas E., Muzzin, J., Lambert, D. J., Bishop, M. J., Rice, B., Wojtas, M., Walsh, M. E., Walsh, M. R., and Taylor, S., Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 6, ERDC TR-06-12, U.S. Army Engineer Research and Development Center, Vicksburg, MS, 2006a.

Pennington, J. C., Jenkins, T. F., Ampleman, G., Thiboutot, S., Brannon, J. M., Hewitt, A. D., Lewis, J., Brochu, S., Diaz, E., Walsh, M. R., Walsh, M. E., Taylor, S., Lynch, J. C., Clausen, J., Ranney, T. A., Ramsey, C. A., Hayes, C. A., Grant, C. L., Collins, C. M., Bigl, S. R., Yost, S., and Dontsova, K., Distribution and Fate of Energetics on DoD Test and Training Ranges: Final Report, ERDC TR-06-13, U.S. Army Engineer Research and Development Center, Vicksburg, MS, 2006b.

Pennington, J. C., Hayes, C., Yost, S., Crutcher, T., Betty, T. E., Clarke J. U., and Bishop, M. J., Explosive Residues from Blow-in-Place Detonations of Artillery Munitions, *Soil Sediments Contam.*, vol. **17**, no. 2, pp. 163–180, 2008a.

Pennington, J. C., Silverblatt, R., Poe, K., Hayes, C., and Yost, S., Explosive Residues from Low-Order Detonations of Heavy Artillery and Mortar Rounds, *Soil Sediment Contam.*, vol. **17**, no. 5, pp. 533–546, 2008b.

Pennington, J. C., Jenkins, T. F., Brannon, J. M., Lynch, J., Ranney, T. A., Berry, J., Thomas, E., Hayes, C. A., Miyares, P. H., Walsh, M. E., Hewitt, A. D., Perron, N., and Delfino, J. J., Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 1, ERDC TR-01-13, U.S. Army Engineer Research and Development Center, Vicksburg, MS, 2001.

Poulin, I., Diaz., E., and Quémerais, B., Airborne Contaminants in Two Antitank Weapons Back Blast Plume: Carl Gustav 84-mm and M72 66-mm, DRDC Valcartier TR 2008-242, Defence Research and Development Canada–Valcartier, Québec, 2008a.

Poulin, I., Diaz., E., and Quémerais, B., Particulate Matter Emitted from the M777 Howitzer During Live Firing, DRDC Valcartier TR 2008-215, Defence Research and Development Canada–Valcartier, Québec, 2008b.

Poulin, I. and Diaz, E., Airborne Particulate Matter Emissions During Live Firing of LG1 Mark II 105-mm Howitzer, DRDC Valcartier TM 2007-297, Defence Research and Development

Canada–Valcartier, Québec, 2008.

Quémerais, B., Diaz, E., Poulin, I., and Marois, A., Characterization of Atmospheric Emission Produced by Live Gun Firing: Test on the Carl Gustav Antitank 84-mm Weapon, DRDC Toronto TR 2007-103, Defence Research and Development Canada–Toronto, Toronto, 2007a.

Quémerais, B., Melanson, L., Ampleman, G., Thiboutot, S., Poulin, I., and Diaz, E., Characterization of Atmospheric Emissions During Live Gun Firing at the Muffler Installation in Nicolet, Lac St. Pierre, Canada: Test on Howitzer 105 mm, DRDC Toronto TR 2007-060, Defence Research and Development Canada–Toronto, Toronto, 2007b.

Robertson, T. J., Martel, R., Quan, D. M., Ampleman, G., Thiboutot, S., Jenkins, T., and Provatas, A., Fate and Transport of 2,4,6-Trinitrotoluene in Loams at a Former Explosives Factory, *Soil Sediment Contam.*, vol. **16**, no. 2, pp. 159–179, 2007.

Robidoux, P. Y., Svendsen, C., Caumartin, J., Hawari, J., Ampleman, G., Thiboutot, S., Weeks, J. M., and Sunahara, G. I., Chronic Toxicity of Energetic Compounds in Soils Determined Using the Earthworm (Eisenia Andrei) Reproduction Test, *Environ. Toxicol. Chem.*, vol. **19**, no. 7, pp. 1764–1773, 2000.

Robidoux, P. Y., Hawari, J., Thiboutot, S., Ampleman, G., and Sunahara, G. I., Chronic Toxicity of Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine (HMX) in Soil Determined Using the Earthworm (Eisenia Andrei) Reproduction Test, *Environ. Pollut.*, vol. **111**, pp. 283–292, 2001.

Robidoux, P. Y., Svensen, C, Sarazin, M., Thiboutot, S. Ampleman, G., Hawari, J., Weeks, J. M., and Sunahara, G. I., Assessment of a 2,4,6-TNT Contaminated Site Using Apporectodea Rosea and Eisenia Andrei in Mesocosms, *Arch. Environ. Contam. Toxicol.*, vol. **48**, pp. 56–67, 2005.

Robidoux, P. Y., Lachance, B., Didillon, L., Dion, F. O., and Sunahara, G. I., Development of Ecological and Human Health Preliminary Soil Quality Guidelines for Energetic Materials to Ensure Training Sustainability of the Canadian Forces, NRC Report No. 45936, National Research Council of Canada, Montréal, 2006.

Rocheleau, S., Lachance, B., Kuperman, R. G., Hawari, J., Thiboutot, S., Ampleman, G., and Sunahara, G., Toxicity and Uptake of Cyclic Nitramine Explosives in Ryegrass Lolium Perenne, *Environ. Pollut.*, vol. **156**, no. 1, pp. 199–206, 2008.

Sarrazin, M., Doddard, S. G., Savard, K., Lachance, B., Robidoux, P. Y., Kuperman, R., Hawari, J., Ampleman, G., Thiboutot, S., and Sunahara, G., Accumulation of Hexahydro-1,3,5-Trinitro-1,3,5-Triazine by the Earthworm Eisenia Andrei in a Sandy Loam Soil, *Environ. Toxicol. Chem.*, vol. **28**, no. 10, pp. 2125–2133, 2009.

Sunahara, G. I., Robidoux, P. Y., Gong, P., Lachance, B., Rocheleau, S., Dodard, S. G., Sarrazin, M., Hawari, J., Thiboutot, S., Ampleman, G., and Renoux, A. Y., Laboratory and Field Approaches to Characterize the Soil Exotoxicology of Polynitro Explosives, Environmental Toxicology and Risk Assessment: Science, Policy and Standardization-Implications for Environmental Decisions: Tenth Volume, ASTM STP 1403, Greenberg, B. M., Hull, R. N., Roberts, Jr., M. H., and Gensemer, R. W. (eds.), ASTM, W. Conshohocken, PA, pp. 293–312, 2001.

Sunahara, G., Lotufo, G., Kuperman, R., Hawari, J. Thiboutot, S., and Ampleman, G., *Ecotoxicology of Explosives*, CRC Press, Taylor and Francis Group, Montréal, 2009.

Taylor, S., Campbell, S., Perovich, L., Lever, J., and Pennington, J., Characteristics of Composition B Particles from Blow-in-Place Detonations, *Chemosphere*, vol. **65**, no. 8, pp. 1405–1413, 2006.

Thiboutot, S., Ampleman, G., Dubé, P., Hawari, J., Spencer, B., and Paquet, L., Protocol for the Characterization of Explosives Contaminated Sites, DREV-R-9721, Defence Research Establishment Valcartier, Val-Bélair, Quebec, 1997.

Thiboutot, S., Ampleman, G., Gagnon, A., Marois, A., Jenkins, T. F., Walsh, M. E., Thorne, P. G., and Ranney, T. A., Characterization of Antitank Firing Ranges at CFB Valcartier, WATC Wainwright and CFAD Dundurn, DREV R-9809, Defence Research Establishment Valcartier, Val-Bélair, 1998.

Thiboutot, S., Ampleman, G., Gagnon, A., and Marois, A., Characterization of an Unexploded Ordnance Contaminated Range (Tracadie Range) for Potential Contamination by Energetic Materials, DREV TR 2000-102, Defence Research Establishment Valcartier, Val-Bélair, Quebec, 2000.

Thiboutot, S., Ampleman, G., Lewis, J., and Brochu, S., Evaluation of Heavy Metals Contamination at CFAD Dundurn Resulting from Small-Arms Ammunition Incineration, DREV TR-2001-127, Defence Research Establishment Valcartier, Val-Bélair, Quebec, 2001a.

Thiboutot, S., Ampleman, G., Martel, R., Paradis, D., and Lefebvre, R., Environmental Characterization of Canadian Forces Base Shilo Training Area (Battleruns) Following GATES Closure, DREV TR 2001-126, Defence Research Establishment Valcartier, Val-Bélair, Quebec, 2001b.

Thiboutot, S., Ampleman, G., and Hewitt, A., Guide for Characterization of Sites Contaminated with Energetic Materials, ERDC-CRREL TR-02-01, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, 2002.

Thiboutot, S., Ampleman, G., Hamel, A., Ballard, J. M., Martel, R., Lefebvre, R., and Downe S., Research on the Environmental Conditions of Groundwater and Surface Water Prevailing in the Training Area at CFB Gagetown, New Brunswick, DRDC Valcartier TR 2003-016, Defence Research and Development Canada-Valcartier, Québec, 2003a.

Thiboutot, S., Ampleman, Lewis, J., Faucher, D., Marois, A., Martel, R., Ballard, J. M., Downe S., Jenkins, T., and Hewitt, A., Environmental Conditions of Surface Soils and Biomass Prevailing in the Training Area at CFB Gagetown, New Brunswick. DRDC Valcartier TR 2003-152, Defence Research and Development Canada-Valcartier, Québec, 2003b.

Thiboutot S., Ampleman G., Brochu S., Martel R., Sunahara, G., Hawari, J., Nicklin, S., Provatas, A., Pennington, J. C., Jenkins, T. F., and Hewitt, A., Protocol for Energetic Materials-Contaminated Sites Characterization, Vol. 2, Final Report No. TTCP WPN-4 KTA 4-28, Quebec, 2003c, available at http://www.em-guidelines.org

Thiboutot, S., Ampleman, G., Marois, A., Gagnon, A., Bouchard, M., Hewitt, A., Jenkins, T., Walsh, M. E., and Bjella, K., Environmental Condition of Surface Soils, CFB Gagetown Training Area: Delineation of the Presence of Munitions Related Residues (Phase III, Final Report), DRDC Valcartier TR 2004-205, Defence Research and Development Canada-Valcartier, Québec, 2004.

Thiboutot, S., Ampleman, G., Marois, A., and Gagnon, A., Caractérisation des sols de surface du champ de tir et secteurs d'entraînement de la Garnison Valcartier, DRDC Valcartier TR 2008-190, Recherche et développement pour la défense Canada–Valcartier, Québec, 2008a.

Thiboutot, S., Ampleman, G., Lapointe, M. C., Brochu, S., Brassard, M., Stowe, R., Farinaccio, R., Gagnon, A., Marois, A., and Gamache, T., Study of the Dispersion of Ammonium Perchlorate Following the Static Firing of MK-58 Rocket Motors, DRDC Valcartier TR 2008-240, Defence Research and Development Canada–Valcartier, Québec, 2008b.

Thiboutot, S., Ampleman, G., Marois, A., Gagnon, A., Gilbert, D, Tanguay, V., and Poulin, I., Deposition of Gun Propellant Residues from 84-mm Carl Gustav Rocket Firing, DRDC Valcartier TR 2007-408, Defence Research and Development Canada–Valcartier, Québec, 2008c.

Thiboutot, S., Ampleman, G., Marois, A., Gagnon, A., and Gilbert, D., Nitroglycerine Deposition from M-72 Antitank Rocket Firing, DRDC TR-2009-003, Defence Research and Development Canada–Valcartier, Québec, 2009.

Thiboutot, S., Ampleman, G., Gagnon, A., Marois, A., Martel, R., and Bordeleau, G., Persistence and Fate of Nitroglycerin in Legacy Antitank Range, DRDC Valcartier TR 2010-059, Defence Research and Development Canada–Valcartier, Québec, 2010.

Thiboutot, S., Ampleman, G., Kervarec, M., Cinq-Mars, A., Gagnon, A., Marois, A., Poulin I., Boucher, F., Lajoie R., Legault, K., Withwell, S., Sparks, T., Eng, J., Cartier, M., and Archambault, P., Development of a Table for the Safe Burning of Excess Artillery Propellant Charge Bags, DRDC TR-2010-254, Defence Research and Development Canada–Valcartier, Québec, 2011.

Thiboutot, S., Ampleman, G., Brochu, S., Poulin, I., Marois, A., and Gagnon, A., Guidance Document: Surface Soils Sampling for Munition Residues in Military Live-Fire Training Ranges, DRDC Valcartier TR 2011-447, 2012.

