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Review of Fate and Transport Processes of Explosives

by James M. Brannon, Tommy E. Myers

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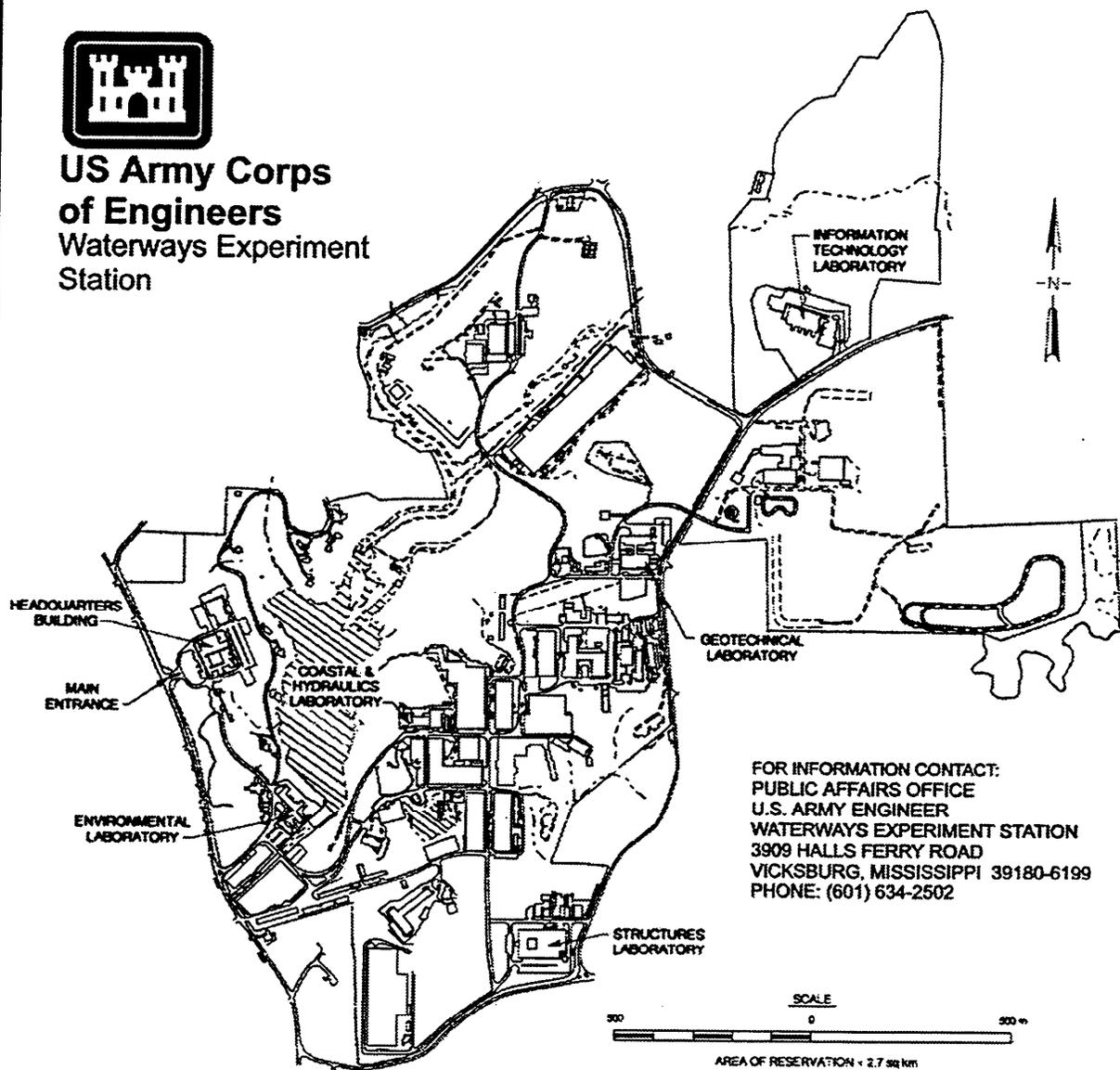
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Preface

The work reported herein was conducted by the U.S. Army Engineer Waterways Experiment Station (WES) for Headquarters, U.S. Army Corps of Engineers (HQUSACE). Funding was provided by the HQUSACE Installation Restoration Research Program (IRRP), Fate and Effects Thrust Area, Work Unit entitled Fate and Transport of Military Unique Contaminants in Soil, Sediment, and Water Ecosystems. Dr. Clem Myer was the IRRP Coordinator at the Directorate of Research and Development, HQUSACE. The IRRP Program Manager was Dr. M. John Cullinane, WES.

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1 Introduction

Many Department of the Army (DA) and other Department of Defense (DoD) installations contain soil, sediment, surface water, and groundwater environments contaminated with explosives. Subsurface and surface contamination by the explosives 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is often associated with munitions manufacturing and with loading, assembling, and packing facilities (Pugh 1982, Spaulding and Fulton 1988). Exposure assessment and risk management of explosives contaminated soil, sediment, surface water, and groundwater require knowledge of the fate and effects of explosives and their transformation products in the environment. By far the most extensive body of work on explosives centers on sorption of TNT and RDX by soils, clay minerals, and drilling muds (Leggett 1985; Loehr 1989; Pennington and Patrick 1990; Brannon et al. 1992; Ainsworth et al. 1993; Haderlein, Weissmahr, and Schwarzenbach 1996). Research on explosives fate and transport processes in surface waters has concentrated on photodegradation of TNT (McGrath 1995), although only the disappearance of TNT was generally monitored due to the unavailability of standards for degradation products. Other environments have been subject to less extensive study.

Interpretation of sorption data for explosives, especially TNT, is confounded by formation of TNT transformation products such as 4-amino-2,6-dinitrotoluene (4A-DNT), 2-amino-4,6-dinitrotoluene (2A-DNT), 2,4-diamino-6-nitrotoluene (2,4-DANT), and 2,6-diamino-4-nitrotoluene (2,6-DANT) (Kaplan and Kaplan 1982). When transformation of the sorbing analyte is neglected, sorption can be overestimated or misinterpreted. This can lead to erroneous conclusions on fate and transport of explosives in the environment.

Processes affecting groundwater transport of TNT include, but are not limited to, advection, hydrodynamic dispersion, biodegradation, abiotic transformations, sorption, and diffusion (McGrath 1995). Not all processes affect TNT subsurface transport equally; therefore, identifying key processes involved and developing accurate descriptors for these processes are critical. In environmental settings other than the subsurface, processes in addition to those identified for the subsurface may be operative. For example, in environmental settings such as surface water and soils exposed to sunlight and air, processes such as volatilization and photolysis may become operative.

Two of the most important processes affecting the fate and transport of explosives are sorption and transformation. TNT solution concentrations either approach steady state in 60 min (Haderlein, Weissmahr, and Schwarzenbach 1996), 24 hr (Pennington and Patrick 1990), or 96 hr (Ainsworth et al. 1993) in soils or rapidly disappear from solution (Price, Brannon, and Hayes 1995). The long equilibration times for TNT solution concentrations that have been reported are due to TNT transformation, competition for sorption sites, and reequilibration with dissolved TNT (Pennington and Patrick 1990; Ainsworth et al. 1993; Pennington et al. 1995b). The rapid disappearance of TNT from solution is due to TNT transformation and irreversible sorption to soil organic matter (Price, Brannon, and Hayes 1995). The present limited understanding of sorption and transformation process rates for TNT is inadequate. The understanding of these processes for RDX and HMX is even more limited. Therefore, development of accurate process descriptors for explosives in the environment are lacking, and the ability to perform exposure assessment, an essential element in risk assessment, is compromised. This report synthesizes recent process results for explosives in the environment and identifies research needs relevant to exposure assessment. A review of the early literature was provided by McGrath (1995). Studies conducted during and after preparation of the McGrath (1995) report are the main focus of this report.

