6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

2,4- and/or 2,6-DNT have been identified in at least 98 of the 1,699 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2007). Information on the other isomers was not available. The number of sites evaluated for DNTs is not known. The frequency of these sites can be seen in Figure 6-1.

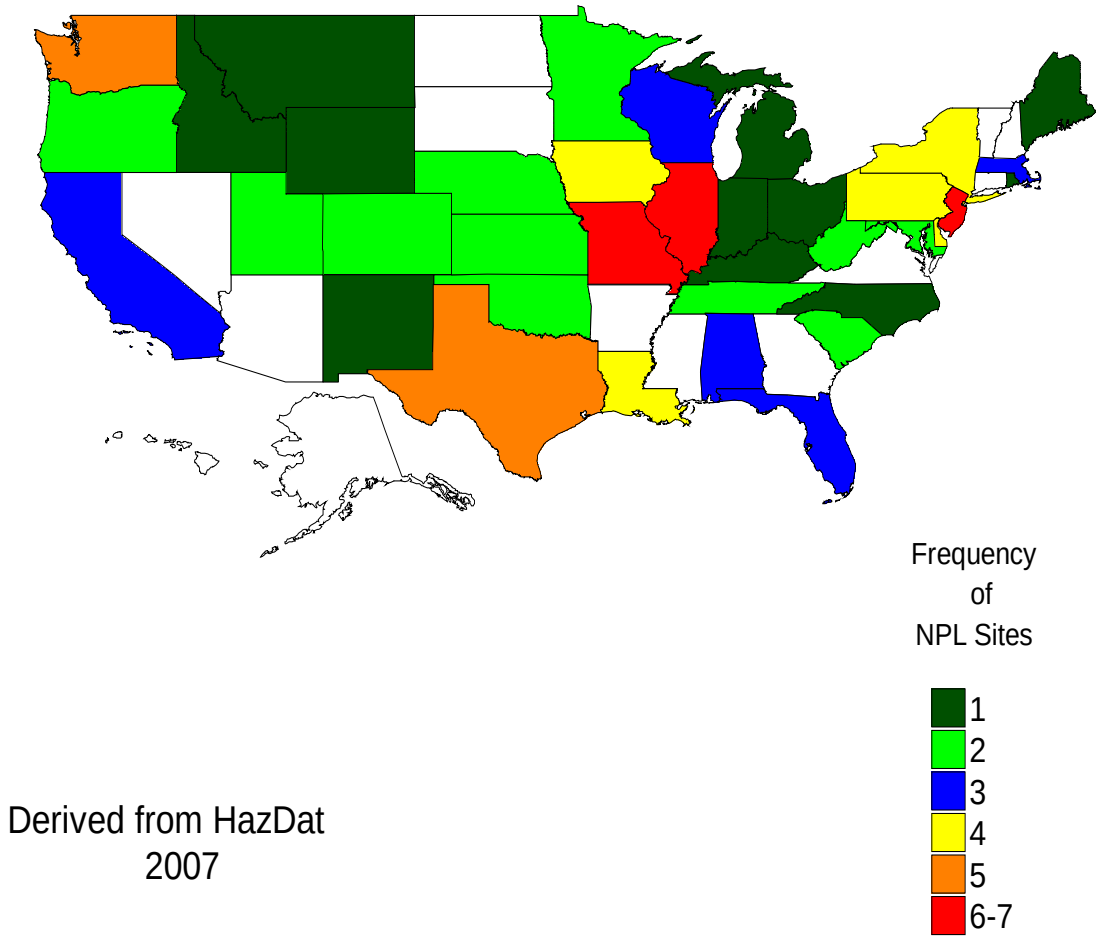
The available data provide a complex and incomplete view of the overall potential for human exposure to isomers of DNT. Little direct knowledge of the magnitude of environmental exposure pathways exists. Data regarding exposure of humans to DNTs have been obtained primarily from the workplace.

DNTs have been found in waste water and groundwater in and around munitions sites (Jenkins et al. 1986), and 4-nitrotoluene and dinitrobenzene, structural analogues of DNTs, are taken up by plants (McFarlane et al. 1987). However, predictions of environmental exposure pathways based on measurements of structural analogues of DNTs are severely limited by the complex abiotic reactions of DNTs in the environment and by the different pathways, rates, and products of biological reduction and/or oxidation of 2,4- and 2,6-DNT.

The relatively low log octanol-water partition coefficients (log K_{ow}) of the DNT isomers (1.98–2.18) suggest that DNTs released to the environment would not bioaccumulate. Measured bioconcentration factors also indicate that DNTs are not expected to bioaccumulate in fish and other aquatic species (Lang 1997; NITE 2002). DNTs are not highly adsorbed to soil or sediment and may leach from the soil surface to groundwater. DNTs are degraded by oxidation, photolysis, and biotransformation in water or soil, resulting in a variety of degradation products. Volatilization is expected to occur slowly from water and soil surfaces and the rate of hydrolysis is negligible.

Studies of occupational exposures to DNTs indicate that inhalation and dermal contact can result in absorption of DNTs into the body. The general population is not expected to be exposed to DNTs unless they reside near a source area, in which case, dermal contact and incidental ingestion pathways are the likely routes of exposure.

Figure 6-1. Frequency of NPL Sites with 2,4- and 2,6-Dinitrotoluene Contamination



6.2 RELEASES TO THE ENVIRONMENT

The Toxics Release Inventory (TRI) data should be used with caution because only certain types of facilities are required to report (EPA 2005). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the TRI only if they employ 10 or more full-time employees; if their facility is included in Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20–39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under RCRA Subtitle C, 42 U.S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis); and if their facility produces, imports, or processes ≥25,000 pounds of any TRI chemical or otherwise uses >10,000 pounds of a TRI chemical in a calendar year (EPA 2005).

Section 112 of the Clean Air Act (CAA) lists 2,4-DNT as one of the original hazardous air pollutants (HAPs) known to cause, or suspected of causing, cancer or other serious human health effects or ecosystem damage (EPA 2000b). EPA's National Emission Inventory (NEI) database collects information about sources that emit criteria air pollutants and their precursors, and HAPs for the 50 United States, Washington DC, Puerto Rico, and the U.S. Virgin Islands (prior to 1999, criteria pollutant emission estimates were maintained in the National Emission Trends [NET] database and HAP emission estimates were maintained in the National Toxics Inventory [NTI] database). The NEI database derives emission data from multiple sources including state and local environmental agencies; the TRI database; computer models for on-road and off-road emissions; and databases related to EPA's Maximum Achievable Control Technology (MACT) programs to reduce emissions of hazardous air pollutants. Using composite data from the NTI database from 1990 to 1993, it was estimated that the annual emissions of 2,4-DNT in the United States was approximately 3.5 tons per year during that time frame (EPA 2000b). Data downloaded from the 2005 NEI indicated that the total emission of 2,4-DNT was approximately 4 tons, with the biggest source arising from nonpoint source waste disposal.