U.S. EPA, Inductively Coupled Plasma–Mass Spectrometry, EPA SW-846 Method 6020A, Revision 0, U.S. Environmental Protection Agency, 1994, accessed March 7, 2012 from http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/6020a.pdf

U.S. EPA, Nitroaromatics, Nitramines and Nitrate Esters by High Performance Liquid Chromatography (HPLC), EPA SW-846 Method 8330B, Rev. 2, 2006, accessed March 7^{th}, 2012 from http://www.epa.gov/epawaste/hazard/testmethods/pdfs/8330b.pdf

U.S. EPA, Inductively Coupled Plasma–Atomic Emission Spectrometry, EPA SW-846 Method 6010C, Rev. 3, U.S. Environmental Protection Agency, 2007, accessed March 8, 2012 from http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/6010c.pdf

Voie, O., Stomseng, A., Johnse, A., Rossland, H. K., Karsrud, T., and Longva K., Veiler for Undersokelse, Risikovurdering, Opprydning og Avhending av Skytebane og Ovingsfelt (Protocol for Investigation, Risk Assessment, Cleanup and Disposal of Shooting Range and Training Area), Forsvaret Forskninginstitutt/Norwegian Defence Research Establishment Report No. FFI 2010/00116 Kjeller, 2010.

Walsh, M. E., Ramsey, C. A., and Jenkins, T. F., The Effect of Particle Size Reduction by Grinding on Sub-Sampling Variance for Explosives Residues in Soil, *Chemosphere*, vol. **49**, no. 10, pp. 1267–1273, 2002.

Walsh, M. E., Collins, C. M., Hewitt, A. D., Walsh, M. R., Jenkins, T. F., Stark, J., Gelvin, A., Douglas, T. S., Perron, N., Lambert, D., Bailey, R., and Myers, K., Range Characterization

Studies at Donnelly Training Area, Alaska: 2001 and 2002, ERDC/CRREL TR-04-3, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, 2004.

Walsh, M. R., Walsh, M. E, Collins, C. E., Saari, S. P., Zufelt, J. E., Gelvin, A. B., and Hug, J. W., Energetic Residues from Live-Fire Detonations of 120-mm Mortar Rounds, ERDC/CRREL TR-05-15, U.S. Army Engineer Research and Development Center, Hanover, NH, 2005.

Walsh, M. R., Ramsey, C. A., Rachow, R. J., Zufelt, J. E., Collins, C. M., Gelvin, A. B., Perron, N. M., and Saari, S. P., Energetic Residues Deposition from a 60-mm and 80-mm Mortars, ERDC-CRREL TR-06-10. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, 2006.

Walsh, M. R., Walsh, M. E., Bigl, S. R., Perron, N. M., Lambert, D. J., and Hewitt, A. D., Propellant Residues Deposition from Small Arms Munitions, ERDC/CRREL TR-07-17, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, 2007a.

Walsh, M. R., Walsh, M. E., and Ramsey, C. A., Measuring Energetic Residues on Snow, ERDC Report ERDC/CRREL TR-09-13, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, 2007b.

Walsh, M. R., Walsh, M. E., Thiboutot, S., Ampleman, G., and Bryant, G., Propellant Residues Deposition from Firing of AT4 Rockets, ERDC Report No. ERDC/CRREL TR-09-13, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, 2009.

Walsh, M. R., Walsh, M. E., Taylor, S., Poulin, I., Thiboutot, S., and Ampleman, G., Explosives Residues on Military Training Ranges, Proceedings of the NATO AVT-177 Symposium on Munition and Propellant Disposal and its Impact on the Environment, Edinburgh, pp. 27-1–27-22, 2011a, accessed March 7, 2012 from http://www.rto.nato.int/abstracts.aspx?RestrictRDP=4.

Walsh, M. R., Thiboutot, S., Walsh, M. E., Ampleman, G., Martel, R., Poulin, I., Taylor, S., Characterization and Fate of Gun and Rocket Propellant Residues on Testing and Training Ranges: Final Report (SERDP ER-1481 phase 2), US Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, Technical Report No. ERDC/CRREL TR-11-132011b.

Zhao, J. S., Fournier, D., Thiboutot, S., Ampleman, G., and Hawari, J., Biodegradation and Bioremediation of Explosives, *Soil Biology, Bioremediation, Phytoremediation and Natural Attenuation*, Vol. 1, Singh A. and Ward, O. (eds.), Springer-Verlag, Berlin, pp. 55–80, 2004.

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EVALUATION OF GIM AS A GREENER INSENSITIVE MELT-CAST EXPLOSIVE

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For years, DRDC Valcartier has invested efforts at developing energetic thermoplastic elastomers (ETPEs) based on linear glycidyl azide polymers to serve as energetic binders and replacing the thermoset matrix in insensitive explosives. It was first observed that introducing ETPEs in their melted form was not an easy task because high and nonpractical viscosities were encountered in the process. It was discovered that 2,4,6-trinitrotoluene (TNT) could be used in its melted form as an organic solvent to dissolve the ETPE and allow its incorporation into the insensitive formulations. Using these ETPEs led to the development of a greener insensitive melt-cast explosive named green insensitive munitions (GIM). This new explosive was intensely studied. The mechanical properties and proportions of ETPE in the formulations were optimized to obtain a melt cast with low viscosity while leading to an insensitive explosive formulation. Work was conducted on GIM explosives to test their performance and sensitivity, fate and behavior with regard to the environment, their recycling capability, and toxicity. This paper describes the results of all experiments conducted so far to test these aspects of GIM explosives. The preparation of the ETPEs and the GIM explosives will also be briefly described.

KEY WORDS: *thermoplastic, elastomer, GAP, XRT, GIM*

NOMENCLATURE

BAMO	bis-3,3-azidomethyl oxetane
BRI-NRC	Biotechnology Research Institute—National Research Council
C4	demolition explosive made of 91% RDX and plasticizer in polyisobutylene
CL-20	2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane
DADNE	1,1-diamino-2,2-dinitroethene
DNAN	dinitroanisole
DOA	dioctyl adipate
DRDC	Defence Research and Development Canada
EC_{20}	effect concentration which causes a 20% inhibition
EC_{50}	effect concentration which causes a 50% inhibition
ETPE	energetic thermoplastic elastomer
FOX 7	Same as DADNE
FOX 12	N-guanylurea-dinitramide
GAP	glycidyl azide polymer
GIM	green insensitive munitions
HMX	high-melting explosive, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine
HTPB	hydroxyl-terminated polybutadiene
INRS-ÉTÉ	Institut National de la Recherche Scientifique, Centre Eau Terre et Environnement
IM	insensitive munitions
LC_{50}	lethal concentration which causes a 50% mortality
NTO	3-nitro-1,2,4-triazol-5-one
PBX	plastic-bonded explosive or polymer-bonded explosive
RIGHTTRAC	revolutionary insensitive, green and healthier training technology with reduced adverse contamination
RDX	research & development explosive, hexahydro-1,3,5-trinitro-1,3,5-triazine
SERDP	Strategic Environmental R&D Program
TDP	Technology Demonstration Program
TNT	2,4,6-trinitrotoluene
XRT	experimental rubbery TNT

1. INTRODUCTION

For the last two decades, insensitive explosives development has been at the heart of research and development work (R&D) in most military organizations. More recently, the development of insensitive explosives raised in importance in Canada because these explosives are safer for the Canadian Forces personnel and they allow interoperability between the Allied Forces. In many countries, efforts are being made to develop and field new insensitive energetic formulations. As an example, the USA has recently developed and put into service an insensitive explosive based on 2,4-dinitroanisole (DNAN) and 3-nitro-1,2,4-triazol-5-one (NTO), but little is known about the environmental toxicity, fate, and behavior of these compounds (Di Stasio,2009; Niles and Doll, 2001; Fung et al., 2009; Samuels, 2009). Because of that, many other explosives are evaluated as potential 2,4,6-trinitrotoluene (TNT) and research and development explosives, e.g., 1,3,5-trinitro-1,3,5-triazine (RDX), replacements. Furthermore, because of the environmental impacts of munitions and energetic materials in general, formulations now need to be greener, meaning that their environmental footprint should be lower than existing formulations. There is still a lot of work to be conducted before the best green and insensitive melt-cast explosive formulation is identified and accepted by the formulators, the managers, and the people concerned by environmental impacts.

The development of insensitive explosives can be separated into two main technologies based on the processes used to produce them. The first process involves the use of a cast-cured polymer-bonded system. These explosives are called "cast-cured explosives" or often "plastic or polymer-bonded explosives" (PBX). This type of explosives used to dominate insensitive munitions (IM) explosive development. The second type of explosives is the melt-cast explosive. In this case, the explosives are melted and cast into shells. More recently, there has been an increased interest for insensitive melt-cast explosives, mostly based on DNAN and NTO. This renewed interest for insensitive melt-cast explosives is related to their lower costs and ease of production, as presently, most of the manufactured explosives are made by melt-cast technology. Furthermore, melt-cast technology is mature and well understood, and as a result, there are much more industrial melt-cast facilities than any other types of casting. While PBXs were previously used in large, high-cost items such as missiles or bombs, new uses have been identified in smaller weapons such as mortars or artillery shells. Pelletier et al. (2009) presented a good example of this in the demonstration of the French RDX/hydroxyl-terminated polybutadiene (HTPB)-based HBU88B in the US 120-mm mortar. New PBX formulations are also being created with tailored properties for specific applications such as boosters or for blast. They either make use of older explosive crystals known for their insensitive properties, such as NTO, or use new promising molecules such as 1,1-diamino-2,2-dinitroethene (DADNE, FOX-7), N-guanylurea-dinitramide (FOX-12), or 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) (Anderson et al., 2009; Bergman et al., 2009; Hatch et al., 2009; Nouguez and Mahé, 2009; Spyckerelle and Eck, 2009). Compared to melt-cast explosives, the cast-cured PBXs are more difficult to process, to recycle, and are generally more expensive.

In 1988, Defence Research and Development Canada (DRDC) Valcartier started investing efforts in the development of insensitive energetic materials. At this time, environmental pressure and the need for interoperability between allied armies gave the momentum for this new area of research. It was soon realized that formulating energetic materials that would be insensitive, environmentally friendly, and produced at low cost was not an easy task. Many efforts were done worldwide to work with glycidyl azide polymer (GAP) as an energetic binder. In 1995, radioactive carbon-14 GAP was prepared to evaluate its degradability (Ampleman et al., 1995). It was demonstrated that

GAP, although insoluble in water, was mineralized at 10–20% by indigenous microbes (Jones et al., 1996). Later in 2004, ATK Alliant Techsystems conducted a study for the Strategic Environmental R&D Program (SERDP) where they found that ETPEs based on GAP and poly-bis-3-azidomethyl oxetane (BAMO) were nontoxic to mice (Cohen et al., 2004; Ampleman et al., 2002) and developed at DRDC Valcartier new energetic thermoplastic elastomers (ETPEs) based mainly on linear GAP to give the insensitive character to the formulations. These energetic thermoplastic elastomers were prepared by using GAP as macromonomers reacted with 4,4'-methylenebis (phenyl isocyanate). By doing so, energetic copolyurethane thermoplastic elastomers were obtained, and these rubbery, physically cross-linked matrices were mixed with secondary explosives which provided the basis for a new generation of insensitive explosives. Many approaches were taken to develop ETPEs, and the complete description of GAP, their synthesis, and the ETPEs obtained from them were published (Ampleman et al., 1988; Ampleman, 2010). Later, the toxicity of these ETPEs was evaluated and it was demonstrated that they were nontoxic and could be considered as a green ingredient (Monteil-Rivera et al., 2008).

The original objective of the ETPE project at DRDC Valcartier was to develop ETPEs that could melt at 85°C and behave as a GAP-cured system to replace TNT in melt-cast formulations. The main problem of incorporating these ETPEs into melt-cast insensitive explosive formulations resides in the fact that the melt-cast process is a solventless process and, in such cases, once melted, ETPEs would give very high mix viscosities. Furthermore, our copolyurethane thermoplastic elastomer decomposes before melting. It was found that melted TNT could act as an organic solvent and was able to dissolve the ETPE matrix, resulting in acceptable processing viscosities. A new insensitive explosive was then prepared. It is only later that the green characteristics became very important because nowadays, it would be unwise to develop an explosive that has a negative environmental footprint.

It is known that TNT is toxic, and the environmental fate and transport of TNT were demonstrated by Sheremata et al. (1999) and Monteil-Rivera et al. (2009). They showed that in the environment, this explosive degrades rapidly by photolysis or biotransformation into 2- and 4-aminodinitrotoluene and other metabolites that form covalent bonds with the organic matter of soils, making it not bioavailable. This means that TNT, once released in the environment, reacts and cannot reach ecological or human receptors, making it less environmentally threatening when used in live firing activities. This was demonstrated on antitank ranges in Canada by Mailloux et al. (2008), as high concentrations of high-melting explosive (HMX), 1,3,5,7-tetranitro-1,3,5,7-tetrazine, were observed while no TNT was, even if the explosive formulation used there was Octol, which is based on both compounds. The idea of dissolving the ETPE in melted TNT was therefore studied and resulted in the development of an insensitive explosive named "XRT" for "experimental rubbery TNT." This explosive was obtained by mixing the ETPE with Composition B. However, the nitramine RDX has proven to be both toxic and highly mobile in the environment, while HMX is much less soluble, toxic, and mobile. Replacing RDX by HMX using Octol instead of Composition B led directly to the development of a new greener insensitive munitions (GIM) recyclable explosive. For this explosive, Ampleman et al. (2003) used GAP of molecular weight 2000 as the macromonomer to obtain the best mechanical properties and melted viscosity for the copolyurethane thermoplastic elastomers used for the GIM preparation. Diaz et al. (2001) studied the structure of the ETPE and confirmed that the best candidate was obtained with GAP 2000. Because ETPEs are recyclable, an easier disposal and reuse of the formulations at the end of their life cycle can be accomplished.

