

# FINAL REPORT

## Photochemical Transformation of Munitions Constituents in Marine Waters

SERDP Project ER-2123

May 2012

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<b>14. ABSTRACT</b> The mechanism and rate photolysis of nitroaromatic compounds was determined in various waters. Solutions of individual nitroaromatic compounds were irradiated using a Suntest CPS+ solar simulator and analyzed using high performance liquid chromatography (HPLC). Photolysis products were separated and identified using solid phase extraction and liquid chromatography/mass spectrometry. The photolysis rates of 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT), and 2,4,6-trinitrotoluene were similar in seawaters from four locations but varied in different estuary waters. Photolysis rates in natural waters were impacted by dissolved organic matter and salinity but not pH or nitrate concentration. The products formed through DNT photolysis included dinitrobenzyl alcohols, dinitrobenzaldehydes, and 2-amino-4-nitrobenzoic acid. When photolyzing these products, the alcohols and aldehydes were photolyzed faster than those of their parent DNT, but 2-amino-4-nitrobenzoic acid was not photolyzed. Toxic products that do not photolyze will accumulate if not transformed by other mechanisms.					
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## List of Acronyms

2A4NBA	2-amino, 4-nitrobenzoic acid
2,4-DNBCHO	2,4-dinitrobenzaldehyde
2,6-DNBCHO	2,6-dinitrobenzaldehyde
2,4-DNBCOH	2,4-dinitrobenzyl alcohol
2,6-DNBCOH	2,6-dinitrobenzyl alcohol
2,4-DNBCOOH	2,4-dinitrobenzoic acid
2,6-DNBCOOH	2,6-dinitrobenzoic acid
2,4-DNT	2,4-dinitrotoluene
2,6-DNT	2,6-dinitrotoluene
ADNT	aminodinitrotoluene
CDOM	chromophoric dissolved organic matter
DNBCHOs	dinitrobenzaldehydes
DNBOHs	dinitrobenzyl alcohols
DOM	dissolved organic matter
HA	humic acid
HPLC	high performance liquid chromatography
LC/MS	liquid chromatography/mass spectrometry
MC	munitions constituent
NaHA	humic acid sodium salt
NOAA	National Oceanic and Atmospheric Administration
TNB	trinitrobenzene
TNT	2,4,6-trinitrotoluene
UXO	unexploded ordnance

## List of Keywords

Photolysis, nitroaromatic compounds, solar simulator, kinetics, TNT, dinitrotoluene, seawater

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## Abstract

### Objectives

The objective of this work was to improve the understanding of photolysis as a mechanism to transform chemical constituents released from munitions. Specifically, the goals were to determine how photolysis rates of 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT), and 2,4,6-trinitrotoluene (TNT) were impacted by water source and specific dissolved materials (nitrate, dissolved organic matter) and to determine the photoproducts and their photolysis rates.

### Technical Approach

Munitions constituents were dissolved in various natural and laboratory waters and in some cases were augmented with nitrate or dissolved organic material (DOM). The solutions were irradiated in thermostated quartz optical cells in a Suntest CPS+ solar simulator. High performance liquid chromatography (HPLC) was used to measure concentrations. Photolysis products were extracted using solid phase extraction and eluded using various solvents. The eluents were analyzed using liquid chromatography/mass spectrometry (LC/MS) to identify the products.

### Results

The impact of water type on photolysis was tested using four near-shore seawater samples, four estuary or river water samples, and ultrapure water. The decline in DNT or TNT concentration due to photolysis was modeled as a first-order process. The photolysis rate constants for each munitions constituent showed little variation in the four seawater samples tested, which had similar salinity and DOM. These rate constants differed by as much as 50% from those found using estuary and river water samples, which have lower salinity and higher DOM. The addition of DOM as humic acid to ultrapure water increased the 2,4-DNT and 2,6-DNT rate constants. The addition of humic acid sodium salt to seawater increased the photolysis rate constants for 2,6-DNT, but it decreased the rate constants for 2,4-DNT. The addition of nitrate enhanced photolysis in ultrapure water, but did not affect photolysis in seawater. For these experiments, the proof-of-concept was achieved in that differences were found in different water types, and one factor affecting the rates is dissolved organic matter. Future work should include testing waters from other Navy locations and determining what additional solutes alter photolysis rates.

The products formed through DNT photolysis included dinitrobenzyl alcohols (DNBOHs), dinitrobenzaldehydes (DNBCHOs), and 2-amino-4-nitrobenzoic acid (2A4NBA). When photolyzing these products, the rate constants for DNBOHs and DNBCHOs were larger than those of their parent DNT, but 2A4NBA was not photolyzed. For these experiments, the proof-of-concept was achieved in that the photolysis mechanism is more clearly understood. Future work should determine other photoproducts and their photolysis rates.

### Benefits

The research conducted herein has shown that munitions constituents will photolyze at different rates in natural waters that vary in salinity and DOM. Upon photolysis, some compounds are produced that photolyze faster than their parent compound and are less likely to accumulate in environment, while other products do not photolyze and will accumulate if not



transformed by other mechanisms. These results have increased our understanding of photodegradation mechanisms of munitions and will help the DoD to assess the environmental impact of unexploded ordnance on coastal ranges and dumping sites and to plan for the future use of these ranges.

## Objective

Previously the Strategic Environmental Research and Development Program (SERDP) had sponsored work on the transport and transformation of munitions compounds (MC) in coastal aquatic systems. In the area of photolysis, recent work has suggested that the rate of transformation of compounds such as 2,4,6-trinitrotoluene (TNT) is rapid in seawater, but very little work has been done to determine what products are formed in a salt water environment and the rate at which those products undergo photochemical decay. Rapid transformation rates of some munitions in marine waters, through photolysis, dilution and metabolism, suggest that these munitions may not pose a long term pollution problem. However, if the transformation products are more toxic than the parent compound, then the liability of the Navy remains. In addition if the transformation pathways and rates are not fully characterized in marine systems, the lack of scientific information could lead to poor remediation and management decisions.

The objective of this limited-scope project was to characterize the photochemical fate of munitions compounds and the kinetics of such reactions at environmentally relevant concentrations in coastal waters. This research effort addresses the objective of the statement of need set forth in ERSON 11-10, which was “to develop an improved understanding of the environmental impacts associated with chemical constituents released from munitions in marine environments. Of particular importance is assessing impacts at environmentally relevant concentrations and understanding dominant fate and transport mechanisms.” Specifically, the goal was to help “assess the predominant fate and transport mechanisms and the kinetics of such reactions at environmentally relevant concentrations in both the water column and the aquatic sediments.”

Laboratory experimentation sought to investigate the photolytic behavior of such compounds in fresh, brackish, and salt water environments that are representative of DoD water training and testing ranges. Natural waters from a variety of coastal systems were examined, for example surface water (euphotic zone) from the Chesapeake Bay, Gulf of Mexico, Charleston Harbor, and Kahana Bay. The munitions and propellants examined included TNT, 2,4-dinitrotoluene (2,4-DNT), and 2,6-dinitrotoluene (2,6-DNT). The overall goals of this proposal were to fill in the data gaps concerning:

1. the mechanism of parent compound transformation,
2. the rates of photolysis of secondary products, and
3. the natural water characteristics that affect transformation rates (salinity, pH, chromophoric dissolved organic matter (CDOM), and nitrate concentration),

and to determine which areas need further investigation. The criteria for success for this Limited Scope project included 1) demonstrating the ability to find which components of natural waters influence photolysis rates and quantifying those rates; and 2) demonstrating the ability to isolate and identify products formed during photolysis and to measure how rapidly these secondary products are photolyzed. The photolysis rate behavior and the mechanisms (products and their photolysis rates) determined in this Limited Scope project and in any follow-on work can be used in conjunction with studies on other transformation processes to model the behavior of munitions in natural systems. A better understanding of photodegradation mechanisms of munitions will help the DoD to assess the environmental impact of UXOs on coastal ranges and dumping sites and to plan for the future use of these ranges.

## Background

### DoD and Regulatory requirements

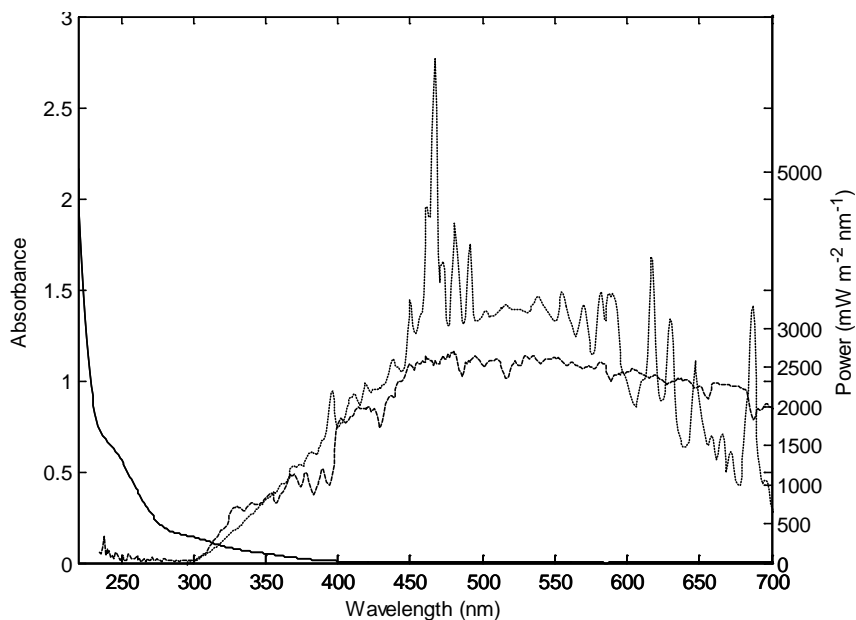
The United States Navy currently possesses 1.29 million acres of active or inactive ranges in their inventory. Though currently only about 230 acres are both underwater and facing response action due to the presence of toxic chemicals, the future cost to DoD of environmental compliance to maintain these ranges may limit their use. A partial list of locations includes Hawaii, California, Alaska, Louisiana, Japan, and Okinawa. In a recent survey by the National Oceanic and Atmospheric Administration (NOAA) of the contaminant levels in Ordnance Reef Wai'anae, Hawaii, they found two propellants at concentrations significantly higher than the detection limit: 2,4-DNT and 2,6-DNT (SRAB, 2007). Previous work in our laboratory and in other laboratories on the photolysis of munitions constituents in marine environments has shown that TNT, 2,4-DNT, and 2,6-DNT are degraded faster in marine waters than in fresh water, and some of the products formed during the photolysis in marine waters have been tentatively identified. Some of these products are more toxic than their parent compound, but their photolysis rates in natural waters under various environmental conditions have yet to be determined. For the Navy to fully assess the impact of munitions on the seawater environment, the products formed during photolysis as well as the photolytic decay of those products in the marine environment need to be determined for a variety of water types. In addition the dependence of the photolysis rates on ambient water characteristics (salinity, pH, CDOM, nitrate) needs to be understood for impact and remediation assessment.

### Photolysis processes

Experimental studies into the photolysis of explosive compounds have focused on freshwater systems with the ultimate goal of enhancing the photolysis process using catalysts or other added components to increase the speed of the reactions (Alnaizy and Akgerman 1999; Bose et al. 1998a, 1998b; Burlinson et al. 1979; Burrows et al. 1989; Celin et al. 2003; Dillert et al. 1995; Ho, 1986; Kaplan et al. 1975; Larson et al. 1996; Larson et al. 2000; Liou et al. 2003; Rodgers and Bunce 2001; Schmelling et al. 1996; Simmons and Zepp 1986; Spangford et al. 1980; Spangford et al. 1983; Zhuang et al. 2008). These additional components include catalysts such as  $\text{TiO}_2$  or additives such peroxide, Fenton's reagent (peroxide and iron (II)), and peroxide and ozone, which are meant to speed up the transformation processes. Elemental iron (zero-valent iron) has also been used to enhance contaminant degradation but this reduction process does not include photolysis (Naja et al. 2008; Oh et al. 2003; Zhuang et al. 2008). All of these photolysis augmentation approaches are applicable to production plant effluent treatment streams or potential treatment approaches for holding lagoons. However all of these would be difficult or cost prohibitive to implement as a mitigation strategy for a coastal or oceanic site. Further, very few studies have examined the photolysis in salt solutions or natural marine systems.

Nitroaromatic compounds (TNT, DNT) absorb electromagnetic radiation in the ultraviolet (UV) range of 200 nm and 400 nm (Bartolo et al. 1979). The absorption spectra increase exponentially with decreasing wavelength, thus the absorption in the environmentally-relevant UV (290 to 400 nm) is much less than at wavelengths <270 nm. The overlap of the absorption spectra of 2,6-DNT in seawater and that of sunlight is shown in Figure 1. While the overlap region is small, there is sufficient energy at wavelengths between 300 and 400 nm to

promote photochemical degradation. Wavelengths less than 300 nm do not penetrate deeply in to surfaces waters, and the presence of dissolved organic matter and particulates in natural water systems can reduce that penetration even more. In the coastal water column, however, the rapid vertical mixing means that sunlight energy may cause much direct photolysis. Coastal salt water systems also have lower concentrations of particulates and dissolved organic matter than those typically found in fresh waters. Even fresh waters can have some photolysis when naturally occurring oxidizing agents or catalysts are present. DiGnazio et al. (1998) hypothesized photodegradation as a partial explanation for nitrate generated from explosives stored in lagoons at the Ammunition Burning Ground at the Crane Naval Surface Warfare Center. It is important, therefore, to determine the rates of photolysis in a variety of waters in which munitions compounds can be found.



