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Molecular Weight Distribution of the Final Products of TNT-Hydroxide Reaction

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Preface

The work reported herein was conducted and supported by the Environmental Quality Technology Program at the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS.

This report was prepared by Ms. Deborah Felt of Applied Research Associates, Inc. (Southern Division); Mr. Lance Hansen of the Environmental Engineering Branch (EEB), Environmental Laboratory (EL), ERDC; Dr. Steven L. Larson of the Environmental Chemistry Branch (EEC), Environmental Laboratory (EL), ERDC. Chemical analyses were performed by the Environmental Chemistry Branch of ERDC.

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1 Introduction

Contamination of groundwater, surface water, and soil by the explosive 2,4,6-trinitrotoluene (TNT) has occurred at military sites throughout the world as a result of the manufacture of explosive compounds, assembly of munitions, and deployment of explosives containing devices. The U.S. Environmental Protection Agency (EPA) has listed TNT as a priority pollutant, with known adverse effects on human health. The removal of TNT, and other explosives, from contaminated sites, where concentrations have ranged as high as 10,000 mg/kg in soil and 100 mg/L in water, has been recommended (Heilmann, Wiesmann, and Stenstrom 1996). Recently, it has been recognized that abiotic removal may provide mechanisms to transform not only parent contaminants, but also toxic end-products generated by reductive transformation of the parent compound. The transformation of 2,4,6-trinitrotoluene (TNT) in basic solutions has been established for many years (Urbanski 1964). The rate of TNT transformation is enhanced at alkaline pH when exposed to ultraviolet light (Dillert et al. 1995), to iron (II) (Brannon, Price, and Hayes 1998), or to a combination of UV light, ozone, and electrohydraulic discharge (Lang et al. 1998). Dunnivant (Dunnivant and Schwarzenbach 1992) reported that TNT degradation caused by Natural Organic Matter (NOM) was increased at elevated pH. Degradation intermediates of TNT were polymerized under alkaline conditions during anaerobic bioremediation of soils (Funk et al. 1993) and at elevated temperatures (Saupe, Garvnes, and Heinze 1997). Emmrich (1999, 2001) has treated TNT-contaminated soil and water at bench-scale with calcium hydroxide and examined factors affecting the kinetics. Early studies in our laboratory have determined the kinetics of the hydroxide-TNT reaction and performed preliminary toxicological studies on the final products (Felt 2000).

The DoD has a need for a low cost, in situ remediation technique for the reduction of risks associated with explosives in soil. One technology that is being investigated for this application is the base-catalyzed transformation of 2,4,6-Trinitrotoluene (TNT) using low-cost agricultural grade lime. This technology has been shown to effectively degrade explosives in a number of situations including demilitarization, explosives in water, and explosives in soils (Emmrich 1999; Felt, Larson, and Hansen 2001). Lime treatment offers several advantages over other remediation technologies: (a) Cost savings due to material handling and energy costs, (b) The equip-

ment needed for this technology is commercially available and easy to use, and (c) Lime treatment eliminates the possible human exposure/toxicity due to inhalation and skin contact that is associated with excavation/ material handling. In order to implement this technology in the field a number of mechanistic investigations as to the reaction between explosives and hydroxide must be understood. A report published by the authors deals with the details of the kinetics of the base hydrolysis of TNT in aqueous systems. The knowledge of the rates of TNT transformation and the temperature dependence of this reaction in the water phase allows for the correct optimization parameters to be assigned for field applications (Felt, Larson, and Hansen 2001). Another stumbling block for field application is the acceptance of innovative technologies by regulating agencies. Many innovative remediation technologies have been shown to be effective, but could not be implemented because of regulators/ public concerns over environmental issues. Lime application to soil is an established agricultural practice and is widely accepted by the public and governmental agencies. A concern that has limited the use of promising innovative technologies is the ultimate fate of the contaminated material following transformation and the environmental risks that are posed due to these residues' presence in the environment. Techniques for determination of the specific classes of transformation products produced by a remedial system and an understanding of the molecular properties of the transformation products are required to satisfy these concerns. The results outlined in this report present basic information about the transformation products in an aqueous solution, while future work will determine the chemical characteristics of TNT transformation products in soil matrices. Efforts are currently underway to determine the classes of transformation products of the base hydrolysis of explosives in soil systems. The findings of this study will be published in a future technical report. This will be followed by an engineering manual for field implementation of base-induced transformation for the treatment of explosives soils.

