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The fate and transport of nitroglycerin in the unsaturated zone at active and legacy anti-tank firing positions

Geneviève Bordeleau [a,*], Richard Martel [a], Guy Ampleman [b], Sonia Thiboutot [b], Isabelle Poulin [b]

[a] Institut National de la Recherche Scientifique, Centre Eau, Terre et Environnement (INRS-ETE), 490 de la Couronne, Quebec City, Qc., Canada G1K 9A9
[b] Defense Research and Development Canada, Valcartier, 2459 Pie-XI Blvd. North, Quebec City, Qc., Canada G3J 1X5

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ABSTRACT

The environmental fate of nitroglycerin (NG) in the unsaturated zone was evaluated in the context of double-base propellant residue deposition at anti-tank training ranges. Fresh propellant residues were collected during live anti-tank training. Surface soils, sub-surface soils and water samples from the unsaturated zone were collected at an active anti-tank range, and at a legacy site where NG-based propellants have been used. Results show that the residues are composed of intact propellant particles, as well as small quantities of NG, dinitroglycerin (DNG) and nitrate which are rapidly dissolved by precipitation, resulting in sporadic pulses of those compounds in water from the unsaturated zone after rain/snow melt events. The dissolved NG and DNG can be progressively degraded in the unsaturated zone, releasing nitrate as an end-product. Over a period of several years, small propellant particles located at the soil surface can be carried downward through the soil pore system by infiltration water, which explains the presence of NG in sub-surface soils at the legacy site, more than 35 years after site closure. NG is no longer leached from these old particles, therefore the detection of NG in sub-surface soils does not signify that groundwater is at risk of contamination by NG.

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1. Introduction

Military training activities can result in the presence of energetic materials (EMs) in soils, and sometimes groundwater and surface water on training ranges. The type, concentrations and spatial distribution of EMs depend on the training activities taking place at a site. In Canada and the United States, soils from several types of training ranges have been sampled, and anti-tank training ranges were found to be among the most contaminated (Jenkins et al., 2006). On these ranges, high explosives such as trinitrotoluene (TNT), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) are mostly found in soils near target areas since these compounds are present in the filling of projectiles, while nitroglycerin (NG) and nitrocellulose (NC) are usually found near firing positions since they are present in the formulation of propellants (Jenkins et al., 2006).

At firing positions, the contamination is due to the incomplete combustion of the propellant. Hence, as the anti-tank ammunition is fired, some propellant residues are expelled backwards from the shoulder launcher. Soot and unconsumed particles of different sizes are thus deposited on the ground, with the highest concentrations found within 30 m behind the firing wall (Walsh et al., 2012). The most common propellants used for anti-tank training are the double-base M7 and AKB 204, which are mainly composed of NG and NC. For these types of propellants, 0.2 and 14% of the original mass of NG is deposited on the ground in the form of residues,

* Corresponding author. Tel.: +1 418 654 2530x4468; fax+1 418 654 2600.
E-mail addresses: genevieve.bordeleau@ete.inrs.ca (G. Bordeleau), richard.martel@ete.inrs.ca (R. Martel), guy.ampleman@drdc-rddc.gc.ca (G. Ampleman), sonia.thiboutot@drdc-rddc.gc.ca (S. Thiboutot).

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respectively (Walsh et al., 2012). Regular training can thus lead to the build-up of propellant concentrations in surface soils. In Canada and the United States, NG concentrations in the order of thousands of mg/kg were reported in surface soils behind firing positions on anti-tank ranges (Jenkins et al., 2006; Thiboutot et al., 2004). NC concentrations have never been reported in this context, as it is not routinely quantified in field studies due to the time-consuming and labor-intensive analytical methods for this compound. Moreover, NC being a non water-soluble polymer, it is usually not considered as a threat to groundwater nor to human health (Jenkins et al., 2005).

After being deposited on the ground, the propellant residues containing NG and NC are subjected to weathering; however, the environmental fate of NG in the unsaturated zone in the context of double-base propellant deposition has been sparsely documented. Sampling of several sites has demonstrated that NG may be present at low concentrations (few mg/kg) in sub-surface soils over a depth of several centimeters (Thiboutot et al., 2004). The presence of NG in sub-surface soils could be due to NG-contaminated water in the unsaturated zone (pore water) being collected as part of the moist sub-surface soil samples. Indeed, a few laboratory studies have shown that part of the NG contained in propellant residues may be leached into groundwater, and that it does not bind irreversibly to low-carbon soils (Bellavance-Godin, 2009; Hewitt and Bigl, 2005). Once dissolved in pore water, NG may be degraded by various species of bacteria and fungi, both under aerobic and anaerobic conditions (Accashian et al., 1998; Christodoulatos et al., 1997; Marshall and White, 2001). The microbial degradation pathway involves the successive loss of nitro (NO_2) groups, thus releasing nitrite (NO_2^-) ions in solution (White et al., 1996). The final denitrated product is glycerol. If the released NO_2^- is not consumed by the microorganisms, it is rapidly oxidized to nitrate (NO_3^-) in the presence of oxygen. Other natural attenuation processes may contribute to NG degradation, however those processes are not well understood (Pennington et al., 2001). A study of the stability of NG in moist, unsaturated soils has shown that the half-life of NG in these conditions would be <1 day (Jenkins et al., 2003). The authors concluded that NG leaching out of propellant residues should not pose a threat to water quality. However, the NG concentrations used in this study were $\leq$0.2 mg/kg, so degradation rates could vary if NG concentrations were higher by a few orders of magnitude.

Overall, while some information is available on individual components of the fate and transport of NG from double-base propellants, the issue has not yet been studied as a whole, and some information gaps remain. For instance, the way that NG migrates vertically in soils is not well understood, and the leaching of NG from propellant and its subsequent degradation has only been observed in the laboratory. Also, while NG was reported to degrade rapidly in the environment, its presence at high concentrations in soils several years after site closure (Brochu et al., 2009) raises questions regarding the protection of groundwater resources. The objectives of this study were therefore to characterize the fate and transport of NG from propellant residues in the unsaturated zone, to determine whether it poses a risk to groundwater quality, and to distinguish the environmental risks associated with active training ranges versus legacy sites. To achieve this, a field study was carried out over a period of three years at the firing positions of two anti-tank training ranges. The first step was the collection of propellant residues from the live firing of anti-tank ammunition, in order to characterize the source term of contamination. Then, the short- and long-term fate of NG on training ranges was investigated through a field study realized at an active anti-tank range (site A), which has been in use for about 35 years, and a legacy anti-tank training range (site L), which has been closed for over 35 years. The field study involved the sampling of soils (surface and sub-surface) and water from the unsaturated zone.