**Figure 1.** Comparison of the spectrum of light produced by the solar simulator (...) with that of natural sunlight times 3 (--), and the absorption spectra of 2,6-DNT in seawater (-). Power spectra were measured with a SPR-4002 spectroradiometer from Luzchem Research, Inc. (O’Sullivan et al., 2010)

### Photolysis in marine systems

A few studies have examined the photolysis of munitions compounds in marine systems where the ionic composition and types of organic matter differ from fresh water systems (Mihas et al. 2007; Nipper et al. 2004; O’Sullivan et al. 2010, 2011). Research in our laboratory has measured the photolysis rates of TNT, 2,4-DNT, and 2,6-DNT in seawater systems (O’Sullivan et al. 2010; 2011). In all cases surface water refers to water in the euphotic zone, which is approximately within one meter of the surface. Our research has shown that photolysis of TNT in natural surface seawater from the Chesapeake Bay follows first order kinetics. We have found that TNT, 2,4-DNT, and 2,6-DNT were photolyzed faster in seawater than in freshwater, and the first-order rate constants depended at least partially on the ionic strength of the aqueous phase.

The rate of photolysis decreased in the order seawater > estuarine water > fresh water >> pure water. The photolysis rate at wavelengths greater than 395 nm was very small. The transformation was largely driven by wavelengths less than 320 nm with some photochemical transformation occurring in the wavelength range from 320 to 395 nm. Photolysis of TNT in ultrapure water, 18 M $\Omega$  cm<sup>-1</sup> Milli-Q water, had a half-life ( $t_{1/2}$ ) of 770 minutes when exposed to sunlight with wavelengths greater than 295 nm. In freshwaters under the same conditions the half-life was 210 minutes, for estuarine water  $t_{1/2}$  was 115 minutes, and in seawater  $t_{1/2}$  was 69 minutes (O'Sullivan et al., 2011). Changes in the photolysis rate did not appear to be driven solely by changes in the ionic strength from fresh to salt waters. In pure NaCl solutions at similar ionic strength as seawater,  $\mu = 0.69$  M, that had been passed through chelex to remove trace metal contamination, the photolysis half-life was 315 minutes, much slower than in seawater, indicating that the increase in ionic strength was not solely responsible for the enhanced photolysis rate in seawater. *It is critical to determine if these TNT photolysis characteristics are repeated in a variety of natural surface waters (i.e. Gulf of Mexico, Charleston Harbor and Kahana Bay surface waters); if natural water constituents influence the photolysis rates; and if this behavior is exhibited by the DNTs.*

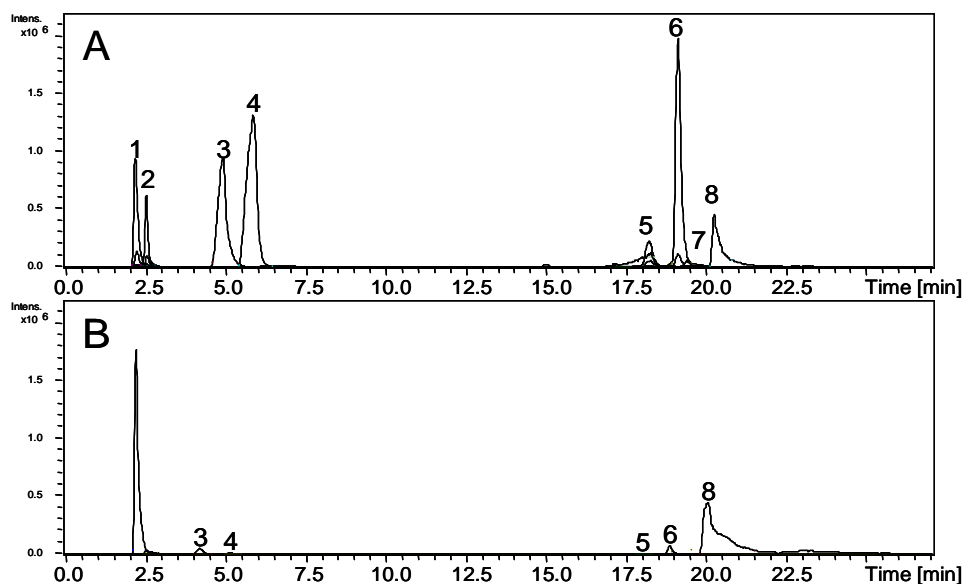
### **Influence of nitrate and CDOM on photolysis rates**

Research to determine the influence of various natural water constituents on photolysis rates suggests that dissolved ions and humic substances can influence those rates. Nitrate has been found to increase the rate of photolysis of several organic compounds (Brezonik and Fulkerson-Brekken 1998; O'Sullivan et al. 2011; Zepp et al. 1987), while the presence of chloride has been found to increase or decrease the photolysis rate depending on the compound being photolyzed (Chiron et al. 2006; Mateus et al. 2000; Mihas et al. 2007). In our previous work under SERDP ER-1431, we measured how ionic substances also change the solubility of nitroaromatic compounds (Luning Prak and Moran 2008; Luning Prak and O'Sullivan 2006, 2007, 2009), significantly reducing their solubility in marine systems relative to pure water. Naturally occurring dissolved constituents will also affect reaction rates of the munitions constituent in addition to altering its solubility. Dissolved organic matter has been found to enhance the photolysis of nitroaromatic compounds in freshwater systems (Mihas et al. 2007, Simmons and Zepp 1986), but other studies suggest dissolved organic matter will lower photolysis rates by scavenging the hydroxyl radical, which is believed to be the main reactant in oxidative photolysis reactions (Brezonik and Fulkerson-Brekken 1998). *Since the influence of dissolved substances on the photolytic behavior cannot be easily predicted from prior work, it is important to quantify their impact for specific munitions constituents in marine and freshwater systems.*

### **Isolation and identification of photolysis products**

In addition to quantifying photolysis rates, determining the mechanism of photolytic decay is critical because photolysis may produce more persistent compounds of greater toxicity. The mechanism of the photolytic decay of several munitions constituents have been reported for freshwater systems (Bose et al. 1998a, 1998b; Burlinson et al. 1979; Burrows et al. 1989; Hawari et al. 2002; Just and Schnoor 2004; Pennington et al. 2007; Peyton et al. 1999; Spanggard et al. 1980; Spanggard et al. 1983). Burrows et al. (1989) report that more than 20 compounds are produced by the photolysis of TNT in fresh water using a mercury lamp. These products include 2,4,6-trinitrobenzaldehyde and azo and azoxy compounds. Recently, Liou et al. (2003) have

determined that TNT degradation follows first order kinetics and has deduced the steps of degradation for the photo-Fenton process in distilled water. The mechanistic pathways determined for freshwater systems with and without iron or peroxide can provide a framework for marine systems, but it is unclear if the solutes unique to marine systems will change the suite of products formed. Some preliminary work has been done in our laboratory to identify products formed during the photolysis of munitions compounds in salt water system. Analysis of irradiated samples of estuarine water from the Chesapeake Bay containing 20 ppm TNT from our laboratory using LC-MS with MS negative and positive ionization modes and auto MS/MS/MS negative ionization mode enabled the identification of several photolysis products. In all photolyzed samples, 3 major peaks and few minor peaks were detected using negative ionization mode (see Figure 2), which were not detectable using positive ionization mode.



**Figure 2.** Extracted ion chromatograms of TNT and its degradation products observed by LC-MS negative ionization mode during photolysis in estuarine-water at 295 nm (**A**) and in dark control (**B**).

Using MS/MS/MS negative ionization mode, the first fragments (MS<sub>2</sub>) show the loss of 44 Da in the products **1** and **2** and 28 Da in the products **4** and **6** suggesting the presence of a carboxyl (COO) and an aldehyde (CO) groups in the molecules, respectively (see Table 1). Fragmentation of compound **3** shows the same initial fragment (MS<sub>2</sub>) as observed with TNT (**8**), but the loss of 17 Da in MS<sub>3</sub> suggest the presence of a hydroxyl group in the molecule (see Table 1). TNT, trinitrobenzene (TNB) and aminodinitrotoluene (ADNT) were confirmed by comparison with standard chemicals, but the other products are still to be determined and need to be assessed in the light of other photochemical pathways (e.g. Burlinson et al., 1979).

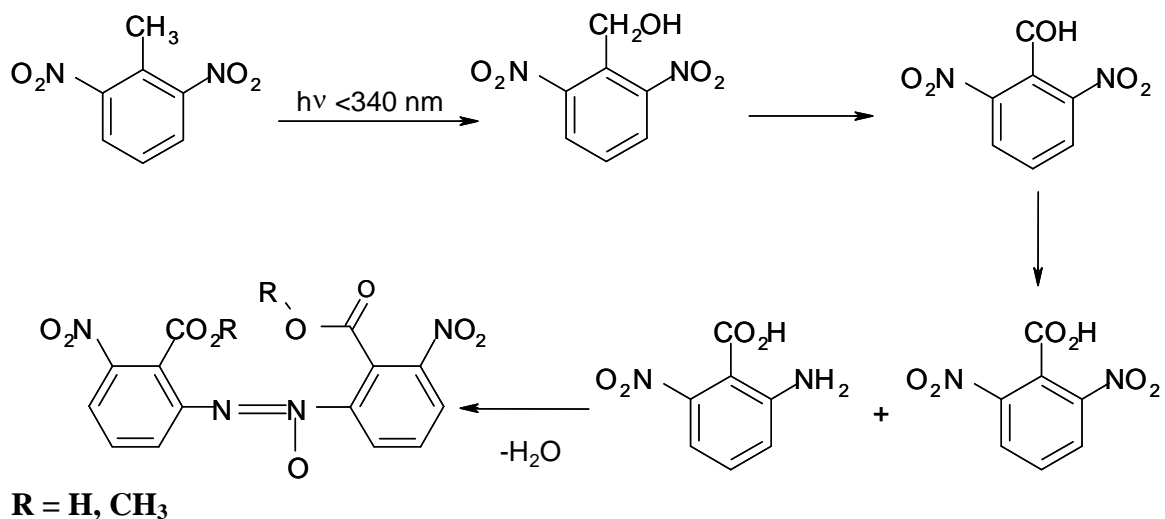
For dinitrotoluenes, we identified 2,4-dinitrobenzaldehyde (2,4-DNBCHO) and 2,6-dinitrobenzaldehyde (2,6-DNBCHO) from the photolysis of 2,4-DNT and 2,6-DNT, respectively, in seawater (O'Sullivan et al. 2010). Figure 3 shows a proposed reaction pathway for the photolysis of 2,6-DNT in seawater based on our work. This pathway is consistent with the pathway reported by Ho (1986) for photooxidation in the presence of the UV light and

peroxide. It is unclear if the products isolated from the photolysis of these compounds in seawater would also be found in other natural water systems that are relevant to the Navy, and as such work needs to be done in this area.

**Table 1.** MS/MS/MS negative ionization mode of TNT and its degradation products observed during photolysis at 295 nm in estuarine Chesapeake Bay surface waters.

Peak #	Retention time (min)	MS m/z	MS2 m/z	MS3 m/z	Proposed molecular weight	Proposed structure
1	2.4	226	182		227	2-amino-4,6-dinitrobenzoic acid, <i>or others</i>
2	2.5	224	180		225	2,6-dinitroso-4-nitrobenzoic acid, <i>or others</i>
3	4.8	226 226	196 196	136 179	227	2-nitroso-4,6-dinitrobenzylalcohol, <i>or others</i>
4	7.2	211	183 and 137		212	2-hydroxy-4,6-dinitrobenzaldehyde; <i>or others</i>
5	17.5	183			<b>213</b>	<b>TNB*</b>
6	19.2	210 210	182 and 136 182 and 136	119	211	2-amino-4,6-dinitrobenzaldehyde, <i>or others</i>
7	19.6	196			<b>197</b>	<b>ADNT</b> (trace)
8	20.3	226	196	136	<b>227</b>	<b>TNT</b>

\* TNB was detected with m/z 183 and 214, a [M-NO] mass fragment ion and an adduct mass, respectively, confirmed with standard compound.



