Chemosphere xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Role of soil organic carbon and colloids in sorption and transport of TNT, RDX and HMX in training range soils

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HIGHLIGHTS

- Explosives particles on operational ranges.
- Explosives reaction with soil organic carbon and clays.
- Colloid-facilitated migration important for TNT but not RDX or HMX.

ARTICLE INFO

Article history:
Received 5 September 2012
Received in revised form 29 January 2013
Accepted 20 March 2013
Available online xxxx

Keywords:
Explosives
Colloids
Organic carbon
Operational training range
Column experiments

ABSTRACT

Contamination of soils and groundwater by munitions compounds (MCs) is of significant concern at many U.S. Department of Defense sites. Soils were collected from operational training ranges in Maryland (APG), Massachusetts (MMR-B and MMR-E) and Washington (JBLM) and sorption and transport studies were conducted to investigate the effects of soil organic carbon (OC) and textural clay content on fate of dissolved MCs (TNT, RDX, HMX). Sorption experiments showed higher distribution coefficients [TNT:42–68 L kg^{-1}, RDX:6.9–8.7 L kg^{-1} and HMX:2.6–3.1 L kg^{-1}] in OC rich soils (JBLM, MMR-E) compared to clay rich soils (MMR-B and APG) [TNT:19–21 L kg^{-1}, RDX:2.5–3.4 L kg^{-1}, HMX:0.9–1.2 L kg^{-1}]. In column experiments, breakthrough of MCs was faster in MMR-B and APG compared to MMR-E and JBLM soils. Among TNT, RDX and HMX, breakthrough was fastest for RDX followed by HMX and TNT for all columns. Defining the colloidal fraction as the difference between unfiltered samples and samples filtered with a 3 kDa filter, ~36%, ~15% and ~9% of TNT, RDX and HMX were found in the colloidal fraction in the solutions from sorption experiments, and around 20% of TNT in the effluent from the transport experiments. Results demonstrate that OC rich soils may enhance sorption and delay transport of TNT, RDX and HMX compared to clay-rich soils. Further, transport of TNT may be associated with soil colloid mobilization.

1. Introduction

Contamination of groundwater by dissolved munitions compounds (MCs) has received increased interest in recent years at operational training ranges of the US and Canada (Brannon and Pennington, 2002; Hatzinger et al., 2004; Bordeleau et al., 2008; Mailloux et al., 2008; Lewis et al., 2009). Ranges used for training troops and testing energetic materials can deposit large quantities of MCs to soil over time. Plumes of dissolved MCs have been recently observed in groundwater at various military facilities (Thiboutot et al., 1998; Jenkins et al., 2001; Clausen et al., 2006). In particular, the components of the most wide-used explosive, Composition B, found in contaminated soils and groundwater are 2,4,6-trinitrotoulene (TNT), hexahydro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX).

Interaction of dissolved MCs with clay has been widely studied in both pure minerals and soils (Haderlein et al., 1996; Hatzinger et al., 2004; Dontsova et al., 2006, 2009). Both 2:1 layered clays such as montmorillonite and illite and 1:1 layered clays such as kaolinite have higher sorption affinity of dissolved MCs compared to Fe and Al-oxides (Haderlein et al., 1996; Weissmahr et al., 1999; Dontsova et al., 2006, 2009). With respect to soils, positive correlations between soils containing higher clay content or higher fine fraction (clay and silt) and sorbed TNT, RDX and HMX have been observed (Monteil-Rivera et al., 2003; Eriksson et al., 2004; Dontsova et al., 2009). Sorption of TNT is also associated with high CEC (Haderlein et al., 1996; Weissmahr et al., 1999; Brannon et al., 2002). Between the different dissolved MCs, TNT has been found to show higher sorption affinity (~170 L kg^{-1}) to clay-enriched

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0045-6535/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2013.03.028

Please cite this article in press as: Sharma, P., et al. Role of soil organic carbon and colloids in sorption and transport of TNT, RDX and HMX in training range soils. Chemosphere (2013), http://dx.doi.org/10.1016/j.chemosphere.2013.03.028

soils/sediments compared to RDX (∼8 L kg^{-1}) and HMX (∼30 L kg^{-1}) (Brannon and Pennington, 2002; Brannon et al., 2002; Monteil-Rivera et al., 2003).

Soil organic carbon (OC) also affects sorption of dissolved MCs considerably. Both particulate and dissolved OC have been observed to associate with MCs, especially TNT (Li et al., 1997; Eriksson and Skyllberg, 2001; Singh et al., 2008, 2010). Increasing OC content in soil has been found to increase sorption and retention of dissolved TNT in soils mixed with compost (Singh et al., 2010; Alavi et al., 2011). In lab and field (transport) experiments TNT, RDX and HMX breakthrough was also found to be delayed in soils with higher OC content (Tucker et al., 2002; Dontsova et al., 2006; Singh et al., 2008; Alavi et al., 2011). The mechanism of sorption appears to be covalent binding of aromatic amines (and nitrogroup containing compounds) such as aniline, TNT, 4-amino-2,6-dinitrotoluene, 2-amino-4,6-dinitrotoluene to soil OC and/or humic substances which can result in irreversible sorption of the latter (Li et al., 1997; Drzyzga et al., 1998; Achtnich et al., 1999; Eriksson and Skyllberg, 2001; Eriksson et al., 2004). However, some studies have also suggested that OC content has little or even a negative effect on sorption of dissolved MCs/nitramine/nitroaromatic compounds (Weissmahr et al., 1999; Brannon and Pennington, 2002; Monteil-Rivera et al., 2003; Charles et al., 2006). Thus, the overall role of OC on sorption of dissolved MCs in soils is unclear and more investigation is needed to provide basic predictability of the role of OC.