2 Transformation Processes Affecting Fate and Transport

Most information on explosives transformation processes in the environment is for surface and subsurface soils. Very little information is available for explosives transformations in other environments. Photolysis of explosives in surface waters is known to rapidly remove the parent compounds from solution via transformation to other compounds (McGrath 1995), but rates are not generally available (Townsend and Myers 1996). McGrath (1995) and Townsend and Myers (1996) provide a synopsis of what is known of photolysis rates and transformation products. Because photolysis-mediated transformations occur rapidly (McGrath 1995; Townsend and Myers 1996), explosives should not persist in surface waters. This section will focus on transformations that are not mediated by photolysis.

TNT

The major factors affecting fate and transport of TNT in the subsurface are transformation, sorption, and irreversible soil binding (Townsend and Myers 1996). Although TNT reductive transformation has been known for some time (McCormick, Feeherry, and Levinson 1976; Kaplan and Kaplan 1982), only recently have TNT reductive transformation products been routinely measured in laboratory and field studies (Townsend, Myers, and Adrian 1995; Price, Brannon, and Hayes 1995; Comfort et al. 1995; Selim, Xue, and Iskandar 1995; Xue, Iskandar, and Selim 1995; Haderlein, Weissmahr, and Schwarzenbach 1996; Myers et al. in preparation).

TNT transformation generally occurs by sequential reduction of nitro groups to amino groups (Figure 1). Commonly observed reductive transformation products include 2A-DNT, 4A-DNT, 2,4-DANT, and 2,6-DANT. 2,4,6-triaminotoluene (TAT) is also possible. The presence of these compounds, except for TAT, has been measured in laboratory column and batch experiments (Ainsworth et al. 1993; Comfort et al. 1995; Selim, Xue, and Iskandar 1995; Townsend, Myers, and Adrian 1995; Price, Brannon, and Hayes 1995) and in experiments where plants and sediments were exposed to water containing TNT (Best and Sprecher 1996). Reduction of

DANT to TAT in cell suspensions has been reported (Preuss and Rieger 1995), but TAT is highly unstable and, therefore, likely to react before it can be collected and analyzed (Preuss and Rieger 1995). In addition, there is evidence that TAT may require $E_h \leq -250$ mV for formation (Rieger and Knackmuss 1995).

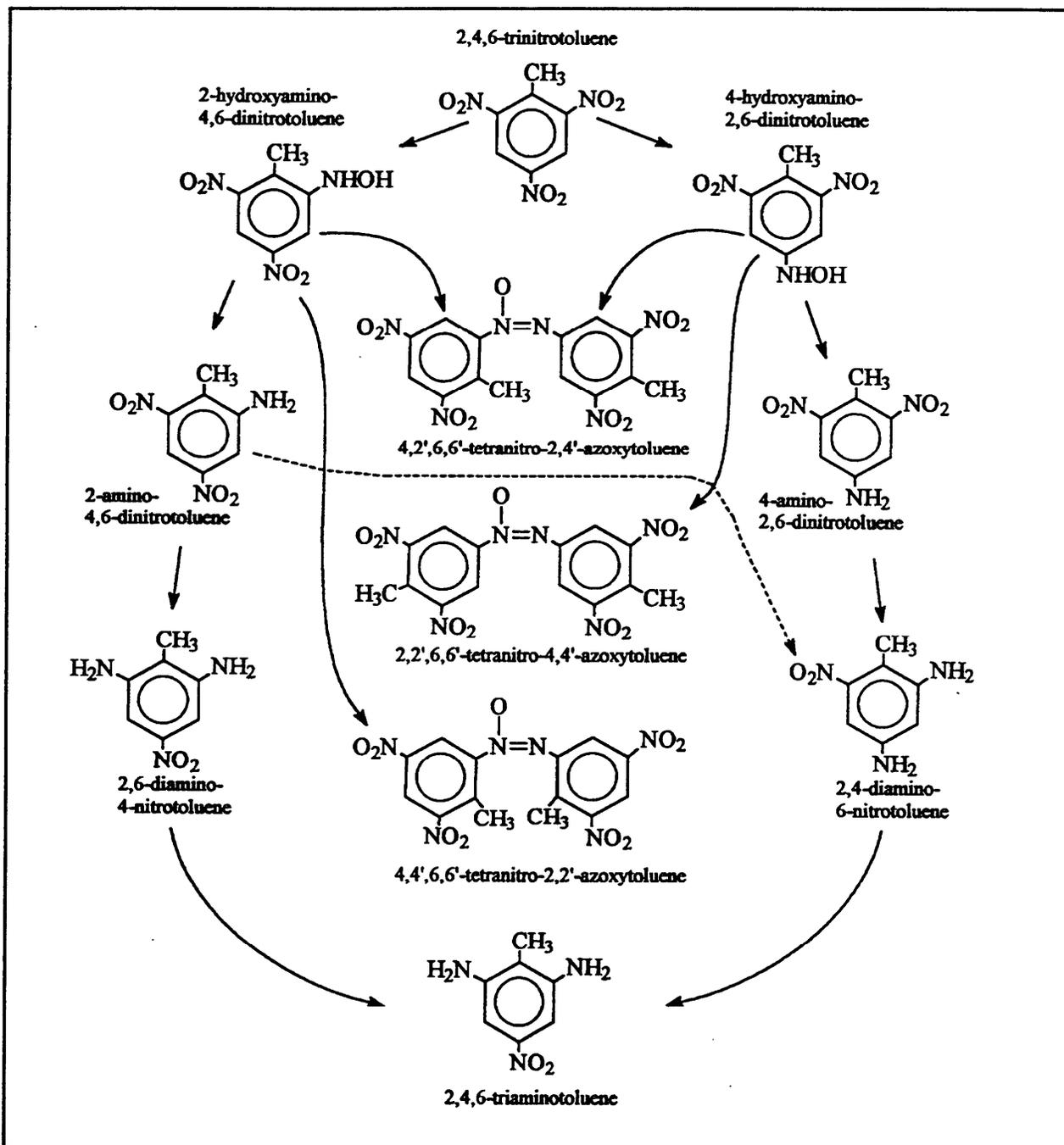


Figure 1. Proposed TNT transformation pathway (from Kaplan and Kaplan 1982)

TNT transformation rates are enhanced significantly under anaerobic conditions (Price, Brannon, and Hayes 1995) (Figure 2). Depending on the Eh, one or two of the nitro groups were reduced to amino groups. TNT was unstable at all of the Eh values tested (+500, +250, 0, -150 mV), but was especially unstable at Eh = -150 mV.