**Figure 3.** Proposed oxidation products and dimmer formation for the photolysis of 2,6-dinitrotoluene in seawater (from O'Sullivan et al. 2010)

## **Photolysis of secondary products formed by the photolysis of TNT and DNT**

Some of the products formed during the photolysis of TNT and DNT may be equally or more toxic than the parent compounds, as enhanced toxicity in bioassays has been observed during the photodegradation of TNT (Davenport et al. 1994). To date no studies have examined the fate and/or chemistry of the secondary products produced from the photolysis of TNT and DNT in marine waters. Characterization of the reaction products in natural estuarine and sea waters is critical to ensure that degradation of a released munitions constituent does not produce a more persistent compound of greater toxicity (i.e., azo, azoxy and nitroso compounds). *To enable the Navy to correctly evaluate and assess the potential impact of UXO, a complete understanding of the naturally produced degradation products and the anticipated levels is necessary.*

Based on the literature, the photolysis rates and mechanisms have been determined in freshwater systems for some munitions constituents, and a few studies have examined the photolysis rate for TNT in seawater systems, but few studies have focused on other munitions constituents. Open questions and data gaps that need to be addressed to achieve a comprehensive understanding of the fate of munitions constituents in marine waters are:

- 1) *a determination of whether the photolysis mechanisms defined in one set of natural waters is relevant for other natural water systems of importance to the Navy,*
- 2) *a confirmation of whether the trends observed in the rate constants for Chesapeake Bay waters can be applied to other surface waters.*
- 3) *a determination of what characteristics of natural waters affect the MC photolysis rates (ambient levels of  $\text{NO}_3^-$ , CDOM, and salinity).*
- 4) *determination of the photolysis rates and degradation products of the secondary products formed from the initial photolysis of the original munitions constituents in seawater systems.*

To address these questions, the work we conducted was broken into four tasks:

Task 1: Examination of TNT and DNT photolysis in a variety of natural surface waters

Task 2: Examination of TNT and DNT photolysis as a function of nitrate, CDOM, and pH

Task 3: Isolation and identification of photolysis products

Task 4: Examination of the photolysis of secondary products formed by the photolysis of TNT and DNT

## **Materials and Methods**

### **Materials**

Photolysis experiments were conducted using 2,4-DNT (Aldrich, 97 % purity), 2,6-DNT (Aldrich, 98 % purity), TNT (Eastman, >97% purity), 2,4-DBCHO (Aldrich, 97 % purity), 2,6-DNBCHO (Aldrich, 98 % purity), 2,4-dinitrobenzoic acid (2,4-DNB $\text{COOH}$ , Aldrich, 98 % purity), 2A4NBA (Chem Services), trinitrobenzene (TNB) (Aldrich, 99.9 % purity), 4-amino, 2,6-dinitrotoluene (Chem Services, 99.5% pure, 1 mg/L in ACN), 2-amino-4,6 dinitrotoluene (Chem Services, 99.5% pure, 1 mg/L in acetonitrile), 2,4-dinitrobenzyl alcohol (2,4-DNBOH Adlab chemicals, LLC, 95 % purity), 2,6-dinitrobenzyl alcohol (2,6-DNBOH, synthesis method given in method section). The synthesis required magnesium sulfate ( $\text{MgSO}_4$ , 97% purity), chloroform, carbon tetrachloride, potassium permanganate, and dimethyl sulfoxide from Aldrich



along with sodium borohydride, sodium carbonate, diethyl ether and sulfuric acid from Fisher Scientific. Methanol was obtained from Pharmco-Aaper and celite 545 from Acros Organics. Stock solutions of the nitroaromatic compounds were prepared in acetonitrile (Baxter Scientific) or in methanol. The 2,6-dinitrobenzoic acid (2,6-DNBCOOH, Aldrich rare chemicals) and other compounds were prepared in methanol for GCMS and LCMS product identification.

Aliquots of the stock solutions were added to either seawater, artificial seawater, salt water with known ions, or ultrapure water prior to photolysis. Ultrapure 18 M $\Omega$  water was generated from either a Milli-Q UV Plus<sup>®</sup> or Barnstead E-pure<sup>®</sup> water system. Seawater was collected from Accomac Canyon off of New Jersey. Seawater and estuary waters were collected from Kahana Bay in Hawaii, from the Mississippi Delta Region, and in Charleston Harbor in South Carolina by Mike Montgomery and colleagues under SERDP grant 2124. Estuary water was also collected from the Chesapeake Bay. All water samples were filtered through a 0.20  $\mu$ m Gelman Pal filters. Salinity and dissolved organic carbon measurements provided by Mike Montgomery are given in Table 2.

**Table 2.** Various marine and estuary waters studied.

Location	Water	Depth (m)*	DOC (mg Carbon/L)*	Salinity*	pH
Kahana Bay, HI	Seawater		0.97	35	8.23
Gulf of Mexico	Miss. River	0.2	5.09	0.2	8.33
	Estuary	0.5	3.53	8	8.40
	Sea water	8	0.91	36	8.15
Charleston Harbor, SC	Estuary 1 (s0)	0.9	4.6	5.6	8.13
	Estuary 2 (A3)	12.4	1.86	28.8	8.00
	Sea water	18.1	0.94	36	8.01

\*data provided by Mike Montgomery

Artificial seawater was prepared from various ionic compounds according to a recipe given by Millero (2006). Sodium chloride (NaCl), sodium sulfate (NaSO<sub>4</sub>), potassium chloride (KCl), boric acid (B(OH)<sub>3</sub>), and magnesium chloride hexahydrate (MgCl<sub>2</sub>·6 H<sub>2</sub>O) were obtained from Fisher and were certified ACS reagent grade salts. Potassium bromide (KBr, 99+ %), sodium fluoride (NaF, 99+ %), strontium chloride hexahydrate (SrCl<sub>2</sub>·6 H<sub>2</sub>O, 99%), and calcium chloride dihydrate (CaCl<sub>2</sub>·2H<sub>2</sub>O, 99.99%) were obtained from Aldrich. Sodium hydrogen carbonate (NaHCO<sub>3</sub>) was obtained from Chemical Commodities Agency, Inc.

To test the effect of additives, humic acid was added to ultrapure water as humic acid (Aldrich) and to seawater as humic acid sodium salt (Aldrich). The nitrate used was NaNO<sub>3</sub> (Fisher Certified ACS). The pH was lowered using trace metal grade hydrochloric acid (Fisher).

## Methods

The photolysis methods used in this work follow those of O'Sullivan et al. (2010). Briefly, cuvettes containing the nitroaromatic compound dissolved in various water types were exposed to the simulated solar radiation using a Suntest CPS+<sup>®</sup> solar simulator equipped a 1.5 kW xenon lamp and a solar standard optical filter (Figure 1). Each cuvette was maintained at a

constant temperature and only exposed to a portion of the solar spectrum by the presence of various Schott long-pass optical filters or maintained in the dark. The long pass filters that were used have nominal 50% transmission at wavelengths of 295, 305, 320, and 395 nm, passing longer wavelengths and absorbing shorter wavelengths.

During each experiment, 30-mL cuvettes (Starna Cells, Inc.) containing the dissolved nitroaromatic compound were exposed to simulated sunlight for a specified amount of time. Aqueous subsamples taken from each cuvette after each irradiation period were analyzed by HPLC using either a modified version of EPA method 8330 (Luning Prak and O'Sullivan 2006, 2007) or a method for polar compounds (Luning Prak and O'Sullivan 2011). The concentration data was used to determine the rate of photolysis.

For some of the samples, the absorbance was measured from 200 to 800 nm using an Agilent 8453 UV-Visible spectrophotometer with 18.2 M $\Omega$  water as the blank. Figure 1 shows the UV-Vis spectra of 2,6-DNT taken in our lab prior to photolysis. The pH of the various waters were measured using an Orion Star pH meter (Thermo Scientific) and the results are included in Table 2. For ultrapure water, KNO<sub>3</sub> was added to enable the measurement of pH, since the meter cannot measure pH when the ionic strength is zero.

Solutions containing humic substances were prepared by two methods. For the humic acid, 35 mg of humic acid was added to a beaker and 70 mL of ultrapure water was added. The solution pH was raised to 10.3 using 2 M sodium hydroxide, and approximately 430 mL of ultrapure water was added. This new solution was mixed for a week and then filtered through a 0.45 micron mixed cellulose ester filters (MFS, Pleasanton, CA). The resulting solution contained 61.8 mg/L of humic acid. This method did not work using seawater. For initial seawater studies, the Accomac seawater was mixed with a small volume of the humic acid in ultrapure water. To prepare seawater solutions containing humic material but not diluted with ultrapure water, humic acid sodium salt was used in place of humic acid, but the pH was not adjusted.

The 2,6-dinitrobenzyl alcohol was synthesized through the reduction of 2,6-DNBCHO (Houlihan et al. 1988). A 0.80 mL solution of 0.2 N NaOH was prepared in ultrapure water and 0.055 g of sodium borohydride was added to it. This solution was slowly added to 0.500 g of 2,6-dinitrobenzaldehyde in 3.75 mL of methanol at room temperature. After stirring the solution for thirty minutes, the solvent was removed by rotovap at 50 °C under a vacuum, yielding tan crystals. Ether was added to the solution until the crystals dissolved and then the solution was dried with anhydrous magnesium sulfate. The solution was filtered through a 0.45  $\mu$ m Millex®-FH syringe filter (Millipore, Inc.) and concentrated on the rotovap until tan crystals formed. Further recrystallization was carried out by dissolving the crystals in about 10 mL boiling chloroform, adding about 5 mL carbon tetrachloride dropwise, prior to cooling the solution in an ice bath. The final product was characterized by <sup>1</sup>H NMR spectroscopy using a JEOL ECX 400-MHz Nuclear Magnetic Resonance Spectrometer. The melting point of the product was taken using a Mel-Temp® Apparatus (Electrothermal, Inc.).

To isolate and identify the photolysis products, the photolysate was extracted using solid phase extraction (SPE) columns, Amino SampliQ Sep-Pak columns (Agilent). The extracted material was then eluted using various solvents such as acetonitrile and methanol. Once the

organic compounds were extracted from the aqueous phase, their identity was determined by liquid chromatography mass spectrometry (LC/MS). LCMS analysis was performed on a Varian 320 MS triple quadrupole mass spectrometer equipped with Varian 212 LC pumps, a ProStar UV/Vis detector, and a model 410 autosampler. The mobile phase was 40%:60% methanol:water with 0.1% formic acid. Separations were performed on a Pursuit XRs® Ultra 2.8 Diphenyl column or C-18 Column (Pursuit XRs 3 150 x 2 mm) with a flow rate of 0.200 mL/min. Nitroaromatic compounds were determined by both absorbance at 254 nm and negative ion mode atmospheric pressure chemical ionization mass spectrometry. Compounds were verified by comparison with commercially available compounds or by compounds synthesized in the lab.

To determine the influence of dissolved species on the photolysis of the munitions compounds, a series of experiments were run that systematically varied the nitrate and dissolved organic matter concentration. These parameters were varied by adding components to marine water or pure water. CDOM augmentation was accomplished by adding humic acid or humic acid sodium salt.

To determine the impact of salinity and temperature on the solubility of the 2,4-DNBCHO and 2,6-DNBCHO, experiments were conducted following the methods of Luning Prak and O'Sullivan (2006, 2007, 2009) and Luning Prak and Moran (2008).

## Results and Discussion

### Task 1: Photolysis in various marine systems:

The goal of this task was to investigate the photolytic behavior of nitroaromatic compounds in fresh, brackish, and salt water environments that are representative of DoD water training and testing ranges. The results discussed below show that the proof of concept was met: photolysis in various water can be measured and water type directly influences photolysis rates. This impact is compound specific. *Since these preliminary studies reveal that various waters have significantly different photolysis rates, future work should investigate waters from other potential Navy sites.*

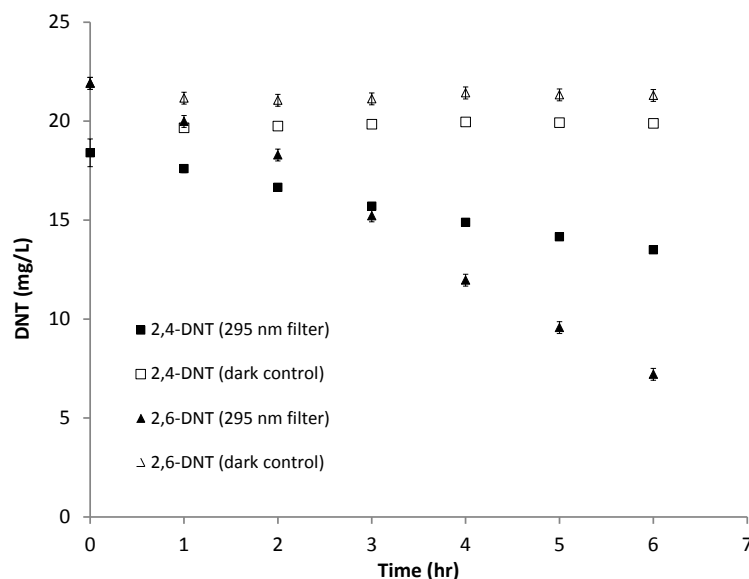
Exposure of the nitroaromatic compounds to simulated sunlight caused the concentration of the nitroaromatic compounds to decrease. Figure 4 shows the concentration of 2,4-DNT and 2,6-DNT in seawater from the Gulf of Mexico under the 295 nm cut-off filter (filled-in symbols) and the dark control (open symbols) after exposure to simulated sunlight. While no change is found in the dark control, approximately 67 % of 2,6-DNT and 27% of 2,4-DNT is photolyzed over the 6-hour period.

