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Environmental fate of explosives

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Abstract

Waste disposal practices associated with military production of weapons, especially before and during World War II, have resulted in significant contamination of soils and ground water with high explosives such as TNT, RDX and HMX. Development of remediation and risk management strategies for these contaminated sites as well as development of approaches for sustainable use of active training and weapons testing sites require an understanding of how the energetic compounds interact with the environment. Factors affecting leaching and transport, microbial degradation, phytotoxicity and plant uptake, and invertebrate and vertebrate toxicity are determinants of ultimate environmental fate and hazard potential. In this article, we will summarize our current understanding of these interactions, identify significant data deficiencies, and briefly discuss the drivers of future research in this area.

Keywords: Explosives; Weapons; RDX; TNT; HMX

1. Introduction

Many US Department of Army and other Department of Defense installations have soil, sediment, surface water, and ground water contaminated with explosives. 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 explosives manufacturing and with loading, assembling, and packing of explosives into munitions items [1,2]. Remediation and risk management of contaminated sites requires knowledge of the fate and transport of explosives and their transformation products in the environment.

In addition to dilution and dispersion, processes important to ground water transport of explosives include biotic and abiotic transformations, covalent bonding to soil organic matter, and adsorption by soils. Not all processes affect explosives subsurface transport equally; therefore, identifying key processes and developing accurate numerical descriptors for these processes are critical to modeling transport and predicting ground water contaminant levels. Transformation of nitroaromatic compounds generally occurs by sequential reduction of nitro groups to amino groups [3]. For example commonly observed reductive transformation products of TNT include 2-amino-4,6-dinitrotoluene (2ADNT), 4-amino-2,6-dinitrotoluene (4ADNT), 2,4-diamino-6-nitrotoluene (2,4DANT), 2,6-diamino-4-nitrotoluene (2,6DANT) (Fig. 1). Transformation can occur through microbially mediated processes or abiotically and is favored under reducing conditions [4,5]. The mono amino transformation products of TNT are common in TNT-contaminated environments whereas the transformation products of RDX and HMX are less frequently observed. Extensive research has been devoted to defining adsorption of TNT and RDX by soils, and clay minerals [6–10]. Interpretation of sorption data for TNT is confounded

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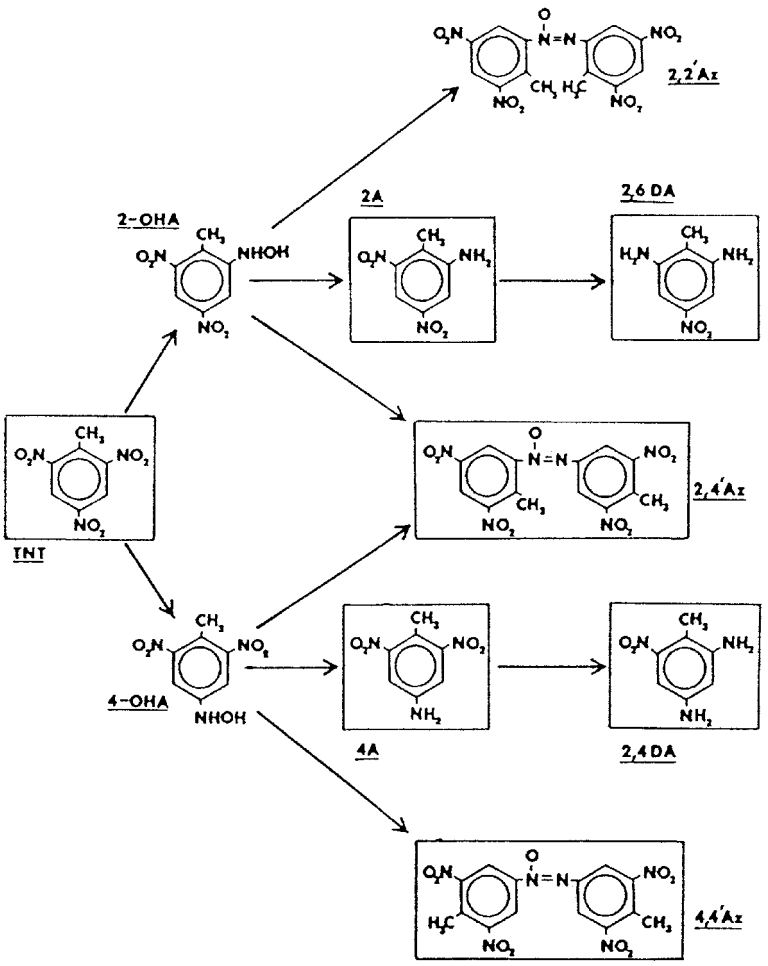