6.2.1 Air

Estimated releases of 7,621 pounds (~3.5 metric tons) of 2,4- and 2,6-DNT to the atmosphere from nine domestic manufacturing and processing facilities in 2013, accounted for about 99% of the estimated total environmental releases from facilities required to report to the TRI (TRI13 2015). These releases are summarized in Tables 6-1 and 6-2. The TRI database does not contain information regarding the other isomers of DNT.

The Great Lakes Regional Air Toxic Emissions Inventory Project estimated that 1,894 pounds of 2,4-DNT were emitted to the air of the Great Lakes watershed in 2002 (Great Lakes Commission 2006). The overwhelming majority of these emissions arose from local point and area sources such as production or use facilities. No data were available for the other isomers of DNT.

Minute amounts of nitrotoluene are formed by the photochemical reaction of toluene, nitrogen oxides, and sunlight (Atkinson et al. 1980). Although DNTs could be formed subsequently, they would be subject to photolysis and would not be likely to accumulate enough to contribute significantly to human exposure.

6.2.2 Water

Estimated releases of 2 pounds (~0.001 metric tons) of 2,4- and 2,6-DNT to the water from nine domestic manufacturing and processing facilities in 2013, accounted for about 0.3% of the estimated total environmental releases from facilities required to report to the TRI (TRI13 2015). These releases are summarized in Tables 6-1 and 6-2. The TRI database does not contain information regarding the other isomers of DNT.

The detection of DNTs in water has been reported (Feltes et al. 1990; Shackelford and Keith 1976; Staples et al. 1985). Both 2,4- and 2,6-DNT are recognized as major components in waste waters from TNT manufacturing facilities (Spanggord and Suta 1982; Spanggord et al. 1982a). DNTs occur in samples of TNT waste waters at concentrations of 0.04–48.6 mg/L (2,4-DNT) and 0.06–14.9 mg/L (2,6-DNT). The occurrence of DNTs in waste waters from other manufacturing uses (e.g., polyurethane forms) has not been reported. The frequency of detection of DNTs in surface waters, as indicated in the STORET database (Staples et al. 1985), is low. Slightly over 1% of the stations reported detectable quantities of DNTs, and the median of positive samples was <10 µg/L (0.01 mg/L). The presence of DNTs was not detected in samples of sediment or biota.

Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use 2,4-Dinitrotoluene[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
IA	1	500	0	0	0	0	500	0	500
IL	1	0	0	0	0	0	0	0	0
IN	3	2	0	0	0	0	2	0	2
KY	1	5,500	0	0	0	0	5,500	0	5,500
LA	1	0	0	0	0	0	0	0	0
OH	1	2	0	0	21	0	2	21	23
TX	3	14	0	0	0	0	14	0	14
UT	1	2	0	0	0	0	2	0	2
VA	2	0	2	0	0	1	2	1	3
Total	14	6,020	2	0	21	1	6,022	22	6,044

[a]The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.
[b]Data in TRI are maximum amounts released by each facility.
[c]Post office state abbreviations are used.
[d]Number of reporting facilities.
[e]The sum of fugitive and point source releases are included in releases to air by a given facility.
[f]Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).
[g]Class I wells, Class II-V wells, and underground injection.
[h]Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.
[i]Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown.
[j]The sum of all releases of the chemical to air, land, water, and underground injection wells.
[k]Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI13 2015 (Data are from 2013)

Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use 2,6-Dinitrotoluene[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
IN	1	1	0	0	0	0	1	0	1
KY	1	1,600	0	0	0	0	1,600	0	1,600
OH	1	0	0	0	21	0	0	21	21
TX	1	0	0	0	0	0	0	0	0
Total	4	1,601	0	0	21	0	1,601	21	1,622

[a]The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.
[b]Data in TRI are maximum amounts released by each facility.
[c]Post office state abbreviations are used.
[d]Number of reporting facilities.
[e]The sum of fugitive and point source releases are included in releases to air by a given facility.
[f]Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).
[g]Class I wells, Class II-V wells, and underground injection.
[h]Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.
[i]Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown
[j]The sum of all releases of the chemical to air, land, water, and underground injection wells.
[k]Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI13 2015 (Data are from 2013)

6.2.3 Soil

Estimated releases of 42 pounds (~0.019 metric tons) of 2,4- and 2,6-DNT to soils from 6 domestic manufacturing and processing facilities in 2013, accounted for about 0.6% of the estimated total environmental releases from facilities required to report to the TRI (TRI13 2015). The TRI database does not contain information regarding the other isomers of DNT. There were no reported releases to underground injection wells. These releases are summarized in Tables 6-1 and 6-2.

The extensive use of DNTs as intermediates in the synthesis of TDI and polyurethane foam is not a reported source of releases to soil. However, DNTs can be contaminants in the soil from explosives, propellants, etc. Residues of DNTs were observed to be deposited onto the surface of military live-fire training soil (Jenkins 2006). As a result, mean surface soil concentrations ranged from <0.001 to 84 mg/kg for 2,4-DNT and from <0.001 to 4.6 mg/kg for 2,6-DNT (Jenkins 2006).

6.3 ENVIRONMENTAL FATE

6.3.1 Transport and Partitioning

The water solubilities of DNTs are moderate (Callahan et al. 1979), and the octanol-water partition coefficients are low (EPA 1982c). As a result, there is a potential for DNTs to leach from soil into groundwater.

The solubility of nitroaromatic compounds in seawater and pure water at different temperatures was examined by Luning Prak and O'Sullivan (2007) and Kholod et al. (2011). Luning Prak and O'Sullivan (2007) found that the solubility in both seawater and pure water was observed to increase with increasing temperatures (5–40 °C) and decrease with increasing salinity (0–100%) for 2,3-DNT and 2,6-DNT. Kholod et al. (2011) found that the Conductor-like Screening model for Real Solvents (COSMO-RS) was effective in estimating the solubility of 2,5-DNT. The same trends that were observed in the experimental values were also observed in the estimated values. These solubility models are useful in the characterization of the fate of nitro compounds in marine systems.

U.S. Army (1980) determined partitioning of 2,4-DNT onto environmental media and found that the soil organic carbon partition coefficient (K_{oc}), the octanol-water partition coefficient (log K_{ow}), and the partition bioconcentration factor (Kb) were 364, 2, and 64, respectively. EPA (1982c) calculated sediment-water partitioning coefficients of 45 and 92 for 2,4- and 2,6-DNT, respectively. Depending on

the nature of the sediment load, the total concentration of DNTs carried in the soil and water column could be high. The low Henry's Law constants for the isomers of DNT (see Table 4-2) suggest that volatilization from water and moist soil surfaces will occur slowly. U.S. Army (1980) used experimentally determined volatilization rate constants of 2,4-DNT obtained under laboratory conditions, to extrapolate a volatilization rate constant for 2,4-DNT in an environmental aquatic water body with a depth of approximately 6.5 feet and ambient temperature of about 20 °C. Using this extrapolated rate constant, a volatilization half-life of >400 days is estimated for 2,4-DNT.