Previous kinetics experiments performed in our laboratory at three different temperatures indicated rapid TNT degradation in aqueous solution at the temperatures used in the study (Felt, Larson, and Hansen 2001). TNT concentration was 100 ppm before base addition and was reduced to below detection limit (0.095 ppm) in <40 min at room temperature, <18 hr at 10 °C, and <48 hr at 0 °C after addition of the base. The study also indicated that the OH-TNT reaction has two components with two rates: a fast component that occurs immediately after the addition of the base to the TNT solution, followed by a slower secondary component. The fast initial reduction rate was not temperature dependent, but the secondary rate was temperature-dependent. Calculated activation energies for the first and second phases of the reaction were 406.20 kJ/mol and 245.18 kJ/mol, respectively. These large activation energies indicate the two components of the OH-TNT reaction are spontaneous reactions. These results validated base-catalyzed TNT transformation as a rapid and effective method to degrade TNT, but research was needed to characterize the transformation products to identify possible fate and effects of the products.

In this phase of our research, we established the identities and chemical properties of the final reaction products. Many factors including chemical speciation of the reaction products, influence the possible fate and effects of the products, and directly impact their transport into groundwater, soil-binding capabilities, and toxicity. The mechanism of the OH-TNT reaction is indicated by the molecular size of the final products. The molecular size can be determined by the distribution of ^{14}C counts in polystyrene equivalent molecular weight fractions. Distribution of counts in the molecular weight fractions also indicates whether TNT has polymerized (counts in large polystyrene equivalent molecular weight fractions), whether the aromatic ring had been cleaved (counts in small polystyrene equivalent molecular weight fractions), or, perhaps that, other reactions might have occurred.

In this study, radiolabeled TNT was challenged with hydroxide and the reaction was allowed to go to completion. The TNT was entirely depleted upon completion of the reaction and all ^{14}C counts were associated with the final reaction products. In order to determine the chemical properties of the transformation products, the ^{14}C labeled products were separated by solvent/solvent extraction and acid/base chemistry and analyzed by scintillation counting. Their distribution in the final reaction mixture, and their polystyrene equivalent molecular weight fractions were determined using gel permeation chromatography (GPC) (Henry 1996; Lee 1988; Barth, Boyles, and Jackson 1996; Fishman, Rodrigues, and Chau 1996).

2 Materials and Methods

Chemicals

The TNT used in this study was universal-labeled ^{14}C -radiolabeled with a specific activity of 26.3 mCi/mmol. This compound was custom-synthesized by New England Nuclear, a division of Dupont Chemical Company. The samples were counted in Ultima Gold scintillation cocktail (Packard Instruments Company, Meriden, CT). Solvents used for extraction were dichloromethane (DCM), HPLC grade, obtained from Burdick and Jackson, and deionized water (Millipore Corp.).

Preparation of Stock Solutions and Standard Curves

TNT

A stock solution was made by diluting 1.37-mg radiolabeled ^{14}C TNT in 100 mL methanol to yield a radioactive concentration of 3.5×10^6 disintegrations per minute (dpm)/mL. This solution was diluted 1:10 with methanol to yield a working solution of 350,000 dpm/mL. Radioactive concentration was confirmed by pipetting representative samples (0.1 mL) of each solution into 20-mL scintillation vials, adding 15-mL scintillation cocktail and counting using a Packard Instruments model 2500 TR. The counter was equipped with a barium external source to enable correction for machine efficiency. The liquid scintillation protocol collected data up to 156 meqV or the maximum energy for ^{14}C . Vials were counted twice for 2 min.