Fig. 1. Biotransformation of TNT in compost [3].

by formation of transformation products. When transformation of sorbing analyte is neglected, sorption can be overestimated, leading to under estimation of ground water contamination.

Explosives are typically degraded very slowly in environmental systems. Observation of mineralization in the environment is complicated by this slow rate and the lack of accumulation of degradation products beyond the transformation products observed at TNT-contaminated sites. Mineralization to very simple compounds such as methane, carbon dioxide and nitrates occurs more readily under anaerobic than under aerobic conditions.

Plants exhibit tolerance to explosives in soils until concentrations reach toxic levels, which vary with soil properties and plant species. TNT tends to accumulate in plant roots, while RDX is readily bioaccumulated by some plant species. RDX has been observed to bioaccumulate in edible portions of several crop plants. Less is known about HMX phytotoxicity, but several authors report bioaccumulation of HMX by plants [11,12].

Explosives generally exhibit moderate-to-low toxicity to the few animal species that have been studied. These include aquatic invertebrates and fish [13–20], salamanders and earthworms [21–27], and mice, rats and dogs [28–32]. Most effects of exposure are sublethal, although LC50 values have been established for earthworms exposed to TNT in soils. This is an active area of research in which a great need exists to broaden the number of species evaluated.

2. Transformation processes affecting environmental fate and transport

Major factors affecting fate and transport of TNT in the subsurface are transformation, sorption, and irreversible soil binding [33]. Although TNT reductive transformation has been known for some time [3,34], only recently have TNT reductive transformation products been routinely measured in laboratory and field studies [5,10,35–39]. Possible TNT transformations include reduction of one, two or all three of the nitro-moieties to amines, and coupling of amino transformation products to form dimmers (Fig. 1) [3]. Formation of the two monoamino transformation products, 2ADNT and 4ADNT, is favored [40] and they are typically observed in TNT-contaminated soils and ground water. Since the diamino products are energetically more difficult to form, they are observed less frequently and typically at lower concentration than the monoamino products [41]. The triamino product is rarely observed not only because it is more energetically difficult to form, but also because once formed, it does not persist, but is likely to be immobilized by chemical reactions with soil components [42] or by microbial degradation [43].

The amino transformation products are amenable to several attenuation mechanisms in soils. These include covalent bonding to functional groups on soil organic matter such as described for similar amines [44–47], reactions at mineral surfaces [10,48,49], sequestration [42], and reversible adsorption [7,8, 39,50]. Although these mechanisms for attenuation of TNT have received attention in laboratory studies in the last several years, little data have been reported on their occurrence in the field beyond detection of the amino transformation products in soil and ground water and declines in TNT concentrations over time [41].

Laboratory studies have demonstrated the effects of several environmental factors on transformation of TNT. Such factors include redox status, pH, organic carbon levels, cation exchange capacity and presence/absence of expandable clays and reducing agents, e.g. divalent iron and manganese. TNT transformation is significantly enhanced under anaerobic conditions, but occurs at a slow rate under aerobic [4,5].

TNT disappeared from the solution phase of slurry tests under highly reduced conditions (Eh $= -150$ mV) following 1 day of incubation [5]. The monoamino and diamino transformation products disappeared rapidly in all tests at all concentrations and pH values. Under aerobic conditions (Eh $= +500$ mV), TNT had completely disappeared from solution after 4 days. Only the monoamino transformation products appeared with maximum concentrations at day 4, but with detectable concentrations through day 14. These results demonstrated that TNT transformation is more rapid under highly reducing conditions (Eh $= -150$ mV) than under oxidizing conditions (Eh $= +500$ mV), but that neither TNT nor its transformation products persist.