Steady-state whole-fish bioconcentration factors (BCFs) of 2,4-DNT measured in carp during two different equilibrium periods were 9.15 and 4.15 (Lang et al. 1997). BCF values of DNT (mixed isomers CAS Registry Number 25321-14-6) measured in carp over a 6-week incubation period were 0.6–2.9 at a nominal concentration of 0.25 ppm and 3.2–21.2 at a nominal concentration of 0.025 ppm (NITE 2002). BCF values of <2.7 were also measured for 3,4-DNT in carp over a 6-week incubation period (NITE 2002). These data suggest that bioaccumulation in fish and other aquatic organisms will be low.

Direct measurement of plant uptake of DNTs has not been made, but plant uptake is predicted to occur based on its low octanol-water partition coefficient. Structural analogy with 1,3-dinitrobenzene and 4-nitrotoluene (McFarlane et al. 1987) suggests that 2,4- and 2,6-DNT would be readily taken up by plants. Plant uptake of related nitroaromatic compounds such as 2,4,6-TNT and its byproduct, 4-amino-2,6-DNT, has also been observed and is inversely proportional to soil organic carbon content (Pennington 1988). The relative concentrations in the plants was root > stem > leaves > seed and food (U.S. Army 1990).

Uptake of 2,4-DNT was observed in a cell suspension culture of separate plantlets, *Senecio jacobaea*, *Saponaria officinalis*, and *Phragmitis australis.* The concentration of 2,4-DNT was reduced to 20 mg/L from 50 mg/L after 17 days by *S. jacobaea* (yellowweed). Concentrations of 2,4-DNT were rapidly decreased after 6 days by *S. officinalis* (soap wort). The reduction products, 4-amino-2-nitrotoluene and 2-amino-4-nitrotoluene were observed after 2 days. No reduction products were observed after metabolism of 2,4-DNT with *P. austrailis* (reed) given that the uptake of 2,4-DNT by *P. australis* was much slower than in the other plantlets (Podlipna et al. 2015).

Root uptake by plants can be inhibited by the increase of sorption to the soil. Sorption can reduce the bioavailability of organic compounds to target organisms. In a bioavailability and phytotoxicity study, the toxicity of 2,4-DNT to the aquatic duckweed plant was significantly reduced by sorption to potassium

smectite clay (Roberts 2007). In general, 2,4-DNT is expected to adsorb to suspended soil and sediment in water based on its K_{oc}. Nitroaromatic compounds adsorb to the soil mainly by forming electron-donor acceptor complexes with clays (Haderlein 1996). In anoxic conditions, sorption of the tested aromatic compounds followed the order of DNTs>ANT>DATs, where monoamines (ANT) and diaminotoluenes (DAT) were the derivatives of DNTs (Yang 2008).

The toxicity of the transformation products of 2,6-DNT was studied by Nipper et al. (2005) in spiked sandy, fine-grained marine sediments and in seawater. In environments with the spiked sediments, toxicity to the micro-algae, *Ulva fasciata,* decreased as 2,6-DNT was biotransformed to 2-amino-6-nitrotoluene. Subsequent studies indicated that toxicity to the copepod *Schizopera knabeni* increased with biotransformation. Therefore, 2-amino-6-nitrotoluene was more toxic than 2,6-DNT to the copepod, and less toxic to the micro-algae. Likewise, in environments with the spiked seawater tests, 2-amino-6-nitrotoluene was also more toxic than its parent compound to the copepod, but not to the micro-algae. These studies indicate that toxicity to the 2,6-DNT degradation products vary with the environment and species.

The Pre-Biologic Screen (PBS) model for ecotoxicologic effects (Gillett 1983) estimates a score (heavy concern, concern, or no concern) for a compound determined by the octanol-water partition coefficient, the Henry's Law constant, and the half-life in the medium of interest. The score indicates the compound's potential for (a) bioaccumulation and multi-media/multispecies effects, (b) bioaccumulation and long-term effects, (c) persistence and interactions in the water column, including plant uptake and leaching, and (d) direct and indirect effects in the atmosphere (e.g., smog formation, plant fumigation, stratospheric modification). Both 2,4- and 2,6-DNT are of concern or heavy concern only for (c), persistence and interactions in the water column, depending on the value used for half-life. Since the degradation of DNTs is so dependent on environmental conditions and the presence of effective microorganisms, the protective view that DNTs are of heavy concern for persistence in water, plant uptake, and leaching to groundwater may be warranted. The lack of concern for bioaccumulation, multimedia/multispecies action, and atmospheric action also appears to be justified.

6.3.2 Transformation and Degradation

6.3.2.1 Air

Based on their rapid photolysis in water, DNTs are presumed to be subject to oxidation of its methyl group, decarboxylation, ring oxidation, and/or nitroreduction in air and sunlight. DNTs are slowly

degraded in the atmosphere by reaction with photochemically produced hydroxyl radicals; the half-life in air is estimated to be approximately 50 days for the DNT isomers (EPA 2011).

6.3.2.2 Water

DNTs may be degraded in water through several mechanisms, including photolysis, microbial biodegradation, ozonation and chlorination, and oxidation by strong oxidants such as hydrogen peroxide, ozone, or oxone (Bausum et al. 1992; EPA 1979; Freedman et al. 1996; Ho 1986; Noguera and Freedman 1996; U.S. Navy 1977). Ho (1986) studied photooxidation of 2,4-DNT in aqueous solution in the presence of hydrogen peroxide and suggested the following degradation pathway of 2,4-DNT: 2,4-DNT → 1,3-dinitrobenzene → hydroxynitrobenzene derivatives → carboxylic acids → CO_2, H_2O, and HNO_3. Oxidation of aqueous 2,4-DNT with hydrogen peroxide or ultraviolet (UV) irradiation alone was very slow, and elimination was not complete. Dillert et al. (1995) reported that degradations of DNTs and several other nitroaromatics were accelerated in irradiated TiO_2 suspensions and that the degradation rates were dependent solution pH and light intensity. At given temperature, pH, and photo intensity, degradation rates were shown to decrease in order of 2-nitrotoluene > nitrobenzene > DNTs > 1,3-dinitrobenzene > TNT > trinitrobenzene, and the degradations followed first-order kinetics. The photocatalytic oxidation of 2,6-DNT in aqueous suspension of TiO_2 produces ammonium and nitrate ions as the predominant species (Kumar and Davis 1997).

The presence and potential toxicity of DNTs in waste water have spurred considerable study of the abiotic and biotic fate of 2,4- and 2,6-DNT. U.S. Army (1980) reported that the half-lives of DNTs in three sunlit natural waters were 3–10 hours, whereas the photolysis half-life in distilled water was 43 hours. At different latitudes and sunlight conditions, they estimated that the photolysis half-life in waters would range from approximately 1.8 days (summer sunlight conditions) to 11.5 days (winter conditions). Simmons and Zepp (1986) found that dissolved or suspended humic substances greatly enhance (10–17 times) indirect photolysis of nitroaromatic compounds with a nitro group ortho to a methyl group.

