



Nitroglycerin degradation mediated by soil organic carbon under aerobic conditions



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ABSTRACT

The presence of nitroglycerin (NG) has been reported in shallow soils and pore water of several military training ranges. In this context, NG concentrations can be reduced through various natural attenuation processes, but these have not been thoroughly documented. This study aimed at investigating the role of soil organic matter (SOM) in the natural attenuation of NG, under aerobic conditions typical of shallow soils. The role of SOM in NG degradation has already been documented under anoxic conditions, and was attributed to SOM-mediated electron transfer involving different reducing agents. However, unsaturated soils are usually well-oxygenated, and it was not clear whether SOM could participate in NG degradation under these conditions. Our results from batch- and column-type experiments clearly demonstrate that in presence of dissolved organic matter (DOM) leached from a natural soil, partial NG degradation can be achieved. In presence of particulate organic matter (POM) from the same soil, complete NG degradation was achieved. Furthermore, POM caused rapid sorption of NG, which should result in NG retention in the organic matter-rich shallow horizons of the soil profile, thus promoting degradation. Based on degradation products, the reaction pathway appears to be reductive, in spite of the aerobic conditions. The relatively rapid reaction rates suggest that this process could significantly participate in the natural attenuation of NG, both on military training ranges and in contaminated soil at production facilities.

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1. Introduction

Nitroglycerin (NG) has often been detected in soils on military training ranges, as a result of incomplete combustion of the propellant used for training activities such as firing of anti-tank rockets, artillery, machine gun grenades, and small arms (Walsh et al., 2012). Once deposited on the ground, the NG located within propellant residues can partially dissolve in infiltration water and migrate downward in the soil profile, eventually reaching the water table, and potentially discharging to surface water bodies. The presence of NG in groundwater and surface water is of concern, as prolonged

Abbreviations: NG, nitroglycerin; NO_2^- , nitrite; NO_3^- , nitrate; DNG, dinitroglycerin; MNG, mononitroglycerin; POM, particulate organic matter; DOM, dissolved organic matter; SOM, soil organic matter (comprises POM and DOM); NDOM, natural dissolved organic matter

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exposure to this compound may cause severe and diverse health effects on humans (Bhaumik et al., 1997), as well as toxicity to microorganisms and wildlife (Burton et al., 1993).

To date, the presence of NG has been very sparsely documented in groundwater on military training ranges. However, at the firing position of an active anti-tank range in Eastern Canada, NG and its common degradation products (dinitroglycerin (1,2- and 1,3-DNG), mononitroglycerin (1- and 2-MNG), nitrate (NO_3^-)) have been detected in water from the unsaturated zone (pore water), at depths up to 5.0 m below ground surface (Bordeleau et al., 2012a). The presence of these degradation products is an indication that natural attenuation of NG is occurring.

Such natural attenuation can be the result of various processes, which have not been fully characterized until now. The two main degradation processes that have been documented for NG are biodegradation (Bernstein et al., 2010; Clausen et al., 2011; Husserl et al., 2010; Jenkins et al., 2003; Pennington and Brannon, 2002) and photolysis (Bedford et al., 1996; Bordeleau et al., 2013; Pennington et al., 2001). Both processes proceed through sequential denitration of the NG molecule, releasing a nitrite (NO_2^-) ion at each step, which can then oxidize to NO_3^- in presence of oxygen. However, in several biodegradation studies, the released NO_2^- was consumed by the microorganisms and was therefore not found in solution (Accashian et al., 2000; Ducrocq et al., 1989; White et al., 1996). Likewise, photolysis of solid NG-bearing propellant particles located at the soil surface was shown to produce relatively little NO_2^- or NO_3^- available for dissolution in infiltration water (Bordeleau et al., 2013). Therefore, these two processes may not satisfactorily explain the high NO_3^- concentrations observed at the anti-tank firing position, which underlines the necessity to better characterize the fate of NG in the subsurface.