Normalized TNT breakthrough curves for different soil types illustrate dramatic differences (Myers and Townsend 1996) (Figure 3). The Tunica silt is a loam (4 percent sand, 82 percent silt, 14 percent clay) from Vicksburg, MS, and the Louisiana Army Ammunition Plant aquifer material (LAAP-D) (22 percent sand, 36 percent silt, 42 percent clay) is from Shreveport, LA. Practically all of the TNT mass introduced to the LAAP-D aquifer material eluted from the column as TNT (95.4 percent), whereas very little of the TNT mass input to the Tunica silt eluted from the column as TNT (<1 percent) (Figure 4). Most of the TNT input to the Tunica silt eluted as measurable transformation products, whereas TNT transformation in the LAAP-D aquifer material was negligible (Figure 5). The transformation data for Tunica silt and LAAP-D aquifer material (Figures 3-5) indicate that caution should be used when interpreting soil column or batch data solely on the basis of TNT, 2A-DNT, and 4A-DNT analyses.

About 16 percent of the TNT input to the Tunica silt was unaccounted for (Figure 5). The TNT loss may be explained by (a) production of unmeasured transformation products such as TAT, (b) formation of azoxy-toluene conjugates or polymers, (c) irreversible binding to soils, and (d) mineralization to CO₂ and H₂O (Myers and Townsend 1996). Irreversible soil binding has been suggested as a mechanism accounting for TNT disappearance in soil column studies (Selim, Xue, and Iskandar 1995; Comfort et al. 1995) and has been shown to account for TNT disappearance in compost (Pennington et al. 1995a) and soil (Price, Brannon, and Hayes 1995) under both aerobic and anaerobic conditions. Irreversible binding to organic matter may therefore be an important mechanism since TNT and most of its transformation products are not extracted by the solvents used in the standard explosives analyses (SW 8330) (Pennington et al. 1995a; Price, Brannon, and Hayes 1995).

TNT transformations in soils can occur both biologically and abiotically. When sterilized and unsterilized soils were used, transformations were observed under both conditions (Pennington and Patrick 1990; Myers et al. in preparation), suggesting the presence of a purely abiotic transformation component. Transformations were far more extensive in unsterilized soils than in sterilized soils. Townsend, Myers, and Adrain (1995) pumped over 150 pore volumes of TNT-contaminated feed solution through Tunica silt in columns and found that TNT transformations were still occurring at the end of the loading step. These data suggest a nonexhaustible process which is consistent with biological transformation. Price, Brannon, and Hayes (1995) demonstrated that Fe⁺² in the presence of a montmorillonite or kaolinite surface resulted in disappearance of TNT. No disappearance of TNT was observed in systems containing montmorillonite, kaolinite, or Fe⁺² alone. Since Fe⁺² alone could not transform TNT, microorganisms and/or surfaces are also needed. Once the initial supply of Fe⁺² is exhausted, maintenance of this abiotic pathway depends upon microbial reduction of Fe⁺³ to Fe⁺² under anaerobic conditions. This, in effect, couples a microbial pathway to the Fe⁺² abiotic pathway.

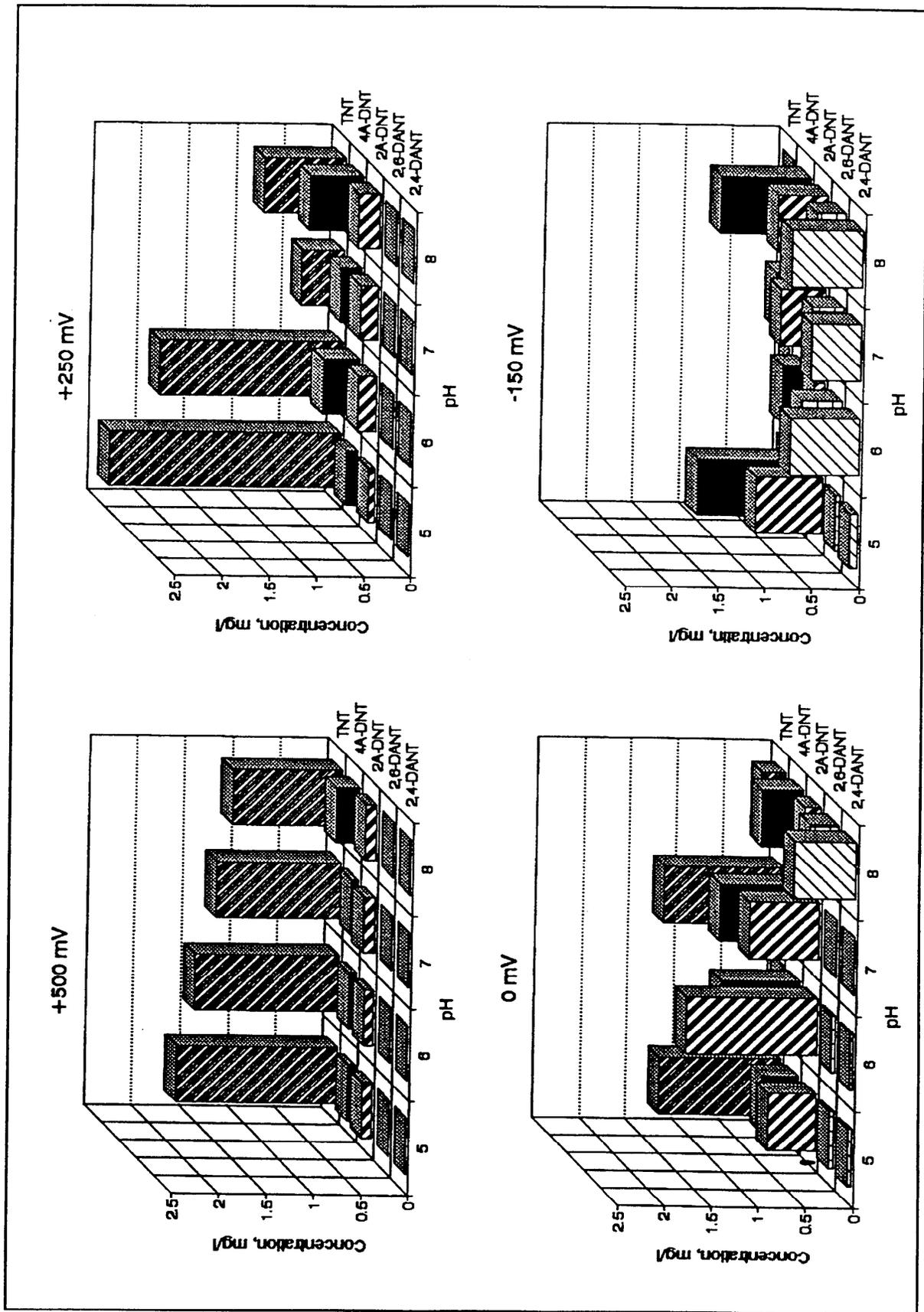


Figure 2. Aqueous mass of TNT and transformation products following one day of incubation (from Price, Brannon, and Hayes 1995)