2. Study sites

The two study sites are located within 5 km of each other, in eastern Canada. The legacy site (Site L) has been closed since 1975. It is located along a river (Fig. 1, right hand part). The firing position is located at around 200 m from the river on the north bank, while the impact area is located both on the north and south banks. Access to the former firing wall is now prevented by a fence located 5 m behind the former concrete firing wall. The pore water monitoring equipment was installed at 6 m behind the firing wall (Fig. 2, right hand part). At this location, the total organic carbon (TOC) content in the surface soil is 4.5%, and the clay content is 0.01% (Table 1). The top part of the soil profile is composed of fine to coarse sand with pebbles. The d_{50}, which represents the diameter of particles at the median of the grain size distribution, is 0.58 mm. Below this, a layer of clayey silt is present and is steeply inclined towards the river. At 7 m behind the firing wall, this layer is located at a depth of 0.8 m; just 1 m further (6 m behind firing wall), the layer is located below 1.3 m in depth. At the location where the water sampling instruments were installed, the water table is located at 1.2 m below ground surface, and drains northward towards the river. The annual groundwater recharge is between 500 and 700 mm.

The active range (Site A) has been used since the 1970's, and is located on the lower part of a mountain (Fig. 1, left hand part). The firing position is situated on a sand terrace on the flank of the mountain. The firing pad extends 20 m behind the firing wall (south) and consists of a regularly maintained gravel road (Fig. 2, left hand part). The pore water sampling equipment was installed at the southern edge of the firing pad, 20.7 m behind the firing wall; soil samples were collected at the same location. The TOC content in the surface soil is 3.8%, and the clay content is 1.4% (Table 1). The soil is composed of fine to coarse sand with pebbles and lenses of silty sand, and the d_{50} is 0.19 mm. South of this location, the topography is steep and keeps decreasing, until it reaches the bottom of the valley at the entrance of the training range (Fig. 1). On the mountain, precipitation water moves down (southward) as surface runoff, and enters the sub-surface at the edge of the sand terrace, upgradient from the firing pad. On the firing pad, the water table is located at approximately 25 m below ground surface during recharge periods, and is absent through most of summer. The annual groundwater recharge rate is between 300 and 380 mm. After reaching the bottom of the valley, groundwater is close to the soil surface and drains to the east towards the same river as site L. The river is located at approximately 3.5 km from site A.

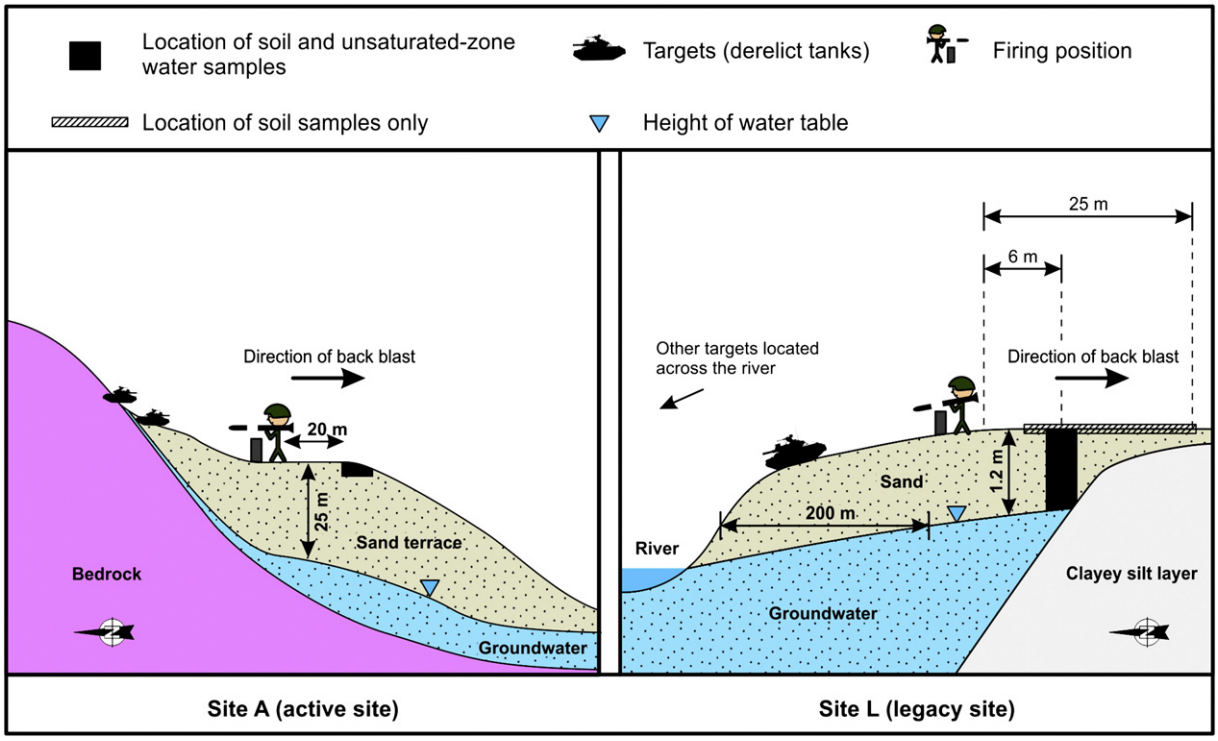

Fig. 1. Simplified conceptual model of study sites L and A (not to scale).

A background location was also selected for the installation of pore water sampling equipment. This site is located just outside site A, several hundred meters away from the firing position. The equipment was installed in a grassy location at the edge of a forested area, which is not in the direction of either the prevailing winds, or surface water