TNT transformations in soils can occur both biologically and abiotically [7,9,51]. The rate of TNT transformation by Fe^{2+} in the presence of montmorillonite or kaolinite increased as pH increased [52]. Products were primarily monoamino and azoxy compounds; however, mass balance using radiolabeled TNT indicated the presence of unextractable products. Suppression of the abiotic Fe^{2+} pathway by addition of EDTA slowed reduction, but the suppression lasted for no more than 24 h.

Studies conducted with aquatic plants demonstrated the presence of mono- and di-amino transformation products of TNT in the aqueous phase of the media [12]. Trinitrobenzene was also observed in the water.

Transformation of RDX through mono-, di-, and trinitroso products has been postulated [53,54]. Such reductions lead to destabilization, ring cleavage, and mineralization of RDX under anaerobic conditions (Fig. 2, [34,55,56]). Degradation intermediates are susceptible to aerobic as well as anaerobic mineralization; however, mineralization is nearly an order of magnitude greater under anaerobic conditions [57]. The nitroso intermediates of RDX have rarely been observed in the field at the few sites where analyses have been conducted for them.

Little is known regarding the transformation of HMX. In laboratory studies HMX is stable under a broad range of redox and pH conditions [57]. First-order transformation rate constants for HMX have been measured in soil column and shake-test experiments [33,57]. Rates constants ranged from 0 to $9.0 \times 10^{-2}\ h^{-1}$. Transformation products of HMX have rarely been detected in environmental samples. However, analyses for transformation products have been limited.

