



## Removal rates of dissolved munitions compounds in seawater



Richard W. Smith\*, Penny Vlahos, Craig Tobias, Mark Ballentine, Thivanka Ariyaratna, Christopher Cooper

University of Connecticut, Department of Marine Sciences, 1080 Shennecossett Road, Groton, CT 06340, United States

### HIGHLIGHTS

- Sediments dramatically increase removal kinetics of dissolved RDX and TNT.
- Removal rates very widely among published studies due to experimental setups.
- Sediment characteristics are proxies for explosive contamination persistence.

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### ABSTRACT

The historical exposure of coastal marine systems to munitions compounds is of significant concern due to the global distribution of impacted sites and known toxicological effects of nitroaromatics. In order to identify specific coastal regions where persistence of these chemicals should be of concern, it is necessary to experimentally observe their behavior under a variety of realistic oceanographic conditions. Here, we conduct a mesocosm scale pulse addition experiment to document the behavior of two commonly used explosives, 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in simulated marine systems containing water and sediments collected from Long Island Sound, CT. The addition of sediments and sediment grain-size had a major influence on the loss rates of all compounds detected. RDX and reduced TNT products were removed from seawater only in the presence of sediment, and TNT degraded significantly faster in the presence of sediment. Both compounds were removed from the system faster with decreasing grain-size. Based on these findings and a thorough review of the literature, we hypothesize that in addition to bacterial abundance and nutrient availability, TNT removal rates in coastal marine waters may be controlled by sorption and rapid surface-mediated bacterial transformation, while RDX removal rates are controlled by diffusion into sedimentary anoxic regions and subsequent anaerobic bacterial breakdown. A comparison of published removal rates of RDX and TNT highlights the extreme variability in measured degradation rates and identifies physicochemical variables that covary with the breakdown of these munitions compounds.

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### 1. Introduction

Coastal military activity has resulted in exposure of marine habitats to munitions compounds in both dissolved and particulate phases (Darrach et al., 1998; Rodacy et al., 2000). Unexploded ordnance (UXOs) enter the marine environment through their use in the field and ongoing training exercises, through incomplete detonation, as well as disposal at sea (Rosenblatt et al., 1991; Morley et al., 2006), and contamination can persist for several decades (Darrach et al., 1998).

2,4,6-Trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) are two of the most commonly used munitions compounds, and are proven toxins in marine systems (Rosen and Lotufo, 2005, 2007, 2010; Ek et al. 2007; Torre et al. 2008; Won et al., 1976; Nipper et al., 2001). Sub lethal bioaccumulation of RDX and TNT in the tissues of marine organisms may also pose a threat to human health from seafood consumption (Belden et al., 2005; Lotufo et al., 2010). The duration of environmental exposure after munitions compounds become solubilized is a function of their residence time in seawater, determined by a number of factors including sediment adsorption, biotic and abiotic transformation, and remineralization (Hawari et al., 2000; Brannon et al., 2005). Therefore, reliable estimates of removal rates of TNT and RDX under a number of geographic locations and oceanographic conditions, has the potential to greatly simplify fate and transport models and/or contaminant management schemes.

A wealth of information exists on the fate of RDX and TNT in terrestrial environments such as soils, groundwater, and surface

\* Corresponding author. Tel.: +1 585 880 1206.

E-mail addresses: [richard.2.smith@uconn.edu](mailto:richard.2.smith@uconn.edu) (R.W. Smith), [penny.vlahos@uconn.edu](mailto:penny.vlahos@uconn.edu) (P. Vlahos), [craig.tobias@uconn.edu](mailto:craig.tobias@uconn.edu) (C. Tobias), [mark.ballentine@uconn.edu](mailto:mark.ballentine@uconn.edu) (M. Ballentine), [thivanka.ariyaratna@uconn.edu](mailto:thivanka.ariyaratna@uconn.edu) (T. Ariyaratna), [christopher.cooper@uconn.edu](mailto:christopher.cooper@uconn.edu) (C. Cooper).

freshwater (Pennington and Patrick, 1990; Bradley et al., 1992; Juhasz and Naidu, 2007; Zheng et al., 2009); yet how the rates and mechanisms of removal translate to the marine environment is not fully understood (Brannon et al., 2005), especially considering the geochemical differences between soils, freshwater sediments and marine sediments (Hedges and Oades, 1997). Also, observed breakdown and transformation (removal) rates in simulated marine systems vary greatly (Yost et al., 2007; Harrison and Vane, 2010; Chappell et al., 2011), outlining the need for additional experiments and a thorough comparison of existing data.

In this study, we examine the loss of RDX and TNT at environmentally relevant concentrations in a realistic simulated marine setting, with a focus on the role of sediments. The observed rates are compared with existing rates to highlight potential sedimentary indicators of munitions persistence, and pathways of removal.

## 2. Methods

### 2.1. Experimental design

Four experimental treatments were used in the study: seawater only – light ( $SW_L$ ); seawater only – dark ( $SW_D$ ); seawater + fine grained sediment ( $SED_{FG}$ ); and seawater + coarse grained sediment ( $SED_{CG}$ ). Two paired mesocosms (70 L glass tanks containing seawater or seawater and sediment) were used for each individual treatment, connected to a common recirculating reservoir (one common reservoir for each treatment, no mixing occurred between treatments) (Fig. 1). Seawater was supplied to the mesocosms directly from Long Island Sound. Sediments used in the  $SED_{FG}$  and  $SED_{CG}$  mesocosms were collected from a Long Island Sound shallow subtidal habitat near Groton, CT, and added to the mesocosms to a sediment thickness of  $\sim 10$  cm depth. The  $SW_D$  treatment, to control for photochemical degradation, was kept in the dark using a black cloth. All other treatments were exposed to ambient light conditions. Sediments and seawater were added to the tanks with active recirculation 2 weeks before the start of the experiment, in order for redox and chemical conditions to stabilize. The seawater was kept recirculating through the mesocosms and reservoirs as a closed system throughout the course of the experiment (see Fig. 2).