Polystyrene molecular weight standards

Polystyrene molecular weight standards were prepared by dissolving 40 mg polystyrene molecular weight standards in 20 mL DCM in a scintillation vial. Polystyrene polymers used for this study had molecular weight

averages of 162, 266, 484, 979, 1180, 2230, 5520, and 10,300 Da (Phenomenex, Torrance, CA). A representative sample (20 mL) of each standard was injected on a Waters HPLC equipped with a Waters 600-M system controller, a Waters 991-MS photodiode array detector (PDA), and a Waters 7 Satellite WISP autosampler using DCM mobile phase. The columns used were a Phenomenex 50 x 7.8mm guard column, Phenogel 5 x103 A (300 x 7.8 mm), and Phenogel 5 m x 50 A (300 x 7.8 mm) columns (Phenomenex, Torrance, CA.). A flow rate of 0.5 mL/min was set for the run time of 40 min, and the detector was set for 254 nm. Retention times for each of the molecular weight standards were noted. A standard curve of polystyrene molecular weight standards yielded an r^2 of 0.9288, a slope of 10.51, and a y-intercept of 12.39.

Gel permeation chromatography (GPC) standards

The GPC analysis used polyethylene glycol (PEG) molecular weight standards to calibrate the molecular weights in the inorganic samples. The working standards were made by dissolving 20 mg of each compound in 40 mL of water. Representative samples (20 mL) of each standard (6,000 to 3,000, 3,000 to 1,500, 1,500 to 1,000, 1,000 to 750, 750 to 500, 500 to 250, 250 to 100, <100 Da) were injected onto a Biosep 600 x 7.8-mm column using the HPLC system previously described. A flow rate of 1 mL/min was used with an aqueous mobile phase, the detector was set at 206 nm, and the run time was 40 min. Pump pressures averaged 1,000 psi, which is normal for a long column and aqueous mobile phase in GPC. Retention times were noted for the peak produced by each standard. A standard curve was generated for the polyethylene glycol molecular weight standards with an r^2 value of 0.9986, a slope of 5.097, and a y-intercept of 17.968.

3 Experimental Design

A flow chart detailing the steps of this experiment is shown in Figure 1. A ^{14}C -labeled TNT solution was challenged with hydroxide and the reaction was allowed to proceed until all TNT had been transformed. All ^{14}C associated with TNT before the reaction was now incorporated into final products (Block 1 on Figure 1). Solvent/solvent extraction was used to separate the final products of the TNT-hydroxide reaction into organic (Block 2 on Figure 1) and inorganic (Block 3 on Figure 1) fractions. Representative samples of all phases in the experiment were counted for ^{14}C concentration by liquid scintillation counting. Count distribution in the organic and inorganic phases indicated the polarity of the final products of the TNT-hydroxide reaction. A representative sample of the inorganic phase of the reaction mixture was neutralized with buffer and separated into organic (Block 4) and inorganic phases (Block 5) by a second solvent/solvent extraction to determine possible organic acid distribution in the final products. The organic (Block 2) and inorganic (Block 3) phases of the radiolabeled final products were separated into polystyrene equivalent molecular weight (mw) fractions (Blocks 6 and 7) using GPC.

Radiolabeled ^{14}C TNT challenge (Block 1)

Radiolabeled working solution (100 mL) was added to four scintillation vials, each containing 1 mL unlabeled TNT solution (100 ppm), to yield solutions with a radioactive concentration of 3.18×10^5 dpm/mL. Three of the vials containing the radiolabeled TNT solution were challenged with 1 mL, 1 N potassium hydroxide (KOH). Water (1 mL) was added to the remaining vial to make an unchallenged TNT control. Reaction mixtures were homogenized by vigorous shaking for 3 sec. The reactions were allowed to proceed to completion (1 week) at 25 °C in the dark. Representative samples (0.1 mL) of the reaction mixtures were counted according to the protocol previously described to determine the initial counts in each vial after the reaction.