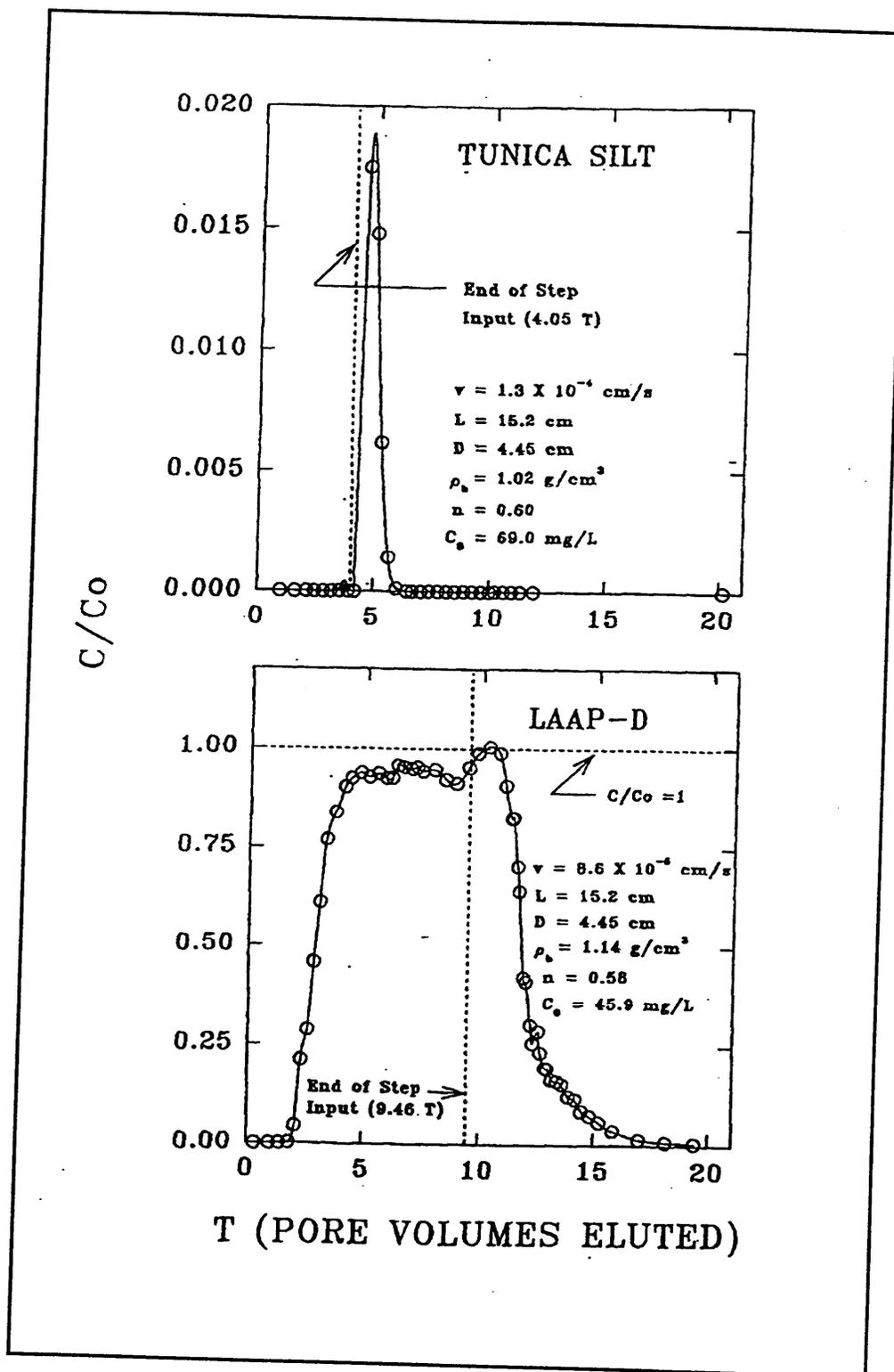


Figure 3. TNT breakthrough curves for Tunica silt soil and Louisiana Army Ammunition Plant aquifer material (LAAP-D) (v = average pore water velocity, L = column length, D = column diameter, ρ_b = bulk density) (from Myers and Townsend 1996)

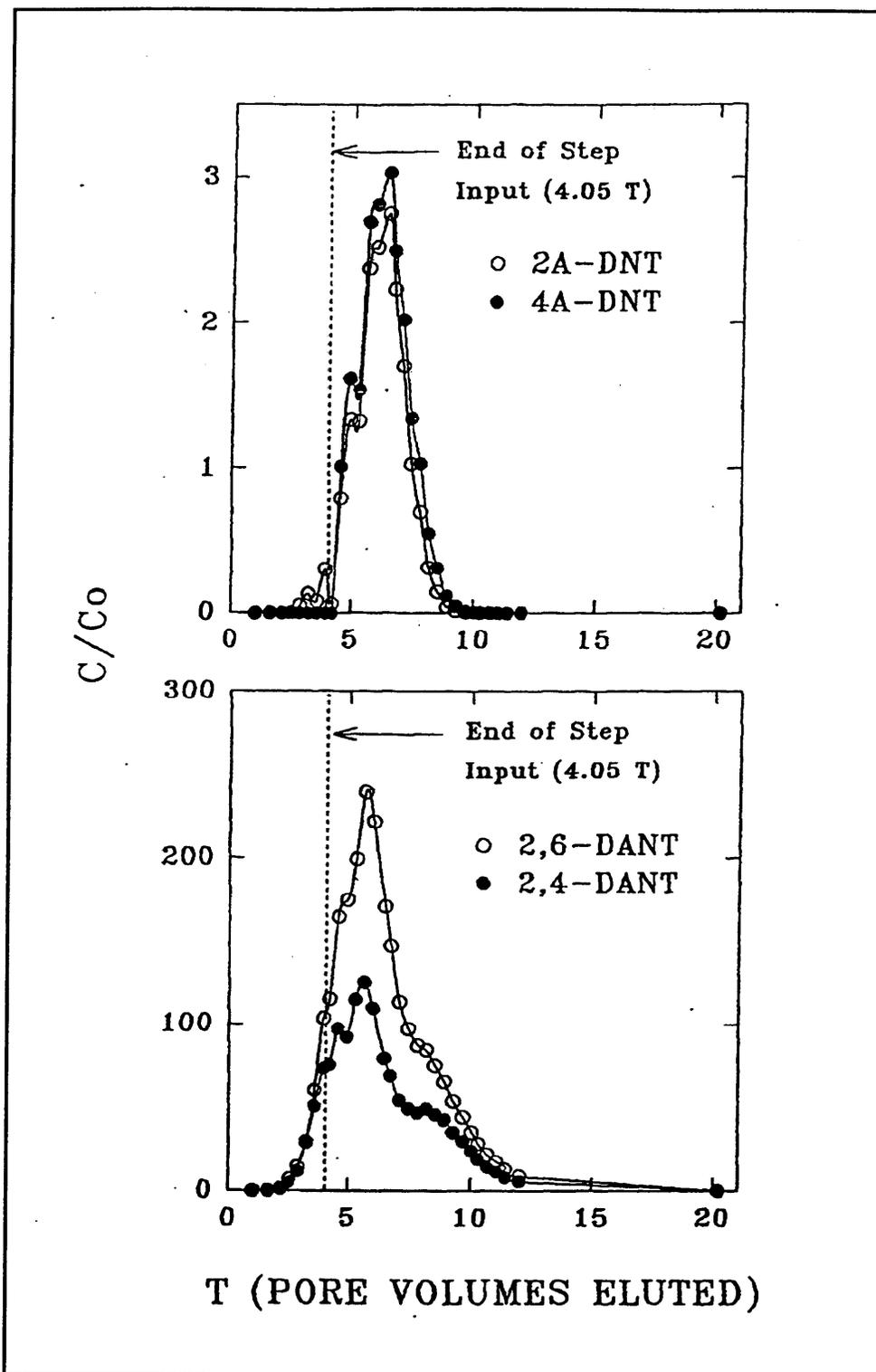


Figure 4. Tunica silt TNT transformation product breakthrough curves for 2-amino-4,6-dinitrotoluene, 4-amino-2,6-dinitrotoluene, 2,4-diamino-6-dinitrotoluene, and 2,6-diamino-4-dinitrotoluene (from Myers and Townsend 1996)