DNTs may be also degraded by ozonation and chlorination. Lee and Hunter (1985) reported that both ozone and chlorine produced <17% reduction of 2,6-DNT, whereas 2,4-DNT was more vulnerable, yielding about 35% reduction by chlorine and 60% reduction by ozone. Contact time did not appear to have any impact on the reduction rates.

Studies have shown that DNTs can be used as a sole carbon source for microorganisms commonly detected in natural waters. Using bay water obtained near an Army munitions facility as inoculum, >90% degradation of 2,4-DNT was observed after 6 days following a 2–3-day lag period (U.S. Army 1980). Under anaerobic conditions, the half-life of 2,6-DNT in non-acclimated sewage was found to be 28 days, with no loss of the compound under aerobic conditions during the same period (Hallas and Alexander 1983). Liu et al. (1984) reported complete biotransformation of 2,4-DNT within 14 days under anaerobic conditions using a fresh sample of activated sludge diluted with distilled water as inoculum. The intermediates of biotransformation were identified as 2-amino-4-nitrotoluene, 4-amino-2-nitrotoluene, 2-nitroso-4-nitrotoluene, and 4-nitroso-2-nitrotoluene. Parrish (1977) investigated 190 fungal species from 98 genera, but found only 5 capable of 2,4-DNT biotransformation. Valli et al. (1992) reported degradation of 2,4-DNT as the sole source of carbon and energy by the lignin-degrading fungus *Phanerochaete chrysosporium* under aerobic conditions, resulting in stoichiometric release of nitrate.

Several additional studies have shown biodegradation of DNTs from microorganisms isolated from areas that are frequently exposed to DNTs and other structurally similar compounds such as TNT (Bausum et al. 1992; Freedman et al. 1996). Bausum et al. (1992) found complete degradation of 20 ppm 2,4-DNT and 20 ppm 2,6-DNT in water samples taken downstream a short distance from the Radford Army Ammunition Plant in Radford, Virginia. A lag time was noted prior to the breakdown for both of the two compounds with 2,4-DNT exhibiting the shorter lag time. Microbial enrichment cultures were developed from the collected water samples by exposing the cultures to increasing concentrations of 2,4- and 2,6-DNT. Degradation and visible turbidity in the suspension medium were noted up to a level of 130 ppm. In a separate but related study, degraded DNTs were shown to be converted to CO_2 with 2,4-DNT conversion occurring at a greater rate than that of 2,6-DNT; concentrations ranged from 0.004 to 10.0 ppm (Bausum et al. 1992). The rate of mineralization to CO_2 was concentration dependent and increased with increasing concentration.

In the Bradley et al. (1994) study, a culture of microorganisms taken from aquifer sediments at an explosives-contaminated site was observed to be capable of transforming 2,4- and 2,6-DNT. Breakdown products from 2,4-DNT degradation included 4-amino-2-nitrotoluene and 2-amino-4-nitrotoluene. Carbon dioxide was released during the degradation process. Aminonitrotoluene isomers were also detected as breakdown products of a solution of 2,4-DNT and ethanol (Freedman et al. 1996). The Freedman et al. (1996) study exposed an inoculum from a wastewater treatment plant at an ammunition plant to a solution of 2,4-DNT and ethanol and a solution of 2,4-DNT and ether. The concentration of 2,4-DNT at each application was 0.55 mM and the concentrations of ethanol and ether were 600 and

142 mg/L, respectively. Ethanol and ether were chosen because they are often found in munitions manufacturing waste-water streams along with 2,4-DNT. As stated above, aminonitrotoluene isomers were detected as products of the solution containing 2,4-DNT and ethanol. The degradation of ethanol was believed to be driving a partial reduction of 2,4-DNT before the oxidation of 2,4-DNT took place. In contrast, ether at the applied concentration slowed the rate of 2,4-DNT degradation. Low chemical oxygen demand during the studies suggests that DNTs were mineralized to a significant degree.

Spanggord et al. (1991) studied the degradation pattern of 2,4-DNT using, water samples obtained from the Waconda Bay located near a TNT manufacturing facility (Volunteer Army Ammunition Plant) in Chattanooga, Tennessee. Samples were enriched with 2,4-DNT and incubated for 5 days. The *Pseudomonas sp.* strain aerobically degraded 2,4-DNT as a sole source of carbon, and the nitro groups were oxidatively removed without prior reduction to the amines. Since this *Pseudomonas sp.* strain used 2,4-DNT as a carbon source, it may be useful for the removal of other nitrotoluenes from contaminated soils or from industrial waste streams. Likewise, it may also be useful since the oxidative removal of the nitro groups bypasses the accumulation of toxic amino derivatives.

The co-metabolism of 2,4-DNT with ethanol, methanol, and acetic acid has been studied under anaerobic conditions (Cheng et al. 1995). High concentrations of ethanol accelerated the reductive transformation of 2,4-DNT by supporting the growth of the anaerobic bacteria. The rate of 2,4-DNT biotransformation was much higher with the addition of ethanol than with the addition of methanol or acetic acid in anaerobic conditions (Cheng et al. 1995). In a culture using a continuous flow laboratory fermentor under anaerobic conditions with both 2,4-DNT and ethanol as substrates, 2,4-DNT was completely transformed to 2,4-diaminotoluene (Cheng et al. 1996). During the biotransformation, two intermediates were formed: 2-amino-4-nitrotoluene and 4-amino-2-nitrotoluene.

2-Amino-4-nitrotoluene and 4-amino-2-nitrotoluene were also formed in the transformation of 2,4-DNT to 2,4-aminotoluene by the marine microbial culture, *Shweanella marisflava* EP1. *S. marisflavi* EP1 acts to reduce 2,4-DNT during respiration under anaerobic conditions by using lactate as an electron donor (Huang et al. 2015).

The products formed from anoxic biotransformation of 2,4-DNT by two denitrifying enrichment cultures with ethanol provided as a primary substrate were characterized in one study (Noguera and Freedman 1997). One culture was developed with inoculum acclimated to 2,4-DNT, the other with activated sludge that was not routinely exposed to nitroaromatic compounds. The acclimated culture consumed 2,4-DNT

twice as fast as the unacclimated culture, with reduction of 2,4-DNT to aminonitrile toluenes as the initial pathway. The principal metabolites identified in the acclimated culture were 6-nitroindazole, 2-nitrotoluene, and 4-nitrotoluene, as well as products from acetylation at the *para* position (4-acetamide-2-nitrotoluene and 4-acetamidetoluene). Reduction of aminonitrotoluenes to 2,4-diaminotoluene also occurred, and its subsequent disappearance resulted in accumulation of significant amount of nonfilterable material in both cultures. The soluble metabolites formed from the unacclimated culture were more hydrophilic. Initial characterization of the highly hydrophilic metabolites indicated approximately equal amounts of negatively-charged and neutral compounds.

