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Sorption and desorption kinetics of nitroglycerin and 2,4-dinitrotoluene in nitrocellulose and implications for residue-bound energetic materials

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ABSTRACT

Energetic materials (EMs) bound to propellant residues can contribute to environmental risk and public health concerns. This work investigated how nitrocellulose, a common binding material in propellants, may control the release dynamics of nitroglycerin (NG) and 2,4-dinitrotoluene (2,4-DNT) from propellant residues. Batch adsorption/desorption experiments on nitrocellulose and re-interpretation on results from past leaching studies involving propellant-bound EMs were conducted. Mechanistic modeling of adsorption/desorption kinetics based on intra-particle diffusion (IPD) predicted aqueous intrinsic diffusivities (D_{iw}) to within a factor of 2 of expected values. Furthermore, the IPD model was able to predict effective diffusivities (D_{eff}) during the early leaching of NG from propellant residues to within a factor of 2 over a 3-log unit range. Prediction of leaching D_{eff}'s associated with fired residues was less successful probably due to the neglect of compositional and morphological heterogeneity within the residues. Close correlations were found between the early and late D_{eff}'s of residue-bound NG and between the fast- and slow-domain rate constants for both EMs, suggesting that the late leaching kinetics of bound-EMs may be empirically assessed from the early kinetics. This work illustrates that, in addition to dissolution, retarded diffusion through nitrocellulose matrix may also limit the overall release and transformation of residue-bound EMs in the field. Implications and limitations of the current study, and the steps forward are also presented.

1. Introduction

Residues containing energetic materials (EMs) or munition constituents (MCs) can pose serious environmental and health hazards when released into the environment (Best et al., 2006; Dodard et al., 2005; Kuperman et al., 2006; Lima et al., 2011). Environmental release of *explosive chemicals* such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and *propellant constituents* such as nitroglycerine (NG), 2,4-dinitrotoluene (2,4-DNT), has been reported at military training ranges (Martel et al., 2009) and former factory sites (Robertson et al., 2007), leading to their presence in soil (Clausen et al., 2010; Jenkins et al., 2006), groundwater (Martel et al., 2009; Robertson et al., 2007) and even coastal tidal zone nearby (Walsh et al., 2010). Clean-up and response cost for active or formerly used military sites in US can cost billions of dollars (Bearden, 2008), comparable to that estimated for other contaminated groundwater sites in US (National Research Council, 2013). EMs contamination is not unique to US as worldwide episodes of surface and subsurface contaminations have also been documented as a result of training, disposal, and storage activities (Linkov et al., 2014; Pichtel, 2012).

A number of studies have suggested that some common EMs may be readily degraded or immobilized in natural environment or engineered systems. Fuller et al. (2004, 2005) reported that peat moss is effective in reducing the dissolved levels of TNT, RDX, and HMX significantly with some degree of mineralization observed. More recently, Bordeleau et al. (2014) reported the rapid and complete degradation of NG in the presence of soil-derived

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particulate organic matter within a week. These findings suggest that under favorable chemical environment, natural attenuation may be a viable option for EM-impacted surface soils.

Field sampling campaigns and investigations, however, suggested that the dispersed EMs may linger on longer than expected. By applying stable C, H, and N isotope analyses to EMs-impacted field soils, Wijker et al. (2013) estimated decadal biodegradation half-life for TNT, 2,4-DNT, and 2,6-DNT. Bausinger et al. (2007) reported residual TNT, 2,4-DNT, and metabolites from the Verdun battlefield at 1–10 mg/kg levels despite they were deposited almost a hundred years ago. These levels are comparable with those found at the firing points in live-fire training ranges (Jenkins et al., 2006) or that employed in laboratory desorption studies (Yamamoto et al., 2004). These studies demonstrated that the dispersed EMs can persist for many decades in the field, despite their rapid degradation and disappearance in laboratory studies.

The discrepancy between EM's long presence in the field and their short laboratory half-lives needs to be reconciled. For better experimental control, many studies have used neat solutions or crystals of EM compounds, rather than taking munition residues collected from the fields, in their studies. These includes investigations on biodegradation (Christodoulatos et al., 1997; Halecky et al., 2014), sorption (Clausen et al., 2011), remediation strategies/applications/technologies (Bordeleau et al., 2014; Fuller et al., 2005, 2004). However, evidence has suggested that the source of EMs can affect the transport/fate behavior of the EMs. Percolation of NG through soils was considerably slower when fired propellant residues was used than with neat solution as the source (Clausen et al., 2010). Similarly, the soil-column breakthrough kinetics were parameterized differently when solid propellants were used as source (Dontsova et al., 2009). In other words, EMs associated with munition residues may behave differently than those exist in the freely dissolved forms.