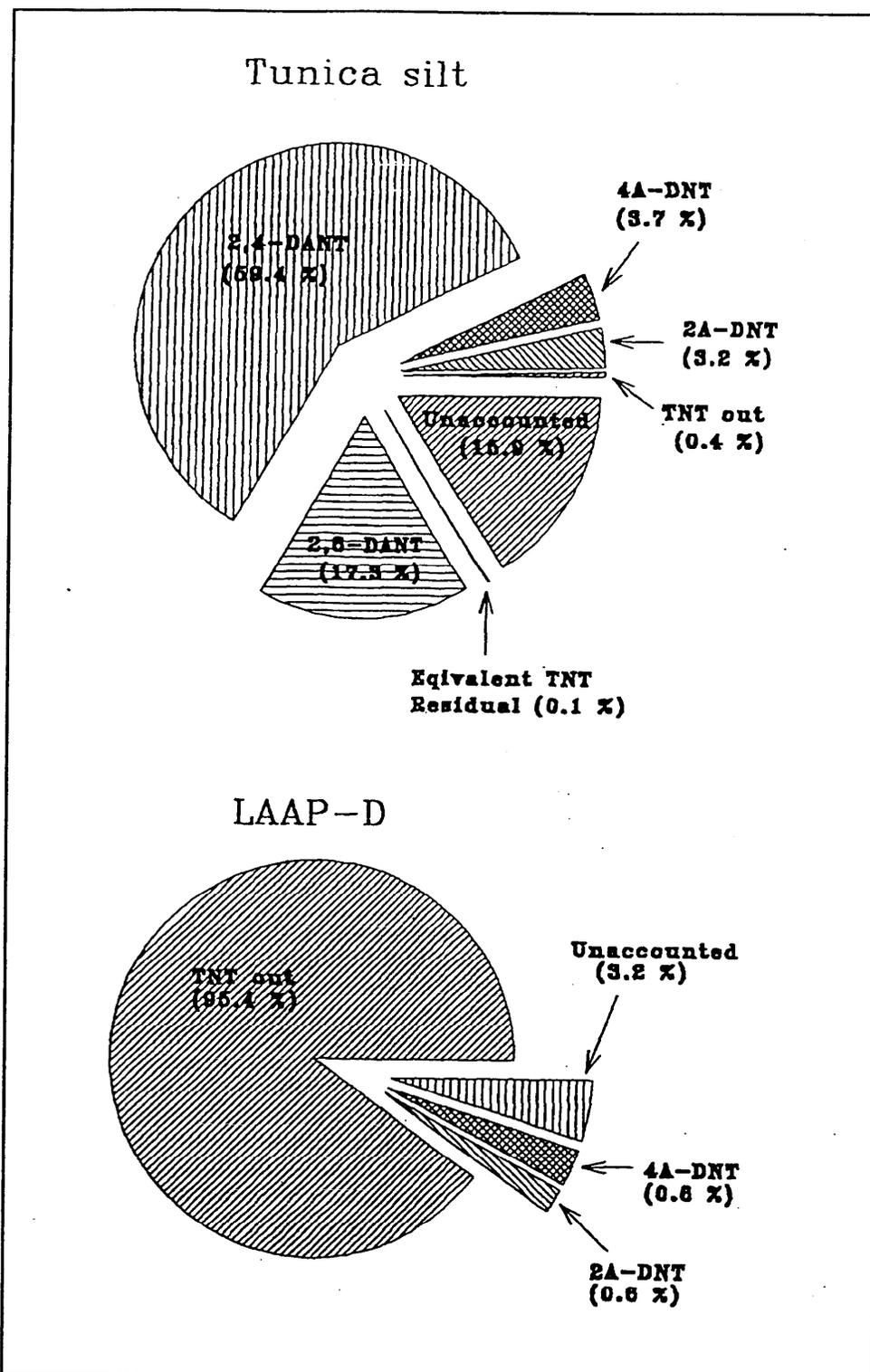


Figure 5. TNT column mole balances for Tunica silt and LAAP-D (from Myers and Townsend 1996)

Subsequent work has shown that the products of the abiotic Fe^{+2} reduction are pH dependent and consist mainly of 2A-DNT, 4A-DNT, and azoxy compounds (Price, Brannon, and Hayes in preparation). The existence of the Fe^{+2} reduction pathway for TNT has been demonstrated in soils (Price, Brannon, and Hayes in preparation). Addition of a chelating agent (EDTA) to bind Fe^{+2} resulted in a nearly 50 percent decrease in TNT disappearance during the first hour of incubation.

Pseudo-first-order disappearance rate constants for TNT (Townsend and Myers 1996) measured in column tests and for TNT and its transformation products measured in batch tests with the same clay soil (Brannon et al. in preparation) (Table 1) agree within an order of magnitude. Disappearance rate constants under anaerobic conditions are generally higher than those under aerobic conditions, resulting in a shorter half-life under anaerobic conditions (Table 1).

TNT transformations in water exposed to plants and sediments produce products similar to those produced with soils, specifically mono- and di-amino reduction products (Best and Sprecher 1996). Removal of nitro groups was not found for any of the 10 plant species tested. The only significant photolysis product reported was trinitrobenzene.

RDX and HMX

Less is known regarding the transformation of RDX and HMX than that of TNT. Research has indicated that RDX is also affected by transformation (McCormick, Cornell, and Kaplan 1981; Myers et al. in preparation). In a proposed pathway scheme for the biodegradation of RDX, McCormick, Cornell, and Kaplan (1981) showed reduction of nitro groups until destabilization and ring cleavage occurrence (Figure 6). The authors also suggested that RDX degradation occurs only under anaerobic conditions and that degradation products would be susceptible to aerobic mineralization. Ongoing studies with radiolabeled RDX (Price, Brannon, and Hayes in preparation) have shown that mineralization of RDX to CO_2 occurs under both anaerobic and aerobic conditions but is approximately an order of magnitude higher under anaerobic conditions. Mass balances for column experiments (Myers et al. in preparation) indicated disappearance of RDX. Although column eluates were not analyzed for RDX transformation products, analysis of soils showed that RDX was not retained in the columns. Myers et al. (in preparation) also observed HMX disappearance, suggesting that HMX biodegradation may have also occurred. Reported first-order RDX and HMX transformation rate constants have been from 0 to $1.0 \times 10^{-1} \text{ hr}^{-1}$ for RDX and from 0 to $9.0 \times 10^{-2} \text{ hr}^{-1}$ for HMX (Townsend and Myers 1996).