Biotransformation of DNT by a *Pseudomonas aeruginosa* strain, which was isolated from the waste water of the Radford Army Ammunition Plant (RAAP) located in Radford, Virginia was observed under both aerobic and anoxic conditions (Noguera and Freedman 1996). The biotransformation was mainly reductive under both of these conditions and was reflective of the cometabolic transformations that can occur in the presence of easily degradable organic matter such as ethanol. *P. aeruginosa* reduced both nitro groups of DNTs resulting in the primary breakdown products of 4-amino-2-nitrotoluene and 2-amino-4-nitrotoluene, with small amounts of 2,4-diaminotoluene also formed. Several DNT metabolites from acetylation of the arylaminos were also identified, including 4-acetamide-2-nitrotoluene, 2-acetamide-4-nitrotoluene, 4-acetamide-2-aminotoluene, and 2,4-diacetamidetoluene.

Clostridium acetobutylicum has received interest in anaerobic TNT bioremediation systems due to their ability to rapidly reduce aryl nitro groups. Results indicated that dihydroxylaminotoluenes are the predominant primary intermediates in the transformation of the DNT isomers by *C. acetobutylicum* and that further metabolism of the dihydroxylaminotoluenes in cell cultures and extracts resulted in the formation of arylamines through hydroxylamine reduction (Hughes 1999).

6.3.2.3 Sediment and Soil

Microorganisms indigenous to surface soils collected at a munitions-contaminated site were reported to transform 2,4- and 2,6-DNT to amino-nitro intermediates within 70 days (Bradley et al. 1994). Another study showed that composting can decrease the concentrations of explosives, such as TNT, in contaminated soil, but neither 2,4- nor 2,6-DNT was detected in the compost (Griest et al. 1993). A study of soil sample handling times indicated that lower temperatures retard the breakdown of 2,4-DNT (Grant et al. 1995). 2,4-DNT was observed to be more stable than TNT in contaminated soils (Grant et al. 1995).

DNTs were not readily biodegradable using a standardized Organisation for Economic Co-operation and Development (OECD) test. 3,4-DNT and mixed isomers of DNT (CAS Registry Number 25321-14-6) achieved 0% of their theoretical biochemical oxygen demand (BOD) over a 14-day incubation period using an activated sludge inoculum and the modified MITI (OECD 301 C) test (NITE 2002). The DT_{50} of 2,4-DNT in an organic soil (82% sand, 13% silt, 5.1% clay, 2.3% organic carbon) was reported as 7 days and the DT_{90} was 191 days (UNEP 2004); however, other studies cited in this report indicated limited degradation of DNT under environmental conditions. In a test system maintained under anaerobic conditions, performed according to EPA-Guideline No. 796.3140, 0% biodegradation was observed within 56 days (UNEP 2004).

In a study conducted by Nishino et al. (1999), the mineralization of 2,4- and 2,6-DNT was examined in soil slurries. DNT-degrading bacteria cultures commonly used in contaminated water systems were examined to see if they were able to degrade DNTs in contaminated soils. It was found that microorganisms indigenous to the soils did not convert DNTs to aminonitrotoluenes during the short incubation times required to mineralize DNTs. DNT-degrading bacteria, however, removed over 99% of the initial DNTs in the soil after 2–3 days of incubation. Disappearance of DNTs was accompanied by $^{14}CO_2$ release and stoichiometric appearance of nitrite.

In another study, soil from a former ammunition plant was anaerobically treated in a laboratory slurry reactor. 2,4-DNT was completely reduced to undetectable levels in the reactor. The contaminated soil was also tested in a larger technical scale where the soil slurry was treated anaerobically and subsequently aerobically to complete the bioremediation process. An overall reduction of > 99% of the contaminants was observed, and ecotoxicological tests showed that the toxicity of the soil could not be detected after the anaerobic/aerobic process (Lenke et al. 1998).

The biotransformation of 2,4- and 2,6-DNT by the indigenous microflora contained in marine sediment from a shipwreck site near Halifax Harbour was studied by Yang et al. (2008). Incubation of 2,4- and 2,6-DNT in anaerobic sediment-water slurries at 10 °C led to the disappearance of both 2,4- and 2,6-DNT and their reduction to their monoamine derivatives in 10 days. The derivatives were progressively reduced even further to 2,4- and 2,6-diaminotoluenes in a series of 50 days for 2,4-DNT and 35 days for 2,6-DNT.

The biodegradation of sorbed 2,4-DNT by the *Burkholderia sp.* strain was examined in a clay-rich aggregated porous medium by Ortega-Calvo et al. (1999). *Burkholderia sp.* exhibited sensitivity to the

cold and was unable to complete the degradation process at low temperatures (Monti 2005). Therefore, *P. fluorescens* was genetically modified (by intergeneric transformation of the DNT genes from the *Burkholderia sp.* strain to the *P. fluorescens* strain) to use 2,4-DNT as the sole nitrogen source to completely degrade the compound (Monti 2005). *P. fluorescens* was shown to be capable of degrading 2,4-DNT in temperatures as low as 10 °C and significantly decreased the toxic effects of 2,4-DNT on specific plants.

The correlation between the mutagenicity and biodegradability of TNT and its analogs, including 2,4- and 2,6-DNT, was reported in Maeda et al. (2007). The umu test using luminescent bacteria was employed to assess the mutagenicity and biodegradability of the nitroaromatic compounds. The *Pseudomonas sp.* strain TM15 bacteria isolated from TNT contaminated soils in Japan was found to biotransform the aromatic compounds harboring three nitro groups efficiently, although 2,4- and 2,6-DNT had low degradation rates. It was demonstrated that the mutagenicity, induced by the nitroaromatic compounds, increased with biodegradability.

In the presence of ultraviolet (UV) exposure, photo-transformation of 2,6-DNT began immediately after simulated solar radiation (SSR) in sandy and fine-grained sediment, with 89% being photo-transferred after 24 hours, and none remaining for photo-transfer after 72 hours (Nipper et al. 2004).

6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to DNTs depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of DNTs in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on DNT levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable. The analytical methods available for monitoring DNTs in a variety of environmental media are detailed in Chapter 7.

6.4.1 Air

Concentrations of DNTs in the ambient air have been reported to be low (0.03–0.1 mg/m^3) or undetectable (Woollen et al. 1985). Occupationally, concentrations of 2,4-DNT found in the stationary air and the personal air of the mechanical plant operating room, rest rooms, and office ranged from <0.1 to 20 $\mu g/m^3$ (<$1x10^{-4}$–0.020 mg/m^3) (Letzel et al. 2003). NIOSH (1980) measured breathing zone air

concentrations of Tg-DNT that ranged from not detected (below detection limits) to 23 μg/m^3 (0.023 mg/m^3) (TWA). Tg-DNT concentrations in area air samples ranged from not detected to 420 μg/m^3 (0.42 mg/m^3) (TWA). NIOSH (1982) reported that area air samples in a manufacturing facility contained TWA concentrations of Tg-DNT that ranged from not detected to 890 μg/m^3 (0.89 mg/m^3). Levine et al. (1985b) also measured personal air samples of 2,4-DNT at 10–440 μg/m^3 (0.01–0.44 mg/m^3) and 2,4- and 2,6-DNT at 50–590 μg/m^3 (0.05–0.590 mg/m^3) in the workplace.