More recently, a technology demonstration program (TDP) named RIGHTTRAC, which stands for “Revolutionary Insensitive Green and Healthier Training Technology with Reduced Adverse Contamination,” was initiated using greener explosives (such as GIM), greener propellants, and a self-destructive device system to produce a greener weapon. A tremendous amount of work has been dedicated to these compounds, in particular, to the GIM explosive. This paper describes the preparation of the ETPEs, the XRT, and mostly the greener explosives GIM. The paper will also present results of the performance characterization, the IM character, the fate and environmental behavior that encompass the dissolution rate, transport and fate in soil and in water, and toxicity measurements.

2. SYNTHESIS, IM TESTS, AND VARIOUS OTHER TESTS

2.1 Synthesis of ETPEs

The preparation of ETPE 2000 was described earlier by Ampleman et al. (2002, 2003) and Diaz et al. (2001). The most important factor to consider in these syntheses is the dryness of the reactants and reaction mixture. Water should be avoided in the reaction and a precise NCO/OH ratio must be observed to get the desired and highest molecular weight for the linear copolyurethane thermoplastic elastomer. When water is present, carbamic acid is formed, and upon decarboxylation, an amine is formed, reacting 100 times faster with isocyanate than the secondary hydroxyl groups of the macromonomer. As a result, chemical crosslinking is formed and lower molecular weights are observed, which renders the polymer insoluble. Having a NCO/OH ratio greater than 1 would also result in chemical crosslinking from allophanate and biuret bond formation, while a NCO/OH ratio lower than 1 would result in lower molecular weight and may give unwanted behavior, as it will be described later. Years ago, 3M was interested in producing our ETPEs based on GAP prepolymers and is at this moment the only source for these products. For the RIGHTTRAC program, a commercial sample prepared by 3M in Minnesota was used for the preparation of the GIM explosives. This sample was prepared using a GAP macromonomer having a molecular weight (M_w) of 2400 g/mol.

2.2 Synthesis of XRT and GIM Explosives

The first formulations of XRT explosives were carried out using a 10% concentration of ETPE 2000 (Ampleman et al., 2003). After refinement of the process and adjustment of the viscosity of the melt-cast mixes, the best results were obtained with a 6% concentration of ETPE 2000. The ETPE 2000 was dissolved in melted Composition B and the mixture was stirred until homogeneity was obtained. The resulting mixture could be poured on a flat surface to make what we refer to as “cookies” upon cooling that could be used later in the filling of shells, or could be poured directly into shells.

The development of the XRT explosives led directly to the preparation of GIM explosives using melted Octol instead of Composition B. HMX is considered more environmentally friendly due to its lower solubility and toxicity. Moreover, as already mentioned, the ETPE is also considered green. In the case of the GIM explosive, the preparation and procedures were almost identical but this time, the concentration of the ETPE 2000 was adjusted at 9.5% to obtain the best results. The concentration of ETPE is a key parameter and must be adjusted to obtain the best IM properties while keeping the melt-cast viscosity at the lowest level possible to allow the use of industrial melt-cast facilities while minimizing the HMX sedimentation. Most efforts were done on the GIM explosive. The following results are related to GIM rather than XRT, even if they are very similar.

In the RIGHTTRAC TDP, two candidates were evaluated for the green explosive—a PBX and the GIM explosive. The GIM explosive was chosen based on its energy, performance, IM characteristics, and environmental footprint. The PBX used for comparison is a Canadian composition called CX-85. The explosive is made of 84.25% HMX and has an HTPB/dioctyl adipate (DOA) binder system cured with isophorone diisocyanate (IPDI). The surface agent system is proprietary. The whole formulation is a small modification of compositions presented before by Hooton (1992). This explosive was deemed a good generic PBX with a decent performance compared to Composition B (because of the HMX) and hence was tested at the same time as the GIM for comparison purposes.

2.3 IM Tests on Explosives

IM tests were conducted at DRDC Valcartier mainly with 105-mm shells filled by either GIM or PBX (CX-85). These tests were also conducted on 105-mm shells filled with Composition B for comparison. Bullet impact, sympathetic detonation, shaped charge jet, and slow cook-off tests were made and the results were analyzed based on a scaling from 1 to 5 and overpressure collected according to Annex A of various NATO STANAGs (2003a,b,c, 2004).

2.4 Bullet Impact

The weapon used for these tests was 0.5 in. armour piercing and the bullet velocity was 850 ± 30 m s^{-1}, as described in STANAG 4241 (2003a). Evaluation of the reactions was done using the air overpressure and characterization of the fragments collected (STANAG 4241, 2003a). Composition B presented type 1 and 2 reactions and failed the test, while GIM and PBX led to type-5 reactions and passed the test. Figure 1 shows that the bullet passed through the shell without reaction in the GIM shell.

2.5 Sympathetic Detonation

During the test, a shell was used as a donor and another was used as an acceptor. Two other witness empty shells were placed in the assembly for confinement (Fig. 2). To evaluate the result, an overpressure sensor was used to measure air pressure. Outcome evaluation was also made by characterizing the size of the fragments collected, in accordance with Annex A of STANAG 4396 (2003b). The projectile with the white cap (C4) is the donor and the acceptor is the one with a fluorescent orange color. The other projectiles were empty and were used only for confinement. Composition B and GIM

FIG. 1: Bullet impact result on GIM explosive.

FIG. 2: Sympathetic detonation setup.

had type-3 reactions and passed the test, while PBX had no reaction and also passed the test.

2.6 Shaped Charge Jet

The test was conducted with the setup illustrated in Fig. 3. The shaped charge was fired and the jet was oriented and directed to the shell. The air-pressure measurement was performed by overpressure sensors. The result evaluation was carried out by these pressures and the size of fragments collected. In all cases, type-1 reaction and multiple fragments were obtained, and none of the formulations passed the STANAG 4526 test (2004).

2.7 Slow Cook-Off

The test was conducted using an oven in which the temperature was measured at the bottom and front, top and rear, top and center, and also in the explosive inside the shell (Fig. 4).

The heating of the sample was done as follows: the experiment started at room temperature and the temperature was increased to 100°C in 30 min, then maintained for 90

FIG. 3: Shaped charge test setup.

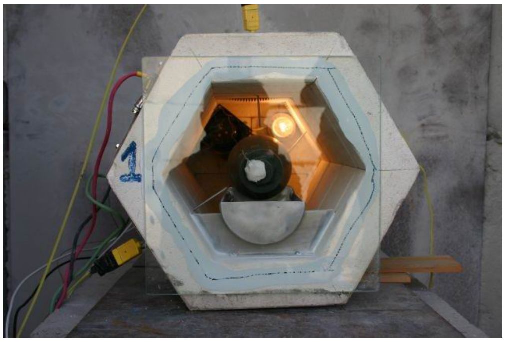

FIG. 4: Oven setup for the slow cook-off.

additional minutes. A heating rate of 25°C h^{-1} was then applied until a reaction occurred. Pressure sensors were installed to measure the overpressure, but no values were observed since only burning reactions were obtained. The evaluation of the results was done visually according to STANAG 4382 (2003c).

Unexpected results were observed for the PBX formulation. In this case, the explosive slowly extruded out of the shell, pushed out by an important quantity of gas formed during the heating period. The extruded material appeared cracked and porous. The released gases were flammable and ignited a fire upon contact with the heater. Following the gaseous ignition, the PBX started burning 2.5 min later. The burning reaction appeared to start into the gas phase instead of the explosives, which is not desirable. Nevertheless, type-5 reactions were observed for all formulations, including Composition B, and all formulations passed the test.

All the IM tests revealed that GIM and PBX have insensitive behavior. In sympathetic detonation, the PBX behaved in a better way, showing no reaction, but the GIM explosive passed the test with a type-3 reaction which is acceptable. For the slow cook-off, even if the PBX passed the test, the formation of flammable gases during the reaction is undesirable.

If these two explosives are insensitive, one would wonder if it is possible to blow them up using the conventional C4 blocks method. Recent experiments were conducted to blow in place 105-mm shells filled with GIM and PBX CX-85 in different setups. All the projectiles went high order using one C4 block (500 g) during the blow-in-place operations. These results will be published later. These experiments demonstrated that it is possible to have an insensitive explosive having a good performance, not reacting to unwanted stimuli and still responding to conventional destruction methods using a C4 block.

3. STABILITY AND PERFORMANCE EVALUATION

In addition to the IM tests, XRT and GIM formulations were evaluated by vacuum stability tests, impact and friction sensitivity (BAM), density, and viscosities of the melted mix measurements. The viscosities were measured directly in the mixer equipped with a temperature control bath at 95°C using a Brookfield rheometer (model LVDV-III+). Helipath T spindles at sizes C and D were in with shear mode (Y) at 5,10, 15, and 20 RPM. Furthermore, performance and shock sensitivity tests (gap tests) were also conducted. All the results from these tests are found in Table 1.

Vacuum stability tests showed a maximum gas evolution for XRT and GIM of 0.8 mL cm^{-3}. Impact sensitivity tests gave for both XRT and GIM a 20 N m value compared to 10, 7.5, and 5 N m for TNT, Octol, and Composition B, respectively. The friction sensitivity tests gave 360 N for XRT and GIM compared to 80, 120, and 240 N for TNT, Octol, and Composition B, respectively. Our best products obtained with Composition B mixed with ETPE 2000 at 6% w/w (XRT) and Octol mixed with ETPE 2000 at 9.5%

TABLE 1: Stability, performance, and IM results for XRT and GIM explosives

Test method	XRT 6%	GIM 9.5%
Vacuum stability	0.8 mL cm^{-3}	0.8 mL cm^{-3}
Drop weight impact	20 N	20 N
Friction	360 N	360N
Density	1.65 g cm^{-3}	1.67 g cm^{-3}
Viscosity	40 poises	50 poises
Detonation velocity	7689 m s^{-1}	7726 m s^{-1}
Detonation pressure	24.2 GPa	24.9 GPa
Plate dent	91.2% Comp B	96% Comp B
Large scale GAP card	167 cards	188 cards

w/w (GIM) have densities of 1.65 and 1.67 g cm^{-3}, and viscosities of 40 and 50 poises, respectively.

Brousseau et al. (2004, 2010) evaluated the performance and showed that the detonation velocity is 7689 and 7726 m s^{-1} for XRT 6% and GIM, respectively. The detonation pressure was calculated at 24.2 GPa for XRT (92% of Composition B) and at 24.9 GPa for GIM (94% of Composition B). The plate dent test confirmed 91.2% Composition B for XRT and 96% Composition B for GIM with 0.76 ± 0.01 cm. Large-scale gap tests revealed a value of 167 cards for XRT 6% while 188 cards were obtained for GIM. As a reference, Composition B has 217 cards for this test. The detonation velocity of the studied mixes is between 94% and 99% of that of Composition B, while the detonation pressure is between 81% and 96% of that of Composition B. In general, the results showed that the XRT and GIM formulations are stable, have a reduced sensitivity to impact and friction, reduced shock sensitivity compared to current melt-cast explosives, that their performance is good, and their behavior in rifle bullet tests is excellent (Diaz et al., 2001).

3.1 Accelerated Aging

Recently, thermal testing was performed on the latest XRT and GIM melt-cast formulations. At the end of the one-week aging process at 70°C, an unacceptable exudation rate of the copolyurethane was observed. After examining in detail the products in these formulations, it was concluded that the commercially produced ETPEs used in these formulations was not fully reacted and that higher molecular weights for the copolymers were needed to pass the exudation test. For the commercial producer, it was safer to do the polymerization reaction at a slightly lower NCO/OH ratio than 1 to ensure that no chemical crosslinking occurred in their batch reactor, but this resulted in a lower molecular weight of the copolymers and also a lower hard segment percentage. This resulted in a softer rubber that had fewer hydrogen bonds, which allows the exudation of the material. The synthesis of the ETPEs was repeated at DRDC Valcartier using GAP 2000 with an exact NCO/OH ratio equal to 1, which led to a higher molecular weight copolymer and a higher hard segment content. No sensitivity testing was repeated, since it is believed that higher molecular weights of the binder having the same structure would not give any differences in the sensitivity tests. As a result, the aging tests were repeated and practically no exudation was observed. Further work is going on to permanently solve this issue.

3.2 Recycling

An important aspect of using thermoplastic elastomers in insensitive explosive formulations is that they allow easy recycling compared to cast-cured PBXs (Poulin et al., 2010, 2011a,b). The most costly ingredients in the XRT and GIM are RDX or HMX. Upon heating, both XRT and GIM formulations can be melted and poured out of the shells if reclamation should be conducted. It was demonstrated that the XRT or GIM products can then be dissolved in ethyl acetate, resulting in the precipitation of the insoluble nitramines. The ETPE and TNT dissolve easily into ethyl acetate while the nitramines are insoluble. Upon filtration, the nitramines were easily recovered (99.9%). The analysis and spectroscopy of these recycled nitramines were identical to the original ingredients; therefore recuperation and reuse could be easily done. The filtrate contained the ETPE and TNT which could be separated using a Soxhlet with hot methanol as the extraction solvent (Diaz et al., 2001).