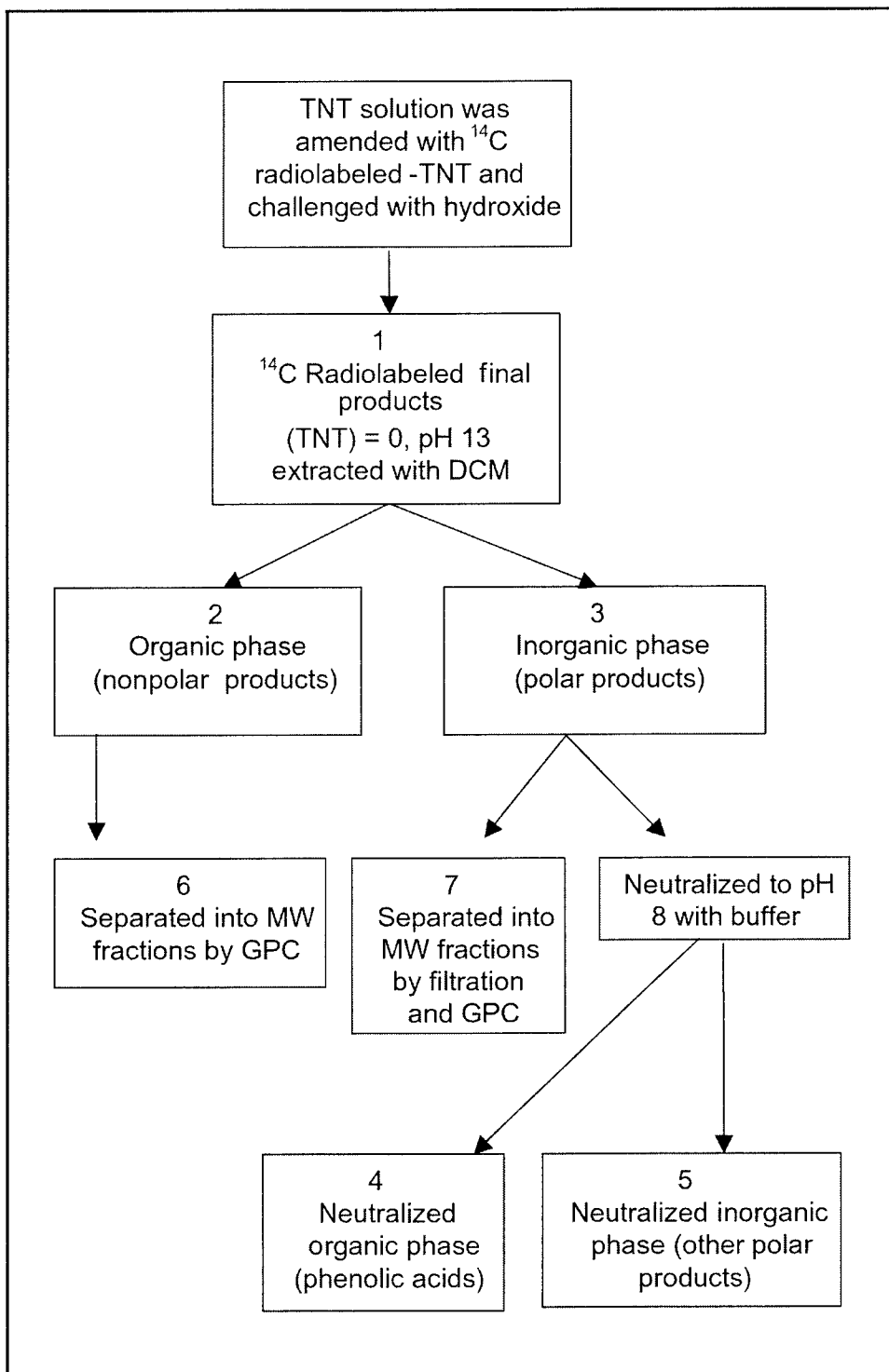


Figure 1. Flow chart for analysis of final products of the OH-TNT reaction

Solvent/solvent extraction of transformation products (Blocks 2 and 3)

After the TNT-hydroxide reaction was completed, 2-mL dichloromethane (DCM) was added to each reaction mixture. Vials were shaken vigorously for 3 sec and the DCM layers were removed. The resulting aqueous layer was extracted three additional times with DCM and the combined DCM layers were rinsed three times with water. The organic (DCM) and inorganic fractions (water) were combined separately. DCM layers were evaporated down to 0.1 mL and then returned to a volume of 350 μ L with DCM. This organic fraction is Block 2 in Figure 1. Representative samples (50 μ L) of the DCM fractions were counted according to the protocol previously described.

The combined water fractions were heated slightly on a hot plate to remove any remaining DCM. The contents of the vials were transferred to calibrated, plastic, centrifuge tubes. Each vial was rinsed several times with water and the rinses were added to the centrifuge tube to transfer all the transformation products. Water phase volumes were brought up to 8 mL in each tube with deionized water, shaken vigorously for 3 sec, and a 1-mL sample was counted by liquid scintillation counting. This inorganic phase is referred to as Block 3 on Figure 1.