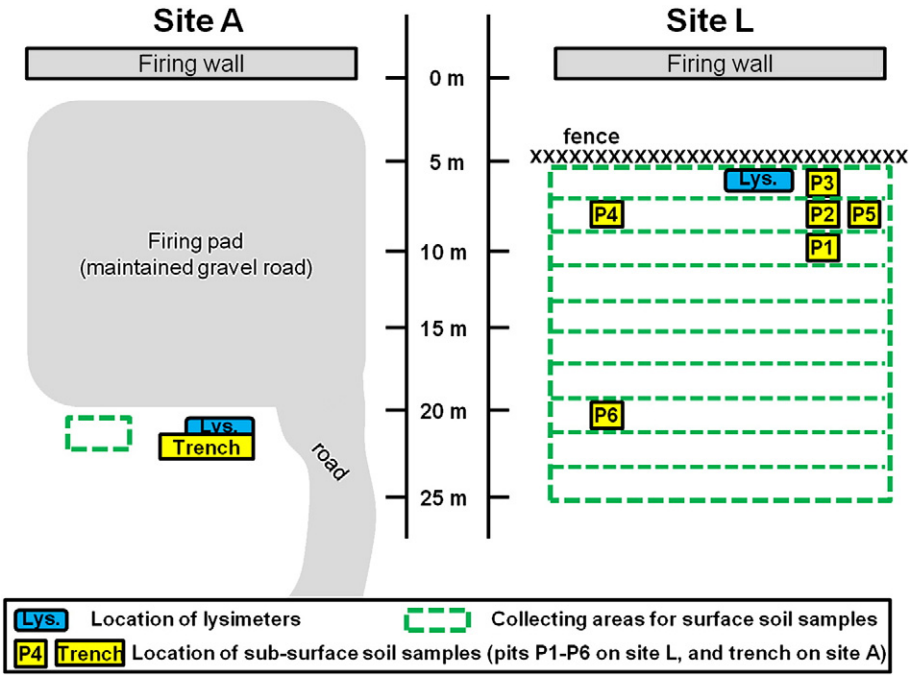

Fig. 2. Topview of sites A and L, with distances (in meters) from the firing wall.

Table 1
Characteristics of the two study sites and the location of the background (BG) lysimeter.

Characteristic	Site L	Site A	BG site
Distance between water sampling equipment and firing wall (m)	6	20.7	n.a.
Depth of water table (m)	1.2	25	n.d.
Annual aquifer recharge (mm)	500–700	300–380	n.d.
TOC content of surface soil (%)	4.5	3.8	2.8
Clay content of surface soil (%)	0.01	1.4	0.2
Median grain size (d_{50}) (mm)	0.58	0.19	0.51

n.a.: not applicable, n.d.: not determined, TOC = total organic carbon.

runoff coming from the firing position. At this site, the surface soil contains 2.8% TOC and 0.2% clay (Table 1).

3. Methodology

3.1. Propellant residue sampling

Propellant residues from the live firing of 84-mm Carl-Gustav anti-tank ammunition were collected on site A. The propellant used was AKB 204, which contains 61% NC, 37.5% NG, and 1.5% ethyl centralite. To collect the residues, a series of aluminum traps and holders designed to resist the back blast were placed on the ground between 5 and 10 m behind each of the two firing bays. The bays are located at both ends of the firing wall. As training proceeded from both bays, propellant residues were expelled rearwards from the shoulder launcher, and were deposited in the traps. The collected residues varied in size, and were mixed with other materials such as sand blown from the ground due to the back blast, as well as broken pieces of plastic used in the ammunition. The residues were not sorted, i.e. the propellant particles were not separated from the other materials present. This was done to avoid losing fine particles. The content of the traps located behind each firing bay was put into two 1-L wide-mouth amber glass bottles, and brought back to the laboratory. In order to estimate the readily-soluble NG, the residues in each of the four bottles were then mixed thoroughly, and for each bottle, a small portion (3 g) was then put in solution using 30 mL of distilled water, shaken for a few minutes, and the insoluble particles were left to settle to the bottom of the vial. A small volume of each solution (1 mL) was collected for the analysis of NG and DNG by high pressure liquid chromatography (HPLC). The remaining solutions were then filtered on Sep-Pak® Vac 12 cm^3/2 g tC18 cartridges (Waters, Mississauga, ON) to remove NG and DNG from solution, before analyzing nitrate and nitrite by ion chromatography. The extraction of NG/DNG prior to nitrate/nitrite analysis was necessary, because their presence would cause an overestimation of the nitrate/nitrite concentrations (Bordeleau et al., 2012). The insoluble residues in the vials were then dried, and the NG concentration in the dry residues was measured by HPLC. The NG, DNG, NO_3^- and NO_2^- concentrations obtained for the four bottles were averaged, and the uncertainty is reported at the 95% confidence level, based on the difference between the results of each bottle.

3.2. Soil sampling

At site L, composite surface soil samples (top 2 cm) were collected over the area located between 5 m and 25 m behind the firing wall. The samples (total mass of 2–2.5 kg each) were composed of 100 sub-samples collected within parallel rectangular areas 16 m wide (width of the firing wall) by 2 m long, starting along the fence and moving southward. They were collected using a stainless steel spoon, as the soil cohesion did not allow the use of a corer. Sub-surface soil samples were collected along the walls of five different hand-shoveled pits (P1–P5) located between 6 and 10 m behind the firing position, and an additional pit (P6) located 20 m behind the firing wall (Fig. 2, right hand part). Each pit measured approximately 0.4×0.4 m, and the samples (400–450 g) were composed of a combination of 12 sub-samples collected at the desired depths. The total depth of the pits varied between 0.4 and 1.0 m. The walls of the pits were cleaned to remove digging debris before sampling. Sampling was done with a stainless steel spoon from the bottom to the top of the pit. The stainless steel spoon was cleaned with acetone and distilled water between samples.

The samples from pit P5 were used for the analysis of NG in the different grain size fractions. For each of those samples, a higher mass (500–800 g) of soil was collected, and dried at room temperature in darkness, before being sieved by manual shaking using the following mesh sizes: 8, 4, 2, 1, 0.5, 0.25, 0.125, and 0.063 mm. The metallic sieves were thoroughly cleaned with running water and compressed air between each sample.

At site A, surface and sub-surface soil samples were collected 20 m behind the firing wall. Representative samples could not be collected closer to the firing wall due to the presence of the gravel firing pad. The surface soil samples (300–350 g) were composed of 12 sub-samples collected within a 1×2 m rectangular area, using a CRREL discrete corer (2.5-cm diameter, 2-cm depth) (Walsh, 2009). A series of sub-surface soil samples (400–450 g) were collected from the north wall of the trench that was dug for the installation of unsaturated zone sampling instruments. Each sample was composed of 12 sub-samples collected with a stainless steel spoon at specific depth intervals over the whole width of the trench wall, which was approximately 3.5 m. The maximum depth that was sampled was 1.2 m below ground surface.

3.3. Pore water sampling

Water sampling in the unsaturated zone was achieved using box and suction lysimeters. First, one box lysimeter was installed at the background location, at a depth of 0.4 m below ground surface. Three box lysimeters were installed at site L (0.1, 0.3 and 0.6 m depths), as well as at site A (0.1, 0.4 and 0.75 m depths). At depths greater than 1 m, the installation of box lysimeters can be difficult; therefore, two suction lysimeters were installed at site A (1.8 and 5.0 m depths) to allow water sampling at greater depth in the unsaturated zone, which extends to approximately 25 m below ground surface. At site L, no suction lysimeter was installed, as the water table was located at 1.2 m below ground surface.