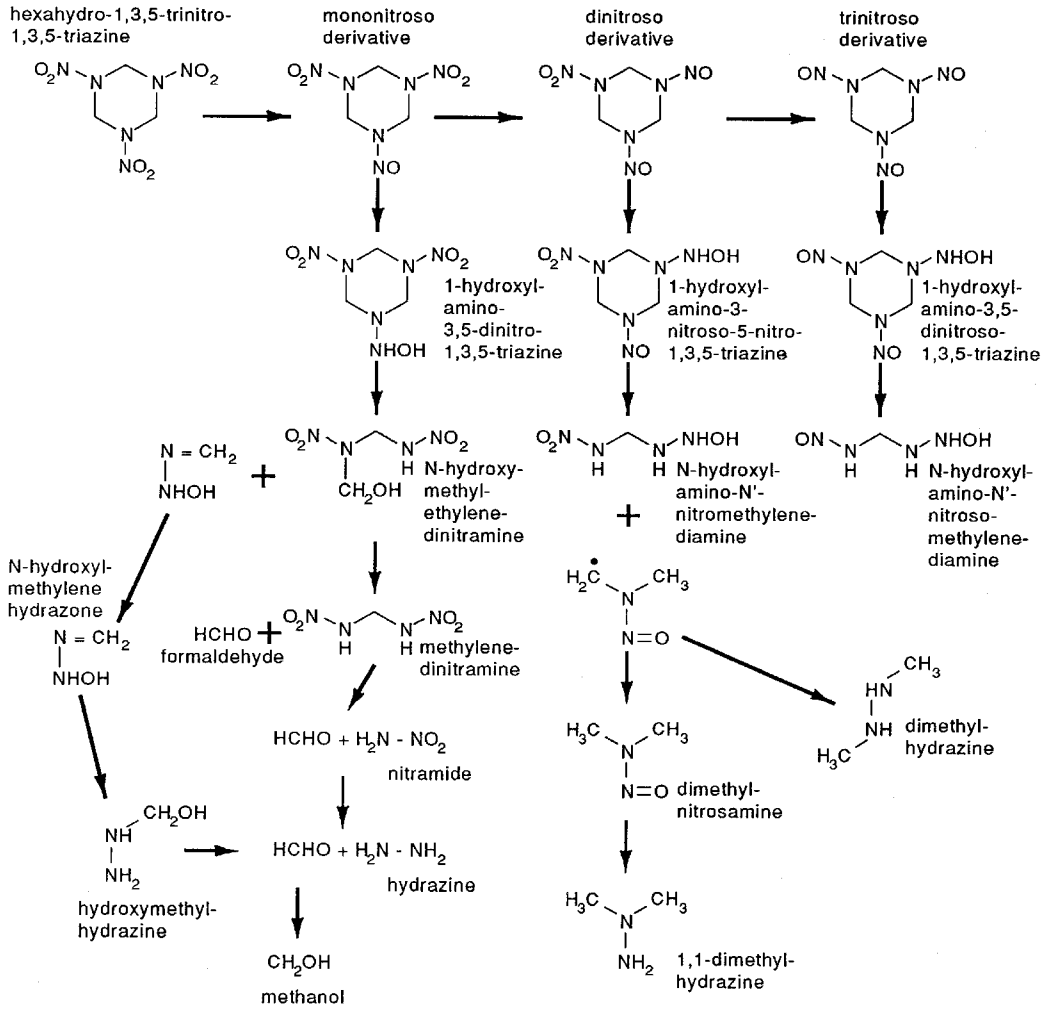

Fig. 2. Anaerobic biomineralization pathway for RDX [34].

3. Sorption processes

TNT can be reversibly sorbed by soils [7,10]. However, reactions that remove TNT from solution and bind TNT transformation products to soil in an unextractable manner can be mistaken for adsorption [5,8,58]. Several investigators have reported batch-determined equilibrium sorption coefficients whose isotherms were well behaved [7,9,10,36,38, 59]. However, recent experiments have shown that TNT in batch tests for some soils may not reach nonzero steady-state concentrations in either soil or dissolved phases due to transformations [4,39]. Some investigators have tried to eliminate the effects of transformation by using (a) short equilibration times [39] (b) poisoning of microbes [8,9], and (c) short equilibration times coupled with poisoning of microbes [7]. Controlling and/or monitoring transformation in batch tests is complicated by the need to define/control redox conditions and microbial activity in tests.

Analysis of solution phase in batch tests may reflect TNT disappearance from solution by sorption and by transformation. Direct measurements of soil phase TNT concentrations showed that steady-state in the sorbed phase for some soils is not reached because

TNT continues to transform, especially under anaerobic conditions [4,39]. Therefore, isotherms based only on solution phase analyses may be misleading. Steady-state conditions for TNT are more likely to be attained in low organic carbon soils, such as those typical of aquifers, than in typical surface soils [41].

In an uncontrolled batch experiment redox conditions are highly variable and depend on the headspace gas, initial concentration of oxygen in the water and soil, microbial activity, organic matter, iron, manganese, sulfur, and numerous other redox-sensitive substances. TNT transformation is more rapid when nitrogen is the headspace gas and de-aired water is used than when air is the headspace gas and air-equilibrated water is used [39].

In some subsurface soils where redox conditions and soil properties do not promote transformation, sorption may be more important than transformation. Haderlein et al. [10] 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 with homoionic K^+- or NH_4^+-clays (up to 21,500 l kg^{-1}) compared to much lower sorption (up to 1.7 l kg^{-1}) 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 dominated by K^+ and Na^+. Therefore, the type of soil or sediment and the ionic strength and composition of the ground water or surface water are important determinants of adsorption.

Haderlein et al. [10] 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 > 2ADNT > 4ADNT > 2,6DANT > 2,4DANT. Testing with a Sharkey clay soil has shown much lower distribution coefficients and a more uniform distribution (within a factor of 2) for TNT and its transformation products [60]. 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 to affect sorption and transport [6,9]. Competition between adsorbed explosives was negligible only in very dilute systems. After the linear range for adsorption was exceeded on clays, explosives with a higher distribution coefficient displaced compounds with a lower distribution coefficient. For example, 2ADNT displaced 2,4DANT from clay sorption sites into the solution phase.