Acid/base separation (Blocks 4 and 5)

A representative sample of the aqueous phase (1 mL) was neutralized with 0.20-mL phosphate buffer (pH 7) to a pH of 8. The buffered sample was extracted three times with DCM and the DCM extracts were combined. Representative samples (0.10 mL) of the DCM (Block 4 on Figure 1) and inorganic (Block 5 on Figure 1) phases were separately counted by liquid scintillation counting.

Separation of organic phase into polystyrene equivalent molecular weight fractions (Block 6)

Using the retention times of the molecular weight standards, collection times for polystyrene equivalent molecular weight fractions of the organic-soluble TNT-hydroxide final reaction products were determined. Representative samples (100 μ L) of the organic (DCM) phase of the 14 C labeled reaction mixtures (Block 2 in Figure 1) were injected on the HPLC. The polystyrene equivalent molecular weight fractions were collected and counted by liquid scintillation counting (Block 6 on Figure 1).

Separation of inorganic phase into polyethylene glycol (PEG) equivalent molecular weight fractions (Block 7)

Two techniques, filtration and GPC, were used to separate the inorganic phase of the final products (Block 3 in Figure 1) of the TNT-hydroxide reaction into molecular weight fractions. Filtration separated the inorganic phase into larger (5,000 to 100,000 Da) PEG equivalent molecular weight fractions. GPC separated the smaller polyethylene glycol equivalent molecular weight fractions (<100 to 6,000 Da).

Separation by filtration. Representative samples (0.75mL) of each inorganic sample (Block 3 in Figure 1) and unchallenged control were pipetted into Biomax centrifugation filtration tubes (Millipore Corporation, Bedford, MA), capped, and the tubes centrifuged for 15 min at 1,200 g. The ultra-filtration membranes, made of regenerated cellulose, were designed to allow molecules of fixed molecular weights, 100 k, 50 k, 30 k, 10 k, and 5 kDa, to pass. After filtration, a representative sample (0.5 mL) was pipetted out of the bottom of the centrifuge tube and counted by liquid scintillation counting according to the protocol previously described (Block 7 in Figure 1).

Separation by GPC. A representative sample (100 mL) of the inorganic phase of the OH-TNT reaction mixture (Block 3) was injected on the high performance liquid chromatography (HPLC) using the instrument protocol previously described. PEG equivalent molecular weight fractions were collected in scintillation vials and the fractions were counted by liquid scintillation counting according to the protocol described previously (Block 7 in Figure 1).

4 Results and Discussion

In this study, a radiolabeled TNT solution was mixed with a basic solution and the reaction was allowed to proceed for 1 week at 25 °C in the dark. This protocol is not contraindicative of the results of the previous kinetic study. In the previous kinetic study, TNT concentration of an aqueous solution was reduced from 100 ppm to below detection limit (0.095 ppm) in <40 min at room temperature after the addition of a basic solution (Felt, Larson, and Hansen 2001). The kinetic study focused only on the transformation of the parent compound, TNT, not on the over-all reaction. Results from a spectroscopic study that followed the OH-TNT reaction over time at four different temperatures indicated the over-all OH-TNT reaction requires at least 2 days to go to completion at room temperature (Felt 2000). A reaction time of 1 week was allowed to ensure the reaction had gone to completion.

Solvent/solvent extraction separates compounds based on their solubility, with nonpolar compounds dissolving in organic solvents and polar, or ionic, compounds dissolving in polar solvents. Most of the final products of the TNT-hydroxide reaction (98 percent) were in the inorganic phase after solvent/solvent extraction, as shown in Table 1, which indicates that the majority of the final products of the TNT-hydroxide reaction are polar compounds.