One potential process that has been very sparsely documented is the degradation of energetic materials mediated by the presence of organic carbon. Indeed, organic carbon was traditionally only considered to cause sorption of energetic materials (Clausen et al., 2011), but in the last decade, it was also recognized to mediate the reduction of organic contaminants by promoting electron transfer (Tratnyek et al., 2001). Such reaction has been documented in a few studies for energetic materials, such as NG, trinitrotoluene (TNT), and 1,3,5-hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). However, these studies focused on degradation in anoxic conditions, which provide favourable conditions for reduction reactions. Such conditions are common in lacustrine or marine sediments, in saturated soils with high organic matter content, or they may be induced in *ex-situ* remediation strategies.

On training ranges, however, most of the NG is located at the soil surface and in the first few centimeters of the soil profile, where soils are unsaturated and conditions are aerobic. One study has shown that unsaturated soils could support degradation of TNT in presence of organic carbon (Singh et al., 2008). Degradation of NG mediated by soil organic matter (SOM) was briefly discussed in another study, but the authors mentioned that aerobic conditions resulted in very slow degradation compared to anaerobic conditions, and they did not explore this reaction further (Saad et al.,

2010). Aerobic SOM-related NG degradation may therefore not be suitable for active remediation strategies, where process efficiency is sought, however in a natural attenuation context where most degradation reactions are slow, it could be a relevant process.

The goal of this study is therefore to determine whether the presence of SOM (in the form of particulate organic matter (POM) and/or dissolved organic matter (DOM)) may significantly participate in the natural attenuation of NG, and the concomitant production of NO_3^- under aerobic conditions. More specifically, the objectives were to: 1) verify whether POM causes sorption and/or degradation of NG; 2) distinguish the roles of POM and DOM in NG degradation; and 3) investigate the degradation mechanism involved. These issues were first investigated through a series of batch-type experiments, where concentrations of NG and its common degradation products were monitored over time. Experimental conditions were chosen to favour NG degradation, i.e. there was permanent contact and stirring of NG solution with soil having a relatively high (up to 4.5%) organic carbon content. The results obtained from batch experiments were then verified in column-type experiments, where conditions were less ideal but more representative of several of the contaminated zones on military ranges, i.e. infiltration of precipitation water into shallow, well-oxygenated contaminated soils with moderate organic carbon content.

2. Experimentals

2.1. Chemicals and reagents

For batch-type experiments, spiking of treatments with NG was achieved using a concentrated (220 mg/L) NG stock solution. The stock solution was prepared by stirring double-base propellant grains (Powder C propellant: 65% NC, 34% NG, and 1% ethyl centralite) in distilled water for 7 days, which causes the dissolution of some of the NG contained in the propellant. The solution was then filtered on a 0.45 μm nylon membrane, and kept at 4 °C in an amber glass bottle. Spiking of experimental treatments with NO_2^- was achieved using a stock solution (5.2 mg N- NO_2^- /L) prepared from ACS-grade NaNO_2 (EMD Millipore, Billerica, MA). For column-type experiments, fragments of AKB 204 propellant (61% nitrocellulose, 37.5% NG, 1.5% ethyl centralite) were used. These fragments were picked from bulk propellant residues collected during the live firing of 84-mm Carl-Gustav anti-tank ammunition (Bordeleau et al., 2012a).

All instruments that had to be in contact with the experimental soils and solutions were cleaned using soapy water, distilled water, and ACS-grade methanol (MeOH; BDH Merck Ltd., Poole Dorset, UK). For removal of NG by solid-phase extraction in aqueous samples, HPLC-grade acetonitrile (EMD Millipore, Billerica, MA) was used to condition the extraction cartridges. For chemical analysis of NG, DNGs and MNGs, OmniSolv LC-MS grade MeOH (EMD Millipore, Billerica, MA) and HPLC-grade acetonitrile were used. Finally, samples for NH_4^+ analyses were acidified using ACS-grade H_2SO_4 (Sigma-Aldrich, St. Louis, MO), while samples for metal analyses were acidified using trace metal-grade HNO_3 (Thermo Fisher Scientific, Waltham, MA).

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