Because of past waste disposal practices, surface soils can present large repositories of explosives, especially where explosives were manufactured, loaded and packaged into shells. Solid explosives, present in soils as chunks, are relatively stable due to their relatively slow dissolution rate [50,61]. When solid explosive was present in batch partitioning tests, the aqueous solubility of the respective explosives controlled solution phase concentrations masking sorption behavior [50].

Sorption of RDX can be described using linear equilibrium sorption isotherms [9,10,39,59,62]. In contrast to TNT, only small amounts of RDX become associated with soil organic matter [57]. 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. with RDX being more mobile than TNT [8]. The soils were sterilized by gamma irradiation; however, abiotic transformation may have influenced results. Radiolabeled RDX remained extractable from soils after 180 days, whereas TNT was absent from the aqueous phase and was unextractable from the soil in the same period. Best et al. [12] reported that RDX removal from water was much less affected by the presence of plants than was TNT removal. However, low oxygen concentrations in the water resulted in increased removal of RDX. This is consistent with observed increases in mineralization due to anaerobic conditions in soils [57]. In general, RDX is sorbed less than TNT by soils [10,33]. RDX has been observed to move beyond TNT in groundwater plumes ([1,2,80]).

Substantially less data are available on the sorption of HMX. In column studies HMX sorption was approximately described using a linear equilibrium

model [39]. HMX is apparently sorbed less than is TNT by soils [33,57].

4. Immobilization of TNT

Evidence for immobilization of TNT in soils with consequent reduction in bioavailability was dramatically illustrated in a plant uptake study using TNT-amended soils [63]. Results revealed the significant reduction in bioavailability of TNT for plant uptake from clay as compared to silt. Other evidence for TNT immobilization was revealed in composting experiments using [^{14}C]TNT-amended soils [3,58,64]. In these studies, significant quantities of unextractable radioactivity and no radiolabeled volatiles or CO_2 were observed. These results confirmed that mineralization of TNT was not occurring during composting, but that immobilization accounted for the observed dramatic reductions in TNT. Further study of the composting process demonstrated that no TNT and very few identifiable products of TNT could be released from the finished compost even with stringent base/acid hydrolysis schemes [65–67]. Similar results were observed when compost was subjected to ultra violet light and repeated aqueous leaching [64]. Microbial degradation studies have shown that the immobilized products of TNT in compost are resistant to mineralization [66,67].

Results of nuclear magnetic resonance techniques using stable isotopes of nitrogen and carbon confirmed covalent bonding of TNT transformation products to functional groups on humic acid [68]. Studies to define the factors governing the characteristics of observed products are on-going.

Immobilization of RDX and other energetic contaminants is limited. Results of high performance liquid chromatographic analysis of compost containing both TNT and RDX indicated much less disappearance of RDX (approximately 30%) than of TNT (>90%) after 20 days [58]. Since RDX is more readily degraded microbially than TNT and no radiolabeled RDX was present in the tests for monitoring of $^{14}CO_2$, disappearance of RDX may have been due to mineralization rather than immobilization. In the same experiment, no significant change in HMX concentration was observed, which suggests that HMX transformation is not significant.

5. Quantitative process descriptors

Process descriptors for modeling of explosives fate and transport in soils are poorly developed because specific reaction mechanisms and their interrelations are incompletely understood [69]. The processes involved may not be operative in all environmental settings [33]. For example, during subsurface transport of explosives, photolysis would be inactive and volatilization should be minimal. Therefore, photolysis should be considered when modeling transport from waste disposal lagoons, but may be unimportant when modeling groundwater transport. Available rate constants for photolysis and volatization are summarized by [69] and references therein.