Sample	Counts in Organic Fraction	Percent Final Products in Organic Phase	Counts in Inorganic Fraction	Percent Final Products in Inorganic Phase
Final reaction products at pH 13	1,439	2	283,797	98
Final reaction products at pH 8	30,000	10.4 ($\Delta + 8.4$)	258,300	89.6 ($\Delta - 8.4$)
Unchallenged TNT control	284,000	93	21,378	7

In contrast, the unchallenged TNT control demonstrated 93 percent of the counts in the organic phase. This correlates with the fact that TNT is a nonpolar molecule. The TNT remaining in the inorganic phase of the unchallenged control (7 percent) after solvent/solvent extraction was probably associated with the small amount of DCM that was miscible in the water after solvent/solvent extraction and the solubility of TNT in water. Lowering the pH of the reaction mixture protonates some of the organic acids, decreasing their solubility in inorganic phase, so that they could be extracted with an organic solvent. Results of the neutralization and subsequent solvent extraction of inorganic phase of the final products of the TNT-hydroxide reaction are also shown in Table 1. Increased counts in the neutralized organic phase compared to the organic phase extracted from the pH 13 reaction mixture indicated the distribution of certain organic acids formed during the TNT-hydroxide reaction. The neutralized organic phase had 8.4 percent more counts than the organic phase extracted before the reaction mixture was neutralized. Organic acids that might have formed during the TNT-hydroxide reaction would have been deprotonated at pH 13 and would have been water-soluble. By lowering the pH to 8, acidic compounds with $pK_a \geq 8$ would have been protonated and would have been less soluble in an inorganic solvent. Therefore, we suggest that 8.4 percent of the final products of the TNT-hydroxide reaction were associated with phenols or other organic compounds with $pK_a \geq 8$, and the remaining 89.6 percent have lower pK_a or were neutral compounds. Other organic acids with pK_a lower than 8, such as the dicarboxylic acids, would have been deprotonated at pH 8 and would have remained soluble in the inorganic solvent. Future work may include reducing the pH of the TNT-hydroxide reaction mixture to pH 5, extracting the resulting reaction mixture with DCM, and counting the fractions to determine the amount of other organic acids in the final TNT-hydroxide reaction mixture.

Both the organic and inorganic fractions (Block 2 and Block 3 in Figure 1) of the final products of the OH-TNT reaction were separated by GPC to determine the distribution of molecular weight compounds in each fraction and to give insight into the chemical pathways of the OH-TNT reaction. When the organic phase reaction products (polar) were separated into size fractions, the majority (67 percent) was in the < 90 Da PEG molecular weight fraction, as shown in Figure 2. In contrast, the majority (70 percent) of ^{14}C counts in the control were in the 250–90 polystyrene equivalent molecular weight fraction, which correlates with TNT's molecular weight (227 Da). This size range only accounted for 23 percent of the reaction products. Final reaction products with PEG molecular weights smaller than TNT (<90) make up 67 percent of the organic phase fraction.

The inorganic fraction (Block 3) of the final products of the OH-TNT reaction were separated into molecular weight fractions in order to determine the size distribution of the polar transformation products. Filtration separated large PEG molecular weight fractions. Radiolabeled counts in the molecular weight fractions separated by filtration did not vary statistically. This indicated that all of the TNT- radiolabeled final products passed