The decrease in concentration of nitroaromatic compounds due to photolysis was modeled as a first-order process:

$$\ln C = -k t + \ln C_0 \quad (1)$$

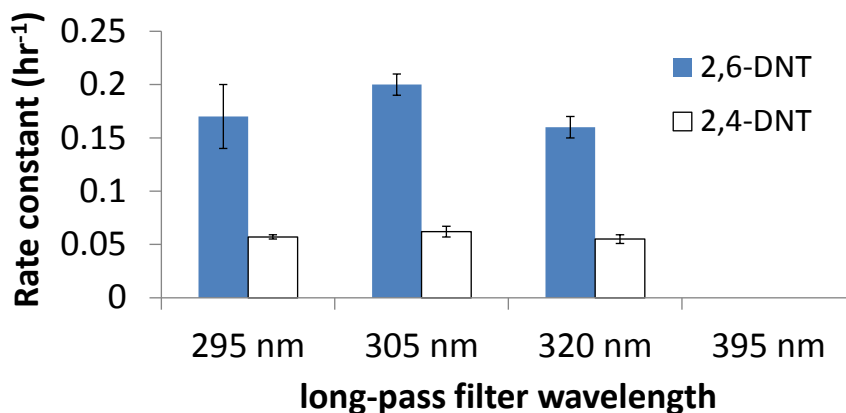
The rate constant for each reaction,  $k$ , was determined by linear regression (Excel, 2010) of this log-linearized form of the rate equation where  $C$  was the concentration at irradiation time  $t$ , and

$C_0$  was the initial concentration. The rate constants for 2,4-DNT, 2,6-DNT, and TNT in the various waters are given in Tables 3, 4, and 5, respectively.



**Figure 4.** Photolysis of 2,4-DNT and 2,6-DNT in Gulf of Mexico seawater off the Mississippi River

One of the variables tested was the effect of different wavelengths of light on the rates of photolysis of the compounds. Wavelengths were varied by using cut-off filters of wavelengths: 295, 305, 320, and 395 nm. For all three compounds, the rate constants were similar under the 295, 305, and 320 nm filters, while the rate constants were smaller or no photolysis was measured under the 395 nm filter as shown in Figure 5 for 2,4-DNT and 2,6-DNT. This shows that the effective wavelengths for photolysis are in the ultraviolet range. At higher wavelengths these compounds do not absorb enough light and the energy may not be high enough to induce photolysis.



**Figure 5.** Impact of long-pass filter wavelength on DNT photolysis rate constant in Accomac Canyon seawater

**Table 3.** Rate constants for photolysis of 2,6-DNT in natural waters (hr<sup>-1</sup>)

Site	Salinity	DOC (mg C/L)	295 nm	305 nm	320 nm	395 nm
Hawaii	35	0.97	0.22 ± 0.01	0.23 ± 0.02	0.20 ± 0.01	0.0074 ± 0.0008
Gulf	36	0.91	0.19 ± 0.02	0.20 ± 0.02	0.19 ± 0.02	NC
Charleston	36	0.94	0.17 ± 0.01	0.23 ± 0.01	0.15 ± 0.01	NC
Acc. Can.	34		0.17 ± 0.01	0.20 ± 0.02	0.16 ± 0.01	NC
Charleston	28.8	1.86	0.28 ± 0.02	0.33 ± 0.02	0.27 ± 0.02	NC
Mississippi	8	3.53	0.27 ± 0.01	0.29 ± 0.01	0.27 ± 0.02	NC
Charleston	5.6	4.6	0.22 ± 0.01	0.23 ± 0.02	0.22 ± 0.02	NC
Mississippi	0.2	5.09	0.23 ± 0.01	0.27 ± 0.02	0.22 ± 0.02	NC

Acc. Can. – Accomac Canyon, off of New Jersey, NC is no change, error is the standard error

**Table 4.** Rate constants for photolysis of 2,4-DNT in natural waters (hr<sup>-1</sup>)

Site	Salinity	DOC (mg C/L)	295 nm	305 nm	320 nm	395 nm
Hawaii	35	0.97	0.061 ± 0.002	0.063 ± 0.003	0.059 ± 0.003	NC
Gulf	36	0.91	0.053 ± 0.001	0.065 ± 0.004	0.056 ± 0.004	NC
Charleston	36	0.94	0.054 ± 0.002	0.063 ± 0.001	0.055 ± 0.002	NC
Acc. Can.	36		0.057 ± 0.002	0.062 ± 0.002	0.055 ± 0.002	NC
Charleston	28.8	1.86	0.059 ± 0.001	0.066 ± 0.002	0.053 ± 0.004	NC
Mississippi	8	3.53	0.051 ± 0.003	0.053 ± 0.002	0.050 ± 0.002	NC
Charleston	5.6	4.6	0.043 ± 0.001	0.048 ± 0.001	0.045 ± 0.001	NC
Mississippi	0.2	5.09	0.040 ± 0.001	0.037 ± 0.001	0.034 ± 0.002	NC

Acc. Can. – Accomac Canyon, off of New Jersey, NC is no change, error is standard error

**Table 5.** Rate constants for photolysis of TNT in natural waters (hr<sup>-1</sup>)

Site	Salinity	DOC (mg C/L)	295 nm	305 nm	320 nm	395 nm
Hawaii	35	0.97	0.43 ± 0.10	0.44 ± 0.14	0.39 ± 0.14	0.046 ± 0.020
Gulf	36	0.91	0.40 ± 0.10	0.37 ± 0.15	0.38 ± 0.09	0.051 ± 0.028
Charleston	36	0.94	0.45 ± 0.03	0.49 ± 0.03	0.40 ± 0.03	0.036 ± 0.003
Chesapeake Bay Estuary water <sup>1</sup>			0.36		0.34	0.04
Susquehanna River water <sup>1</sup>			0.20		0.20	0.02

(1) O'Sullivan et al. (2011), NC is no change

The impact of seawater on photolysis rates depended on the nitroaromatic compounds. For 2,6-DNT and 2,4-DNT no differences in the rate constants were found for Accomac Canyon, Charleston Harbor, Gulf of Mexico, and Hawaii seawaters (Tables 3 and 4). These seawaters have similar salinity (~33), DOC (~0.95 mg carbon/L), and pH (~8.1). When comparing these values to values reported for these compounds in Mid-Atlantic Bight seawater (0.052 hr<sup>-1</sup> for 295 nm filter), the values for 2,4-DNT in the current study are slightly higher (~ 0.055 hr<sup>-1</sup> for 295 nm filter) but within the reported error (O'Sullivan et al. 2010). For 2,6-DNT, however, the rate

constants determined in water from the Mid-Atlantic Bight ( $0.35 \text{ hr}^{-1}$  for 295 nm filter) were higher than those found for the Accomac Canyon, Charleston Harbor, or the Gulf of Mexico ( $\sim 0.19 \text{ hr}^{-1}$  for 295 nm filter). Similarly, the rate constants for the photolysis of TNT photolysis in Charleston Harbor, Gulf of Mexico, and Hawaii seawaters were the same,  $\sim 0.40 \text{ hr}^{-1}$  for 295 nm filter. These values, however, were significantly lower than those found for Mid-Atlantic Bight seawater,  $0.75 \text{ hr}^{-1}$  for 295 nm filter (O'Sullivan et al. 2011). The Mid-Atlantic Bight seawater had a similar salinity (34), less dissolved organic matter ( $0.063 \text{ mg C/L}$ ) and possibly other differences than those of the seawaters tested herein.

In estuary waters, the rate constant behavior was also compound specific. For the 2,4-DNT, the rate constants tended to decline as the salinity declined and DOC increased. The largest rate constant,  $0.066 \text{ hr}^{-1}$ , was found under the 305 nm filter for Charleston estuary water with a salinity of 28.8 and  $1.86 \text{ mg C/L}$  DOC. Under this filter, 2,4-DNT dissolved in estuary water with a salinity of 0.2 and  $5.09 \text{ mg C/L}$  had a much smaller rate constant,  $0.037 \text{ hr}^{-1}$ . This result is similar to previous research on TNT, also shown in Table 5, where the photolysis rate declined as the water moved from Mid-Atlantic Bight seawater, to Chesapeake Bay estuary water, to Susquehanna River water (head waters of the Chesapeake Bay). In contrast, estuary water photolysis rate constants for 2,6-DNT were higher than those in the seawaters tested herein. Within the estuary water samples, the rate constants declined as salinity declined and dissolved organic carbon increased.

## **Task 2: Influence of nitrate, CDOM, and pH on photolysis rates**

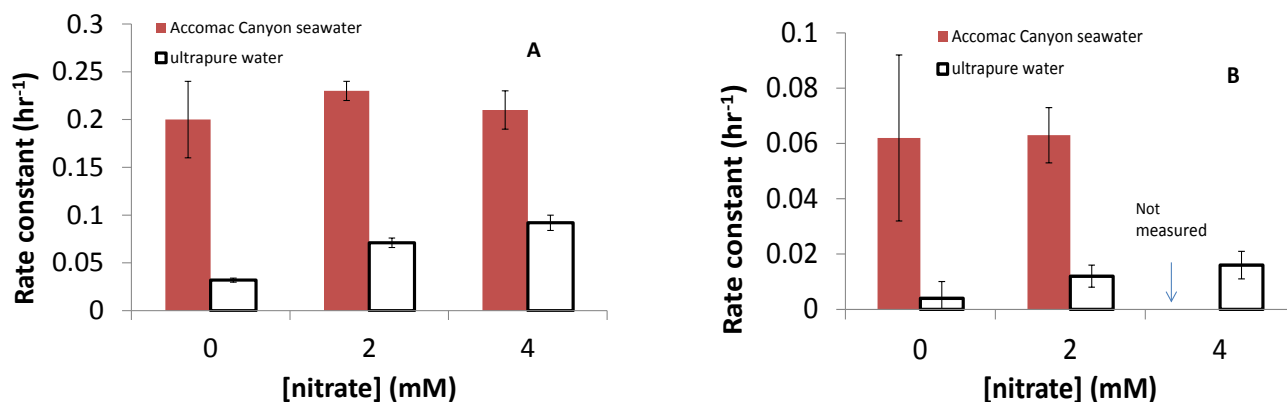
The goal of this task was to investigate how nitrate, CDOM, and pH affect the photolysis rate. The results discussed below show that the proof of concept was met: nitrate was shown to enhance photolysis rates when added to ultrapure water but not to seawater; dissolved organic matter addition in the form of humic acid was shown to enhance the photolysis of 2,6-DNT in seawater and ultrapure water and 2,4-DNT in ultrapure but to hinder photolysis or have no effect on 2,4-DNT photolysis in seawater; and lowering pH slightly enhanced the photolysis of 2,4-DNT and 2,6-DNT, but not TNT. *Since these preliminary studies reveal that dissolved organic matter alters the photolysis rates in seawater, future work should quantify how DOC concentrations vary in marines systems of interest, determine what other components of DOC impact photolysis, and determine the impact of DOC on the photolysis of other munitions constituents or secondary degradation products.*

In the absence of adding nitrate, the 2,6-DNT and 2,4-DNT photolysis rate constants in seawater are much higher than those in pure water (Figure 6 and Table 6). This result is consistent with previous work that has shown that increasing ionic strength increases the photolysis rate constant of 2,6-DNT (O'Sullivan et al. 2010) and has been attributed to the primary salt effect. The salt effect may enhance reaction rates by stabilizing a transition complex (Gardiner 1969). An anionic transition species has been found in the photolysis of 2,6-DNT (Burlinson et al. 1979; Langmuir et al. 1969). It can be speculated that the ions in the seawater are stabilizing the DNT anions, enhancing their photolysis rates.

**Table 6.** Rate constants for photolysis of 2,4-DNT and 2,6-DNT in various aqueous phases to which nitrate was added ( $\text{hr}^{-1}$ )

Reactant	Solvent	$[\text{NO}_3^-]$ (mM)	295 nm	305 nm	320 nm	395 nm
2,6-DNT	Ultrapure water		$0.043 \pm 0.006^1$	$0.032 \pm 0.002^1$	$0.026 \pm 0.001^1$	NC
		2	$0.064 \pm 0.004$	$0.071 \pm 0.005$	$0.055 \pm 0.004$	NC
		4	$0.081 \pm 0.005$	$0.092 \pm 0.008$	$0.067 \pm 0.004$	NC
	Accomac Canyon Seawater		$0.17 \pm 0.03$	$0.20 \pm 0.04$	$0.16 \pm 0.03$	NC
		2	$0.19 \pm 0.01$	$0.23 \pm 0.01$	$0.18 \pm 0.01$	NC
		4	$0.18 \pm 0.01$	$0.21 \pm 0.02$	$0.17 \pm 0.01$	NC
2,4-DNT	Ultrapure water		NC <sup>1</sup>	NC <sup>1</sup>	NC <sup>1</sup>	NC <sup>1</sup>
		2	$0.009 \pm 0.001$	$0.012 \pm 0.001$	$0.008 \pm 0.001$	NC
		4	$0.016 \pm 0.001$	$0.016 \pm 0.001$	$0.013 \pm 0.001$	NC
	Accomac Canyon Seawater		$0.057 \pm 0.002$	$0.062 \pm 0.005$	$0.055 \pm 0.004$	NC
		4	$0.062 \pm 0.002$	$0.063 \pm 0.004$	$0.059 \pm 0.003$	NC

(1) O'Sullivan et al., 2010.