The box lysimeters consisted of square open-top custom-made boxes made of either polyvinylidene fluoride (PVDF) or stainless steel (see Fig. 1 in Supplementary materials). They measured 0.3 × 0.3 m in width, and 0.4 m in height, and had a small hole at the bottom. The hole was fitted with a *Teflon*® connector, to which a *Teflon*® tubing (6 mm) was attached. Soil was prevented from entering the tube by a stainless steel screen (mesh of 125 μm) placed over the hole at the bottom of the lysimeter. The tubing led to a 10-L glass bottle placed in an access manhole. To install the box lysimeters, a trench was dug (3.5 m long × 1.5 m deep). For each lysimeter, a cavity corresponding to the size of the lysimeter was dug in the wall of the trench at the desired depth. The soil was removed in successive 5-cm layers and placed on clean plastic sheets. The box lysimeters were then filled with the soil layers in their original order, and were inserted in their respective cavity on the trench wall. Care was taken to fill the space between the wall of the lysimeters and the wall of the trench completely with soil, in order to avoid empty spaces which could affect the infiltration of precipitation water. An access manhole (0.9 m diameter) was placed in the trench. The *Teflon*® tubing leaving from the bottom of each lysimeter was directed to a hole drilled on the side of the access manhole. The trench was then backfilled completely. Water samples from the box lysimeters were collected directly from the 10-L glass bottles after each significant rainfall event. They were put in amber glass bottles and frozen until analysis.

The suction lysimeters (Soilmoisture Equipment Corp., model Y1920F1L12T-B02M2) were composed of a hollow porous ceramic cup, connected to a hermetically closed *Teflon*® cylindrical collector and two tubings (6 mm diameter) leading from the lysimeter to the ground surface (see Fig. 2 in Supplementary material). The first one, made of polyethylene (PE), was used to create a vacuum and to push air through the collector. The second one, made of *Teflon*®, was used for water sampling. The suction lysimeters were installed in a borehole drilled at an angle of 67° from the horizontal plane, so that the infiltrated water could flow through an undisturbed soil profile before reaching the lysimeter. The lysimeter collector was placed at the bottom of the borehole, and glass beads (*Potters industries Inc.*, model A2900, 30 μm microns) were put around it, in order to ensure a good hydraulic contact with the surrounding media. Bentonite pellets were used to fill the rest of the borehole to the top, thus preventing preferential infiltration. A trench was dug between the top of the borehole and the access manhole. The two small tubings were buried in the trench, and entered the manhole through a hole drilled on its side. The two small tubings were closed using *Norprene*® flexible tubes and plastic clamps. To sample water from the suction lysimeters, a vacuum of 50 centibars was applied to the collection collector through the PE tubing, using a manual vacuum pump, while the *Teflon*® tubing remained tightly closed. The PE tubing was closed to maintain the vacuum for a period of around 24 h. Then, both tubings were opened, and air was pushed through the PE tubing using the manual pump set in reverse mode. Water was thus pushed out of the lysimeter collector through the *Teflon*® tubing, and was collected into 200-mL amber glass bottles.

Over the course of the study, a total of 27 pore water samples were collected at site L, and 70 at site A, which included 15% duplicates. At site L, all samples were analyzed for NG, and 12 of them were analyzed for NO_2^-/NO_3^-. At site A, all samples were analyzed for NG, NO_2^-/NO_3^-, as well as for the combined concentration of dinitroglycerin isomers (1,2-DNG and 1,3-DNG), and mononitroglycerin isomers (1-MNG and 2-MNG).

3.4. Chemical analyses

3.4.1. Sample preparation

All water samples were kept frozen and away from light until analysis. For NG analyses, water samples from site L (volume 0.4 L) were pre-concentrated on Oasis HLB 3 cm^3/500 mg cartridges (Waters, Mississauga, ON). The NG was then eluted from the cartridge using 5 mL of methanol. Then, a volume of 1 mL of sample was mixed with 1 mL of ultrapure water. The solution was vortexed, and filtered at 0.45 μm. These samples were then analyzed by HPLC. At site A, water samples were analyzed for NG, DNGs and MNGs by liquid chromatography-mass spectrometry (LC-MS/MS), which allows a detection limit in the same range as with the HPLC method, but without having to pre-concentrate the samples. In this case, samples were prepared by mixing a sample volume of 250 μL with 250 μL of methanol. This method, which was developed over the course of the study, was preferred over the HPLC method for site A, because the sample volume that could be retrieved from the lysimeters was often very limited (due to the low aquifer recharge rate at this site), which resulted smaller samples to be pre-concentrated, and thus to a poor detection limit compared to site L.

Soil samples for NG analyses were dried at room temperature in darkness and sieved through a 10-mesh sieve (2 mm), and the oversize fraction was discarded. The sub-2 mm fraction was ground using a LM2-P mechanical grinder (ESSA, Belmont, WA, Australia). A 10-g sub-sample was then collected in triplicate, put into amber glass vials and mixed with 20 mL of acetonitrile. A vortex was applied for 1 min, followed by a sonication period of 2 h in a cooled (18 °C) ultrasonic bath. After sonication, the samples were left to settle for 30 min. Two milliliters of the acetonitrile was collected from the vial, and 2 mL of 0.5% $CaCl_2$ solution was added, in order to precipitate the NC which might otherwise interfere with the analysis. The extracts were then filtered at 0.45 μm and analyzed by HPLC.

Exceptionally, in order to determine whether NG migrated in the sub-surface in dissolved form or in the form of solid particles at site L (Section 4.3.2), a different protocol was used for selected soil samples collected at site L. These samples (400–450 g) were collected and analyzed in duplicate. They were not ground, and each one was spread on a table, and two 10-g composite sub-samples (built from 10 increments of approximately 1-g) were collected from each sample. The first 10-g sub-sample was extracted with acetonitrile, as described above. For the second 10-g sub-sample, extraction of NG was rather done using a 2 M aqueous KCl solution (Prokopy, 2001). This protocol is routinely used for the extraction of NO_3^- from soils (e.g. Rock et al., 2011). Before applying this aqueous extraction method, preliminary tests were done on a soil that had been spiked with a NG solution, which had then been evaporated at room temperature. For the preliminary tests, a 10-g sub-sample of the spiked soil was extracted using five aliquots of KCl (50 mL each). Each aliquot was kept separately

for NG analysis. Because all of the NG was recovered in the first two aliquots, for the actual field samples from site L, only three aliquots of 50 mL of KCl solution were used instead of five. For each aliquot, the slurry was agitated for 15 min using an automated hand-shaker, and was then centrifuged for 10 min. The supernatant was collected using a disposable-tip pipette, and was filtered at 0.45 μm. The three aliquots were then mixed together for a single NG analysis. After the KCl extraction, the soil samples were dried and extracted again with acetonitrile, in order to verify whether non KCl-extractable NG remained in the soils. All extracts were analyzed by HPLC. The uncertainty on the average concentrations was calculated at the 95% confidence level, based on the standard deviation between duplicates.