Fate of organic contaminants can also be enhanced by colloid-facilitated migration (McCarthy and Zachara, 1989; Sen and Khilar, 2006). A large range of colloids can exist in soils and groundwater such as (hydr)oxides, weathering products of clay, mineral precipitates, biocolloids and organic matter (McCarthy and McKay, 2004). A number of studies have reported colloid-facilitated transport of organic contaminants such as atrazine (Barton and Karathanasis, 2002), polyaromatic hydrocarbons (Marvin et al., 2004), phenanthrene (Laird et al., 1994) and nitro group containing pesticides such as pendimethalin (Petersen et al., 2002; Lapworth et al., 2005). Interaction of contaminants mainly included associations with clay/fine fractions and OC (Petersen et al., 2002; Dontsova et al., 2006; Sen and Khilar, 2006). Higher sorption coefficients of TNT and RDX were observed with water dispersible colloids compared to the whole soil, as well as higher sorption of MCs with water dispersible colloids enriched in OC (Dontsova et al., 2009). These studies suggest that colloid-facilitated transport may be important for MCs as well.

Despite significant interest in MCs, challenges remain in determining which geochemical parameters primarily influence fate of MCs in soil or whether colloid-facilitated transport of MCs is possible. Studies combining both sorption and transport of dissolved MCs in range soils are also few and the fate of RDX and HMX in particular is not yet clear. Thus, the objectives of the present research were to (1) identify how contrasting sorbents (mainly OC and clay) affect the fate of dissolved MCs (TNT, RDX and HMX) in range soils, and (2) to identify and determine the potential for colloid-facilitated transport of MCs.

2. Materials and methods

2.1. Soils collection and characterization

Bulk soils for all experiments were sampled from B and adjacent horizons from operational training ranges at three US Department of Defense (DoD) sites: Aberdeen Proving Ground near Edgewood, MD (APG), Joint Base Lewis-McChord near Lakewood, WA (JBLM) and Massachussetts Military Range (MMR) near Sandwich, MA. At MMR, soils were collected from B (>20 cm depth) and E (9–20 cm depth) horizons from the same profile and are referred to as MMR-B and MMR-E. The B horizon at APG was sampled at depths over 20 cm, and samples from within (5–20 cm depth) and below the root zone (>50 cm depth) were collected at JBLM. All soils were air-dried, homogenized, and sieved to <2 mm and characterized for total organic carbon (TOC), cation exchange capacity (CEC), soil pH, iron (Fe) oxide content and fine fractions (clay and silt) (Table 1, for soil characterization details see Supporting Information (SI) S1). There was no detectable contamination of the sampled soils by TNT, RDX or HMX.

2.2. Reagents

TNT salt was obtained from the Chem Service Inc. (Pennsylvania) and RDX and HMX were obtained from the Stanford Research Institute. Separate solutions of TNT (60 mg L^{-1}), RDX (30 mg L^{-1}) and HMX (3 mg L^{-1}) were prepared in a background of 10 mM NaCl and readjusted for respective indigenous soil pH for all experiments.

2.3. Sorption experiments

Separate sorption experiments were conducted in triplicate over a concentration range of 0–60 mg L^{-1} for TNT, 0–12 mg L^{-1} for RDX and 0–2.5 mg L^{-1} for HMX by equilibrating 0.5 g soil with 30 mL of reagent solutions in the dark. The dissolved MC-soil mixtures were equilibrated for 48 h (25 °C and 100 RPM) on a horizontal shaker. After 48 h, the samples were filtered with a 0.45 μm nylon filter (Pall Inc., USA) and prepared for analysis of TNT, RDX and HMX. There was <5% change in pH of the supernatant at the end of the sorption experiments. There was no sorption of TNT, RDX or HMX on the 0.45 μm nylon filter (SI S2.1 Table S1).

Additional sorption experiments included (1) a competitive sorption study by adding TNT, RDX and HMX in the same experimental vial and comparing it with systems where TNT, RDX and HMX were added separately (SI S2.2 Table S2), (2) an extended sorption study to determine potential degradation of the dissolved MCs (SI S2.3 Table S3).

2.4. Column experiments

Transport of the dissolved MCs was studied using a flow rate of 10 mL h^{-1} through soils packed in plexiglass columns of dimensions 2 cm diameter and 10 cm length. Each column was filled with 30 g soil, and 2.5 g of sand at both top and bottom. Columns were saturated with the background solution (10 mM NaCl) at the respective soil pH at a flow rate of 2 mL h^{-1} for several days to remove entrapped air. Subsequently, the columns were wrapped in foil to prevent photodegradation and equilibrated for 48 h at 10 mL h^{-1}, after which the injection of a single solution with dissolved MCs (3, 5 and 1 mg L^{-1} TNT, RDX, and HMX respectively) in 10 mM NaCl was initiated. Breakthrough was considered complete once concentration of MCs in the effluent was equivalent to that of the influent. Breakthrough was continued for up to ∼200

Table 1
Soil characteristics.

Soils	TOC (%)	Fine fraction (%)		Fe-oxide (%)	pH	CEC (cmol kg^{-1})
		Clay	Silt			
APG	0.2	6.9	3.8	0.6	4.6	1.8
MMR-B	0.2	9.7	20.2	0.7	4.3	1.8
MMR-E	3.0	1.5	31.3	0.5	3.8	3.9
JBLM	4.2	<1	27.3	1	5.2	7.1

TOC: Total organic carbon; CEC: Cation exchange capacity.

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