Environmental fate of propellant-bound EMs also depends on the nature of the EMs – whether they are freely dissolved or bound. Recently, we have demonstrated (Kuo et al., 2017) that nitrocellulose, a major binding matrix for energetic components in a variety of propellants (Clausen et al., 2010; Steinberger and Drechsel, 1969; Taylor et al., 2012), is almost 10 times more effective in sorbing NG and 2,4-DNT than soil organic carbon. Preliminary investigation also suggested that breakthrough kinetics of EMs originated from propellant residues or particles in column studies can be better explained when sorptive binding of EMs to nitrocellulose is considered (Kuo et al., 2017). The analysis agreed with the drip and batch tests performed by Taylor et al. (2012), which showed that NG encased in propellant grains was released much slower than expected without considering binding to nitrocellulose. These pieces of evidence together suggest that nitrocellulose may have a critical role in determining how fast bound propellant-EMs may be released into the environment. Earlier nitrocellulose diffusion findings have limited applicability as these studies worked with hourly timescale (Drechsel et al., 1953; Lewis, 1978; Lewis and Roberts, 1982), focused on elevated temperatures (Brodman et al., 1975), or used organic co-solvent (Winkler and Starks, 1988). A systematic investigation on the dynamics of EM transport in and out of nitrocellulose is thus needed.

This study aims to explore the role of nitrocellulose in the leaching of residue-bound NG and 2,4-DNT, two commonly encountered propellant-EMs. The uptake and desorption dynamics of NG and 2,4-DNT through military grade nitrocellulose matrix was investigated in model batch experiments at various conditions and analyzed using empirical and mechanistic kinetic models. Kinetic observations reported from other leaching studies were then re-interpreted using the acquired kinetic characterization and understanding. Specifically, three questions were examined: (i) Can the adsorption and desorption kinetics of NG and 2,4-DNT be modeled mechanistically based on their sorption isotherms and the system properties such as dissolved concentration and solid-to-water ratio? (ii) Can the leaching behavior of EMs from propellant residues (both fired and unfired) be explained by the sorptive interaction between EMs and nitrocellulose? (iii) Is it possible to relate desorption kinetics at later times to that in the early times? Raw manufactured nitrocellulose was preferred over propellant grains as it afforded better experimental control, greater compositional homogeneity, and shorter sorption/desorption duration. This study intends to explore these possibilities and questions using nitrocellulose, rather than live-fired particles, as a model matrix. Compositional heterogeneity and variable combustion history of different residue particles make them difficult to be used in controlled laboratory setting.

2. Materials and methods

2.1. Chemicals

Nitrocellulose (12.55% nitrogen and 26.66% moisture) was obtained from Esterline Defense Technologies (EDT), Coachella, CA. The material was manufactured by Hanwa Corporation (Seoul, South Korea) and certified as military grade. An aqueous stock solution (497.3 ± 0.7 mg/L) of nitroglycerin (NG) was provided by the Redford Army Ammunition Plant (Redford, VA). Crystalline 2,4-dinitrotoluene (2,4-DNT) was obtained from Sigma-Aldrich (97%). Sodium azide (NaN_3) was obtained from MP Biomedicals, LLC. NG and 2,4-DNT standards were purchased from AccuStandard Inc. (New Haven, CT). These standards were used for the verification of the NG stock solution and the preparation of calibration solutions for HPLC analysis. Deionized water (18 MΩ cm resistance) was used for the preparation of all solutions. HPLC grade methanol was obtained from Acros Organics. All chemicals and stock solutions were stored (PTFE-lined caps) in the dark at room temperature until further use. Standards, calibration solutions, and samples were stored in dark at 5 °C when not used. All experimental solutions (i.e., tests, controls, and blanks) and calibration standards contained 0.01 M NaN_3 as biocide. Glass vessels were used in the preparation and conducting of all experiments.

2.2. Characterization of nitrocellulose fiber

Dimensions of nitrocellulose fibers were determined from analyzing the microscopic images of the shipped fiber. Images were taken with a digital camera (Canon EOS Digital Rebel XTi with a Canon EF-S600 mm f/2.8 Macro USM lens; Lake Success, NY). Images were viewed and analyzed in digital image viewer (Paint.net, 2016) at magnifications of 3–4 × the original. Dimension was first quantified in number of pixels and then normalized to the number of pixels representing 1 mm. Pixel analysis suggested that the individual fibers had an average diameter of 48 ± 8 μm (n = 15) and an average length of 410 ± 190 μm (n = 30). Hydration volume (i.e., the volume of water required to fully hydrate a given mass) of nitrocellulose was measured to be 2.80 $g_{wat}/g_{nitrocellulose}$ (Kuo et al., 2017).

2.3. Sorption kinetics of NG and 2,4-DNT onto nitrocellulose

Sorption kinetics of NG and 2,4-DNT onto nitrocellulose were examined. For NG, kinetic experiments were conducted at five nitrocellulose-to-water ratios (R_{NC} = 260, 650, 1430, 2880, and 7010 $mg_{nitrocellulose}/L$) for 240 h in glass vials or bottles with Teflon-lined screw-on caps. 70 mL of solution containing 17.4 mg/L NG was added to each vessel. Masses of nitrocellulose (0.484, 0.199, 0.099,