6.4.2 Water

DNTs are rarely detected in public drinking water supplies. 2,4-DNT and 2,6-DNT are priority pollutants, and amendments to the Safe Drinking Water Act require that they be monitored for by large community water systems (CWSs) and non-transient non-community water systems (NTNCWSs) and a statistically representative sample of qualifying small CWSs and NTNCWSs (EPA 2008a, 2008b). Contaminant occurrence data collected under the First Unregulated Contaminant Monitoring Regulation (UCMR 1) showed only a single detection of DNTs. Since the health reference level (0.05 μg/L or 5x10^{-5} mg/L) for each isomer was below the minimum reporting level of 2 μg/L (0.002 mg/L), the data were reported as only as detections exceeding this level. Among the small public water systems (797 tested), there were no detections of 2,4-DNT in 3,251 samples taken, and there was only 1 detection out of 30,513 samples obtained from large systems throughout the United States (3,076 tested). This single detection of 333 μg/L (0.333 mg/L) was in a surface water sample obtained from an entry point source at a large public water system in the State of Tennessee (EPA 2008b). 2,6-DNT was not detected in any of the 33,765 samples (both large and small systems) for which it was tested. A total of 3,873 public water systems were tested for 2,6-DNT, of which 1,970 relied on ground water sources and 1,903 relied on surface water sources (EPA 2008b).

DNTs have been detected in surface water and groundwater near source locations such as munitions sites. Concentrations of 2,4- and 2,6-DNT obtained from a small brook and the Losse River, Germany adjacent to a former ammunition plant were 0.5–13.0 and 0.1–7.6 μg/L (5x10^{-4}–0.013 and 1x10^{-4}–0.0076 mg/L), respectively (Feltes et al. 1990). Two ponds located on a closed munition site in Germany had concentrations of 2,4-DNT ranging from 0.8 to 1.2 μg/L (8x10^{-4}–0.0012 mg/L) and concentrations of 2,6-DNT ranging from 0.07 to 0.3 μg/L (7x10^{-5}–3x10^{-4} mg/L) (Feltes et al. 1990). Monitoring studies at three polluted locations of the Elbe River in Germany found concentrations of 2,4-DNT of 0.1–1.3 μg/L (1x10^{-4}–0.0013 mg/L), while concentrations of 2,6-DNT were 0.08–0.5 μg/L (8x10^{-5}–5x10^{-4} mg/L) (Feltes et al. 1990). Sohr et al. (1995) reported 2,4- and 2,6-DNT concentrations of 0.7 and 3.1 μg/L

($7x10^{-4}$ and 0.0031 mg/L), respectively, at contaminated warfare sites in Germany. Other less-contaminated sites contained 28 ng/L ($2.8x10^{-6}$ mg/L) 2,4-DNT and 19 ng/L 2,6-DNT ($1.95x10^{-5}$ mg/L) (Sohr et al. 1995). In the seawater of Dokai Bay in Japan, 2,4- and 2,6-DNT were measured at levels of not detected (ND)–206 and ND–14.8 µg/L (ND–0.206 and ND–0.0148 mg/L), respectively, in an area receiving effluent from an industrial plant (Hashimoto et al. 1982). 2,3-DNT was also detected, but at much lower levels (ND–0.412 µg/L) (ND–$4.12x10^{-4}$ mg/L). DNT levels as high as 10,000 µg/L (10 mg/L) were reported in potable groundwater at the Joliet Army Ammunition Plant located in Will County, Illinois (EPA 2008a). The dates that these levels were obtained are not known. Levels were also reported as 3,200 (3.2 mg/L) and 2,700 mg/L (2.7 mg/L) in 1989 (Agency for Toxic Substances and Disease Registry 2009); however, current levels of DNTs may be significantly lower. 2,3-, 2,5-, 3,4-, and 3,5-DNT isomers were identified in both monitoring wells and a few private water supply wells near the Badger Army Ammunition Plant site in Wisconsin (EPA 2008a).

6.4.3 Sediment and Soil

Hoke et al. (1993) reported that only low concentrations of 2,4- and 2,6-DNT were detected in sediment of the Great Calumet River-Indian Harbor. Concentrations of 2,4-DNT in sediment pore water ranged from the detection limit of 0.01 to 0.07 µg/L ($1x10^{-5}$–$7x10^{-5}$ mg/L). 2,4-DNT concentrations in sediment pore water ranged from 0.1 to 1.7 µg/L ($1x10^{-4}$–0.0017 mg/L). 2,6-DNT was not detected in sediment samples (limit of detection [LOD]=0.01 µg/L or $1x10^{-5}$ mg/L) and subsequently was not analyzed for in sediment pore water. 2,4-DNT and 2,6-DNT were identified in bed sediment collected from 20 major river basins in the United States for the 1992–1995 sampling period (Lopes and Furlong 2001). The maximum detected concentrations were reported as 170 µg/kg for 2,4-DNT (detected in 0.6% of 519 sites sampled) and 93 µg/kg (detected in 1% of 518 sites sampled) for 2,6-DNT.

Concentrations ranging from <0.1 mg/kg (detection limit) to 117 mg/kg of 2,4-DNT were found at the Joliet Army Ammunition Plant, in Joliet, Illinois, an NPL site. 2,6-DNT was detected on this site at concentrations ranging from <0.1 to 8 mg/kg (Simini et al. 1995). The concentrations of 2,4- and 2,6-DNT were reported as 19 and 1.38 g/kg, respectively, in soil samples obtained at the Volunteer Army Ammunition Plant located in Chattanooga, Tennessee and levels of 2,4- and 2,6-DNT were reported as 8.9 and 0.48 g/kg, respectively, in soil samples obtained at the Badger Army Ammunition Plant located in Wisconsin (UNEP 2004). The concentration of 2,4-DNT in soil samples at the Gyttorp facility in Sweden, which was used for explosives manufacturing from 1864 to 1995 was 4 g/kg (UNEP 2004). The concentrations of 2,4- and 2,6-DNT measured in soil samples obtained from the decommissioned TNT

manufacturing facility in Hessisch Lichtenau Germany were reported as 3.6 and 2.5 g/kg, respectively (UNEP 2004).

Residues of DNTs were detected on the surface of military live-fire training soil (Jenkins 2006). Mean surface soil concentrations ranged from <0.001 to 84 mg/kg for 2,4-DNT and from <0.001 to 4.6 mg/kg for 2,6-DNT at 23 military firing ranges in the United States and Canada (Jenkins 2006).