3.4.2. Analysis of NG, DNGs, and MNGs

Analyses of NG by HPLC were done at the hydrogeology laboratory of INRS-ETE, according to a modified version of USEPA method 8330B (USEPA, 2006), as described in Martel et al. (2009). Analyses were performed with a HPLC Agilent (Santa Clara, CA) HP 1200 equipped with a G1322A degasser, a G1311A quaternary pump, a G1329A autosampler and a G1315D UV diode array detector monitoring at 205 nm. The solvent was a mixture of water and methanol (50:50 v/v), at a flow rate of 1 mL/min. The column temperature was maintained at 25 °C during the analysis, and the injection volume was 20 μL. For water samples, the detection limit was 4 μg/L; for soil samples, it was 0.3 mg/kg. For the KCl extraction of soil samples, the detection limit was 0.1 mg/L in the KCl solution, which corresponds to 1.25 mg/kg in the original soil.

The NG, DNG and MNG analyses by LC-MS/MS were also done at INRS-ETE, using a Thermo Scientific LC-MS/MS (Waltham, MA) equipped with a Finnigan surveyor Autosampler plus, a Finnigan surveyor LC pump plus and a TSQ Quantum access mass spectrometry system detector with APCI source. A Thermo Hypersil Gold Phenyl column (100×2.1 mm, 3 μm particle size) was used to separate the analytes. Mobile phase was a mixture (30:70, v/v) of ammonium acetate solution and ammonium acetate-methanol with a flow rate of 300 μL/min and an injection volume of 20 μL. The concentration of the ammonium acetate in the final mixture was 1 mM. The parent molecule and fragmented product masses were respectively 196.115 and 59.070 for MNGs, 241.077 and 59.030 for DNGs, 286.058 and 62.060 for NG, and 289.056 and 63.000 m/z for the internal standard, which consisted in ^{15}N-labeled NG. For NG, the detection limit was 2.1 μg/L, and the quantification limit was 7 μg/L. The uncertainty on the results was ±19%. For MNGs and DNGs, the detection limit was 2.3 and 1.2 μg/L, respectively, and the quantification limit was 7.8 and 4.1 μg/L, respectively. The uncertainty was ±13% for both MNGs and DNGs.

3.4.3. Nitrate (NO_3^-) and nitrite (NO_2^-)

NO_3^- and NO_2^- ions were determined by ion chromatography (IC) using the ICS-2000 chromatograph from Dionex (Sunnyvale, CA) with 4 mm PAC AS18 ion exchange resin. The system maintained a constant pressure of 1964 psi, a flow rate of 1 mL/min of 23 mM KOH, a column temperature of 30 °C, and a current of 60 mA at the suppressor. Results are reported as N–NO_3^- and N–NO_2^-, to allow a direct comparison and/or addition of the concentrations of both ions, which do not have the same mass. The detection limit was 0.01 mg/L N–NO_3^- and 0.002 mg/L N–NO_2^-.

4. Results and discussion

4.1. Propellant residues

The average NG concentration in the aqueous solution containing the AKB 204 residues was determined to be 251 (±7) mg/L. This corresponds to the readily-soluble NG, which was deposited on the ground as part of very fine particles, instead of being trapped within the larger, insoluble propellant particles. Considering the volume of water that was used (30 mL), a mass of 7.8 (±0.2) mg of NG was therefore measured in the solution. In the remaining, dried residues, 116 (±4) mg of NG was measured. Hence, 7% (±1%) of the total NG that was collected was in a readily-soluble form, and 93% (±1%) remained trapped in the residue particles.

Additionally, in the solution MNGs were not detected, but DNGs were detected at an average concentration of 2.65 mg/L, for a total mass in solution of 0.08 mg. Therefore, incomplete combustion of the propellant also releases small quantities of readily-soluble DNGs, but this amount is almost two orders of magnitude lower than the amount of readily-soluble NG. NO_2^- and NO_3^- concentrations in the solution were also measured. The average concentration was 1.77 (±0.05) mg/L for N–NO_3^- and 0.16 (±0.01) mg/L for N–NO_2^-, for a total of 1.93 (±0.06) mg/L N-($NO_2^- + NO_3^-$), and a mass of N-($NO_2^- + NO_3^-$) in solution of 0.06 (±0.002) mg. The dissolved N-($NO_2^- + NO_3^-$) was therefore mainly constituted of NO_3^- (92%), with only a minor proportion of NO_2^- (8%). Moreover, the NO_2^- should oxidize rapidly to NO_3^- when dissolved in the oxygen-rich water of the unsaturated zone.

This demonstrates that the firing of anti-tank ammunition results in the deposition of fragmented propellant particles, as well as small amounts of readily-soluble NO_3^-, DNGs and NG. The mass of NG deposited per munition can be computed as follow:

$$\text{Mass of NG/munition} = (\text{Mass of propellant})(\text{NG content of propellant})(\text{Deposition rate})$$

where:
Mass of propellant used for each ammunition = 370 g
NG content of AKB 204 propellant = 37.5%
Deposition rate for Carl-Gustav ammunition = 14% (according to Walsh et al., 2012).

Hence, the firing of a Carl-Gustav munition resulted in 19.4 g NG being deposited on the ground, of which 1.4 g (7%) was readily-soluble, and 18.0 g (93%) was found within larger particles. The amount of DNGs and N–NO_3^- can be computed from the proportions of these compounds and NG in the solution obtained with the residues, such that:

$$\text{Mass of DNG or N–}NO_3^-\text{/munition} = (\text{Mass of readily soluble NG/munition})/(\text{Ratio of readily soluble NG to DNG or N–}NO_3^-\text{ in the solution})$$

where:
Mass of readily-soluble NG/munition = 1.4 g

Ratio of readily-soluble NG to DNG = 97.5
Ratio of readily-soluble NG to N–NO_3^- = 141.8.