4. ENVIRONMENTAL EVALUATION OF GIM

The release of munitions constituents and their transformation products from unburned deposited residues may lead to contaminated soils, surface water bodies or groundwater. These residues may be deposited upon firing or released from UXOs that were cracked, corroded, or suffered low-order detonations. Factors that govern the transport, fate, and impact of these contaminants in soil include dissolution, sorption, abiotic transformation, biotransformation, volatilization, bioaccumulation, and toxicity. Our main collaborators from Biotechnology Research Institute (BRI) investigated the behavior of the complete GIM formulation and compared it to that of Octol (Hawari et al., 2009). GIM (HMX/TNT/ETPE: 51.5/40.7/7.8) was prepared at DRDC Valcartier and supplied to BRI for this study.

4.1 Dissolution Tests

To evaluate dissolution and fate of TNT and HMX in GIM samples, batch and dripping tests were performed with GIM samples (Hawari, 2009; Monteil-Rivera et al., 2010). In batch experiments, the concentrations of TNT and HMX measured at equilibrium agreed well with the solubility values calculated for each component using the correlations previously established to relate aqueous solubilities of HMX and TNT with temperatures (Lynch et al., 2001). Moreover, the TNT dissolution rate clearly decreased upon renewing of the aqueous supernatant with fresh distilled water, whereas the dissolution rate of HMX remained more or less constant throughout the successive washings. A similar phenomenon was previously observed by Lever et al. (2005), who reported that the slow dissolution of RDX controlled the dissolution of Composition B (RDX/TNT/wax, 60/39/1) particles by limiting the exposed area of TNT. In the present case, HMX, which is the major component of GIM, dissolved less rapidly than TNT and had its dissolution limited by its low solubility in water. As a result, the nitramine was left at the periphery of GIM pieces as the only explosive to dissolve, while TNT was concentrated at the center of the pieces. The dissolution rate of TNT was hampered by its limited exposure to water.

The total amount of TNT released during four sequential runs conducted at 29.3°C represented 98.4% of the TNT initially introduced, thus suggesting that the presence of ETPE did not prevent TNT from dissolving from a GIM particle that was fully immersed in an aqueous solution. This phenomenon would take place in the case where GIM particles would fall into a small pond or other surface water bodies. The total amount of HMX released under the same conditions corresponded to 2.8% of the HMX initially present. Attempts to detect any ETPE degradation products in the aqueous filtrate obtained at 22.5°C using liquid chromatography–mass spectroscopy (LC-MS) did not show any significant peaks when scanning from 200 to 3000 Da and using both positive and negative ionization modes, thus suggesting the absence of ETPE dissolution in aqueous solutions. This confirmed the green character attributed to these ETPEs.

In order to evaluate the long-term changes in the composition of GIM and to understand the dissolution process, an experiment was set up where a parallelepipedic piece of GIM (115 mg) was deposited on a glass funnel and exposed to a continuous water flow maintained with a peristaltic pump at a rate of 0.5 mL min^{-1}corresponding to $\sim$19 drops per min. Outflow samples were collected in glass flasks covered with aluminum foil and flasks were changed every 24 h for 3 weeks and then every 7 days for 49 weeks. Each water fraction was analyzed for TNT and HMX by high-pressure liquid chromatography–ultraviolet spectroscopy (HPLC-UV). For comparison, a similar experiment was conducted with an Octol particle but using a nylon mesh to hold the whole fragile solid in the funnel and applying the same water flow (0.5 mL min^{-1}).

The leakage of TNT and HMX from Octol or GIM particles was modelled using an equation based on Fick's diffusion law and on the retardation of the faster-dissolving compound by the slower-dissolving one, as initially proposed by Lynch et al. (2003). The model allowed predicting well the dissolution data of Octol but was less appropriate to fit the data of GIM, likely due to a physical transformation and rearrangement of the remaining solid. Indeed, it was found that upon TNT dissolution, the ETPE shrinks and tends to protect the constituents from further dissolution (Fig. 5). A complete description and discussion of these results can be found in the literature (Hawari et al., 2009; Monteil-Rivera et al., 2010).

These experiments demonstrated that GIM solubilized more regularly and more slowly than Octol. The presence of the energetic binder ETPE in GIM prevented particles from collapsing and retarded the dissolution of TNT and HMX by limiting their exposure to water. In GIM, like in Octol, the dissolution rate of solid particles was governed by the compound that dissolved at a slower pace, i.e., HMX in Octol and HMX and ETPE in GIM. Despite the not-fully-satisfactory predictions obtained for GIM, the present findings demonstrate that ETPE decreases the risk of explosives leakage from solid explosive particles. It should thus help in maintaining unexploded particles intact in the field and hence facilitate their physical removal by environmental site managers.

4.2 Transport of GIM and its Components in Two Soils

Transport of GIM and its individual components was studied in batch and column experiments. Two soils were used: a sandy soil, named “DRDC-08,” coming from DRDC training range that contains little organic matter, and a Webster clay loam, named “WCL,” provided by Edgewood Chemical Biological Center (ECBC). Both soils were described in Monteil-Rivera et al. (2011), together with typical batch and column experiments.

The octanol-water partition coefficients (K_{ow}) and the soil/water distribution coefficients (K_d) were measured for HMX and TNT with DRDC-08 and WCL soils. Aerobic conditions were selected due to the aerobic nature of the DRDC-08 soil. The K_{ow} value of HMX was found to be approximately 30 times lower than that of the reported value for TNT, indicative of the larger affinity of the nitroaromatic chemical for organic matter (Johnson et al., 2009). Sorption experiments conducted with HMX or TNT and DRDC-08 soil yielded low K_d values (0.07 for HMX; 0.19 for TNT), suggesting a

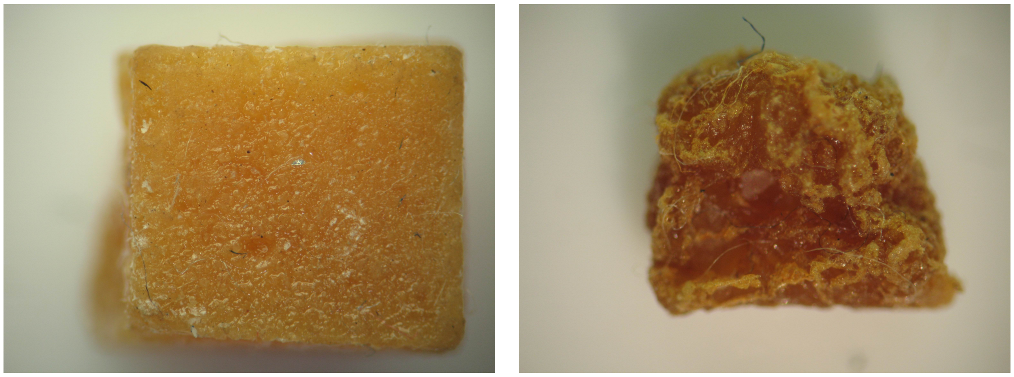

FIG. 5: Microscopic photographs of a piece of GIM before (left) and after 47 weeks (right) in dripping test.

limited sorption of both chemicals onto this soil (less than 4% for TNT). TNT K_d was about 1 order of magnitude lower than other values previously reported by Monteil-Rivera et al. (2009) for TNT sorption in various soils, consistent with the low content of clay or organic matter in DRDC-08 soil. In contrast, HMX and TNT exhibited a stronger affinity for WCL soil. Despite a K_{ow} value for HMX more than 10 times smaller than that of TNT, K_d values of the same order (5.78 for HMX; 4.58 for TNT) were obtained for both chemicals with WCL soil. The higher content of clay in WCL soil (28% vs 2% in DRDC-08 soil) along with the type of clay phases present in this soil are probably responsible for the stronger sorption of HMX. This result confirms our previous observation that clay rather than organic matter governs the immobilization of nitroamines such as RDX, HMX, and CL-20 onto soil, whereas TNT can bind in a lesser extent to both types of solid materials (Monteil-Rivera et al., 2003).

Column experiments were conducted using solutions of either HMX or TNT in both soils. Flow from top to bottom was selected to allow easy introduction and removal of the solid compositions. Sodium chloride was added as a tracer at a concentration of 5 mg L^{-1}. The soil column was saturated with a $Ca(NO_3)_2$ solution, and the pore volume determined as the volume necessary to fill the packed column was found to be around 18 mL for each prepared column. The pure background electrolyte solution was replaced by solutions containing HMX (3.5 mg L^{-1}) or TNT (50 mg L^{-1}) and the tracer. For the column involving solid formulation, the regular flow was stopped, formulation powder (50 mg) was introduced on the top of the soil between two layers of glass wool and a Nylon membrane (125 μm), and flow was restored using a solution containing the tracer.

Breakthrough curves plotted on a time basis for HMX and TNT in DRDC-08 soil confirmed the high mobility of the two explosive components in the sandy soil. When a column experiment was conducted with solid GIM deposited at the top, TNT and HMX also co-eluted with chloride ions, thus confirming their negligible retention on DRDC-08 soil. However, the concentration of each of the two energetic chemicals did not remain constant in the outflow samples. TNT concentration decreased fast throughout the experiment, while HMX concentration decreased very slowly. These findings are in line with the dissolution processes observed in the dripping experiment, thus suggesting that transport of TNT and HMX released from GIM particles in DRDC-08 soil is governed by dissolution. Mass balance calculation from outflow concentrations during the 56-h experiment yielded 11.7 % and 1.5% releases of TNT and HMX, respectively, from the total amounts present in the powder after 56h. The breakthrough curve for HMX in WCL soil showed a neat retardation in this soil compared to the chloride ion, in agreement with the higher K_d value measured in WCL soil.

In conclusion, neither TNT nor HMX was retained by DRDC-08 soil, suggesting that the transport of the two components from the munitions formulations would be governed by dissolution only. On the other hand, both chemicals exhibited some affinity toward WCL, suggesting that the transport of these components in this soil would be influenced by both dissolution and adsorption.

4.3 Fate of GIM Explosives and Their Individual Components

The batch sorption experiments were also used to evaluate the degradability of the individual components of GIM (HMX and TNT) in DRDC-08 and WCL soils under both sterile and nonsterile conditions. No loss of HMX was observed in either DRDC-08 or WCL soil after 3 months, thus indicating its high stability in soil. TNT appeared to be stable in DRDC-08 soil with only an 8% mass loss after 3 months. However, when the experiment was conducted in WCL soil, TNT had completely disappeared after 23 days, whether the loss happened to be biotic or of chemical origin, resulting in a degradation rate of 0.185 d^{-1}. The amino- derivatives, 2-ADNT and 4-ADNT, were identified in both the aqueous and soil fraction, yet the final mass balance was very poor.

Exposure of formulations to sunlight in the field may lead to various extents of photodegradation in the solid form or in solution once individual components have leaked into the environment. Irradiation experiments were conducted using artificial sunlight generated from a SolSim solar simulating photoreactor (Luzchem Research, Inc., Canada), with a total irradiance of 590,000 mW m^{-2}. Aqueous solutions of HMX (4.2 mg L^{-1}) or TNT (10.7 mg L^{-1}) in deionized water were irradiated at 25°C until complete degradation, whereas solid dry particles of GIM formulations were irradiated for 48 h in the dry state. At the end of the exposure, the particle was suspended in water in order to quantify the water-soluble products identified during the individual component studies (HMX and TNT). A second particle was dissolved in acetonitrile in order to establish mass balances of HMX and TNT. In addition, the pictures of particles were taken prior and after exposure to determine any physical changes.

HMX photodegradation under simulated solar light was fast enough (k_{HMXSS} = 0.41 d^{-1}; $t_{1/2\ HMXSS}$ = 1.7 d) to allow complete disappearance of the nitroamine in approximately 1 week (Hawari et al., 2010). The kinetics measured using simulated solar light are more appropriate to predict the HMX photodegradation in the environment and they demonstrate that HMX should degrade over a week scale if present in soluble form in surface water. HMX photodegradation with solar light led to the formation of formaldehyde and formic acid through initial denitration followed by ring cleavage, as supported by the detection of nitrite, nitrate, ammonia, and 4-nitro-2,4-diazabutanal (NDAB). This product distribution is similar to the one previously determined for HMX photodegradation using irradiation at fixed wavelengths (Monteil-Rivera et al., 2008). Mass balances obtained after 7 days showed that carbon mass balance (92%) was higher than the nitrogen one (71%), likely due to the loss of nitrogen in gaseous products such as N_2O or NH_3. TNT photodegradation using the solar simulator gave a rate constant estimated at k_{TNTSS} = 3.28 d^{-1} ($t_{1/2TNTSS}$ = 0.21 d), 10 times higher than the rate measured for HMX photodegradation. TNT photodegradation led to the formation of formaldehyde, formic acid, nitrite, nitrate, and ammonia. However, poor mass balances (C 4.4%; N 12.4%) were obtained after 72 h when considering only these small end-products, suggesting the formation of other products. Analysis of the irradiated aqueous solutions by HPLC-MS revealed the presence of numerous other products of TNT that were identified based on their mass spectra. Most of the identified products were azo or hydrazo dimer forms of TNT, which indicates a tendency of TNT to dimerize, and eventually polymerize further upon exposure to solar light.