Each of the mesocosms received single pulse additions of concentrated TNT and RDX in methanol (10 mL) simultaneously, targeting environmentally relevant concentrations of  $0.3 \text{ mg L}^{-1}$  for RDX and  $1.3 \text{ mg L}^{-1}$  for TNT (Jaramillo et al., 2011). This method of addition may slightly inhibit annamox rates at resulting methanol concentrations but not denitrification (Jensen et al., 2007), and inhibition was likely ephemeral. Samples were taken for explosive

measurements for a period of 28 ( $SW_L$  and  $SW_D$ ) to 45 ( $SED_{FG}$  and  $SED_{CG}$ ) d.

### 2.2. Water chemistry

Dissolved oxygen (DO), salinity, and temperature in the water column were monitored with a YSI probe. Munitions sampling and analysis methods were adapted from EPA method 8330 (US EPA, 1996) as modified by Agilent. Briefly, 5 mL of methanol were immediately added to a 5 mL seawater sample, shaken and filtered through a  $0.45 \mu\text{m}$  PTFE syringe tip filter.  $20 \mu\text{L}$  of the solution was injected onto an Agilent 1200 series ultra-violet high-performance liquid chromatography (UV-HPLC) equipped with a Zorbax Eclipse column ( $4.2 \times 150 \text{ mm}$ ,  $3 \mu\text{m}$ ; Agilent) maintained at  $30^\circ\text{C}$ . Munition compounds were eluted isocratically with 25% MeOH and 75% ammonium formate buffer (pH 6) at a flow rate of  $1.7 \text{ mL min}^{-1}$ . UV peak areas at 254 nm were identified based on retention time and converted to  $\text{mg L}^{-1}$  concentrations with an external calibration curve containing 14 munitions compounds (EPA Mix A:EPA Mix B, 1:1, Accustandard). All values are reported as  $n = 4$  (two water samples from each mesocosm, two mesocosms per treatment), and precision was on the order of approximately 1% (Supplementary Table 2).

Rate constants ( $k$ ) and half-lives of munitions compounds, when degradation was observed, were calculated by fitting a first-order best-fit exponential curve to the time series profiles with Sigmaplot v.11.

### 2.3. Sediment chemistry

Sediments were sampled at the beginning and end of the experiment for percent organic carbon, grain-size, and munitions concentrations. Freeze-dried sediment was analyzed for %OC using the acid fumigation and EA method of Hedges and Stern (1984). For grain size characterization,  $\sim 2 \text{ g}$  of sediment was passed through a series of sieves ranging in size from 2 mm to  $63 \mu\text{m}$ . The mass of each size fraction was converted to particle “counts” assuming a perfectly spherical shape and a density of  $2.65 \text{ g cm}^{-3}$ , typical of aluminosilicates. Sediment that passed through the  $63 \mu\text{m}$  sieve was deemed to be the silt/clay fraction. Munitions were extracted following a method adapted from US EPA (1994). Briefly, 2 g of freeze-dried sediment was extracted by sonicating for 1 h with acetonitrile at a 2:1 liquid to solid ratio. The extract was filtered through a  $0.45 \mu\text{m}$  PTFE syringe tip filter, and a  $3 \mu\text{L}$  aliquot was injected into the HPLC.

## 3. Results and discussion

### 3.1. Mesocosm geochemistry

The temperature of the LIS water used in all the tanks remained stable at  $\sim 19^\circ\text{C}$ . (Supplementary Table 1). Salinity was initially  $\sim 31$ , and increased linearly to  $\sim 35$  to 38 in all the mesocosms as water evaporated over the long duration of the experiment. The water column of all treatments remained aerobic: DO values ranged from  $3.0$  to  $8.1 \text{ mg L}^{-1}$ , with the lowest values observed in  $SED_{FG}$ .

Coarse-grained sediments in  $SED_{CG}$  and  $SED_{FG}$  contained 0.03% and 0.38% OC (w/w) and 0.5% and 26.5% silt/clay (particle counts), respectively. In both treatments with sediments, no munitions compounds were detected in sediment extracts, and therefore the rest of the discussion is based around dissolved values in the water column.

The nearly identical behavior of RDX, TNT, and TNT derivatives in  $SW_L$  and  $SW_D$  suggests that ambient light levels in our

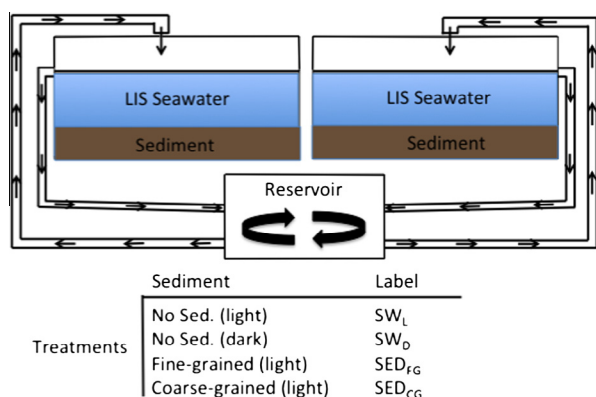


Fig. 1. Diagram of a single recirculating mesocosm. Arrows indicate the direction of water flow.

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