Development of mathematical process descriptors for transport of explosives in the subsurface has been initiated [33,35,37,69]. Sorption coefficients are available for clay minerals with various saturating cations [10]. Sorption and transformation are two of the major processes affecting the fate and transport of explosives in the subsurface and will also be important in other environmental settings. Agreement between observed and model breakthrough curves for thin-disk soil columns suggested that simple formulations of sorption and reaction in transport models for TNT capture the main effects of these processes, even at high solution concentrations [35]. A sorption term, in addition to an irreversible disappearance term, is needed to obtain good model fits for TNT breakthrough curves in columns [9,35–37,39]. Equilibrium-controlled sorption (linear and nonlinear) has been the preferred model formulation for TNT sorption in column studies and has worked well for a wide range of average pore water velocities [9,35,37,39].

Modeling of TNT fate and transport in environments other than the subsurface may require additional formulations. For example, fate and transport of TNT in surface waters may well require additional terms for photodegradation or the activities of plants and animals.

6. Microbial degradation

While readily transformed, TNT is only slowly mineralized in soils and ground water. Several mineralization pathways have been reviewed by [36]. Anaerobic

mineralization through TAT to trihydroxytoluenes, polyphenols, ρ-cresol and acetate has been reported [53,54]. Evidence of mineralization in soils or ground water is scarce. Results of studies in which aquifer soils were challenged with carbon-14 labeled TNT and RDX revealed that the native microflora from two sites possessed limited potential for attacking and degrading these compounds [41]. Furthermore, the limited degradation proceeded at a very slow rate. RDX is more readily degraded than TNT, especially under anaerobic conditions [53,70–72]. Final products may include methanol and hydrazines, and under methanogenic conditions, methane [34,56,73]. Relatively little is known concerning the degradation of HMX, but results of the few observations suggest that HMX is recalcitrant to mineralization, yielding mono- and di-nitroso intermediates only and transforming under anaerobic conditions only [70,74].

7. Phytotoxicity and bioaccumulation in plants

Many plants are tolerant to explosives in soil and water until concentrations reach toxic levels that are dependent upon plant species. In a study designed to develop aquatic plants for phytoremediation of explosives in ground water, surface water, or in constructed wetlands, lethal concentrations of TNT and RDX in water were 5–7 and 5–6 mg l^{-1}, respectively [12]. Growth of emergent plants was reduced when ground water concentrations were 1.5 mg RDX l^{-1}, while growth of the submersed species remained normal [75]. Toxicity of TNT in soils is controlled by soil properties such as clay and organic carbon content. Yields in yellow nutsedge (*Cyperus esculentus*) were significant reduced when concentrations of TNT in a silty soil exceeded 200 mg kg^{-1} [63]. However, in a high clay soil, yields were unaffected until soil concentration reached 400 mg kg^{-1}. An inverse correlation between soil clay and organic carbon content and absorption of TNT by bush bean has also been reported [76]. In a study of plant uptake of TNT and RDX from a contaminated site soil, tolerance to elevated concentrations were in the order (most to least tolerant) of corn stover > tomato vine > nutsedge > corn ears > tomato fruit > lettuce [11]. All of these plants died in soils containing 580 mg RDX kg^{-1} and 1720 mg TNT kg^{-1}. Effects of RDX and TNT were not separated. No data on phytotoxicity of HMX were found.

TNT tends to accumulate in plant roots with limited transport to other plant organs. In the bush bean study mentioned above, roots accumulated significantly more TNT than leaves, stems, pods, or seeds [76]. In soils amended with 10 mg TNT kg^{-1}, seeds accumulated <0.6 mg kg^{-1} during the 60-day test, while leaves, stems, pods and roots accumulated up to 9.0, 24.0, 0.6, and 104.0 mg kg^{-1}, respectively. A survey of native plants at a TNT contaminated site indicated no explosives in aboveground plant tissues, but accumulation of TNT, 2ADNT and 4ADNT in some roots [77]. Poplar tree cuttings also take up significant concentrations of TNT from contaminated soil and water with most of the contamination residing in the roots [78].