Analysis after 48-h photolysis of formulations in the dry form showed a 19% loss of HMX and a 29% loss of TNT from the initial GIM particle. This result suggests that photodegradation of the formulation components can occur even in the absence of water. None of the small end-products previously identified during the aqueous photolysis of HMX or TNT were detected in aqueous washings of the dry irradiated formulation particles, thus suggesting the occurrence of different reactions in the dry state with gaseous processes being predominant. LC/MS analysis of the aqueous extract of the GIM particle showed most of the azo (and hydrazo) compounds identified in TNT photodegradation experiments along with additional chemicals of higher molecular weights that were not identified. The acetonitrile extracts could not be used for identification of products due to the high concentration of TNT and HMX in these extracts. Comparing microscopic images of GIM before and after photolysis did not reveal significant morphological changes (Fig. 6), except for a neat darkening of the orange color of GIM, likely due to the color of TNT photoproducts.

In conclusion, two potential degradation processes were investigated for the individual water-soluble components (HMX and TNT) of the studied explosive GIM formulation. Both chemicals appeared to be stable in nonsterile DRDC-08 soil but less stable in nonsterile WCL soil, when incubated in the dark. In particular, TNT had completely disappeared after a 3-week incubation in nonsterile WCL soil. Although controls were not performed under sterile conditions in WCL, loss of TNT in this soil likely resulted from biotransformation by indigenous microorganisms. Photolysis conducted under conditions that are representative of natural sunlight was found to be a fast transformation process for both studied chemicals, HMX and TNT. Although photolysis was found to be faster in aqueous media, significant losses of TNT and HMX also occurred when dry

FIG. 6: Microscopic photographs of a GIM piece before (left) and after (right) a 48-h photolysis.

solid formulations were exposed to sunlight, thus suggesting that photodegradation is a process that will play a major role in the transformation of explosive components of formulation particles exposed to sunlight. If dissolution experiments are carried out in real enlightened conditions, photolysis will definitively have to be taken into account, since it may affect mass balances before the components have even entered into water and soil.

4.4 Outdoor Experiments

To complete the understanding of the fate and behavior of the GIM explosive formulation in real environments, Côté and Martel (2011), from the Institut National de la Recherche Scientifique (INRS), performed outdoor experiments on GIM explosives. Outdoor dissolution tests were conducted by submitting the ground GIM formulation to natural conditions on glass-fritted funnels. The rainwater and melted snow were collected under the fritted funnels, and the dissolved compounds were analyzed. A physical description of the energetic materials (EM) and mass balance were performed before and after outdoor weathering. All the water samples were analyzed at INRS and at DRDC Valcartier laboratories. The GIM explosive formulation was ground with a 10-mesh sieve to mimic what would normally be found in training areas as a more realistic situation. One should keep in mind though that grinding the GIM formulations increased its surface of exposure and represents a worst case scenario. The particle size was measured in water with a laser diffraction analysis system (Malvern Mastersizer, 2000 from Worcestershire, UK) and gave values between 120 and 600 μm. Pictures of the formulations before and after grinding are shown in Fig. 7. Ground GIM particles (10 g) were exposed to weathering for 546 days. The GIM explosive formulation samples were put on the glass-fritted funnels on July 8, 2009. By the end of summer 2010, it was decided to let the experiments run for another year. The residues from each sample were weighed, observed, photographed, and analyzed to draw final conclusions on the effect of their exposure to weathering.

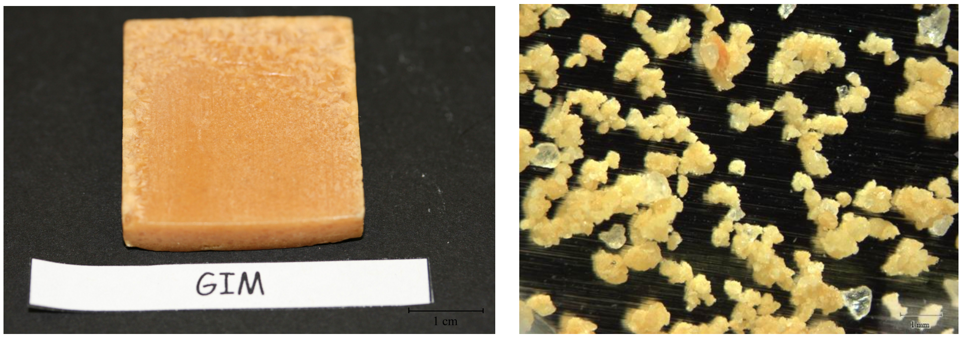

FIG. 7: GIM explosive before (left) and after grinding (right).

The tables containing many large glass-fritted funnels that were used as the setup for the outdoor experiments are shown in Fig. 8. The use of big amber glass sampling bottles (2.5 L) helped to decrease the number of samples during the infiltration periods and prevented spills during heavy rains. However, it did not prevent the bottle from breaking under freezing conditions in winter. All the bottles did break during the winter and were changed at the end of spring. No water samples were lost because the film in these plastic-coated bottles protected water from spilling.

Results indicated that in the first 274 days (August 2009 to April 2010), the GIM formulation released 7.0 mg (0.14% of initial mass) of HMX. After 274 days, the behavior

FIG. 8: Outdoor setup for GIM exposure.

of the GIM formulation changed and at the end of the 546-day period, GIM had released a cumulative mass of 38 mg HMX (0.7% of initial mass), which is an increase in dissolution rates. BRI stated that the dissolution of HMX was more or less constant and this is not what INRS observed in its experiment. It is highly possible that photodegradation occurred during the INRS experiment, changing the way HMX was made available for dissolution. For TNT, after 274 and 546 days of exposure, 7% and 24% (900 mg) of the initial mass of TNT was dissolved. In their dissolution-rate experiments, BRI mentioned that most of the TNT (96%) was dissolved after a year. In the INRS experiment, the GIM samples were not continuously exposed to water and as a result, less TNT came out of the GIM sample in a real outdoor environment. This means that GIM, once exposed to a natural environment, will take a longer time to expose it constituents to receptors and eventually will have the time to degrade, adsorb, and become less toxic. Furthermore, in the INRS experiment, TNT is not fully recovered, meaning that degradation and transformation occurred in the glass-fritted funnels, showing that the fate and behavior may be consistent with our hypothesis of having a greener explosive that leaches TNT derivatives that bind to soil. The ongoing study on the aged GIM sample in soils will answer these questions.

5. ECOTOXICOLOGICAL EVALUATION OF GIM

To determine if a new explosive formulation such as GIM is green, its toxic effects to relevant target organisms must be evaluated. BRI conducted a tremendous amount of work and a complete description of these ecotoxicological studies can be found in Hawari et al. (2011). The main objectives of the ecotoxicological assessments were to conduct terrestrial, aquatic, and benthic ecotoxicity assays and to assess the adverse effects of the GIM formulation as compared to Composition B, which was used as the reference explosive formulation. Direct soil contact toxicity tests included ryegrass seedling emergence and growth inhibition, earthworm lethality, and earthworm avoidance behavior. Benthic toxicity tests using the Organization for Economic Cooperation and Development (OECD) amended artificial sediments included mussel lethality and sublethal immunologic response, as well as amphipod crustacean lethality and growth tests. Toxicity of the explosive formulation was also assessed using soil leachate samples by measuring bioluminescence inhibition in the bacteria *Vibrio fischeri* (Microtox assay), and growth inhibition of freshwater algae and duckweed. For the purpose of the present paper, preliminary results and main conclusions using only GIM and Composition B formulations will be described and can be found in Table 2.

5.1 Equilibrium Studies

As demonstrated earlier, the GIM explosive formulation contains energetic materials covered with a polymer, which makes the energetic substances safer to handle but which

TABLE 2: Toxicity results for soil leachates, soil, and benthic microorganisms

Toxicity tests	**GIM**	**Comp B**
Leachates from soils amended at 10,000 mg/kg		
Microtox: bioluminescence inhibition	2.0% V/V	2.4% V/V
Freshwater algae growth inhibition	1% V/V	1% V/V
Freshwater plant growth inhibition	79–97%	85–98%
Soil organisms		
Ryegrass growth seedling emergence	Ec_{20} 705 mg/kg	Ec_{20} 77 50 mg/kg
Ryegrass growth seedling emergence	Ec_{50} 3782 mg/kg	$Ec_{50} >$ 10,000 mg/kg
Ryegrass shoot growth (dry mass)	Ec_{50} 736 mg/kg	Ec_{50} 750 mg/kg
Earthworm exposed at 1000 and 10,000 mg/kg	100% mortality	100% mortality
Earthworm avoidance test at concentrations of		
100 mg/kg	7%	20%
1000 mg/kg	100%	93%
10,000 mg/kg	100%	100%
Ec_{50}	295 mg/kg	290 mg/kg
Benthic organisms		
Mussel survival in sediments at 10,000 mg/kg	30%	50%
amphipod *Hyallela azteca* survival and growth	Lc_{50} 402 mg/kg	Lc_{50} 495 mg/kg
	Ec_{50} 255 mg/kg	Ec_{50} 255 mg/kg

also prevents their dissolution into water or soil when released into the environment. A standardized method was developed for the amendment of formulations to soil without the use of organic solvents, which could alter the configuration of the polymers. Because the polymers may affect the solubility of the energetic constituents, the homogeneity and soil–water equilibrium were determined at nominal concentrations of 10, 100, 1000, and 10,000 mg/kg. Preliminary results indicate that both total extractable and bioavailable HMX were relatively stable and homogeneous over time in all GIM soil treatments. Total extractable TNT was also relatively stable and homogeneous over time at GIM soil treatment concentrations of 1000 and 10,000 mg/kg. At 100 mg/kg GIM soil treatment, both total extractable and bioavailable TNT became relatively stable after 3 days. Considering these data, it was decided to hydrate and equilibrate the GIM soil samples at room temperature during 3 days prior to the initiation of the toxicity tests. The same tests were repeated with Composition B and a 7-day period was chosen to hydrate and equilibrate the soil samples prior to the toxicity tests.

Similarly, sediment–water equilibrium and bioavailability studies were conducted prior to the initiation of the benthic toxicity tests using the OECD artificial sediment (OECD, 2004a,b). Preliminary results indicate that HMX and TNT concentrations stabilized after 7 days of water contact with the GIM-amended sediment. The same methodology and conditions were used for the Composition B-amended sediment and an equilibrium period of 7 days was therefore performed for both formulations prior to the introduction of the organisms.

5.2 Toxicity of GIM-Amended Soil Leachates to Aquatic Organisms

The Microtox test measures the inhibition of bioluminescence of the marine bacteria *V. fischeri*. Preliminary data indicate that both GIM- and Composition B-amended soil leachates significantly inhibited the marine bacteria bioluminescence. The EC_{50} values of soil leachates amended with GIM or Composition B at 10,000 mg/kg were similar, i.e., 2.0% and 2.4% v/v, respectively. The toxicological values are expressed as soil leachate volume per volume of diluant (salted water).

Leachates of both GIM- and Composition B-amended soil showed significant inhibition of the freshwater algae *P. subcapitata* growth. Both GIM and Composition B soil leachates amended at 10,000 mg/kg had similar toxicities, with EC_{50} values around 1% v/v. The toxicological values are expressed as soil leachate volume per volume of algal medium. Because TNT was measured in both GIM and Composition B soil leachates, we hypothesized that the toxicity of leachates of amended soil samples observed using the Microtox and algae growth assays is related to the presence of TNT. To test this hypothesis, results of both assays were expressed as the amount of TNT measured in the soil leachates (Hawari et al., 2011). Initial data indicated that, for the Microtox test, the toxicity (inhibition of bioluminescence expressed as concentration of TNT) of the samples was slightly lower than the toxicity of pure TNT. For the algae growth assay, both GIM and Composition B curves converged and followed the toxicity of pure TNT dissolved in water. The discrepancy of results between TNT as a pure compound and that contained in the explosive formulation may probably be attributed to the presence of other compounds such as HMX, or RDX.

In the duckweed *Lemna minor* growth inhibition test, GIM and Composition B soil leachates had a high inhibition effect on the *L. minor* growth, with inhibition percentages ranging between 78–97% and 85–98%, respectively. These results are consistent with those measured with the Microtox and the fresh water algae growth inhibition assay.

5.3 Toxicity of GIM to Soil Organisms

The effects of the explosive formulation-amended soil to terrestrial plants were investigated. Seedling emergence of ryegrass in the negative (water) controls was between 92% and 95%, which complies with the quality control requirements. Initial data indicated that seedling emergence EC_{20} and EC_{50} values of GIM and Composition B formulations are 705 and 3782 mg/kg, and 7750 and $>$10,000 mg/kg, respectively. The calculated EC_{50} values for shoot growth (dry mass), which is a more sensitive toxicity endpoint than seedling emergence, were 736 and 750 mg/kg, respectively. Based on these results, both GIM and Composition B had significant and equivalent toxic effects on ryegrass growth. The toxic effect of GIM and Composition B on terrestrial higher plants could be related to the presence of TNT in both formulations. The total extractable concentrations of TNT were systematically greater in the Composition B-amended soil samples than in the GIM-amended soil samples. However, the toxic effects of both formulations on ryegrass growth were not significantly different, indicating that the toxicity is rather related to the bioavailable portion of TNT.

The GIM- and Composition B-amended soils at concentrations of 1000 or 10,000 mg/kg soil induced 100% mortality of earthworms. Hence, GIM and Composition B formulations were both lethal to earthworms at nominal concentrations of 1000 mg/kg and above. This effect can again be attributed to the presence of TNT measured in the amended soils at concentrations above 100 mg/kg.