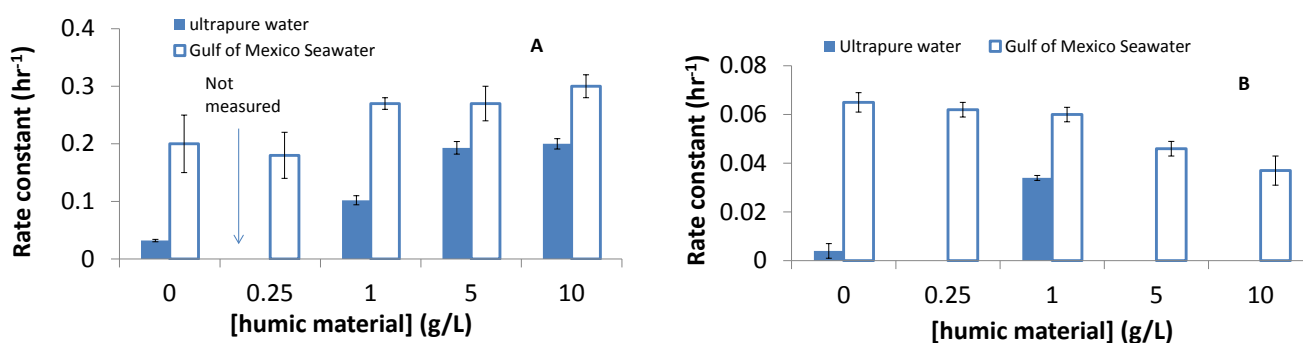
**Figure 6.** Impact of nitrate concentration on the rate constant for (A) 2,6-DNT and (B) 2,4-DNT when photolyzed in Accomac Canyon seawater and ultrapure water under the 305 nm cutoff filter

The presence of nitrate in the aqueous phase caused the photolysis rates of 2,6-DNT and 2,4-DNT in pure water to increase, while it did not change the photolysis rate of 2,6-DNT in filtered seawater (Tables 6). As seen in Figure 6A, the rate constant for 2,6-DNT increases from  $0.032 \pm 0.0021 \text{ hr}^{-1}$  to  $0.092 \pm 0.008 \text{ hr}^{-1}$  as nitrate concentration in ultrapure is increased from zero to 4 mM, but no change is seen when nitrate is added to seawater. Figure 6B shows similar results for 2,4-DNT, namely the addition of nitrate increased the photolysis of 2,4-DNT dissolved in ultrapure water but not in filtered seawater (Table 6).

Nitrate has been shown to produce hydroxyl radicals when exposed to UV light (Einschlag et al. 2009), and these radicals can react with the dissolved species, enhancing the photodegradation rate. Nitrate, however, can also reduce the degradation rate by reacting with

hydroxyl radicals that could have reacted with the dissolved species (Dzengel et al. 1999). The addition of nitrate to the seawater appears to neither create an additional amount of hydroxyl radicals nor consume a significant amount of hydroxyl radicals to alter the rate. The rate of photolysis in seawater (ionic strength = 0.682 mol/kg) is higher than that of pure water, suggesting that either the dissolved ions or organic matter in the seawater are changing the reaction pathway or creating an additional pathway for degradation. It could be hypothesized that these other pathways may mask or negate the impact of the nitrate. Since these altered or additional pathways are not present for the pure water system, the added nitrate to the pure water system causes the reaction rate to increase, suggesting that in this case the nitrate may be causing additional hydroxyl radicals to form to increase the rate of reaction.

The impact of dissolved organic matter on photolysis rates depended on the nitroaromatic compound and the water type. As shown in Figure 7, CDOM in the form of humic acid enhanced 2,6-DNT and 2,4-DNT photolysis in pure water (Table 7A and 7B, dark bars). In seawater, however, CDOM in the form of humic acid and humic acid sodium salt increased the photolysis of 2,6-DNT, while either having no impact or lowering the rate constant for the photolysis of 2,4-DNT. The humic acid was tested in Accomac Canyon seawater, while the humic acid sodium salt was tested in Gulf of Mexico seawater. Humic acid did not dissolve very well in seawater, so it was only used as a preliminary test. Humic acid results were consistent with humic acid sodium salt (Table 7). Increasing the concentration of humic acid sodium salt did not result in a proportional increase in rate.



**Figure 7.** Impact of the humic material concentration on the rate constant for (A) 2,6-DNT and (B) 2,4-DNT when photolyzed in Gulf of Mexico seawater and ultrapure water. Only one concentration of humic material was tested for 2,4-DNT in the ultrapure water.

Naturally occurring dissolved organic matter can affect reaction rates of the munitions constituents due to physical and chemical processes. Physically, dissolved organic matter (DOM) itself absorbs light and can reduce the depth of penetration of light into natural aquatic systems, thereby limiting photolysis. Chemically, dissolved organic matter can influence the concentration of hydroxyl radicals, which are believed to be the main reactant in oxidative photolysis reactions. Dissolved organic matter has been shown to lower photolysis rates by scavenging the hydroxyl radical (Brezonik and Fulkerson-Brekken 1998). In other studies, dissolved organic matter has been found to enhance the photolysis of nitroaromatic compounds



in freshwater systems (Mihás et al. 2007, Simmons and Zepp 1986), thereby suggesting that the hydroxyl radicals have increased.

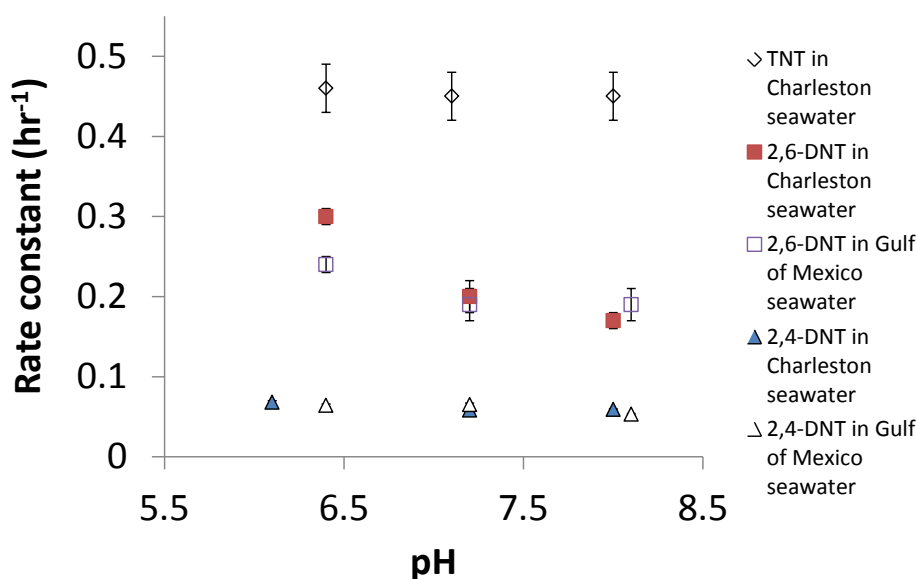
The concentrations of humic material used in this study captured the range of values found in nature. Humic substances (humic and fulvic acids) make up approximately 30% of the total dissolved organic carbon in seawater and 50% in river water. In seawater and river water systems, the concentrations of humic substances ranges from 0.06 to 4.0 mg carbon/L, with wetlands containing as high as 30 mg carbon/L (Thurman, 1985). The complex nature of these substances makes determining a molar mass very difficult, but studies with commercially available humic material have shown that approximately 69% of the humic acid sodium salt (Aldrich) is carbon by mass and 63% of humic acid (Aldrich) is carbon by mass (Malcolm and MacCarthy 1986). For river water, the 4 mg carbon/L of humic substances translates to approximately 6 mg humic acid/L.

**Table 7.** Rate constants for photolysis of 2,4-DNT and 2,6-DNT in various aqueous phases to which dissolved organic matter was added ( $\text{hr}^{-1}$ )

Reactant	Solvent	Humic material added (mg/L)	295 nm	305 nm	320 nm	395 nm	
2,6-DNT	Ultrapure water	none	$0.043 \pm 0.006^1$	$0.032 \pm 0.002^1$	$0.026 \pm 0.001^1$	NC	
		HA: 1	$0.091 \pm 0.008$	$0.102 \pm 0.008$	$0.096 \pm 0.009$	NC	
		HA: 5	$0.163 \pm 0.009$	$0.193 \pm 0.011$	$0.161 \pm 0.008$	$0.007 \pm 0.001$	
		HA: 10	$0.180 \pm 0.009$	$0.200 \pm 0.009$	$0.173 \pm 0.009$	$0.083 \pm 0.009$	
	Accomac Canyon	none	$0.17 \pm 0.03$	$0.20 \pm 0.04$	$0.16 \pm 0.03$	NC	
		HA: 1	$0.29 \pm 0.02$	$0.30 \pm 0.02$	$0.19 \pm 0.02$	NC	
	Seawater Gulf	none	$0.19 \pm 0.04$	$0.20 \pm 0.05$	$0.19 \pm 0.04$	NC	
		NaHA: 0.25	$0.19 \pm 0.03$	$0.18 \pm 0.04$	$0.19 \pm 0.01$	$0.0077 \pm 0.0011$	
		NaHA: 1.0	$0.25 \pm 0.01$	$0.27 \pm 0.01$	$0.22 \pm 0.02$	$0.010 \pm 0.002$	
		NaHA: 5.0	$0.27 \pm 0.01$	$0.27 \pm 0.03$	$0.25 \pm 0.02$	$0.061 \pm 0.017$	
		NaHA: 10	$0.29 \pm 0.02$	$0.30 \pm 0.02$	$0.26 \pm 0.02$	$0.023 \pm 0.003$	
	2,4-DNT	Ultrapure water	none	NC <sup>1</sup>	NC <sup>1</sup>	NC <sup>1</sup>	NC <sup>1</sup>
			HA: 1	$0.030 \pm 0.001$	$0.034 \pm 0.001$	$0.028 \pm 0.001$	NC
Accomac Canyon		none	$0.057 \pm 0.002$	$0.062 \pm 0.005$	$0.055 \pm 0.004$	NC	
		HA: 1	$0.055 \pm 0.004$	$0.058 \pm 0.005$	$0.040 \pm 0.002$	NC	
Seawater Gulf		none	$0.053 \pm 0.002$	$0.065 \pm 0.004$	$0.056 \pm 0.004$	NC	
		NaHA: 0.25	$0.061 \pm 0.003$	$0.062 \pm 0.003$	$0.056 \pm 0.003$	$0.0044 \pm 0.0011$	
		NaHA: 1.0	$0.059 \pm 0.003$	$0.060 \pm 0.003$	$0.054 \pm 0.003$	$0.0049 \pm 0.0010$	
		NaHA: 5.0	$0.042 \pm 0.001$	$0.046 \pm 0.003$	$0.041 \pm 0.007$	$0.0024 \pm 0.0006$	
		NaHA: 10	$0.055 \pm 0.013$	$0.037 \pm 0.006$	$0.042 \pm 0.008$	$0.0043 \pm 0.0009$	

(1) O'Sullivan et al. 2010. HA: Humic acid NaHA: humic acid sodium salt

The impact of pH on photolysis rates was found to be compound specific. The range of pH values tested was from the natural seawater pH of approximately 8.0 down to 6.4. Though a pH value of 6.4 is low for seawater, this lower value was included for comparison with ultrapure water, which had a pH of 6.35. As shown in Figure 8, lowering the pH to 6.4 did not change the photolysis rate constant for TNT, but increased the rate constants for 2,4-DNT and 2,6-DNT (Table 8). Previous work has shown that the TNT and DNT rate constants in ultrapure water with a pH of 6.35 are smaller than in seawater (O’Sullivan et al. 2010, 2011). The result shown here suggests that pH did not cause the differences between ultrapure water and seawater systems. For the intermediate pH value of 7.2 tested here, the rate constants for 2,4-DNT and 2,6-DNT were the same or slightly higher than the those of seawater without pH adjustment. Since natural seawater is unlikely to have a pH of 7.2, the impact of pH on the rate of photolysis is not significant.



**Figure 8.** Impact of the pH on the rate constant for TNT, 2,6-DNT, 2,4-DNT when photolyzed in Gulf of Mexico seawater and Charleston Harbor seawater.

### Task 3: Isolation and identification of photolysis products

The goal of this task was to isolate and identify products from the photolysis of nitroaromatic compounds. The results discussed below show that the proof of concept was met: photolysis products (2,6-DNBOH, 2,6-DNBCHO, 2,4-DNBOH, 2,6-DNBCHO, and 2A4NBA) were successfully separated from mixtures and their identity was confirmed using commercially available standards and compounds synthesized in the current research effort. *Further work will be needed to isolate and identify other photolytic products to determine if the mechanisms proposed for freshwater systems apply to seawater systems.*

The photolytic pathways for 2,4-DNT and 2,6-DNT were studied in ultrapure water and seawater systems. The proposed photolytic pathway for DNT involves transforming the DNT into the dinitrobenzyl alcohol, which is transformed into the dinitrobenzaldehyde (See Figure 3).

The proposed mechanism then involves the conversion of aldehyde into a carboxylic acid. To confirm this proposed mechanism, standards for the alcohol, aldehyde, and acid were needed. While 2,6-DNBCHO, 2,4-DNBCHO, 2,4-DNBCOOH, 2,6-DNBCOOH, and 2,6-DNBCOOH (rare chemical library) are commercially available, the alcohols had to be synthesized. The 2,4-isomer was custom synthesized by Adlab chemicals, LLC, while the 2,6-isomer was synthesized in-house.