6.4.4 Other Environmental Media

Neither 2,4- nor 2,6-DNT were detected in samples of fish obtained from Lake Michigan tributaries and Grand Traverse Bay (Camanzo et al. 1987). DNTs were monitored for, but were not detected in, fish from Great Lakes harbors and tributaries in Ohio and Wisconsin (DeVault 1985).

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Sources of exposure to DNTs for the general population include processing facilities that manufacture or process DNTs, as well as hazardous waste sites that release this chemical. Populations residing near ammunition or explosive manufacturing facilities may be exposed to contaminated groundwater or soil. Exposure pathways to DNTs include dermal contact and incidental ingestion pathways. Since DNTs are not frequently detected in air, inhalation exposure to the general population is expected to be low. Occupational exposure to DNTs may occur from its use in the manufacture of toluene diisocyanate, in the production of explosives, in the manufacture of azo dye intermediates, and in organic synthesis in the preparation of toluidines and dyes (IARC 1996). Exposure may also occur at facilities that store or dispose the substance. Occupational exposure will involve inhalation, dermal contact, and incidental ingestion, with inhalation the most likely exposure pathway.

Studies on occupational exposure to DNTs are limited. Levine et al. (1985b) evaluated the 7-hour TWA personal exposure of workers to Tg-DNT and measured urinary metabolites of DNTs at a DNT manufacturing plant. Breathing zone exposure level of production unit operators to both 2,4- and 2,6-DNT averaged 0.26 mg/m^3 ($2.6x10^{-4}$ mg/L). Air exposure concentrations of loaders, who load storage tanks, collect samples, and perform cleaning tasks, averaged 0.32 mg/m^3 ($3.2x10^{-4}$ mg/L). Exposure of maintenance mechanics averaged 0.12 mg/m^3 ($1.2x10^{-4}$ mg/L), and the exposure of acid-stripper operators was 0.06 mg/m^3 ($6x10^{-5}$ mg/L). The highest personal air monitoring concentrations and levels of urinary metabolites were found to be for loaders, followed by process operators. The levels of urinary metabolites of DNTs in loaders and operators exceeded those that would have resulted from the inhaled

concentrations, although the workers wore gloves for operations that might have led to dermal exposure. Woollen et al. (1985) carried out biological monitoring studies of 28 workers at an explosives factory. The 2,4-DNT metabolite, 2,4-dinitrobenzoic acid was not detected or was present at very low levels in urine samples prior to the start of work; however, it was detected in all post-shift urine samples. The weakly mean post-shift urine concentration of 2,4-dinitrobenzoic acid was 17 mg/L. Concentrations of 2,4-DNT in air samples of the plant ranged from 0.02 to 2.68 mg/m^3 ($2.0x10^{-5}$–0.00268 mg/L). It was concluded that air concentrations could not solely account for the observed excretion levels of the metabolite, 2,4-dinitrobenzoic acid, indicating probable dermal uptake or inadvertent ingestion.

A cross-sectional study with 82 employees who dismantled military waste at the mechanical plant in Saxony, Germany was undertaken by Letzel et al. (2003). The maximum concentrations of 2,4-DNT in the ambient air was 20 µg/m^3 (0.02 mg/m^3). The maximum concentrations in the urine of workers regularly exposed to the ammunition were 2.1 µg/L (0.0021 mg/L) for 2,4-DNT, 95 µg/L (0.095 mg/L) for 2,4-dinitrobenzoic acid, and 3.6 µg/L (0.0036 mg/L) for 2,6-DNT.

In another study, Levine et al. (1986a) reported increases of heart disease among workers at two ammunition plants; one of which is located in Joliet, Illinois and the other located in Radford, Virginia. DNTs were manufactured and purified at the plant in Joliet, Illinois and were used in single-base propellant formulations at the plant in Radford, Virginia.

OSHA established an 8-hour TWA Permissible Exposure Limit (PEL) for DNTs (mixed isomers) as 1.5 mg/m^3, with skin designation to indicate the potential significant contribution to the overall exposure by the cutaneous route (OSHA 2013). The American Conference of Governmental Industrial Hygienist (ACGIH)'s Threshold Limit Value (TLV) for DNTs (mixed isomers) is 0.2 mg/m^3 ($2x10^{-4}$ mg/L), with skin notation (ACGIH 2014). TLV is the time-weighted average concentration for a conventional 8-hour workday and a 40-hour workweek to which it is believed that nearly all workers may be repeatedly exposed without adverse effect. The National Institute of Occupational Safety and Health (NIOSH) determined the Recommended Exposure Limit (REL) for DNTs (mixed isomers) as 1.5 mg/m^3 (0.0015 mg/L), with skin designation (NIOSH 2015).

6.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans. Differences from adults in susceptibility to hazardous substances are discussed in Section 3.7, Children's Susceptibility.

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults to avoid hazards (NRC 1993).

No studies are available that monitor the level of exposure of children to DNTs. No measurements have been made of DNTs or their metabolite levels in amniotic fluid, meconium, cord blood, or neonatal blood to test for prenatal exposure, nor have measurements been made of DNTs or metabolite levels in breast milk. However, because of the low octanol-water partition coefficients of DNTs and excretion in the urine, they are not expected to accumulate in maternal tissues.

Although DNTs can degrade in the environment, they have been detected at high levels at artillery sites or ammunition producing facilities. Therefore, children playing in soil contaminated with DNTs have the potential to be more exposed than adults, both because of this behavior and because of their larger skin surface area in proportion to their body weight for dermal absorption. Also, children drinking well water contaminated with DNTs might be exposed to more of the chemical than adults would be due to the fact that children drink more fluids per kilogram of body weight than adults. Significant dietary exposure is unlikely as DNTs are not expected to accumulate in animal tissues. However, ingestion of vegetables and crops grown in DNT-contaminated areas could be a source of exposure.

There were no studies that examine potential exposure of children from their parents work clothes, skin, hair, tools, or other objects removed from the workplace. No information is available concerning exposure from consumer products because DNTs are used mainly for military and industrial purposes.

Although DNTs are genotoxic in *in vivo* test systems, they have been found to be negative in dominant lethal mutations (U.S. Army 1979) and spermatocyte DNA repair (Working and Butterworth 1984). There is no evidence that exposure of parental germ cells to the active forms of DNTs could plausibly occur since DNTs do not accumulate in tissue.

6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In addition to individuals who are occupationally exposed to DNTs (see Section 6.5), there may be groups within the general population that have potentially high exposures (higher than background levels) to DNTs. These populations include individuals living in proximity to sites where DNTs were produced or sites where DNTs were disposed, and individuals living near one of the NPL hazardous waste sites where isomers of DNT have been detected in some environmental media (HazDat 2007).

Based on the available information, it appears that the highly-exposed populations would be workers exposed in manufacturing facilities.