The effects of the explosive formulation-amended soils on earthworm avoidance behavior showed that there was a significant avoidance response. An avoidance percentage above 60% is considered to be significant. At amended soil concentration of 100 mg/kg, the avoidance behavior was 7% for GIM and 20% for Composition B. At higher concentrations of 1000 and 10,000 mg/kg, avoidance was 100% for GIM and 93 and 100% for Composition B, respectively. The EC_{50} avoidance values were 295 mg/kg for GIM and 290 mg/kg for Composition B. In conclusion, significant avoidance response was measured for both GIM and Composition B at formulation concentrations of 1000 mg/kg and above. Once more, toxicity could be related to TNT leaching out of the formulations.

5.4 Toxicity of GIM to Benthic Organisms

The 7-day exposure to GIM- and Composition B-amended sediments indicated that both formulations had deleterious effects on mussel survival. At the 10,000 mg/kg amended sediment treatment, 30% and 50% lethality were measured in GIM- and Composition B-amended sediments, respectively.

The effects of the explosive formulations on mussel phagocytic activity following the 7-day exposure to GIM-amended sediments were not so clear, and no significant difference in the hemocyte cellular viability was measured as compared to negative control. However, a significantly higher number of hemolymph cells/mL (cellularity) was measured in the 1000 and 10,000 mg/kg concentrations as compared to negative control. A significant decrease in the phagocytic efficiency (hemocyte cells that have engulfed three latex beads or more) was measured in the negative control and at 10 and 10,000 mg/kg GIM-amended sediments as compared to mussel initial phagocytic efficiency. Following the 7-day exposure to Composition B-amended sediment, no significant effect was measured in mussel phagocytic activity, hemocyte viability, and cellularity as compared to negative control.

Results of the amphipod *Hyallela azteca* survival and growth assays indicated that GIM caused 100% mortality at 1000 mg/kg or more. The LC_{50} and growth EC_{50} values for GIM were 402 and 255 mg/kg, respectively. Composition B-amended sediments caused similar inhibition of amphipod survival and growth, with LC_{50} and growth EC_{50} values of 495 and 514 mg/kg, respectively. Results indicate that both GIM and Composition B had similar deleterious effects on the growth and survival of the amphipod at concentrations of 100 mg/kg and above.

5.5 Conclusions of the Ecotoxicological Evaluation of GIM

To summarize these preliminary ecotoxicological results, GIM and Composition B were highly toxic to the *Vibrio fischeri* marine bacteria (Microtox assay), to the freshwater algae *P. subcapitata*, and to the freshwater plant *Lemna minor*. Similar results were observed for the terrestrial plant toxicity test, i.e., both GIM and Composition B had significant and equivalent toxic effects on ryegrass growth. Earthworm mortality (100%) was observed after the 14-day exposure in the GIM- and Composition B-amended soils at concentrations of 1000 mg/kg and above. Significant avoidance response was measured in earthworms at GIM and Composition B concentrations of 1000 mg/kg and above. Similar results were obtained using the benthic organisms, i.e., mussel *Elliptio complanata* and amphipod *Hyallela azteca*. Both GIM and Composition B had deleterious effects on mussel survival, as well as on the survival and growth of the *H. Azteca*. No clear effect could be measured using the mussel hemocyte phagocytic activity assay.

The toxic effect of GIM and Composition B appears to be related to the presence of TNT in both formulations at concentrations greater than 260 mg/kg. The concentrations of total extractable TNT were systematically greater in the Composition B-amended soil samples than in the GIM-amended soil samples. However, the toxic effects of both formulations on ryegrass growth, earthworm survival, and avoidance response were not significantly different, indicating that the toxicity is rather related to the concentrations of bioavailable TNT, which did not significantly differ in both explosive formulations at 1000 and 10,000 mg/kg soil treatments.

All toxicity tests were conducted with freshly prepared GIM that was exposed directly to the organisms. Because these tests were performed in a closed environment, TNT leached out from the formulations and exerted its toxicity on the test species. Our approach of developing a green explosive containing TNT is based on the fact that TNT is transformed rapidly by microbial activity or by chemical reactions (demonstrated in earlier sections) into derivatives that bind to organic matter of the soil. This is why mass balances are often poor in our experiments. In the real environment of training or firing munitions containing GIM explosive, once GIM is deposited on the soils by UXO cracking, it is believed that TNT contained in the GIM formulation will transform by sunlight or other means into its metabolites that will bind to the soils, becoming non bioavailable and therefore nontoxic. Toxicity experiments are currently ongoing with GIM that was aged in soil prior to the initiation of the toxicity tests.

6. CONCLUSIONS

Copolyurethane thermoplastic elastomers were prepared using glycidyl azide polymers as macromonomers reacted with 4,4’ methylenebis-phenyl isocyanate (MDI). It was found that the ETPEs could be dissolved in melted TNT, allowing their incorporation in either Composition B- or Octol-type explosives in the melt-cast process. This generated a new family of innovative recyclable insensitive melt-cast explosives named “XRT” and “GIM.” Recyclability, insensitivity testing, performance evaluation, and processing demonstrated that these explosives can be processed in existing melt-cast facilities, be recycled, and can perform almost with the same energy as that of Composition B. It was found that the best compromise for the energy and the mechanical properties of the insensitive melt-cast XRT explosive was the copolyurethane thermoplastic elastomer ETPE 2000 at 6% weight in the formulation. To produce a green insensitive explosive, HMX was introduced in the formulation instead of RDX, so mixing the ETPE at 9.5% with melted Octol generated upon cooling a greener insensitive explosive named “GIM.” Consequently, these ETPEs offer interesting avenues in the production of insensitive explosives.

Insensitive evaluation of the GIM explosive was carried out and bullet impact, sympathetic detonation shaped charge, and slow cook-off tests were conducted. In addition to this, vacuum stability, impact and friction sensitivity (BAM), density, and viscosities of the melted mixes were measured. Furthermore, performance and shock sensitivity tests (gap tests) were also conducted (Table 1). All the insensitivity tests demonstrated that GIM is insensitive to all tests except the shaped charge test that was not passed. Blow-in-place tests of 105 mm filled with GIM were done in another study where high-order detonations were observed with all items blown by one block of C4. These results will soon be available.

For the RIGHTTRAC project, in the thermal aging tests of the XRT and GIM explosives, unacceptable exudation was observed, jeopardizing the chances of GIM explosives to be used as an insensitive explosive. After careful investigation, it was realized that the source of the problem was the ETPE itself. For these formulations, commercially produced ETPEs were used and revealed to be less than ideal for our application. The synthesis of the ETPEs was repeated at DRDC Valcartier at an exact NCO/OH ratio equal to 1, and this led to a higher molecular weight copolymer with a higher hard segment content. As a result, the aging tests were repeated with new formulations using this latter polymer, and no exudation or at least acceptable exudation was observed.

Environmental evaluation of the GIM explosive was achieved and it was demonstrated that in the GIM products, the ETPE is slowing down the dissolution process of

TNT and this phenomenon becomes more important with time since as a result of TNT dissolution, the products are shrinking. This increases the proportion of polymer in the product and its ability to minimize further dissolution and leaching. It was observed by BRI that TNT was almost completely dissolved from GIM in a year in immersed experiments, while INRS showed that after 1.5 years of outdoor exposure, only 24% of the TNT was leached out from the formulation.

The toxicity of GIM was tested in soil using earthworms and a terrestrial plant (ryegrass), in soil leachate using aquatic organisms (Microtox, freshwater algae, and an aquatic plant *Lemna minor*), and in sediment using benthic organisms (mussels and an amphipod *Hyalella azteca*). Preliminary results indicated that the GIM formulation was toxic to all receptors in all toxicity tests, presumably due to the exposure to TNT that leached out from the formulation (Table 2).

As mentioned, the ETPE slows down the dissolution of TNT and in that sense, it reduces the impact on the environment compared to Octol, since the concentrations of TNT leaching out of the GIM products are lower over a longer period of time. GIM was developed by DRDC Valcartier as a green explosive, based on the low solubility of HMX and on the fact that TNT should rapidly phototransform into insoluble dimers and oligomers or biotransform into amino derivatives that bind to the soil organic matter. In training scenarios, GIM would eventually be released on the ground and be exposed to sunlight and microbes. It would thus be interesting to verify if a soil exposed to GIM is still toxic after weathering and aging when most TNT is expected to be transformed and immobilized in soil. Therefore, a new set of experiments has been initiated using a controlled aging and weathering process prior to the initiation of the toxicity assays. Toxicity tests will include terrestrial organisms (earthworms and plants) using GIM weathered and aged in soil, aquatic organisms using soil leachate samples, and benthic amphipod *Hyalella azteca* using sediment samples. These results will be published elsewhere.

Finally, it was demonstrated that GIM explosive has a good performance, almost equivalent to Composition B, a good chemical stability, and is insensitive to most of the tested stimuli. It is easy to prepare in conventional melt-cast facilities, has good mix viscosity, and can be used to easily fill projectiles. It was demonstrated that freshly amended GIM was toxic to all target organisms tested. Nonetheless, we still believe that GIM is a greener explosive. Further tests are ongoing to demonstrate that once released into the environment, TNT from GIM will transform and bind to organic matter and become nontoxic, making GIM a viable option as a greener explosive.

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REFERENCES

Ampleman, G., Marois, A., and Brochu, S., Approaches to energetic thermoplastic elastomers using glycidyl azide polymers, Third issue of the series, *Rec. Res. Developments Macromol. Res. Research Signpost*, vol. **3**, p. 355, 1988.

Ampleman, G., Thiboutot, S., Lavigne, J., Marois, A., Hawari, J., Jones, A. M., and Rho, D., Synthesis of 14c-labelled hexahydro-1,3,5-trinitro-1,3,5-triazine (rdx), 2,4,6-trinitrotoluene (TNT), nitrocellulose (NC), and glycidyl azide polymer (GAP) for use in assessing the biodegradation potential of these energetic compounds, *J. Label. Comp. Radiopharm.*, vol. **36**, no. 6, pp. 559–563, 1995.

Ampleman, G., Marois, A., and Désilets, S., Energetic copolyurethane thermoplastic elastomers, Can. Pat., 2,214,729, (2003); European Patent Appl. No. 0020188.2-2115 Sept 2000; US Pat. 6,479,614 B1, 2002.

Ampleman, G., Brousseau, P., Thiboutot, S., Diaz, E., and Dubois, C., Insensitive melt-cast explosive compositions containing energetic thermoplastic elastomers, US Patent 6,562,159, 2003.

Ampleman, G., Development of a new generation of insensitive explosives and gun propellants, *Int. J. Energetic Mater. Chem. Propul.*, vol. **9**, no. 2, pp. 107–132, 2010.

Anderson, P., Balas, W., Nicolich, S., Capellos, C., Pincay, J., and Stiehl, L., Development, optimization, and application of combined effects explosives, *Proc. of the 2009 Insensitive Munitions and Energetic Materials Technology Symp.*, Tucson, AZ, USA, 2009.

Bergman, H., Pettersson, A., Ostmark, H., Stenmark, H., and Bergvall-Laitala, C., FOX-7: An IM candidate–Where are we today?, *Proc. of the 2009 Insensitive Munitions and Energetic Materials Technology Symp.*, Tucson, AZ, USA, 2009.

Brousseau, P., Ampleman, G., Trudel, S., and Dubé, P., Bullet impact tests on an insensitive melt-cast explosive composition, *Proc. of the 2004 Insensitive Munitions and Energetic Materials Technology Symp.*, San Francisco, CA, USA, 2004.

Brousseau, P., RIGHTTRAC technology demonstration program: Preliminary IM tests, *Proc. of the 2010 Insensitive Munitions and Energetic Materials Technology Symp.*, Munich, Germany, 2010.

Cohen, A., Cramer, M., Akester, J., and Fawcett, W., Environmentally friendly advanced gun propellants, ATK Alliant Techsystems final report for SERDP, SERDP PP, Report no. 1363, 2004.

Côté, S. and Martel, R., Environmental behavior of green gun propellants and main charge explosive formulations, INRS Phase 3B Final Report no. R-1231, 2011.

Di Stasio, A., Qualification testing of the insensitive TNT replacement explosive IMX-101, *Proc. of 2009 Insensitive Munitions and Energetic Materials Technology Symp.*, Tucson, AZ, USA, 2009.

Diaz, E., Brousseau, P., Ampleman, G., and Thiboutot, S., Less sensitive melt-cast explosives based on energetic thermoplastic elastomers, DREV TR 2001-185, Defence Research Establishment Valcartier, Quebec, Canada, 2001.

Fung, V., Teague, C., Wilson, A., Robinson, C., and Vinh, P., Development and optimization of a production scale process for the manufacture of IMX-101 explosive at Holston Army ammunition plant, *Proc. of the 2009 Insensitive Munitions and Energetic Materials Technology Symp.*, Tucson, AZ, USA, 2009.

Hatch, R., Braithwaite, P., Seidner, N., and Wright, J., Development of cast-cured explosives for composition B replacement, *Proc. of the 2009 Insensitive Munitions and Energetic Materials Technology Symp.*, Tucson, AZ, USA, 2009.

Hawari, J., Monteil-Rivera, F., Radovic, Z., Deschamps, S., Paquet, L., Beaulieu, C., Halasz, A., Sunahara, G., Rocheleau, S., Sarrazin, M., Bergeron, P. M., Joly, M., and Savard, K., Environmental aspects of RIGHTRAC TDP-green munitions, BRI Report no. 49958, 2009.