Hence, the firing of a Carl-Gustav munition also resulted in the deposition of 0.01 g of readily-soluble DNGs, and 0.01 g of readily-soluble N–NO_3^-. On training ranges, this should translate into pulses of NO_3^-, DNGs and NG in infiltration water shortly after training events. Most of the NG, however, is deposited in the form of unconsumed propellant residue particles. Part of the NG in the residue particles can leach out over time and dissolve in infiltration water; the exact amount depends on the size and shape of the particles (Hewitt and Bigl, 2005).

4.2. Surface soils

The presence of NG in surface soils was investigated at both sites. At site L, NG was detected over the whole sampled area, with the highest concentration (4500 mg/kg) at 5–7 m behind the firing wall. This concentration is surprisingly high, considering that the site has not been used in the last 35 years. Concentrations then decrease with increasing distance from the firing position, except for an increase in concentrations between 13 and 17 m. Further than 17 m behind the wall, concentrations decreased again, and reached 22 mg/kg at 25 m behind the wall. On site A, soil samples were only collected at 20 m from the firing wall, due to the presence of a gravel firing pad between the firing wall and this location; concentrations in the three composite samples varied between 240 and 590 mg/kg, with an average of 390 mg/kg. This is similar to the NG concentration at the same distance from the wall on site L (370 mg/kg).

4.3. Sub-surface soils

The vertical migration of NG was evaluated from sub-surface soil samples collected on each of the two sites. At site L, for pits P1–P5 (located between 6 and 10 m behind the firing wall), NG was detected in 32 of the 37 samples, down to a depth of 1.0 m below ground surface; samples were not collected past this depth, as the water table was located just below. Similarly, in pit P6 (20 m behind the firing wall), NG was detected in six out of seven samples, down to the maximum sampled depth of 40 cm. In pits P1–P5, NG concentrations in the first 5 cm of soil were above 1000 mg/kg. On average, 75% of the NG was located within the first 5 cm (Table 2). The concentrations dropped rapidly between 0 and 20 cm (Fig. 3), with 99% of the NG being located within this depth interval. At depths greater than 20 cm, NG concentrations rarely exceeded 10 mg/kg. Also, NG concentrations measured in soils below 20 cm did not continue to decrease steadily; the concentration profile plateaued from 20 to 60 cm in depth in all pits. It is therefore clear that NG at site L did migrate vertically in the soil profile. The plateaued NG concentration for deeper samples (20 to 60 cm) could be due to maintenance work that had been done on the firing pad at the time that this site was used, or to preferential channels in the ground where a few propellant particles might have penetrated. In any case, the presence of NG in sub-surface soils more than 35 years after site closure raises questions as to whether groundwater is still at risk of contamination. However, at site A, the results were different. NG was detected only in the first two depth intervals (0–2 and 2–5 cm depths) at concentrations of 240 and 5 mg/kg, respectively. Therefore, 98% of the NG was located within the top 2 cm of soil, with the remaining 2% being located in the layer at the 2–5 cm depth (Table 2).

Table 2
Cumulative percentage (%) of the total mass of NG in the sampled soil profiles, at different depths.

Site	Proportion of NG	Depth from ground surface (cm)				
		0–2	0–5	0–10	0–15	0–20
Site A	Average (%)	98	100	–	–	–
	Std. dev.	2	0	–	–	–
	n	2	2	–	–	–
Site L	Average (%)	35	75	93	97	99
	Std.dev.	0	15	7	5	1
	N	1	5	6	5	5

n: number of samples, std.dev: standard deviation.

The fact that vertical migration in soils deeper than 5 cm was observed only at site L is surprising, considering that on site A, new residues are being regularly deposited and can leach NG into pore water, while the residues at site L are old, so most of the available NG should already have leached out. The absence of vertical migration on site A cannot be attributed to the lower NG concentrations at the soil surface, because vertical migration was observed at site L in pit P6, where NG concentrations in surface soils were comparable to the concentrations at site A. The TOC content of surface soils at both sites is similar, so adsorption of NG onto organic particles cannot be responsible for the limited migration at site A. Some factors that differ between both sites are the time that has elapsed since the residues were deposited at the soil surface, and the annual groundwater recharge rate. If these are the main factors governing the vertical migration of NG in soils, it could mean that the NG in sub-surface soil samples was present in the form of solid propellant particles rather than dissolved NG adsorbed onto soil particles. The small propellant particles could have migrated downward through the pore system with infiltration water over the years. If this is the case, the smaller particles should have proceeded further down than the larger particles. This was investigated by analyzing the NG present in the different grain size fractions of the soil.

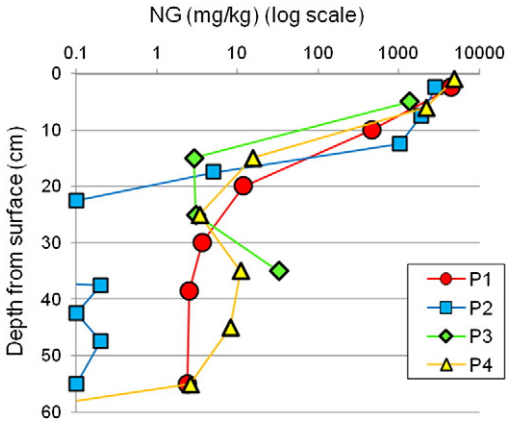

Fig. 3. Vertical NG migration in soils of pits P1–P5 at site L, at a distance of 6 to 10 m behind the firing wall (log scale).

4.3.1. Distribution of NG in the grain size fractions

The grain size distribution of NG was measured in the AKB 204 propellant residues that were collected at site A, and in surface soils and sub-surface soils from pit P5 on site L (Fig. 4). In the AKB 204 residues, most of the NG mass was located within the larger fractions, i.e. between 0.250 and 8 mm. For soil samples, NG was not detected in the 2–8 mm fraction. In the surface soil sample, most of the NG was found in the larger fractions (larger than 0.250 mm). Then, as the depth of the samples increases, the proportion of NG decreases in the coarser fractions, and increases in the finer fractions. This supports the hypothesis that NG moves down the soil profile in the form of non-dissolved propellant fibers, rather than as dissolved NG molecules leaching from the propellant at the soil surface. However, the decrease observed in Fig. 4 is not very pronounced, so further investigation was needed in order to confirm this hypothesis. In the following section, the hypothesis was therefore tested using a second approach.