Members of the general population are likely to be exposed only if they are near a local source of contamination, such as an industrial discharge or an abandoned waste site. There is also the possibility of exposure to DNTs from the gradual turnover of former military bases to local communities for public use. DNTs do not appear to be widespread in the environment, and they were not frequently detected at hazardous waste sites.

6.8 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of DNTs is available. Where adequate information is not available, ATSDR, in conjunction with NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of DNTs.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

6.8.1 Identification of Data Needs

Physical and Chemical Properties. Information regarding the physical and chemical properties of a chemical is essential for estimating the partitioning of the chemical in the environment. Information on the physical and chemical properties of DNTs is presented in Chapter 4 and the data appear to be adequate (HSDB 2012). The isomers of DNT have many similar traits, including identical molecular weights, but 2,4-DNT has higher melting and boiling points and a greater solubility in water than 2,6-DNT (HSDB 2012). DNTs are generally produced as a technical-grade mixture comprised of 95% 2,4- and 2,6-DNT and 5% other substances.

Production, Import/Export, Use, Release, and Disposal. According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit substance release and off-site transfer information to the EPA. The TRI, which contains this information for 2013, became available in October 2014. This database is updated yearly and should provide a list of industrial production facilities and emissions.

USITC statistics on synthetic organic chemical production (USITC 1987) do not describe DNT production. Uses of DNTs appear to be well characterized (HSDB 2012). The most commercially important use of DNT is as a chemical intermediate in the production of toluene diisocyanate, a precursor to polyurethane polymers (HSDB 2012). DNTs are recognized as potentially hazardous chemicals and are subject to a variety of regulations (see Chapter 8), but disposal practices and restrictions are not adequately documented.

Environmental Fate. The low octanol-water partition coefficients of the DNT isomers predict that DNTs released to the environment would not bioaccumulate and would be weakly bound to soil organic matter. Bioconcentration data also supports the notion that 2,4-DNT is not bioaccumulative in fish (NITE 2002; Lang 1997). The relatively low volatility and high solubility of DNTs indicate that they will tend to remain in water for long periods of time unless acted upon by light, oxygen, or biota, creating the potential for transportation to groundwater or surface water (Jenkins et al. 1986). DNTs have been found in waste water and groundwater in and around sites where munitions have been historically used (Jenkins et al. 1986; Spanggord and Suta 1982; UNEP 2004). The occurrence of DNTs in waste water from other manufacturing uses such as polyurethane forms has not been reported.

Given the importance of information about the behavior of DNTs in the water column, and the extensive range of available information relative to that topic (EPA 1982c; Gillett 1983; Hashimoto et al. 1982, 1984; Jenkins et al. 1986; U.S. Army 1980), the absence of substantive information about DNT releases to, or fate in, soils and air is less troublesome than it might be for many chemicals. Data on the persistence of DNTs in the vadose zone (the unsaturated zone lying between the ground level and the top of the groundwater) and groundwater are needed, as well as measured rates of plant uptake and metabolism. Because of the structurally specific nature of biotransformations, more information on the fate of DNT metabolites would be welcome.

Bioavailability from Environmental Media. No information is currently available that describes the bioavailability of DNTs in food. Data on bioavailability of soil/sediment residues would be helpful. Neither 2,4- nor 2,6-DNT were detected in samples of fish obtained from Lake Michigan tributaries and Grand Traverse Bay (Camanzo et al. 1987). DNTs were not detected in fish from Great Lakes harbors and tributaries in Ohio and Wisconsin (DeVault 1985).

Food Chain Bioaccumulation. Limited information indicates that DNTs are not widely distributed in the environment. Residues of DNTs have a low frequency of detection in water samples. These data indicate that bioaccumulation may not be an area of concern (Callahan et al. 1979; EPA 1982c). The log K_{ow} values for 2,4- and 2,6-DNT are 1.98 and 2.10, respectively (Callahan et al. 1979; EPA 1982c), indicating that bioaccumulation is not likely to occur. BCFs also indicate that DNTs are not expected to bioaccumulate in fish (NITE 2002; Lang 1997). Degradation of DNTs forms a variety of products. Additional information would help to confirm or refute indications of low potential for bioaccumulation of DNTs in foods.

Exposure Levels in Environmental Media. Reliable monitoring data for the levels of DNTs in contaminated media at hazardous waste sites are needed so that the information obtained on levels of DNTs in the environment can be used in combination with the known body burden of DNTs to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

The sparse information base suggests that widespread contamination by DNTs has not occurred (Staples et al. 1985). DNTs were detected at very low frequencies in drinking water (EPA 2008b). Analyses of wastewaters indicate that local contamination may occur (Feltes et al. 1990; Shackelford and Keith 1976; Spanggord and Suta 1982; Spanggord et al. 1982a). DNTs were also present in the sediment and soil near source areas (Hoke 1993; Simini 1995; Jenkins 2006).

Exposure Levels in Humans. No studies of exposure of the general population were found, and the occupational studies (Levine et al. 1985b; Woollen et al. 1985) are inadequate to ascertain "background" or nonoccupational exposure. Based on available information, the highly-exposed populations are those workers exposed in manufacturing facilities. Members of the general population are likely to be exposed only in that they are near a local source of contamination. Toxicokinetic data on occupationally- and environmentally-exposed humans will be helpful. Measurements of DNTs and their metabolite levels in blood and urine will be useful to provide an estimate of internal dose of exposure.

This information is necessary for assessing the need to conduct health studies on these populations.

Exposures of Children. No exposure or body burden studies have been conducted on children; consequently, it is not known if children differ from adults in their weight-adjusted intake of DNTs, or if unique exposure pathways for children exist. Since DNTs are not a widespread environmental contaminant, there are only two likely potential sources of exposure for children. Children living near a DNT-contaminated site might be exposed if DNTs have moved offsite in contaminated environmental media. If such a situation were identified, further site-specific studies of children's exposure could be conducted. Children whose parents work in manufacturing facilities that produce or use DNTs and are occupationally exposed to significant quantities of DNTs might potentially be exposed to DNTs transported home on their parents' work clothes, skin, hair, tools, or other objects removed from the workplace. If such a significant occupational exposure setting were identified, they might be the subject of a take-home exposure study.

Child health data needs relating to susceptibility are discussed in Section 3.12.2, Identification of Data Needs: Children's Susceptibility.

Exposure Registries. No exposure registries for 2,4- and 2,6-DNT were located. This substance is not currently one of the compounds for which a sub-registry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for sub-registries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to this substance.

The development of an exposure registry would provide valuable data on exposure levels and frequency. In addition to providing information on exposure levels and duration, a registry would be useful in identifying sources of exposure such as hazardous waste sites and manufacturing and use facilities. Knowledge about exposure levels and sources would be valuable in developing strategies to control unnecessary sources and these exposures. The ability to correlate sources and exposure levels with health effects would be useful in identifying disease conditions that may result from exposure to the chemical.

6.8.2 Ongoing Studies

No ongoing studies sponsored by NIH or EPA were identified for DNTs.