Hawari, J., Radovic, Z., Monteil-Rivera, F., Paquet, L., Halasz, A., Sunahara, G., Robidoux, P. Y., Rocheleau, S., Dodard, S., Savard, K., Beaulieu, I., Bergeron, P. M., Berube, V., Dumas, J., Sarrazin, M., Bensir, N., and Soumis-Dugas, G., Environmental aspects of RIGHTRAC TDP-green munitions annual report, BRI-NRC Report no. 50014, 2010.

Hawari, J., Radovic, Z., Monteil-Rivera, F., Paquet, L., Halasz, A., Sunahara, G., Robidoux, P. Y., Rocheleau, S., Dodard, S., Savard, K., Beaulieu, I., Bergeron, P. M., Berube, V., Dumas, J., Sarrazin, M., Bensir, N., and Soumis-Dugas, G., Environmental aspects of RIGHTRAC TDP-green munitions, BRI-NRC Report no. 53361, 2011.

Hooton, I., Low-vulnerability characteristics of an HMX-based explosive, Advisory Group for Aerospace Research and Development Conf. Proc. 511, Insensitive Munitions, paper presented at the Propulsion and Energetics Panel, 78th A Specialists' Meeting, Bonn, Germany, pp. 10–1 to 10–6, 1992.

Johnson, M. S., Salice, C. J., Sample, B. E., and Robidoux, P.-Y., Bioconcentration, bioaccumulation, and biomagnification of nitroaromatic and nitramine explosives in terrestrial systems, In *Ecotoxicology of Explosives*, pp. 227–252, CRC Press, Boca Raton, FL, 2009.

Jones, A. M., Labelle, S., Paquet, L., Hawari, J., Rho, D., Samson, R., Greer, C., Lavigne, J., Thiboutot, S., and Ampleman, G., Assessment of the aerobic biodegradation potential of RDX, TNT, GAP, and NC, In *Environmental Biotechnology: Principles and Practice*, Moo Young, M., Anderson, W. A., and Charabarty, A.M., Eds., Kluwer Academic Publishers, Dordrecht, pp. 368–381, 1996.

Lever, J. H., Taylor, S., Perovich, L., Bjella, K., and Packer, B., Dissolution of composition B detonation residuals, *Environ. Sci. Technol.*, vol. **39**, pp. 8803–8811, 2005.

Lynch, J. C., Myers, K. F., Brannon, J. M., and Delfino, J. J., Effects of pH and temperature on the aqueous solubility and dissolution rate of 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), *J. Chem. Eng. Data.*, vol. **46**, pp. 1549–1555, 2001.

Lynch, J. C., Brannon, J. M., Hatfield, K., and Delfino, J. J., An exploratory approach to modeling explosive compound persistence and flux using dissolution kinetics, *J. Contam. Hydrol.*, vol. **66**, pp. 147–159, 2003.

Mailloux, M., Martel, R., Gabriel, U., Lefebvre, R., Thiboutot, S., and Ampleman, G., Hydrogeological study of an antitank range, *J. Environ. Qual.*, vol. **37**, pp. 1468–1476, 2008.

Monteil-Rivera, F., Groom, C., and Hawari, J., Sorption and degradation of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) in soil, *Environ. Sci. Technol.*, vol. **37**, pp. 3878–3884, 2003.

Monteil-Rivera, F., Deschamsps, S., Halasz, A., Paquet, L., and Hawari, J., Environmental fate of the new explosive formulation, GIM, Final Report no. BRI-NRC 49931, 2008.

Monteil-Rivera, F., Halasz, A., Groom, C., Zhao, J.-S., Thiboutot, S., Ampleman, G., and Hawari, J., Fate and transport of explosives in the environment: A chemist's view, In *Ecotoxicology of Explosives*, Sunahara et al., Eds., Chap. 2, pp. 5–35, Taylor and Francis, London, 2009.

Monteil-Rivera, F., Deschamps, S., Ampleman, G., Thiboutot, S., and Hawari, J., Dissolution of a new explosive formulation containing TNT and HMX: Comparison with octol, *J. Hazard. Mater.*, vol. **174**, pp. 281–288, 2010.

Monteil-Rivera, F., Radovic-Hrapovic, Z., Halasz, A., Paquet, L., Ampleman, G., Thiboutot, S., and Hawari, J., Environmental fate of triethylene glycol dinitrate, *Environ. Eng. Sci.*, vol. **28**, pp. 70–79, 2011.

Niles, J. and Doll, D., Development of a practical reduced sensitivity composition B replacement, *Proc. of the 32nd Intl. Annual Conf. of ICT*, V28, Karlsruhe, Germany, 2001.

Nouguez, B. and Mahé, B., Tailored sensitivity explosive formulations, *Proc. of the 2009 Insensitive Munitions and Energetic Materials Technology Symp.*, Tucson, AZ, USA, 2009.

OECD, Guideline 218, Sediment–Water chironomid toxicity test using spiked sediment, In *OECD Guidelines for Testing of Chemicals*, Paris, p. 21, 2004a.

OECD, Guideline 219: Sediment–water chironomid toxicity test using spiked water, In *OECD Guidelines for the Testing of Chemicals*, Paris, p. 21, 2004b.

Pelletier, P., Brousseau, P., Carillo, A., Patel, C., and Mahé, B., Studies of HBU88B manufactured with CONUS RDX, *Proc. of the 2009 Insensitive Munitions and Energetic Materials Technology Symp.*, Tucson, AZ, USA, 2009.

Poulin, I., Brochu, S., and Brassard, M., Laboratory testing on recycling of energetic materials in a new generation of explosives and propellants, *SERDP and ESTCP's Partners in Environmental Technology Technical Symp. and Workshop*, Washington, DC, USA, 2010.

Poulin, I., Brochu, S., and Diaz, E., New Canadian munitions: Recycling tests for main charge explosive and gun propellant, *Proc. of the 42nd Intl. Annual Conf. of the Fraunhofer ICT*, Karlsruhe, Federal Republic of Germany, 2011a.

Poulin, I., Brochu, S., Tanguay, V., and Diaz, E., Demilitarisation of new insensitive and green munitions: Recycling and open-detonation, Paper no. 30, NATO AVT-177/RSY-027, *Symp. on Munition and Propellant Disposal and its Impact on the Environment*, Edinburgh, UK, 2011b.

Samuels, P., Common low-cost explosive insensitive munitions program phase 2: Explosive replacement for composition B, *Proc. of the 2009 Insensitive Munitions and Energetic Materials Technology Symp.*, Tucson, AZ, USA, 2009.

Sheremata, T.W., Thiboutot, S., Ampleman, G., Paquet, L., Halasz, A., and Hawari, J., Fate of 2,4,6-trinitrotoluene and its metabolites in natural and model soil systems, *Environ. Sci. Technol.*, vol. **33**, pp. 4002–4008, 1999.

Spyckerelle, C. and Eck, G., An insensitive substitute for composition A3, *Proc. of the 2009 Insensitive Munitions and Energetic Materials Technology Symp.*, Tucson, AZ, USA, 2009.

STANAG 4241 PPS, *Edition 2–Bullet Impact*, *Munition Test Procedures*, NATO NSA/0389-PPS/4241, 2003a.

STANAG 4396 PPS, *Edition 2–Sympathetic Reaction*, *Munition Test Procedures*, NATO NSA/0392-PPS/4396, 2003b.

STANAG 4382 PPS, *Edition 2–Slow Heating, Munitions Test Procedures*, NATO NSA/0391-PPS/4382, 2003c.

STANAG 4526 PCS, *Edition 2–Shaped Charge Jet, Munitions Test Procedure*, NATO NSA/1144-PCS/4526, 2004.

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GAS TEMPERATURE MEASUREMENT AT THE EXIT PLANE OF A TYPICAL GAS TURBINE COMBUSTOR

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This paper describes an attempt to use a technique called thin filament pyrometry (TFP) to measure simultaneously multiple temperature lines at the exit plane of a gas turbine combustor. This technique diverges significantly from the widely used setup that characterizes the TFP method [W. M. Pitts, H. C. Smyth, and D. A. Everest in 27th Symp. (Intl.) on Combustion, The Combustion Institute, pp. 563–569, 1998; V. Vilimpoc and L. P. Goss in 22nd Symp. (Intl.) on Combustion, The Combustion Institute, pp. 1907–1917, 1988; W. M. Pitts in 26th Symp. (Intl.) on Combustion, pp. 1171–1179, 1996; P. B. Kuhn, B. Ma, B. C. Connelly, M. D. Smooke, and M. B. Long in Proc. 33rd Int. Symp. on Combustion, pp. 743–750, 2010]. Although the same physics apply, the approach will be discussed to indicate required changes. The experiment will utilize multiple 15-μm β-SiC fibers, which will be simultaneously imaged at 10,300 points over a total length of 525 mm. Typically, the measurable temperature range is known to be between 500 and 2100 K with the proper filter, the temperature range having a spatial resolution of ∼100 μm, a temporal resolution of 1.5 ms, and an accuracy of 1.5 ± 1.0 K for temperature on the order of 2000 K [Kuhn et al., 2010]. Unlike usual TFP experiments, the filament will be calibrated with a thermocouple, with data from a Fourier transform infrared (FTIR) gas analyzer allowing a thermochemical equilibrium calculation to provide low but sufficient accuracy. Temperature at different positions along the filament will then be determined by recording relative emission intensities and assuming that the filament acts as a gray body emitter. The calibrated TFP would then be used to make a multiple-filament temperature measurement across the exit plane of a typical combustion chamber at various operating conditions. For each flame type, emissions measured with an FTIR and a calibration done with thermocouples are both necessary to provide knowledge of flow temperature and molecular composition. The flow conditions need to be well characterized to provide enough accuracy with the technique. Most studies were done with laminar diffusion flames. The case under study is a highly turbulent high-speed gas flow. The convective properties are to be validated and the mechanical resistance of the 15-μm β-SiC fibers is to be demonstrated under relatively much harsher conditions.

KEY WORDS: *gas temperature measurement, combustor exit plane, aero-gas turbine*

1. INTRODUCTION

Knowledge of the temperature field at the exit plane of a turbine combustor is of great significance for many reasons. The most important one is linked to the hot point on the turbine blades, which needs to be between 50% and 80% of the blade length, depending on the manufacturer and blade design, to prevent failure of the blade. When introducing a new technology in the combustor, one must determine the effect on the temperature profile for all operating conditions. Yet, a usual way to do so is by sweeping the exit plane with thermocouples and to post-process the data for radiation correction. This process is laborious, but gives satisfactory results. This experiment is a feasibility study to apply the thin filament pyrometry (TFP) technique to measure the complete temperature field in a snapshot, thus allowing rapid diagnostics for a wide range of operating conditions, fuels, igniters, etc.

2. TFP

The electromagnetic thermal radiation emitted from a thin filament is used to characterize the local gas temperature. Silicon carbide fibers, 15 μm in diameter, with very low thermal conductivity, high emissivity, and very good thermal and mechanical strength, are ideal for this purpose. Past studies (Kuhn et al., 2010; Pitts, 1996; Pitts et al., 1998; Vilimpoc and Goss, 1988) are related and summarize the methodology based on the following laws. A heated β-SiC fiber is adequately approximated as a gray body for which the spectral emissive power E_g can be written as follows (known as Planck's law):

$$E_g(\lambda, T) = \frac{2\pi\varepsilon hc^2}{\lambda^5\left[e^{hc/\lambda kT} - 1\right]},$$

where λ is wavelength, T is temperature, ε is the apparent emissivity for the fiber, h is Planck's constant, c is the speed of light, and l is Boltzmann's constant. The relative light intensity emitted by the heated fiber is recorded using a photodetector having a wavelength- dependent response R. The overall signal S generated by the detector as a function of temperature is given as

$$S(T) = k_{\text{exp}}\int_{\lambda_1}^{\lambda_2} E_g(\lambda, T)R(\lambda)d\lambda,$$

where k_{exp} is an experimental coefficient assumed to be independent of wavelength. The range of wavelengths for integration covers the sensitivity range of the detector. According to Wien's law, the maximum emissive power for the high-temperature gases will range from 2900 to 2070 nm for temperature between 1000 K and 1400 K. To give a better idea of the work done in the past on the TFP technique (Pitts, 1996), Fig. 1 illustrates an experimental setup used to study the dynamic response of a fiber with a flickering laminar diffusion flame. The loudspeaker induces an oscillation in the fuel velocity that can be related directly to the flame flicker frequency. A β-SiC fiber is stretched

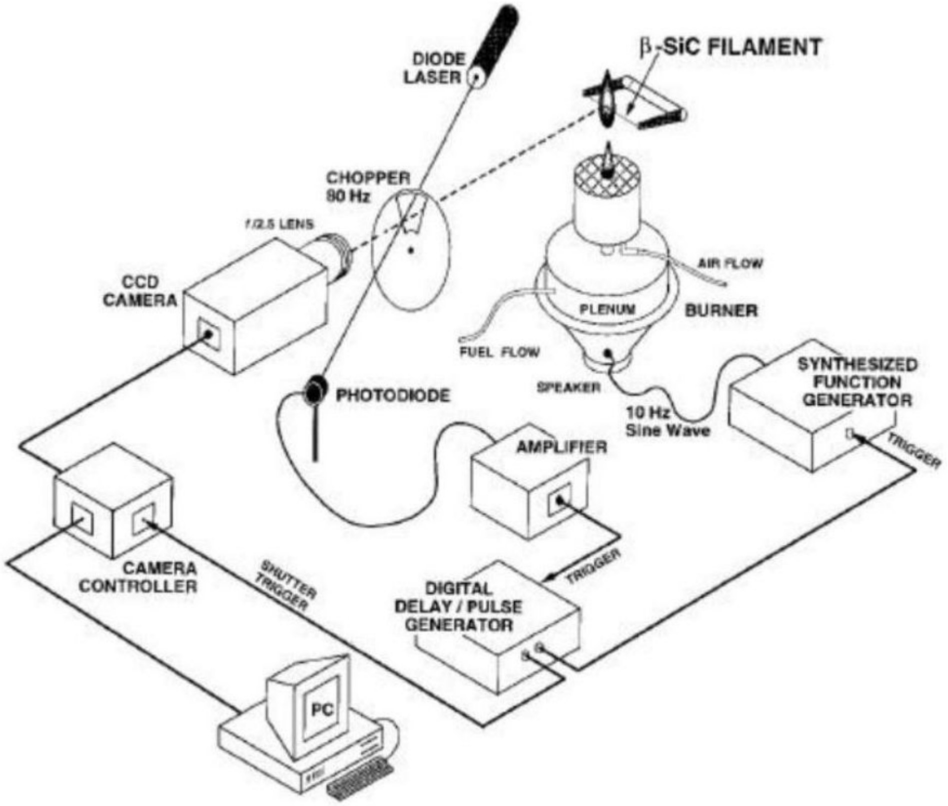

FIG. 1: An example for the TFP setup as reported in Pitts (1996).

between two pieces of metal shim stock that provide tension to maintain the fiber taut as its length changes with heating. The fiber is positioned horizontally downstream of the fuel tube and passes through the burner centerline. A mechanical chopper is used to reduce the integration time down to 1 ms and capture images corresponding to flicker frequency.