Table 1
First Order Rate Coefficients for Disappearance of TNT and TNT Transformation Products from Aerobic and Anaerobic Soil (Brannon et al. in preparation)

Compound	K, hr ⁻¹	Std. Error	r ²	t ^{1/2} , hrs
Aerobic Conditions				
TNT, abiotic	0.0053 ¹	0.0007	0.784	131
TNT, biotic	0.0163 ²	0.002	0.939	43
2A-DNT	0.0067	0.0013	0.696	103
4A-DNT	0.0113	0.0023	0.686	61
2,4-DANT	0.0208	0.002	0.908	33
2,6-DANT	0.0167	0.0008	0.974	41
Anaerobic Conditions				
TNT, abiotic	0.0058 ³	0.0005	0.936	119
TNT, biotic	0.062 ¹	0.01	0.95	11
2A-DNT	0.048	0.004	0.944	14
4A-DNT	0.047	0.007	0.861	15
2,4-DANT	0.013	0.0024	0.772	55
2,6-DANT	0.034	0.0018	0.975	21
¹ Regression uses data from 2 hours and up. ² Regression uses data from 1 hour and up. ³ Regression uses data from 6 hours and up.				

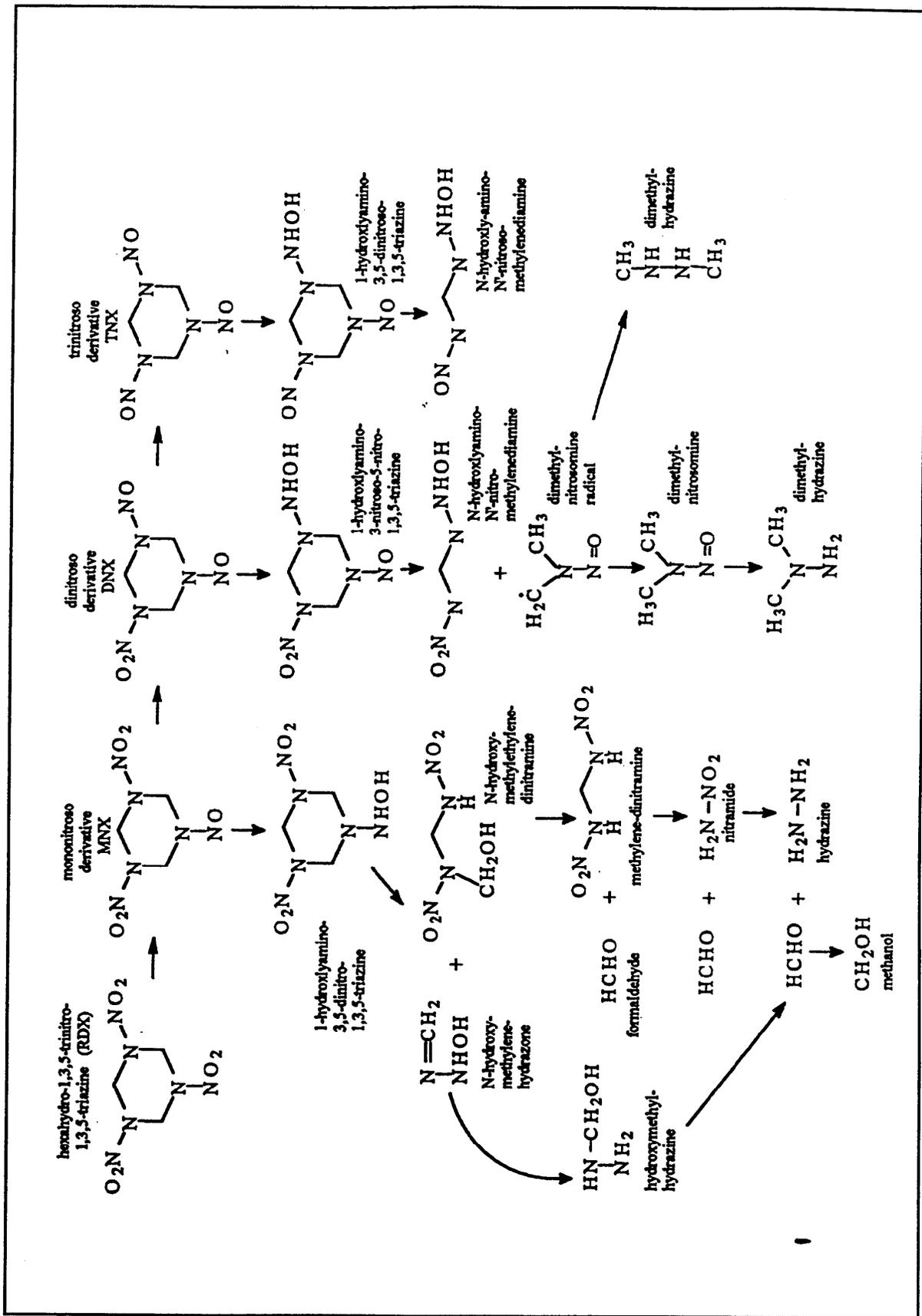


Figure 6. Proposed RDX transformation pathway diagram (from McCormick, Cornell, and Kaplan 1981)

3 Sorption Processes Affecting Fate and Transport

Sorption is a process that can and does occur in any environment, although the relative significance of sorption in relation to other processes may vary. Whether the sorption is reversible or irreversible will depend on environmental and geochemical conditions as well as the nature of the sorbing material.

TNT

TNT can be sorbed in a reversible manner (Haderlein, Weissmahr, and Schwarzenbach 1996, Pennington and Patrick 1990) and can also undergo reactions, which can be mistaken for sorption, that remove TNT from solution and bind TNT transformation products to soil in an unextractable manner (Pennington et al. 1995a; Brannon et al. 1992; Price, Brannon, and Hayes 1995). Several investigators (Leggett 1985; Pennington and Patrick 1990; Ainsworth et al. 1993; Xue, Iskandar, and Selim 1995; Comfort et al. 1995; Haderlein, Weissmahr, and Schwarzenbach 1996) have reported batch-determined equilibrium sorption coefficients whose isotherm plots were well behaved in all respects and appeared reliable. However, recent experiments (Price, Brannon, and Hayes 1995; Myers et al. in preparation) also showed that TNT in batch tests for some soils may not reach nonzero steady-state concentrations in either soil or dissolved phases due to transformation reactions.

Two radically different perspectives on partitioning of TNT between soil and water phases emerges. One portion of the literature on batch TNT sorption highlights measurement of constants for equilibrium partitioning of TNT between soil and water phases. The other portion emphasizes TNT transformation and the absence of equilibrium concentrations in soil and water phases. Some have tried to eliminate the effect of transformation by using (a) short equilibration times (Myers et al. in preparation), (b) short equilibration times coupled with poisoning of microbes (Pennington and Patrick 1990), and (c) poisoning of microbes (Ainsworth et al. 1993; Brannon et al. 1992). Causes for these radically different perspectives

include confusion over sorbed TNT concentrations (unmeasured transformation products), poorly-defined redox conditions during batch testing, and soils with different properties and microbial activities.

Some studies have measured both dissolved and soil phase TNT concentrations (Ainsworth et al. 1993; Price, Brannon, and Hayes 1995; Myers et al. in preparation) while other studies measured only TNT dissolved phase concentrations (Leggett 1985; Pennington and Patrick 1990; Xue, Iskandar, and Selim 1995). In the absence of measured soil phase TNT concentrations, sorbed concentrations are calculated by difference, that is, the TNT that disappears from the water phase is assumed to have been sorbed by the soil phase. Thus, calculated sorbed concentrations reflect both TNT disappearance from solution by sorption and transformation (unmeasured). The direct measurements of soil phase TNT concentrations (Myers et al. in preparation; Price, Brannon, and Hayes 1995) showed that equilibrium in the sorbed phase for some soils is not reached because TNT continues to transform, especially under anaerobic conditions.