4.3.2. KCl-extractable NG

To further investigate whether NG migrates in sub-surface soils in the form of propellant fibers, a comparison of the amount of NG recovered by aqueous (KCl) and organic (acetonitrile) extractions was realized. The rationale is that if NG had transited through the soil profile in dissolved form, it would be reversibly sorbed to soil grains and could be extracted with the KCl solution. On the other hand, if NG is bound within old propellant fibers, it could only be extracted using acetonitrile, which dissolves the NC matrix. Therefore, in this case NG should not be detected in the KCl aqueous extract.

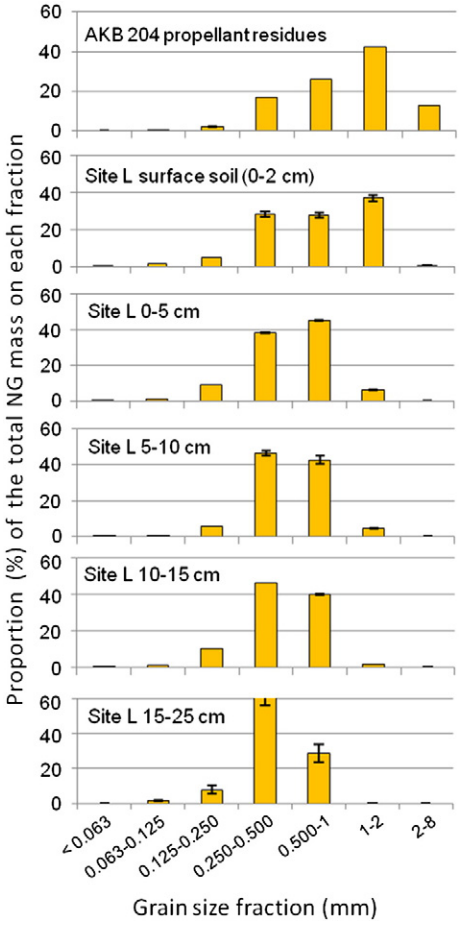

Fig. 4. Distribution of NG on the different grain size fractions in the AKB 204 residues, and in sub-surface soils from pit P5 at site L.

The tests were done on soil samples collected at two different depths (5–10 and 10–15 cm below ground surface) in pit P5 at site L. The NG concentrations in the soil samples (as determined by the acetonitrile extraction performed on one of the two 10-g sub-samples collected within each sample) were 1184 (±201) mg/kg for the 5–10 cm depth, and 156 (±27) mg/kg for the 10–15 cm depth. Then, the aqueous extractions were performed on the second 10-g sub-sample collected within each sample, and NG was not detected in any of the aqueous extracts. After the aqueous extractions, the NG concentration in these soil sub-samples was 1336 (±227) mg/kg at 5–10 cm in depth, and 136 (±23) mg/kg at 10–15 cm in depth. The recovery of NG using acetonitrile therefore varies between 87% (±15%) and 113% (±19%) of the initial concentration. The high uncertainty is due to the fact that NG analyses were done on 10-g sub-samples collected within soil samples that had not been ground. Grinding was not possible because it would have broken down the propellant fibers and released NG that should normally be bound within the fibers. NG contamination in soils on training ranges is known to be very heterogeneous, therefore the difference between the concentrations before and after aqueous extractions can be attributed to heterogeneity of the contamination.

Despite the heterogeneity, it is clear that the NG present in sub-surface soils was not extractable by the KCl solution. This confirms that NG migrated vertically in soils in the form of small NC-embedded non-dissolved propellant fibers. Therefore, finding NG in sub-surface soils at legacy sites is not an indication that groundwater is at risk of contamination, but it is rather an indication that NG has been present at this site for several years, and that the site conditions (recharge rate, grain size distribution) were adequate to promote the migration of particles through the pore system.

4.4. Water from the unsaturated zone

To confirm that groundwater contamination was indeed not occurring at site L, 27 pore water samples from the unsaturated zone were collected over one year. NG was not detected in any sample, while nitrate concentrations varied between 0.03 and 0.74 mg/L N–NO_3^-, and nitrite concentrations were always near the detection limit. Among the 12 samples analyzed for nitrate, five exceeded the maximal estimated background concentration of 0.22 mg/L N–NO_3^-. This concentration was calculated at the 99% confidence level (Student's t-test), from all nitrate concentrations measured in samples from the background lysimeter. It therefore appears that while NG is not a concern for groundwater at legacy sites, the propellant residues at the soil surface might still be releasing nitrate. This could be due either to slow photodegradation of NC (Devore et al., 1929), or to aging of the propellant, where nitro groups are slowly released from NC (Auer et al., 2005).

At site A, anti-tank training activities are still taking place, so fresh propellant residues are regularly being deposited. To verify whether NG leaches out of those residues, 70 water samples from the unsaturated zone were collected over two years, for the analysis of NG, DNGs and MNGs, as well as NO_2^-/NO_3^-. NG was detected in 10 samples, at a maximum concentration of 840 μg/L. Four of the samples had concentrations above the detection limit but below the quantification limit. MNGs and DNGs were detected in 34 samples, at a maximum concentration of 84 μg/L; six of those samples had concentrations below the quantification limit. Nitrite concentrations were always near or below the detection limit. Nitrate concentrations varied between 0.01 and 8.66 mg/L $N–NO_3^-$. Overall, 71% of the samples had nitrate concentrations above the maximal background level.

The sporadic detection of NG and its degradation products suggests that NG leaches out of the propellant residues over a short period after the residues are deposited on the ground surface; however, the facts that NG concentrations were often below the quantification limit, and that water was not present in all lysimeters on the same dates, do not allow a direct comparison of NG concentrations at different depths on the same dates. In fact, more information can be gained by looking at the proportion of samples with NG/DNG/MNG detection, or with NO_3^- concentrations above the maximal background level, at each depth (Fig. 5).

NG, DNGs and MNGs were detected in a large proportion of the samples near the soil surface; the presence of degradation products (DNGs and MNGs) near the soil surface may appear surprising. These degradation products could come either from the incomplete combustion of the propellant (DNGs only), or from degradation processes taking place at the soil surface, such as photodegradation. Interestingly, the proportion of NG/DNG/MNG detection in samples decreases as depth increases (Fig. 5). For example, at 10 cm below ground surface, 89% of the samples contained MNGs/DNGs, compared to 22% at a depth of 5.0 m. For NG, the proportions at these two depths are 33% versus 13%. Because those samples were collected in the unsaturated zone and the contaminant source zone is located above, dilution by pristine water, which could be observed in the saturated zone, is not possible. Instead, these decreasing proportions indicate that degradation of NG is occurring. Contrary to NG/DNG/MNG, the proportion of samples with NO_3^- concentrations above background levels increases with increasing depth (Fig. 5). Because NO_3^- is being released through NG degradation, this increasing proportion with increasing depth supports the hypothesis that NG is being degraded in the unsaturated zone through natural attenuation processes. Attenuation of NG has been observed before in soils, in the presence or absence of microorganisms (Clausen et al., 2011; Jenkins et al., 2003; Xu et al., 2010). Nitrate concentrations in pore water samples at site A never exceeded the drinking water guideline of 10 mg/L $N–NO_3^-$ (Health Canada, 2010; USEPA, 2009). However, because nitrate is persistent under oxidizing conditions, these concentrations contribute to the nitrate load in aquifers, where nitrate from several sources can combine.