To adapt this technique to different flow conditions in our experiment, due to flame interaction and electromagnetic absorbance of the participating gas and to possible change in emissivity of the fiber with temperature and with soot deposition, two narrow-band filters, 3.99 and 4.25 μm, will be used to measure the temperature. With the assumption that the emissivity will be the same at these two wavelengths, there is no longer the need to know the emissivity. A measure of the background using the two filters will remove the emissions coming from the flame and from the surrounding walls. The emissions from the fibers will then be detectable and the relative intensities will be linked to a temperature based on a look-up table. The thermocouple calibration will be the basis of this table (Brochez et al., 2004; Choi et al., 1994; Duvaut, 2008; Laviolette, 1999; Fissan and Pfender, 1973; Roberts et al., 2011; West and Westwater, 1953).

3. GAS ANALYSIS WITH AN FTIR

The FTIR provides a precise (2%) gas composition measurement. A calculation detailed in Laviolette (1999) gives a quick iterative procedure to determine the gas temperature assuming frozen equilibrium for the gas sample. The molar balance equation can be written as follows:

$$\begin{aligned}\Phi \mathrm{C}_X\mathrm{H}_Y\mathrm{O}_Z + \beta \mathrm{O}_2 + 3.76\beta \mathrm{N}_2 \rightarrow & \; a\mathrm{CO}_2 + b\mathrm{CO} + c\mathrm{H}_2\mathrm{O} + d\mathrm{O}_2 + e\mathrm{NO} \\ & + f\mathrm{NO}_2 + g\mathrm{N}_2 + p\mathrm{C}_X\mathrm{H}_Y\mathrm{O}_Z,\end{aligned}$$

with β defined as

$$\beta = X + \frac{Y}{4} - \frac{Z}{2}.$$

The total number of moles for dry (S_{dry}) and wet (S_{wet}) gases is given by

$$S_{\text{dry}} = a + b + d + w + g,$$

$$S_{\text{dry}} = a + b + c + d + +e + f + g + p.$$

The FTIR gives the concentrations χ:

$$\chi_{\mathrm{CO}_2} = \frac{a}{S_{\text{dry}}};\ \chi_{\mathrm{CO}} = \frac{b}{S_{\text{dry}}};\ \chi_{\mathrm{O}_2} = \frac{d}{S_{\text{dry}}};\ \chi_{\mathrm{H}_2\mathrm{O}} = \frac{w}{S_{\text{dry}}};$$

$$\chi_{\mathrm{NO}} = \frac{e}{S_{\text{wet}}};\ \chi_{\mathrm{NO}_2} = \frac{f}{S_{\text{wet}}};\ \chi_{\mathrm{CHO}} = \frac{p}{S_{\text{wet}}}.$$

From the species balance, there are four additional equations:

Carbon:

$$a + b + pX = \phi X,$$

Hydrogen:

$$2c + pY = \phi Y,$$

Nitrogen:

$$g = 3.76\beta - \frac{e}{2} - \frac{f}{2},$$

Oxygen:

$$Z\phi + 2\beta = 2a + b + c + 2d + e + 2f + Zp.$$

A solution of this system of equations gives the number of mole per species. The temperature is finally obtained once the energy balance is completed using the normalized enthalpies:

$$\sum_{j_{\text{reactant}}} N_j \bar{h}_j = \sum_{j_{\text{products}}} N_j \bar{h}_j$$

This is true as long as thermal losses can be considered negligible, which is nearly the case in the current experiment. The actual system has 10 unknowns with 11 equations. This makes this set of equations a hyperstatic system to procure a better accuracy.

4. THERMOCOUPLE CALIBRATION

In addition to the FTIR emission data, a temperature mapping will be performed using type K sheathed thermocouples with no further attempt for radiation correction at this level. Accuracy on the order of 50 K is sufficient for this stage of the study.

5. EXPERIMENTAL SYSTEM

Figure 2 is a schematic of the experimental setup. Note that a gas probe or a thermocouple will be in lieu of the β-SiC mesh for the specific measurements presented above. The generic combustor rig in use has similar operating conditions to actual gas turbine combustors. Four strings are stretched horizontally and five are stretched vertically. The fibers are imaged onto a cooled (238 K) infrared (IR) camera using a 50 mm f/2.5 lens focused such that each of the 15 × 15 μm pixels corresponds to 150 × 150 μm in the image plane. A 640 × 170 pixel area of the array corrected with reference black bodies at 1500 K and 300 K to have a uniform response will be used. Pixel intensities will be digitized with 32-bit accuracy and will be saved in ASCII format for later analysis. The electromagnetic flux will be filtered with two narrow-band filters at 3.99 and 4.25 μm to diminish the uncertainty on the fiber emissivity and to remove the flame background from the signal. Also, a 10% neutral filter will be used to avoid detector saturation. The operating condition will vary between 1000 and 1300 K.

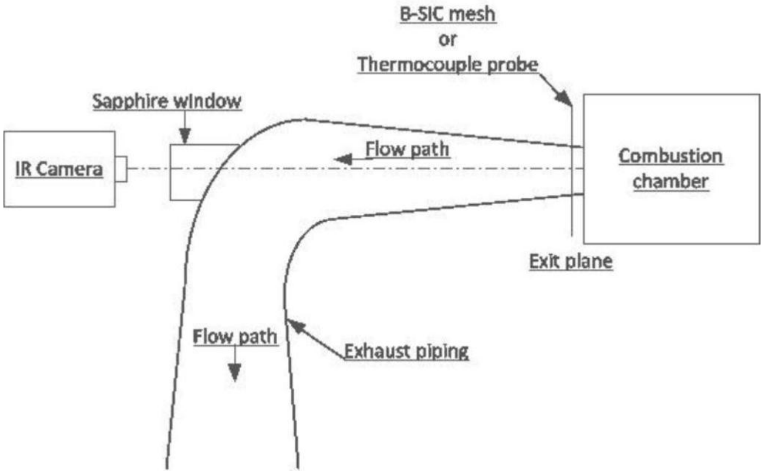

FIG. 2: Schematic of the experimental setup.

6. ANALYSIS PROCEDURE

The first step is to record the relative intensity along each fiber. For every operating condition in the combustion chamber, and for every setting of the optics between the IR detector and the hot gases, it is necessary to take a recording without the mesh of fibers. This allows correcting for a zero offset and for background emission by subtracting the signal to the TMP (thin mesh pyrometry) recording.

The next step is to relate relative emission to temperature. Because there are no data available for the case in hand, it is necessary to create a look-up table for temperature.

Two techniques will be used to approximate the gas temperature in the flow field as accurately as possible. First, sheathed thermocouples will be used to sweep the exit plane. No radiation correction will be applied at this stage other than the existing technology inherent to measurements with a thermocouple. This will provide a measurement in the 1000–1300 K range with a 50 K uncertainty. A coordinate system is established with 20 points to be scanned with all the measurement techniques.

In closing, the FTIR gas analysis provides a precise measurement of the main combustion gases present at the sampling point, on the order of 1%–2% for the concentration of each gas identified. The probe in use consists of three concentric tubes. The central tubes are for drawing the combustion gas sample while the two other circuits are for water cooling. The probe needs to be cooled to avoid melting, and the gas needs to be cooled down as fast as possible to stop the reaction. The frozen equilibrium is then achieved and is sent to the gas analyzer. With the calculation shown previously, we know the possible maximum temperature for each probed point.

7. CONCLUSIONS

The current experimental setup with an enclosed, very turbulent diffusion flame differs greatly from the original experiment reported in the literature that was done with an opened free buoyant laminar diffusion flame. Due to temperatures and velocities inherent to the exhaust of a typical gas turbine combustor, the challenge is definitely of significance. The walls of this exhaust duct, the hot combusting gases in the cavity, and the walls around the cavity of the combustor are all great emitters of electromagnetic flux, compared to the thin 15-μm β-SiC filament fibers. Furthermore, in order to get a temperature mapping at the exit place, the IR camera needs to be aligned with the flow. This adds more complexity to the setup with more unknown factors that need to be addressed. The hot volume of burning gases will greatly influence the electromagnetic flux as seen by the IR camera at the exit of the combustor, thus making the signal harder to analyze; hence the need for the 3.99 and 4.25 nm filters. These regions of the spectrum are less affected by the overall emissions from the gases or the walls of the combustion chamber. Currently, the dynamic response for the planar temperature measurements is not part of this planned study in order to concentrate on the efforts dealing with very harsh environment typical of gas turbine combustor exhaust conditions. Using larger diameter fibers is also an option to consider in case the 15-μm β-SiC filaments get damaged at an unreasonable rate. The accuracy and resolution are to be characterized by further developing the methodology presented in the literature to respond to industrial concerns with planar temperature measurements in difficult surroundings that is also in great demand to validate numerical simulation results.

REFERENCES

Brochez, S., Delvosalle, C., and Marlair, G., A two-thermocouples probe for radiation corrections of measured temperatures in compartment fires, *Fire Safety J.*, vol. **39**, pp. 399–411, 2004.

Choi, M. Y., Hamins, A., Mulholland, G. W., and Kashiwagi, T., Simultaneous optical meadurement of soot volume fraction and temperature in premixed flames, *Combust. Flame*, vol. **99**, no. 1, pp. 174–186, 1994.

Duvaut, Th., Comparison between multiwavelength infrared and visible pyrometry: Application to metals, *Infrared Phys. Technol.*, vol. **51**, no. 4, pp. 292–299, 2008.

Fissan, H. J., and Pfender, E., A probe system for spectrometric determination of temperature and concentration distributions in combustion gases, *Int. J. Heat Mass Transfer*, vol. **16**, no. 5, pp. 991–1001, 1973.

Kuhn, P. B., Ma, B., Connelly, B. C., Smooke, M. D., and Long, M. B., Soot and thin-filament pyrometry using color digital camera, in *Proc. 33rd Int. Symp. on Combustion*, Vol. 33, Tsinghua University, Beijing, China, pp. 743–750, Sep. 16–30, 2010.

Laviolette, M., *Mesure Non-Intrusive de la Temperature de Flamme*, Université Laval, Quebec, 1999.

Pitts, W. M., Thin-filament pyrometry in flickering laminar diffusion flames, in *Proc. 26th Symp. (Intl.) on Combustion*, Vol. 1, Naples, Italy, pp. 1171–1179, July 28–Aug. 2, 1996.

Pitts, W. M., Smyth, H. C., and Everest, D. A., Effects of finite time response and soot deposition on thin filament pyrometry measurements in time-varying diffusion flames, in *Proc. 27th Symp. (Intl.) on Combustion*, Vol. 1, Boulder, CO, USA, pp. 563–569, Aug. 2–7, 1998.

Roberts, I. L., Coney, J. E. R., and Gibbs, B. M., Estimation of radiation losses from sheathed thermocouples, *Appl. Therm. Eng.*, vol. **31**, pp. 2262–2270, 2011.

Vilimpoc, V. and Goss, L. P., SiC-based thin-filament pyrometry: Theory and thermal properties, in *Proc. 22nd Symp. (Intl.) on Combustion*, Vol. 22, University of Wahsington, Seattle, WA, USA, pp. 1907–1917, Aug. 14–19, 1988.

West, W. E., Jr. and Westwater, J. W., Radiation-conduction correction for temperature measurements in hot gases, *Ind. Eng. Chem.*, vol. **45**, no. 10, pp. 2152–2156, 1953.