Eh is a major environmental factor affecting TNT transformation but has not been measured during batch testing with the exception of the study by Price, Brannon, and Hayes (1995). Redox conditions in an uncontrolled batch experiment are highly variable and depend on the head space gas, initial concentration of oxygen in the water and soil, organic matter, iron, manganese, sulfur, and numerous other redox-sensitive substances. TNT transformation is more rapid when nitrogen is the head space gas and deaired water is used than when air is the head space gas and air-equilibrated water is used (Myers et al. in preparation). Since TNT is unstable in soil at any Eh (Price, Brannon, and Hayes 1995), TNT transformation may have occurred in other studies (Leggett 1985; Pennington and Patrick 1990; Selim and Iskandar 1994), but the significance of transformation on these sorption data appears to be minimal because sorption times were short and based on attainment of steady-state concentrations in solution.

In situations where redox conditions and soil properties do not promote transformation of TNT, as in some subsurface situations, sorption may be a more important factor than transformation affecting TNT fate and transport. Haderlein, Weissmahr, and Schwarzenbach (1996) reported equilibration times of 30-60 min and fully reversible surface adsorption of TNT and its transformation products on clay minerals. High adsorption constants were measured for TNT and its transformation products with homoionic K^+ - or NH_4^+ -clays (up to 21,500 L/kg) compared to much lower sorption (up to 1.7 L/kg) when Ca^{+2} , Na^+ , Mg^{+2} , or Al^{+3} was the exchangeable cation. These results suggest that the sorption behavior in freshwater and saline waters may be very different. In freshwater environments dominated by Ca^{+2} , sorption of TNT and its transformation products to soils, sediments, and suspended sediments may be lower than that observed in a saline environment where K^+ is present in higher concentrations than Ca^{+2} , but Na^+ is even more common and preferentially exchanges to displace K^+ . In considering the fate and transport of TNT and its transformation products, not only is the type of soil or sediment important, but also the ionic strength and composition of the groundwater or surface water in which the soil or sediment resides.

Haderlein, Weissmahr, and Schwarzenbach (1996) showed that TNT and its degradation products may exhibit very different mobilities in subsurface environments where specific adsorption to clay minerals can be a dominant sorption process. Distribution coefficient values for aqueous TNT and its transformation products on a K^+ saturated montmorillonite decreased in the order TNT > 2A-DNT > 4A-DNT > 2,6-DANT > 2,4-DANT (Haderlein, Weissmahr, and Schwarzenbach 1996). Testing with a Sharkey clay soil has shown much lower distribution coefficients and a more uniform distribution (within a factor of two) for TNT and its transformation products (Brannon et al. in preparation). Therefore, depending upon the characteristics of the sorbent, TNT transformation products may either be more mobile than TNT or show similar mobility.

Competitive adsorption between TNT, its degradation products, and other explosives has been postulated as a process that can effect their sorption and transport (Loehr 1989; Ainsworth et al. 1993). For clay minerals, the competition efficiency of explosives and their degradation products parallels their relative distribution coefficient values (Haderlein, Weissmahr, and Schwarzenbach 1996). Competition between adsorbed explosives is negligible only in very dilute systems (Haderlein, Weissmahr, and Schwarzenbach 1996). After the linear range for adsorption is exceeded on clays, explosives with a higher distribution coefficient will displace compounds with a lower distribution coefficient. For example, 2A-DNT will displace 2,4-DANT from clay sorption sites into the water phase (Haderlein, Weissmahr, and Schwarzenbach 1996).

Soil column studies have shown that a sorption term, in addition to an irreversible disappearance term, is needed to obtain good model fits for TNT breakthrough (Ainsworth et al. 1993; Selim, Xue, and Iskandar 1995; Townsend, Myers, and Adrian 1995; Comfort et al. 1995; Myers et al. in preparation). Equilibrium-controlled sorption (linear and nonlinear) has been the preferred model formulation for TNT sorption in column studies (Ainsworth et al. 1993; Selim, Xue, and Iskandar 1995; Townsend, Myers, and Adrian 1995; Myers et al. in preparation) and has worked well for a wide range of average pore water velocities.

Modeling of TNT fate and transport in environments other than the subsurface may require additional formulations. For example, fate and transport in surface waters may well require additional terms to adequately describe the behavior of TNT because of additional sink terms such as photodegradation or the activities of plants. Sediments containing plants removed TNT from water more rapidly than did sediment alone (Best and Sprecher 1996).

Surface soils highly contaminated with TNT are another area where formulations that adequately describe TNT fate and transport in the subsurface may require modification. Surface soils are generally large repositories of explosives at munitions loading facilities because of past waste disposal practices. Explosives are relatively stable in surface soils because of the presence of solid product in the soils (Pennington et al. 1995b) and the toxicity of high explosives concentrations to soil organisms (Bradley and Chapelle 1995). Solution phase concentrations of TNT, RDX, and HMX in soils containing high concentrations of these components, including a high proportion as free product, were controlled by the

aqueous solubility of the respective explosives (Pennington et al. 1995b). Solution phase concentrations in soils with lower concentrations of explosives were controlled by partitioning (Pennington et al. 1995b). Desorption partitioning resulted in nearly linear desorption isotherms for three TNT degradation products, 4A-DNT, 2A-DNT, and trinitro benzene (TNB) (Pennington et al. 1995b).

RDX

Sorption of RDX can be described well using linear equilibrium sorption isotherms (Leggett 1985; Ainsworth et al. 1993; Selim and Iskandar 1994; Haderlein, Weissmahr, and Schwarzenbach 1996, Myers et al. in preparation). Substantially less data are available on the sorption of HMX; but, in column studies (Myers et al. in preparation), HMX sorption was approximately described using a linear equilibrium model, although some evidence of nonequilibrium or nonlinearity was observed. In general, RDX (Haderlein, Weissmahr, and Schwarzenbach 1996; Townsend and Myers 1996), N,2,4,6-tetranitro-N-methylaniline (tetryl) (Haderlein, Weissmahr, and Schwarzenbach 1996), and possibly HMX are sorbed to a lesser extent than is TNT (Townsend and Myers 1996). In contrast to TNT, only small amounts of RDX become associated with soil organic matter (Price, Brannon, and Hayes in preparation). Desorption of radiolabeled TNT and RDX over time was complex but was also consistent with field observations on the relative mobility of TNT and RDX, i.e., RDX is more mobile than TNT (Brannon et al. 1992). Even though the soils were sterilized by gamma irradiation, abiotic production of transformation products that were not assayed may have influenced results. However, at the end of 180 days, radioactivity could not be detected in either water or methanol extracts of soils to which ^{14}C labeled TNT had been added. Radioactivity from added ^{14}C labeled RDX remained extractable from soils following 180 days of incubation. Behavior of RDX in settings other than the subsurface may be affected by many of the same factors as are those in the subsurface. Best and Sprecher (1996) reported that RDX removal from water was much less affected by the presence of plants than was TNT. However, low oxygen concentrations in the water resulted in increased removal of RDX (Best and Sprecher 1996) relative to high dissolved oxygen concentrations. This is consistent with observed increases in mineralization due to anaerobic conditions in soils (Price, Brannon, and Hayes in preparation).