**Table 8.** Rate constants for photolysis of TNT, 2,6-DNT, 2,4-DNT at various pH values ( $\text{hr}^{-1}$ ) in seawater under 295 nm filter and in dark control

Site	Solute	pH	295 nm	Dark
Charleston	TNT	8.0 ± 0.1	0.45 ± 0.03	NC
		7.1 ± 0.1	0.45 ± 0.03	
		6.4 ± 0.1	0.46 ± 0.03	NC
	2,6-DNT	8.0 ± 0.1	0.17 ± 0.01	NC
		7.2 ± 0.1	0.20 ± 0.02	
		6.4 ± 0.2	0.30 ± 0.01	NC
	2,4-DNT	8.0 ± 0.1	0.059 ± 0.001	NC
		7.2 ± 0.1	0.058 ± 0.004	
		6.1 ± 0.2	0.068 ± 0.002	NC
Gulf	2,6-DNT	8.1 ± 0.1	0.19 ± 0.02	NC
		7.2 ± 0.1	0.19 ± 0.02	NC
		6.4 ± 0.1	0.24 ± 0.01	NC
	2,4-DNT	8.1 ± 0.1	0.053 ± 0.001	NC
		7.2 ± 0.1	0.065 ± 0.002	NC
		6.4 ± 0.1	0.064 ± 0.002	NC

NC is no change

The synthesis of 2,6-dinitrobenzyl alcohol was successful. The product formed from the reduction of 2,6-DNBCHO had a melting point of 96-98 °C, which compares well to the literature value of 96 °C for 2,6-dinitrobenzyl alcohol (Mori et al. 1986). The results of the  $^1\text{H}$  NMR (ppm,  $\text{CDCl}_3$ ): 8.08-8.02 (m, 2 H, Ar H-3,5); 7.65-7.59 (m, 1 H, Ar H-4); 7.23 (d, 2 H, H-7); 4.94-4.89 (t, 1 H, O-H) match those found in literature for 2,6-dinitrobenzyl alcohol (Mori et al., 1986). A percent yield of 30.56 % was obtained through this synthesis process. This alcohol, along with the purchased compounds, were then used in analyzing photoproducts.

The product mixture formed by the photolysis of 2,4- and 2,6-DNT is yellow in color, while the original DNTs are colorless in solution. The mixture was passed through an amino Sep-pak and subjected to a sequential solid phase extraction scheme to isolate different fractions of the products. The eluent fractions were analyzed by LCMS. The identity of the products was determined by matching the retention times and MS/MS spectrometry of the known compounds with compounds in the product mixture. The optimized conditions are given in Table 9 for the MS/MS analysis using the C-18 column and the diphenyl column including the parent ion captured (Q1) in the first quadrature and the optimal daughter mass (Q3) formed by bombarding the captured parent ion. Based on the resulting fragments, most product ions were missing part of a nitro group, while the 2,6-DNBA product ion appears to have undergone a decarboxylation.

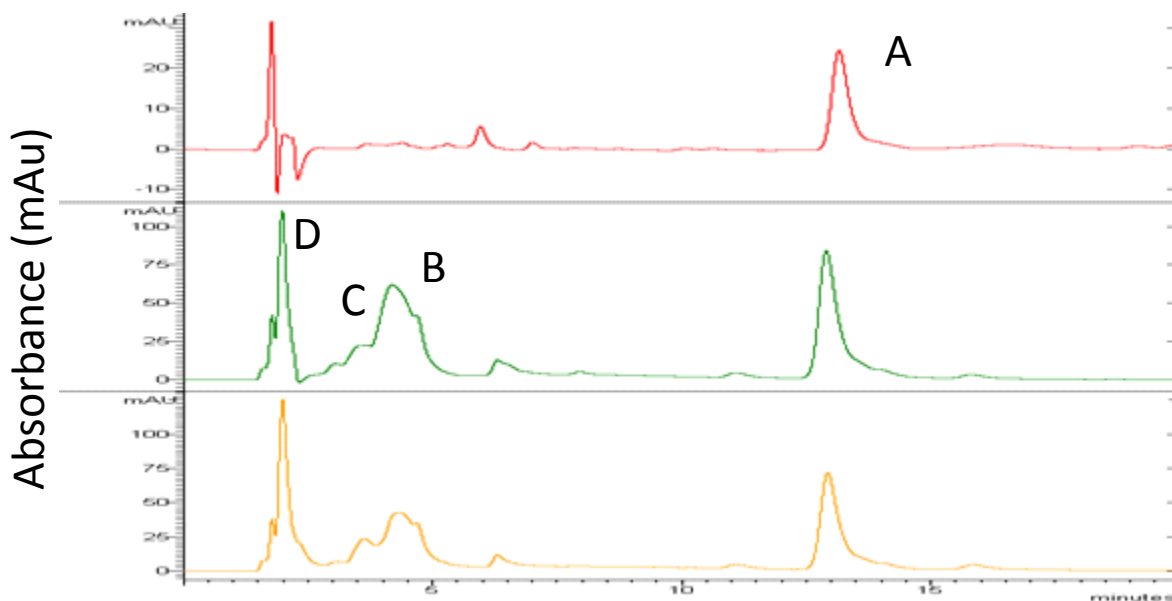
**Table 9.** LC/MS/MS parameters for selected compounds

	Q1 mass m/z	Q3 mass m/z	Precursor / Product Ion	CE (Volt)	Diphenyl Retention Time (min)	C-18 Retention Time (min)
2,4-DNBOH	197.7	134.6	[M-H] <sup>-</sup> / [M-H-NO <sub>2</sub> -OH] <sup>-</sup>	-6.5	9.6	
2,4-DNBCHO	195.5	137.6	[M-H] <sup>-</sup> / [M-H-NO-CO] <sup>-</sup>	-11.5 -12.5	13.0	4.1
2A4NBA	180.6	136.7	[M-H] <sup>-</sup> / [M-H-CO <sub>2</sub> ] <sup>-</sup>	-9.4	14.0	
2,4-DNBCOOH	210.8	166.3	[M-H] <sup>-</sup> / [M-H-CO <sub>2</sub> ] <sup>-</sup>	-5.5	9.7	
2,6-DNT	181.5	151.6	[M-H] <sup>-</sup> / [M-H-NO] <sup>-</sup>	-6.5		13.3
2,6-DNBOH	197.6	167.7	[M-H] <sup>-</sup> / [M-H-NO <sub>2</sub> ] <sup>-</sup>	-5.5 -9.0	8.3	3.7
2,6-DNBCHO	195.5	137.7	[M-H] <sup>-</sup> / [M-H-NO-CO] <sup>-</sup>	-10.0 -12.5	10.9	4.7
2,6-DNBCOOH	211.5	167.6	[M-H] <sup>-</sup> / [M-H-CO <sub>2</sub> ] <sup>-</sup>	-6.0	6.5	2.2

CE: collision energy

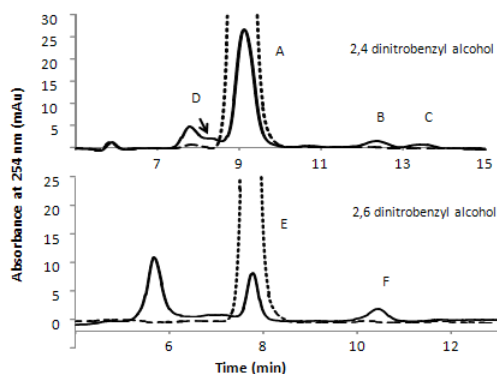
The compounds also eluted based on their polarity, with the very polar 2,6-DNBA eluting at 2.2 minutes and the least polar 2,6-DNT taking 13.3 minutes on the C-18 column.

The C-18 column liquid chromatography scans of extracts from the photolysis of 2,6-DNT in seawater show the presence of a mixture of compounds. Figure 9 shows the LC scans from the uv-vis detector for seawater solution containing 2,6-DNT before (top figure) and after photolysis in the absence (middle figure) and presence of added nitrate (lower figure). The 2,6-DNT, labeled as “A,” appears at a retention time of 13.3 minutes. Upon photolysis in filtered seawater, peaks labeled as “B” and “C” appear at 4.7 min and 3.7 min, respectively. Peak “B” has the same retention time as 2,6-DNBCHO and “C” has the same retention time as 2,6-DNBOH. To confirm the identity of the products, the retention times and MS/MS spectrometry of the known compounds were compared with those of the product mixture. Using this analysis, compounds “B” and “C” were confirmed as being 2,6-DNBCHO and 2,6-DNBOH. The peak labeled as “D” has the same retention time on the LC using the uv-vis detector as that of DNBCOOH, 2.2 min. Its identity, however, could not be confirmed by MS/MS. The detection of a 2.5 ppm standard of 2,6-DNBCOOH gives a small MS/MS signal, so smaller quantities may not be detected by the method. The photolyzed solution containing nitrate does not provide a significantly different result from the non-nitrate sample on both the chromatogram and the MS/MS output. Therefore, under the extraction conditions tested, a difference in pathway is not evident.



**Figure 9.** LC chromatogram for unphotolyzed 2,6-dinitrotoluene, photolyzed 2,6-dinitrotoluene, and photolyzed 2,6-dinitrotoluene with a 2 mM nitrate addition. The sample was photolyzed under a 305 nm light filter and was extracted in acetonitrile. Data were collected at 254 nm wavelength.

The degradation pathway shown in Figure 3 for 2,6-DNT can also apply to the 2,4-isomer. If that pathway is correct, the photolysis of the 2,4-dinitrobenzyl alcohol (2,4-DNBOH) should produce 2,4-dinitrobenzaldehyde (2,4-DNBCHO) and the other products. Figure 10 shows the phenyl column LC scans from the uv-vis detector for seawater solution containing 2,4-DNBOH before (top figure, dotted line) and after photolysis for 60 minutes (top figure, solid line). The alcohol, labeled as “A,” appears at a retention time of 9.1 minutes. Upon photolysis in filtered seawater (dark line), peaks labeled as “B” and “C” appear at 12.2 min and 13.4 min, respectively. Peak “B” has the same retention time as 2,4-DNBCHO and “C” has the same retention time as 2A4NBA. To confirm the identity of the products, the retention times and MS/MS spectrometry of the known compounds were compared with those of the product mixture. Using this analysis, compounds “B” and “C” were confirmed as being 2,4-DNBCHO and 2A4NBA. The peak labeled as “D” has the same retention time on the LC using the uv-vis detector as that of DNBCOOH, 8.38 min. Its identity, however, could not be confirmed by MS/MS. The detection of a 2.5 ppm standard of 2,4-DNBCOOH gives a small MS/MS signal, so smaller quantities may not be detected by the method. When comparing the photolysis of 2,4-DNBOH in ultrapure water with that in seawater, fewer peaks appear on the chromatogram for the ultrapure water (not shown). No 2,4-DNBCHO was found by either the uv-vis detector or by MS/MS, and a small amount of 2A4NBA was detected by both uv-vis and MS/MS.



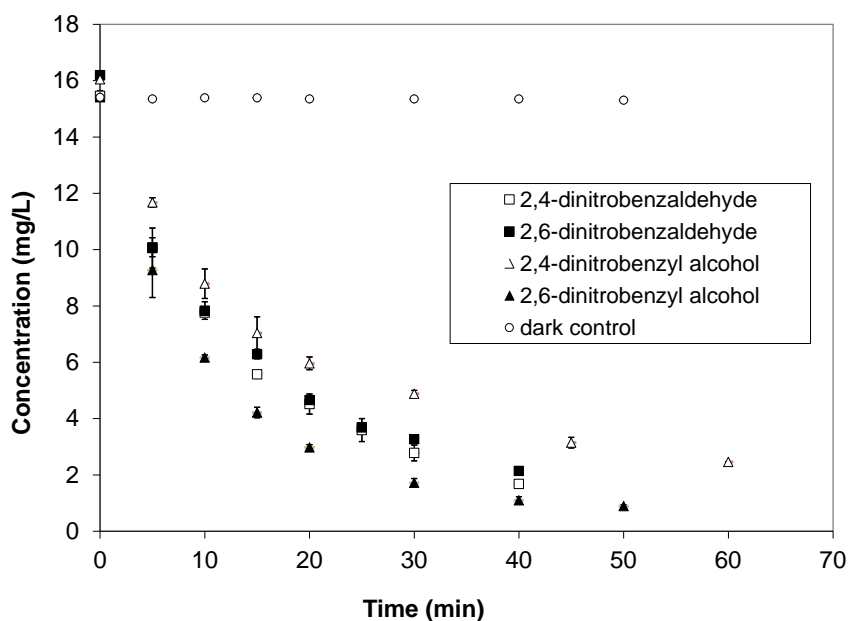
**Figure 10.** LC chromatograms of the initial 2,4-dinitrobenzyl alcohol in filtered seawater (top figure, dotted line) and after 60 minutes of irradiation (top figure, solid line), and of the initial concentration of 2,6-dinitrobenzyl alcohol in filtered seawater (bottom figure, dotted line) and after 50 minutes of irradiation (bottom figure, solid line)

In a manner similar to 2,4-DNBOH, the photolysis of 2,6-DNBOH should produce 2,6-DNBCHO and 2,6-DNBCHOH. Figure 10 shows the LC scans from the uv-vis detector for seawater solution containing 2,6-DNBOH before (bottom figure, dotted line) and after photolysis for 60 minutes (bottom figure, solid line). The alcohol, labeled as “E,” appears at a retention time of 7.7 minutes. Upon photolysis in filtered seawater (dark line), a peak labeled as “F” appears at 10.3 min. This peak has the same retention time as 2,6-DNBCHO, and its identity was confirmed by MS/MS using the parameters in Table 9. No peak appears at 6.5 min, which is the retention time for 2,6-DNBCHOH. Analysis of the products formed by photolyzing 2,6-DNBOH in ultrapure water also show that the aldehyde is formed, but the acid could not be detected.