RDX is readily bioaccumulated by plants. When grown in soil contaminated with 58 mg RDX kg^{-1}, lettuce accumulated 1200, nutsedge 62, tomato fruit 7, corn kernels 6, and corn stover 56 mg RDX kg^{-1} plant tissue [11]. RDX was also taken up by eleven species of aquatic plants grown in explosives contaminated ground water [12]. Plant uptake of HMX from soil (8.6 mg HMX kg^{-1}) by lettuce (43 mg kg^{-1}), corn stover (4.3 mg kg^{-1}), and yellow nutsedge (6.0 mg kg^{-1}), has been reported [11]. In the same study tomatoes and corn kernels did not take up HMX. Plant uptake of HMX from ground water phytoremediation systems by several wetland plants was reported by Best et al. [12].

8. Animal toxic and sublethal effects

Much more data are available concerning toxicity of TNT and RDX than of other explosives. The explosives in general exhibit moderate-to-low toxicity for most receptors. An excellent review of animal toxicity was provided by Talmage et al. [79]. Since that review, significant research has been initiated to better define environmental effects by focusing on potentially useful indicator species.

Determination of sublethal and chronic toxicological effects in terrestrial ecosystems often relies upon results of earthworm bioassays. Earthworm toxicity was defined in a series of recent articles by Robidoux et al. [24–26] and Renoux et al. [27]. Acute toxicity

as determined by survival of earthworms was inversely related to TNT concentration in soil [24]. Earthworms failed to survive >9000 mg TNT kg^{-1} soil. For TNT-spiked soils the lowest-observed-effect-concentration (LOEC) was 110 mg kg^{-1} dry soil and the no-observed-effect-concentration (NOEC) was 55 mg kg^{-1} [25]. For RDX-spiked soil, the LOEC was 95 mg kg^{-1} and the NOEC was <95 mg kg^{-1}. The concentration of TNT at which 50% of earthworms died (LC50) in a forest sandy soil over 14-days was 143 mg kg^{-1} [27]. TNT was transformed to 2ADNT, 4ADNT, 2,4DANT, and 2,6DANT in earthworm tissues. Dermal uptake was a significant exposure route for TNT. Fecundity (total and hatched number of cocoons, number of juveniles and their biomass) was reduced (LOEC = 280 mg kg^{-1} dry soil) at different concentrations of HMX, but no mortality occurred [26].

The salamander, *Ambystoma tigrinum*, has been suggested as a bioindicator of effects in the evaluation of toxicity of explosives at contaminated sites [21–23]. Dermal exposure was determined to be the most important exposure pathway for uptake of TNT from contaminated soil by the salamander [21]. Trace amounts of TNT were detected only in the skin and liver of exposed salamanders, while 2,6DANT was found only in liver and kidney tissues [22]. Skin was concluded to be important in the primary reduction of TNT. When salamanders were exposed to TNT in soil (1 ppm) and fed earthworms exposed to TNT in the same soil, no differences between controls and treated animals were observed for weight gain, organ to body weight ratios, function of splenic phagocytic cells, nor peripheral hematological parameters [23]. However, the liver exhibited heavily pigmented iron-rich phagocytes (melanomacrophages) and growth rate was slower during treatment.

Recent mammalian studies have been conducted on mice and rats ([29,30], respectively). When as much as 601 mg TNT per kg body weight was fed to white-footed mice over a 14-day period, no mice died [29]. Several indicators of nonspecific immunity, including increased spleen weight, were related to dose. Results of studies of the hispid cotton rat suggest that hepatic enzymes and hemolytic anemia may be useful biomarkers of terrestrial contamination by explosives [30]. Increased spleen weight, hemolytic anemia and elevated methemoglobin, and increased weight and histological changes of the liver were among the effects reported. Some of the above researchers and others are currently exploring the mammalian toxicity of RDX and other explosives.

9. Future research

The driver for future research in this area will expand from cleanup mandates for explosives manufacturing and munitions development to sustaining military readiness by appropriately managing training and testing ranges in an environmentally responsible manner. Assessing the potential for explosives contamination and the potential for exposure of environmental and human receptors resulting from various military activities will be necessary. Research will be needed to refine environmental and human health risk assessment methods and develop tools for effective management of necessary military training operations to minimize adverse environmental and human health effects.

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