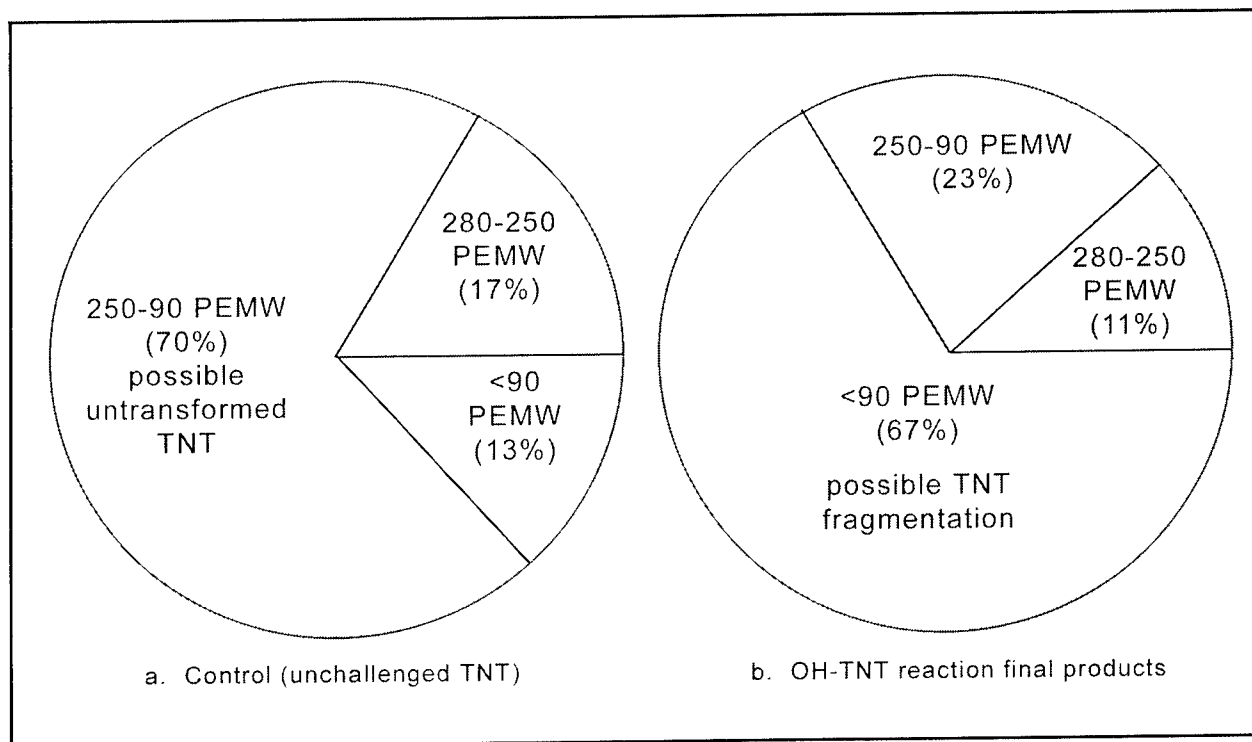


Figure 2. Distribution of polystyrene equivalent molecular weight (PEMW) fractions in the organic phase

through the filters and that all the polar final products of the TNT-hydroxide reaction were molecules $<5,000$ Da.

Radiolabel counts were recorded in all of the smaller PEG equivalent molecular weight fractions (100-1000 Da) of the inorganic phase of the TNT-hydroxide reaction mixture that were separated by GPC (Figure 3).

This indicates that the polar final products of the TNT-hydroxide reaction varied in molecular weight. The 1,000 to 6,000 Da fractions of the TNT residue made up 40 percent of the radiolabel activity, which may indicate that some of the final products of the TNT-hydroxide reaction are large molecules and that TNT polymerized when challenged with hydroxide. An equal amount (44 percent) of the activity in the inorganic phase was in the <100 molecular weight fraction, indicating that 44 percent of the final products in the inorganic phase after solvent/solvent extraction of the TNT-hydroxide reaction mixture were compounds that were smaller than TNT.

To summarize and compare the distribution of molecular weight fractions of all final products (polar and nonpolar) of the OH-TNT reaction, results from all molecular weight fractions were combined in Table 2. Final products in the <100 PEMW fraction made up 44 percent of the final reaction mixture. This is the fraction smaller than TNT. A universally-labeled TNT was used in our reaction, therefore simple cleavage of the methyl group accounted for only 15 percent of the ^{14}C mass balance. The