#### **Task 4: Examination of the photolysis of secondary products formed by the photolysis of TNT and DNT**

The goal of this task was to quantify the rate of photolysis of secondary products formed by the photolysis of TNT and DNT. The results discussed below show that the proof of concept was met: photolytic decay was found for some secondary products but not for others. The rates of decay were compound specific. Those compounds that did not degrade by photolysis could either accumulate or be transformed by other processes in natural systems such as microbial decay. *Since these preliminary studies reveal that photolysis rates of secondary products are compound specific, future work should quantify the photolysis rates of other secondary product and examine the impact of mixtures of nitroaromatic compounds on photolysis rates.*

Exposure of some of the nitroaromatic compounds to simulated sunlight caused these compounds to disappear. As shown in Figure 11, the concentration of dinitrobenzaldehydes and dinitrobenzyl alcohols in filtered seawater decreased upon exposure to light with wavelengths greater than 295 nm, and less than 25% remained after 45 minutes of exposure. No change was observed for the dark control samples as shown for 2,6-DNBOH. For the 2,4-DNBCHOH or 2A4NBA, no concentration change was measured over a 9-hour or 4.8-hour exposure time, respectively (not shown).



**Figure 11.** Photolysis of 2,4-DNBOH, 2,4-DNBCHO, 2,6-DNBOH and 2,6-DNBCHO in filtered Gulf of Mexico seawater using 295 nm cut-off filter and the dark control (○).

The first-order rate constants for the photolysis of 2,4-DNBOH, 2,4-DNBCHO, 2,6-DNBOH, and 2,6-DNBCHO in the various waters under the different cutoff filters are given in Table 10. When comparing the photolysis of the various isomers, the rates for the aldehydes were similar but those of the alcohols differed. For example, when comparing the photolysis of the aldehydes in seawater under the 295 nm filter, the rate constant for 2,6-DNBCHO,  $2.9 \pm 0.4 \text{ hr}^{-1}$ , is similar to that of 2,4-DNBCHO,  $3.1 \pm 0.3 \text{ hr}^{-1}$ . In contrast, under the same conditions the rate constant for 2,6-DNBOH,  $4.3 \pm 0.7 \text{ hr}^{-1}$ , is higher than that of 2,4-DNBOH,  $1.8 \pm 0.4 \text{ hr}^{-1}$ . A faster rate for the 2,6-isomer is similar to the faster rates found for the parent compounds. In fresh water and seawater samples, 2,6-DNT is photolyzed faster than 2,4-DNT (Burlinson et al. 1979; Simmons and Zepp 1986; O'Sullivan et al. 2010). The alcohols also have larger confidence intervals for their rate constant. It may be that a first-order fit does not represent all the data as well as it does for the aldehydes.

When comparing the photolysis behavior of these dinitrobenzaldehydes and dinitrobenzyl alcohols with those of their parent dinitrotoluenes, similarities and differences are found. In both cases, the resulting rate constants for each compound are similar for the 295 nm, 305 nm, and 320 nm cutoff filters but much smaller for the 395 nm cut-off filter. The differences arise in the influence of the aqueous phase on the rate of reaction and on the magnitude of the rate constants. The photolysis of 2,4-DNT and 2,6-DNT is faster in filtered seawater than in ultrapure water (O'Sullivan et al. 2010). For 2,6-DNT, the rate constant in filtered seawater under the 305 nm filter of  $0.42 \pm 0.2 \text{ hr}^{-1}$  is an order of magnitude higher than the value in ultrapure water,  $0.032 \pm 0.002 \text{ hr}^{-1}$ . For 2,4-DNT, the rate constant in seawater under the 305 nm filter,  $0.054 \pm 0.006 \text{ hr}^{-1}$  (O'Sullivan et al. 2010), is approximately six times higher than the rate constant measured herein for the 2,4-DNT dissolved in ultrapure water,  $0.0084 \pm 0.0018 \text{ hr}^{-1}$ . O'Sullivan et al. (2010)

measured no change in the 2,4-DNT over a 3.5 hr time period, while the current experiment photolyzed a sample for 12 hours to capture some degradation. In contrast to the photolysis of the parent DNTs, the aqueous phase did not change the photolysis rate of the dinitrobenzyl alcohols or dinitrobenzaldehydes studied herein.

**Table 10.** Rate constants for the photolysis of the photolytic products of 2,4-DNT and 2,6-DNT ( $\text{hr}^{-1}$ )

Solute	Solvent	Cutoff Filter				Dark Control
		295 nm	305 nm	320 nm	395 nm	
2,6-DNBCHO	E-pure water	$2.7 \pm 0.4$	$2.9 \pm 0.3$	$2.8 \pm 0.3$	$0.14 \pm 0.08$	NC
	Chesapeake Bay	$2.9 \pm 0.3$	$2.9 \pm 0.4$	$2.7 \pm 0.6$	$0.25 \pm 0.03$	NC
	Estuary water					
	Seawater (Accomac)	$2.7 \pm 0.6$	$3.0 \pm 0.5$	$2.9 \pm 0.5$	$0.22 \pm 0.07$	NC
	Seawater (Gulf)	$2.9 \pm 0.4$	$3.1 \pm 0.5$	$2.9 \pm 0.3$	$0.20 \pm 0.02$	NC
	Artificial seawater	$3.6 \pm 0.4$	$3.9 \pm 0.7$	$3.5 \pm 0.5$	$0.28 \pm 0.06$	NC
2,4-DNBCHO	E-pure water	$3.4 \pm 0.4$	$3.7 \pm 0.4$	$3.4 \pm 0.4$	$0.26 \pm 0.06$	NC
	Chesapeake Bay	$2.9 \pm 0.4$	$3.0 \pm 0.4$	$3.0 \pm 0.3$	$0.26 \pm 0.06$	NC
	Estuary water					
	Seawater (Accomac)	$3.4 \pm 0.8$	$3.7 \pm 0.8$	$3.3 \pm 0.7$	$0.35 \pm 0.30$	NC
	Seawater (Gulf)	$3.2 \pm 0.3$	$3.2 \pm 0.3$	$3.0 \pm 0.2$	$0.23 \pm 0.05$	NC
	Artificial seawater	$3.6 \pm 0.5$	$3.8 \pm 0.4$	$3.4 \pm 0.5$	$0.28 \pm 0.11$	NC
2,4-DNBCOOH	E-pure water	NC	NC	NC	NC	NC
	Seawater (Accomac)	NC				NC
2A4NBA	E-pure water	NC				NC
	Filtered seawater	NC				NC
2,4-DNT	E-pure water		$0.0084 \pm 0.0018$		NC	NC
2,6-DNBOH	E-pure water	$4.6 \pm 1.0$	$4.5 \pm 1.2$	$4.3 \pm 0.9$	$0.42 \pm 0.01$	NC
	Chesapeake Bay	$4.0 \pm 0.8$	$4.2 \pm 0.9$	$4.0 \pm 0.8$	$0.40 \pm 0.02$	NC
	Estuary water					
	Seawater (Gulf)	$4.4 \pm 0.7$	$3.9 \pm 1.4$	$4.0 \pm 1.0$	$0.43 \pm 0.05$	NC
2,4-DNBOH	E-pure water	$2.3 \pm 0.4$	$2.3 \pm 0.5$	$2.3 \pm 0.3$	$0.14 \pm 0.01$	NC
	Chesapeake Bay	$1.8 \pm 0.2$	$1.8 \pm 0.2$	$1.8 \pm 0.2$	$0.11 \pm 0.02$	NC
	Estuary water					
	Seawater (Gulf)	$1.8 \pm 0.4$	$1.9 \pm 0.4$	$1.8 \pm 0.3$	$0.17 \pm 0.03$	NC

Errors are the 95% confidence interval of the slope from plots of  $\ln C$  vs time.

NC indicates that concentrations varied by less than the analytical error over the course of the experiment.



The photolysis of the alcohols and aldehydes is faster than the DNTs. In seawater solutions under the 305 nm filter, the rate constants for the 2,6-DNT (O'Sullivan et al., 2010), 2,6-DNBOH, and 2,6-DNBCHO are  $0.42 \pm 0.02 \text{ hr}^{-1}$ ,  $3.9 \pm 1.4 \text{ hr}^{-1}$ , and  $3.1 \pm 0.5 \text{ hr}^{-1}$ , respectively. Under similar conditions, the rate constants for the 2,4-DNT, 2,4-DNBOH, and 2,4-DNBCHO are  $0.054 \pm 0.006 \text{ hr}^{-1}$ ,  $1.9 \pm 0.4 \text{ hr}^{-1}$ , and  $3.1 \pm 0.3 \text{ hr}^{-1}$ , respectively. A faster photolysis rate for nitroaromatic alcohols and aldehydes than the parent nitrotoluene was also found by Burlinson et al. (1979) who reported that 2,4,6-trinitrobenzyl alcohol and 2,4,6-trinitrobenzaldehyde were more photosensitive than their parent 2,4,6-trinitrotoluene.

Photolytic transformation of TNT produces 2,4,6-trinitrobenzene, 2-amino 4,6-dinitrotoluene, and 4-amino 2,6-dinitrotoluene. Photolysis of these compounds dissolved in ultrapure water or in Accomac Canyon filtered seawater was studied under the 295 nm filter and in dark control (Table 11). Of these three products, only the 4-amino 2,6-DNT showed significant photolysis under the 295 nm filter, with a rate constant of  $0.07 \text{ hr}^{-1}$ .

**Table 11.** Rate constants for photolysis experiments of the secondary products from TNT photolysis in ultrapure water and Accomac Canyon seawater ( $\text{hr}^{-1}$ )

Solute	Solvent	Cutoff Filter	
		295 nm	Dark control
TNB	Ultrapure water	NC	NC
	Seawater	NC	NC
2-amino 4,6-dinitrotoluene	Ultrapure water	$0.0027 \pm 0.0002^1$	NC
	Seawater	$0.0031 \pm 0.0003^1$	NC
4-amino 2,6-dinitrotoluene	Ultrapure water	$0.068 \pm 0.002$	NC
	Seawater	$0.065 \pm 0.002$	NC

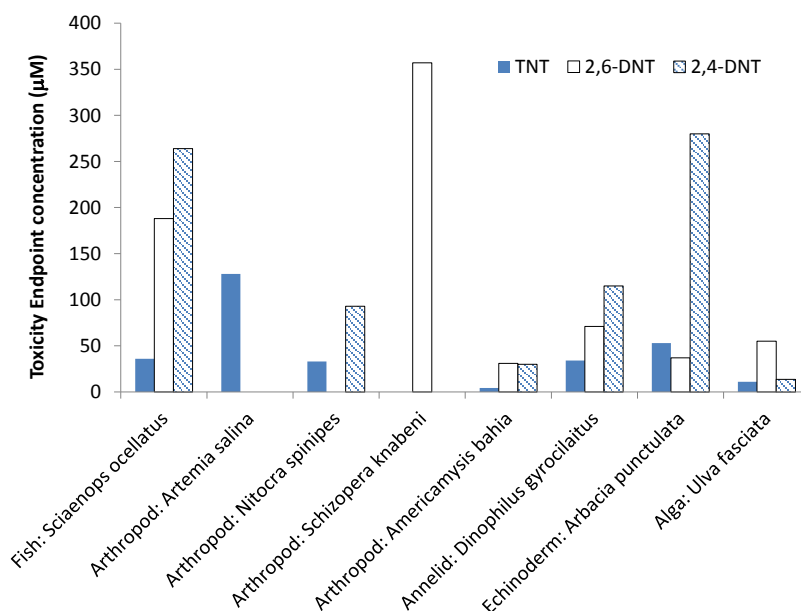
Errors are the 95% confidence intervals of the slope from plots of  $\ln C$  vs time.

NC indicates no change in various sample concentrations during 6 hours of irradiation (TNB) or 8 hours (amino DNTS), <sup>(1)</sup> less than 0.4 mg/L decline over 8 hours

When assessing the impact of the parent compounds on environmental systems, understanding what products are formed and their rate of transformation is important. The result that the more toxic products, the dinitrobenzaldehydes, are photolyzed faster than their parent compounds suggests that in the presence of sunlight, these toxic products will not accumulate in high quantities. Other products, such as the trinitrobenzene, which do not photolyze significantly and are toxic, may accumulate if not transformed by other processes such as microbial decay. If they are not being degraded by means other than photolysis, they remain an issue for the US Navy.