4 Mathematical Process Descriptors

Process descriptors for explosives are poorly developed because specific reaction mechanisms and their interrelations are poorly understood (McGrath 1995). Townsend and Myers (1996) have recently reviewed developments in formulating model descriptors for subsurface transport of explosives. They focused on the sources and sinks term in the equation describing one-dimensional solute transport. Figure 7, adapted and expanded from Townsend and Myers (1996), generalizes the processes involved in the fate and transport of explosives in the subsurface, surface, aquatic, and wetland environments. All sources and sinks in Figure 7 may not be operative in all environmental settings. For example, during subsurface transport of explosives, photolysis would be inactive and volatilization should be minimal. However, these processes should be considered during fate and transport evaluations that involve exposure to sunlight and the

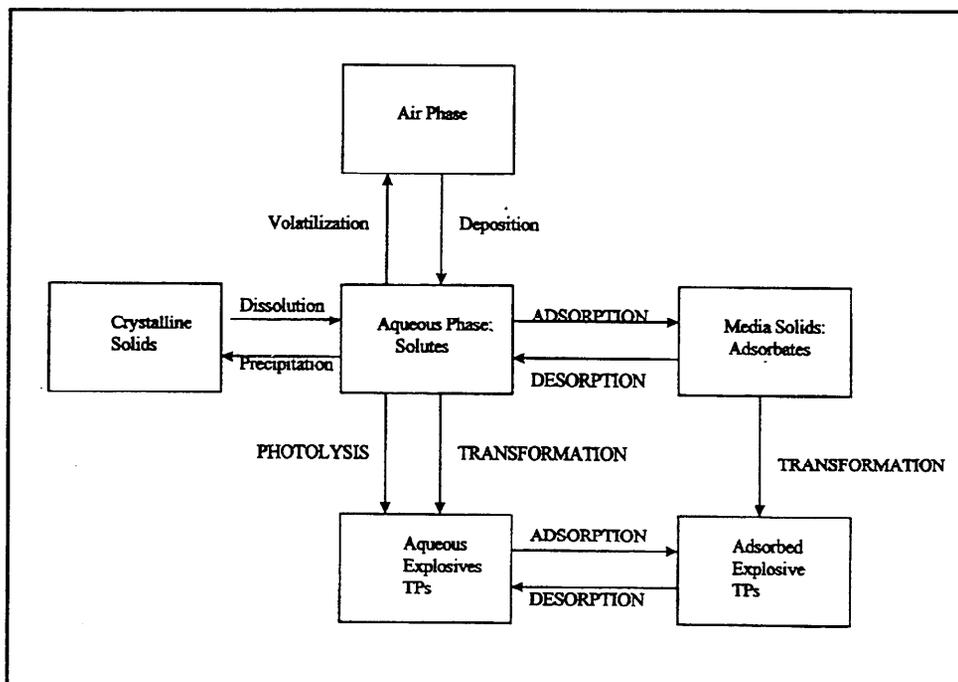


Figure 7. Phases for TNT, RDX, and HMX (after Townsend and Myers 1996)

atmosphere. Available rate constants for representative explosives for photolysis and volatilization are summarized by McGrath (1995) and references therein. Volatilization of TNT from surface soils should be relatively minor (Pennington et al. 1992).

Mathematical process descriptors for transport of explosives are more fully developed for the subsurface than for other environmental settings (McGrath 1995; Townsend and Myers 1996; Townsend, Myers, and Adrian 1995; Selim, Xue, and Iskandar 1995). Townsend and Myers (1996) update presently known coefficients and rate constants for sorption, biodegradation, volatilization, photolysis, etc. for TNT, RDX, and HMX presented in McGrath (1995). Additional sorption coefficients are available for clay minerals with various saturating cations (Haderlein, Weissmahr, and Schwarzenbach 1996) and surface soils (Brannon et al. in preparation). Descriptors for processes other than photolysis are generally lacking for aquatic and wetland environments, and do not include production of transformation products. However, sorption and transformation process descriptors for soils may be modified to encompass other environmental settings if the effects of differing environmental conditions, such as Eh, are considered.

Sorption and transformation are two of the major processes affecting the fate and transport of explosives in the subsurface (Townsend and Myers 1996) and will be equally important in other environmental settings. Disappearance of explosives from water exposed to sediments and plants (Best and Sprecher 1996) demonstrate the importance of these processes in aquatic and wetland environments. TNT is more reactive than RDX in the subsurface and less subject to sorption (Spaulding and Fulton 1988). This also appears to be the case in aquatic and wetland environments (Best and Sprecher 1996). Results of Spaulding and Fulton (1988) at Cornhusker Army Ammunition Plant showed that RDX is much more persistent than TNT in the subsurface. Describing RDX transport has been more successful than efforts to describe TNT when independently determined (batch) parameters were used (Selim, Xue, and Iskandar 1995), probably due to negligible transformation and irreversible sorption. TNT was strongly retained by soils during column tests, although unanalyzed diamino transformation products may have contributed to this finding since soil measurements were not conducted, while only limited retention of RDX was observed (Selim, Xue, and Iskandar 1995). Agreement between observed and model breakthrough curves for thin-disk soil columns suggests that simple formulations of sorption and reaction in transport models for TNT can capture the main effects of these processes, even at high solution concentrations (Townsend, Myers, and Adrian 1995). Others (Comfort et al. 1995) showed that TNT sorption and degradation are concentration-dependent and the assumptions of linear adsorption and adsorption-desorption singularity commonly used in transport modeling may not be valid for prediction of TNT transport in munitions-contaminated soils. The conflicting recommendations for subsurface modeling of explosives fate and transport are probably a result of differing experimental design of the column and batch tests used to provide model input. Because the redox potential within columns cannot be controlled and was not measured, the degree of reduction, which strongly affects TNT transformation rate, cannot be gauged. This points to the complexity of explosives fate and transport, even in the subsurface where the most information exists.

Extension of the knowledge gained from subsurface transformation and sorption of explosives will, however, provide a starting point for other environments. Quantification of the most important processes operative in aquatic and wetland environments, including sorption and transformation, is needed. This will allow development of process descriptors for surface soils and aquatic and wetland environments.

5 Conclusions

Most of the information available on fate and transport of explosives is for the subsurface environment. The information available for the subsurface shows that transformation and sorption are two of the most important environmental processes affecting the fate and transport of TNT. For RDX and other explosives, additional processes such as mineralization to CO_2 may also be important, while processes such as sorption may be less important.

Redox potential strongly affects the rate and products resulting from explosives transformation. Sorption can be affected significantly by cation substitution on clay minerals, and competitive sorption can affect the mobility of explosives and their degradation products.

Recent findings show that considerable work remains to be conducted, even in the subsurface. At present, we possess a good qualitative understanding of the processes that are operative in soils and aquifer materials and an inferential understanding of the processes that may be occurring in other environments. Translating this qualitative understanding and speculation into quantitative mathematical process descriptors is impeded by the nature of the information available and will require additional process level research.

6 Recommendations

Below is a list of recommendations.

- a.* During fate and transport studies of explosives, transformation products should be measured because of their importance to fate, transport, and sorption of explosives.
- b.* Environmental conditions such as Eh and pH should be measured to aid in interpretation of data and development of process descriptors from research results in various environments.
- c.* Fate, sorption, and transformation studies should be conducted with TNT in surface waters and surface soils in addition to subsurface soil environments to determine the importance of these processes in these environments.
- d.* Fate, sorption, and transformation studies should be conducted with RDX and HMX in various environments.

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