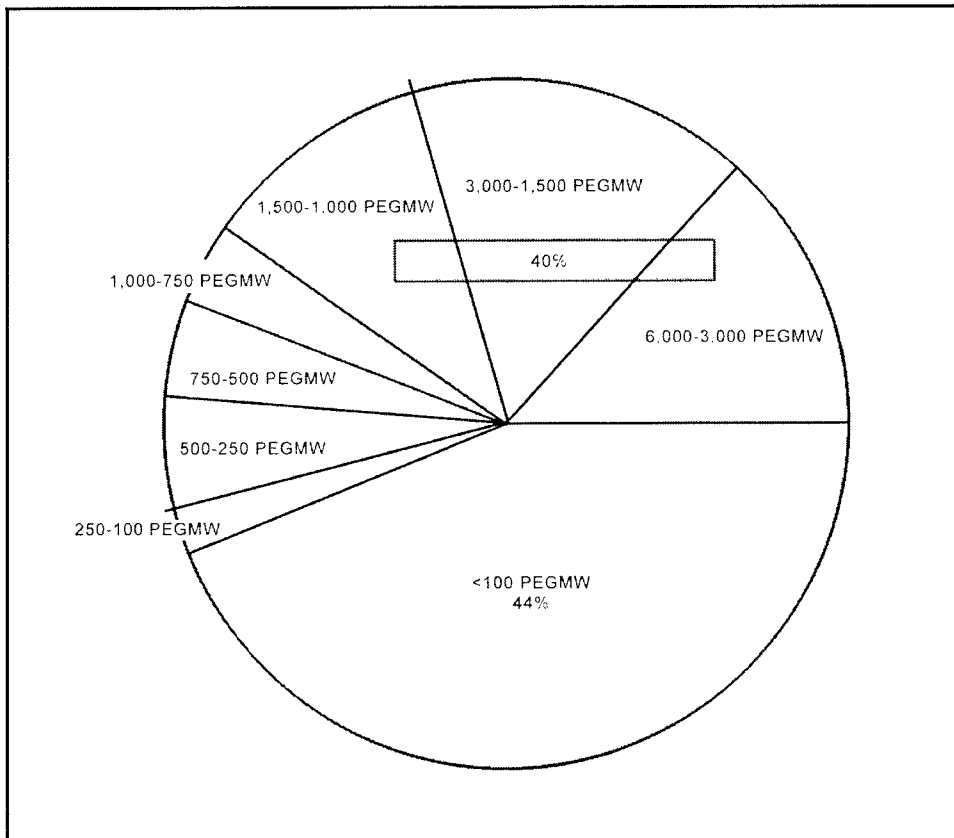


Figure 3. Distribution of polyethylene glycol molecular weight (PEGMW) fractions in the inorganic phase of the extracted OH-TNT reaction mixture. Data represents the mean and standard deviation of three replicates.

remaining 31 percent would appear to indicate that cleavage of the nitroaromatic ring occurred during the reaction of TNT with the hydroxide.

Significant amounts of the final products of the TNT-hydroxide reaction were found in the 6,000-1,000 PEMW fractions, indicating large molecular weight molecules that might have been formed by TNT polymerization. TNT polymerization has been established under alkaline conditions at high temperature. Our results indicate that polymerization also occurs at ambient temperature, and it is the pH, not the temperature, that is the significant factor for polymerization. Large molecules, such as we've found, may be less likely to transport into groundwater, effectively stabilizing the contamination. Our previous research has found the final products to be less toxic than the parent compound. This could be because their size results in a lower bioavailability.

Conclusions from a previous kinetic study provided activation energies, reaction rates at different temperatures, and information concerning the reaction mechanism of the OH-TNT reaction in aqueous solution (Felt, Larson, and Hansen 2001). The results outlined in this report chemically characterize the transformation products of the OH-TNT reaction.

Step	Product Phase	Description/Molecular Weight Range	Percent of ¹⁴C Mass Balance
2	Organic phase	Nonpolar	2
6		280-250 PEMW	11
6		250-90 PEMW	23
6		<90 PEMW	67
3	Inorganic phase (filtration) (GPC)	Polar	98
4		Phenolic acids	10
5		Other polar compounds	90
7		>6,000 PEMW	0
7		6,000-3,000 PEMW	13
7		3,000-1,500 PEMW	16
7		1,500-1,000	11
7		1,000-750	4
7		750-500	5
7		500-250	5
7		250-100	2
7		<100	44

While individual TNT-hydroxide reaction products were not identified in this study, much information was obtained concerning the structure of reaction products and the reaction pathways. In the future, liquid chromatography-mass spectroscopy could be used to identify individual final products. Identification of individual reaction products would yield further knowledge on the fate and effects of the TNT-hydroxide reaction products on the environmental system.

Lime treatment of explosive-contaminated soils is potentially an effective remediation technology. It offers lower costs than other remediation methods, eliminates material handling, and the necessary equipment is readily available. Future research planned to validate the use of this technology for soil remediation include studies using radiolabeled tracers to track TNT transformation products in soils, pilot-scale (lysimeter) studies, toxicity studies, and the identification of individual transformation products in soil matrices using liquid chromatography-mass spectroscopy.

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