The toxicity of the parent nitrotoluenes has been studied using various freshwater organisms, but few estuary and marine organisms have been tested (Nipper et al. 2009). Based on a summary by Nipper et al. (2009), Figure 12 shows that the concentrations at which TNT becomes toxic to marine or estuary organisms range from 4 to 130  $\mu\text{M}$  for TNT, while the ranges for 2,6-DNT are from 31 to 360  $\mu\text{M}$  and for 2,4-DNT are from 30 to 380  $\mu\text{M}$ . In the photolysis work presented here, the concentrations of TNT, 2,6-DNT, and 2,4-DNT were 88  $\mu\text{M}$ , 100  $\mu\text{M}$ ,

and 100  $\mu\text{M}$ , respectively, which are within this toxicity range. Toxicity is defined in different ways for each organism. LC-50 is the concentration at which half of the population dies, while EC-50 is the concentration at which half of the population is affected. The organisms shown in Figure 12 include one marine fish (*Sciaenops ocellatus*, 48-hr EC-50 for embryo survival), one marine arthropod (*Artemia salina*; 24-hr LC-50), three estuary arthropods (*Nitocra spinipes*, *Schizopera knabeni*, *Americamysis bahia*, all 96-hr LC-50), one marine annelid (*Dinophilus gyrociliatus*, 7-day LC-50); one Echinoderm (*Arbacia punctulata*, 48-hr EC-50 for embryo development); and one alga species (*Ulva fasciata*, 96-hr EC-50 for zoospore germination). Based on these few studies, Nipper et al. (2001 and 2009) proposed an interim water quality criteria (WQC) for the protection of marine life to be 0.276 and 0.125  $\mu\text{M}$  TNT for acute and chronic exposure, respectively. No values have been reported for 2,4-DNT and 2,6-DNT. Concern is also emerging over the impact of munitions on corals, and Albright (2011) suggests that coral may be getting cancer from the explosive residue in the water. Other researchers are currently being funded by SERDP (ER-2125) to help assess the impact of munitions on coral.



**Figure 12.** Toxicity of TNT, 2,6-DNT, and 2,4-DNT to various marine and estuary organisms. No bar means that the data were not reported for that compound.

The true impact of munitions constituents in marine conditions depends on the proximity of the organisms to the corroded munitions case. Given that the solubility values of the TNT, 2,6-DNT, and 2,4-DNT are 380  $\mu\text{M}$  (20  $^{\circ}\text{C}$ ), 675  $\mu\text{M}$  (19  $^{\circ}\text{C}$ ), 697  $\mu\text{M}$  (20  $^{\circ}\text{C}$ ) (Luning Prak and O'Sullivan 2006, 2007), respectively, the greatest toxicity threat is for organisms growing near the casings, where little dilution or photolysis has taken place. Certain organisms may be attracted to the bomb casings because they provide shelter or a place to hide from predators.

If photolysis or microbial degradation of munitions constituents takes place, the parent compound will disappear and the daughter products may then react. In the case of the toxic dinitrobenzaldehydes formed by DNT photolysis, the aldehydes photodegrade quickly and are

less likely to be a problem. Photoproducts that are not degradable, either microbially or photochemically, remain a problem. For example, TNB is a photoproduct of TNT that does not photodegrade readily, and TNB is toxic with a proposed WQC for freshwater of 0.282 and 0.050  $\mu\text{M}$  for acute and chronic exposure, respectively (Nipper et al. 2009). No WQC have been determined for marine waters.

### Seawater solubility of 2,4-dinitrobenzaldehyde and 2,6-dinitrobenzaldehyde

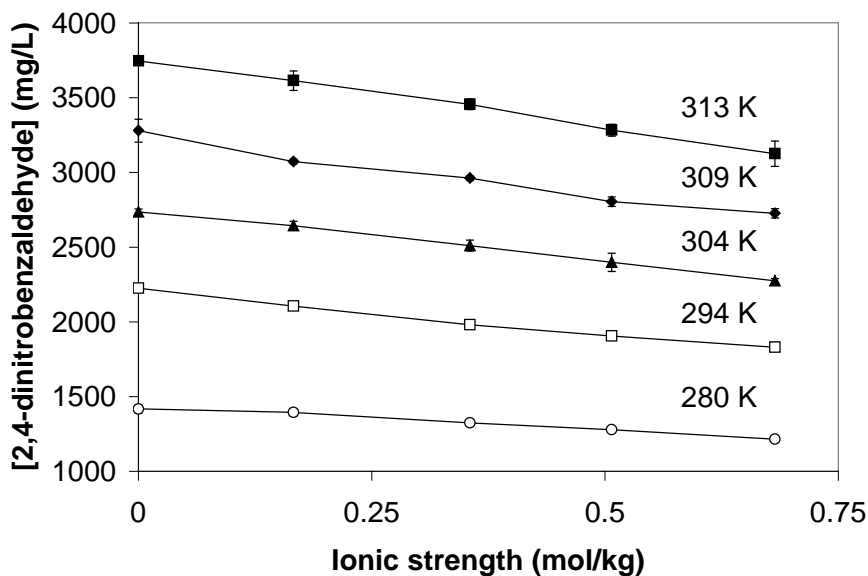
One factor that can influence the photolysis and other reactive pathways is the amount of material that can dissolve in the aqueous phase. An examination of impact of ionic strength and temperature on the solubility of 2,4-DNBCHO and 2,6-DNBCHO revealed that their solubilities declined as the concentration of seawater increased from 0% to 100% (ionic strength = 0.682 mol/kg), and as temperature decreased (Figures 13 and 14) (Luning Prak and O’Sullivan 2011). When the solubility of neutral compounds decreases in the presence of inorganic salts, the process is commonly called “salting-out” (see review in Xie *et al.*, 1997). When a solution contains a complex mixture of salts such as seawater, the salting-out effect can be quantified using a version of the Setschenow equation, which relates organic compound solubility to solution ionic strength,  $I$  (mol  $\text{kg}^{-1}$ ):

$$\log(S_w/S) = K_s' I \quad (2)$$

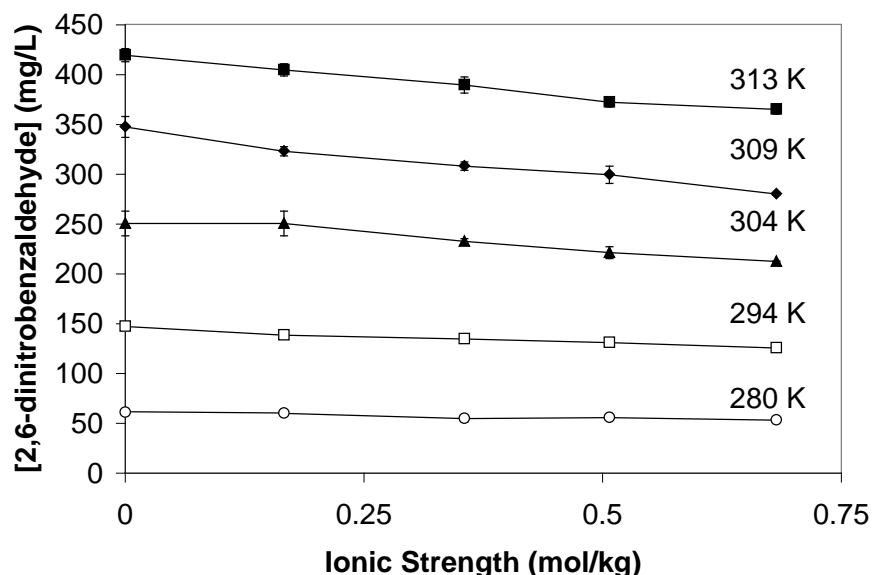
where  $S_w$  is the solute solubility in pure water ( $\text{mg L}^{-1}$ ),  $S$  is the solute solubility in the salt solution ( $\text{mg L}^{-1}$ ), and  $K_s'$  is a salting-out parameter ( $\text{kg mol}^{-1}$ ) (Luning Prak and Moran 2008; Luning Prak and O’Sullivan 2006, 2007, 2009; Sada et al., 1975). The ionic strength,  $I$ , is defined by

$$I = \frac{1}{2} \sum_i C_i Z_i^2 \quad (3)$$

where  $C_i$  is the concentration of ion  $i$  (mol  $\text{kg}^{-1}$ ) and  $Z_i$  is the charge on ion  $i$ .



**Figure 13.** Influence of temperature and ionic strength on the solubility of 2,4-DNBCHO



**Figure 14.** Influence of temperature and ionic strength on the solubility of 2,6-DNBCHO

Values of the salting-out parameter based on eq 2 for 2,6-DNBCHO, ( $0.10 \pm 0.02$ )  $\text{kg}\cdot\text{mol}^{-1}$ , and 2,4-DNBCHO, ( $0.12 \pm 0.01$ )  $\text{kg}\cdot\text{mol}^{-1}$ , do not vary significantly with temperature (Table 12). These salting-out coefficients for dinitrobenzaldehydes are similar to ( $0.11 \pm 0.01$ ,  $0.12 \pm 0.01$ ) for 2,4-DNT and 2,6-DNT, respectively (Luning Prak and O’Sullivan 2006, 2007). As with the pure water systems, the solubility of 2,6-DNBCHO and 2,4-DNBHO in seawater solutions increased with increasing temperature. These results show that seawater conditions can influence the solubility of products formed by photolysis as well as the parent compound. For 2,6-dinitrobenzaldehyde and 2,4-dinitrobenzaldehyde, the solubility values are likely to be much higher than would be produced during photolysis and therefore would not precipitate out.

**Table 12.** Salting-out Parameters,  $K_s'$ , for 2,6-Dinitrobenzaldehyde (1) and 2,4-Dinitrobenzaldehyde (2) at Various Temperatures,  $T^a$

1			2		
$T/K$	$K_s'$	SE	$T/K$	$K_s'$	SE
	$\text{kg}\cdot\text{mol}^{-1}$			$\text{kg}\cdot\text{mol}^{-1}$	
280.0	0.089	0.033	280.3	0.11	0.003
294.0	0.082	0.007	294.2	0.12	0.007
303.9	0.11	0.007	303.8	0.13	0.002
308.5	0.12	0.012	308.6	0.11	0.011
313.4	0.090	0.011	313.4	0.12	0.006

<sup>a</sup>SE: standard error

## Conclusions and Implications for Future Work

This research presented herein has partially addressed some of the data gaps in achieving a comprehensive understanding of the fate of munitions constituents in marine waters. For the data gap of *confirming whether the trends observed in the rate constants for one water body, such as the Chesapeake Bay, can be applied to other surface waters*, this study has shown that rate constants for the photolysis of 2,4-DNT, 2,6-DNT, and TNT are similar in seawaters with similar salinity and dissolved organic matter, but differ in natural waters with lower salinity and higher dissolved organic matter. Future work should investigate seawaters from other Navy sites that have different dissolved organic matter concentration. The exact nature of the dissolved organic matter should be investigated.

For the data gap of *determining what characteristics of natural waters affect the MC photolysis rates (ambient levels of  $\text{NO}_3^-$ , CDOM, and salinity)*, this study has shown that adding nitrate enhanced the photolysis of 2,6-DNT and 2,4-DNT in ultrapure water but not in seawater. The photolysis rates of 2,4-DNT and 2,6-DNT were faster in seawater than in ultrapure water. The addition of humic acid sodium salt to seawater enhanced the photolysis rate of 2,6-DNT, but lowered the photolysis rate of 2,4-DNT. Humic acid is only one component of dissolved organic carbon in natural systems. Future work should investigate how photolysis changes when other forms of dissolved organic matter are added to natural water systems. Natural water systems also vary in temperature. Future work should determine the impact of temperature on photolysis rates.

For the data gap of *determining the photolysis rates and degradation products of the secondary products formed from the initial photolysis of the original munitions constituents in seawater systems*, this study has separated and identified a few photoproducts in the DNT photolysis pathways including 2,4-DNBOH, 2,6-DNBOH, 2,6-DNBCHO, and 2,4-DNBCHO, and 2A4NBA. When photolyzing these products, the rate constants for 2,4-DNBOH, 2,6-DNBOH, 2,6-DNBCHO, and 2,4-DNBCHO were larger than those of their parent DNT, but 2A4NBA was not photolyzed under the conditions studied. The result that the more toxic products, the dinitrobenzaldehydes, are photolyzed faster than their parent compounds suggests that in the presence of sunlight, these toxic products will not accumulate in high quantities. Other products, such as the 2A4NBA from 2,4-DNT photolysis or TNB from TNT photolysis, which do not photolyze significantly, may accumulate if not transformed by other processes such as microbial decay. If they are not being degraded by means other than photolysis, they remain an issue for the US Navy. The impact of ionic strength of a seawater solution and temperature on the solubility of 2,4-DNBCHO and 2,6-DNBCHO was also measured. Their high solubility values suggest that these materials would not precipitate out after being formed. Future work should continue to isolate other compounds formed and determine their photolysis rates. Additional solubility work can help to assess if precipitation of these compounds is a possibility.

For the data gap of *determining of whether the photolysis mechanisms defined in one set of natural waters is relevant for other natural water systems of importance to the Navy*, the results partially address this data gap. Mechanism information includes rates as well as photoproducts formed. The photolysis rates of the parent nitroaromatic DNTs have been found to vary with water type while photolysis rates of the daughter products did not. Some differences were found

in which photoproducts were isolated from ultrapure water and seawater. Specifically, 2,4-DNBCHO was isolated from 2,4-DNBOH photolyzed in seawater but not in ultrapure water, and fewer peaks were found on the HPLC scan for the photolysis reaction in ultrapure water. These differences may be caused by differences in extraction behavior between ultrapure water and seawater or by differences in the mechanisms which produce a greater number of products when photolysis occurs in seawater or allow a more rapid reaction of the aldehyde in the ultrapure water system. Future work should include isolation and identification of products from other natural waters to confirm similar behavior.

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