Based on the results presented above, Fig. 6 shows a simplified conceptual model for the fate and transport of NG and its degradation products from unburned propellant grains ejected in the back-blast of shoulder-held anti-tank munitions at active and former firing positions.

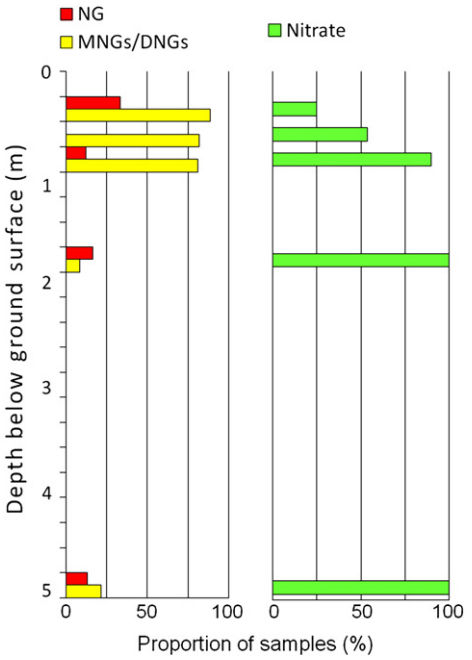

Fig. 5. Proportion (%) of groundwater samples (n = 70) from the unsaturated zone at site A with NG/MNG/DNG detection, or with NO_3^- concentrations above the maximum background level.

5. Conclusion

The environmental fate of NG was studied in the context of double-base propellant residues being deposited on the soil surface at anti-tank range firing positions. Results showed that: 1) Firing of each Carl-Gustav anti-tank weapon resulted in the ejection of small quantities of NO_3^- (0.01 g), DNGs (0.01 g) and NG (1.4 g) that were deposited on the ground and were available for rapid dissolution by infiltration water; the rest of the NG (18 g) was deposited in the form of unburned propellant particles of various sizes; 2) some of the NG within these propellant particles can leach out into pore water over a relatively short period of time; 3) the dissolved NG degrades through natural attenuation processes as it migrates down in the unsaturated zone, thus releasing nitrate as an end-product; 4) small propellant particles located at the soil surface may migrate downward in the soil profile over several years, if hydrogeological conditions are favorable (high water infiltration rate, coarse grain size distribution); 5) at legacy sites, high NG concentrations in surface and sub-surface soils do not pose a threat to groundwater quality, as the NG is embedded deeply within old fibers and does not dissolve anymore; however, small amount of nitrate might still be slowly released due to aging of the propellant.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jconhyd.2012.09.001.

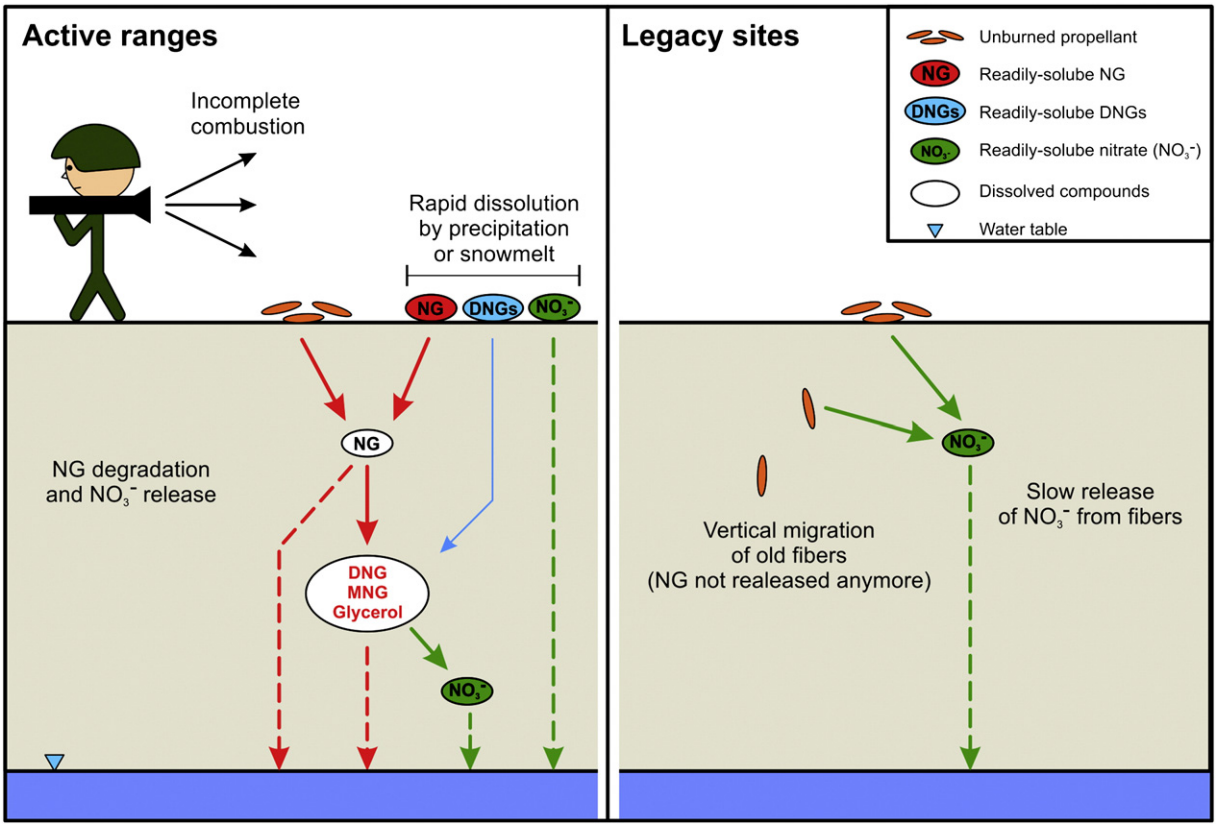

Fig. 6. Conceptual model of the fate and transport of NG and NO_3^- from propellant at active and former anti-tank firing positions.

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