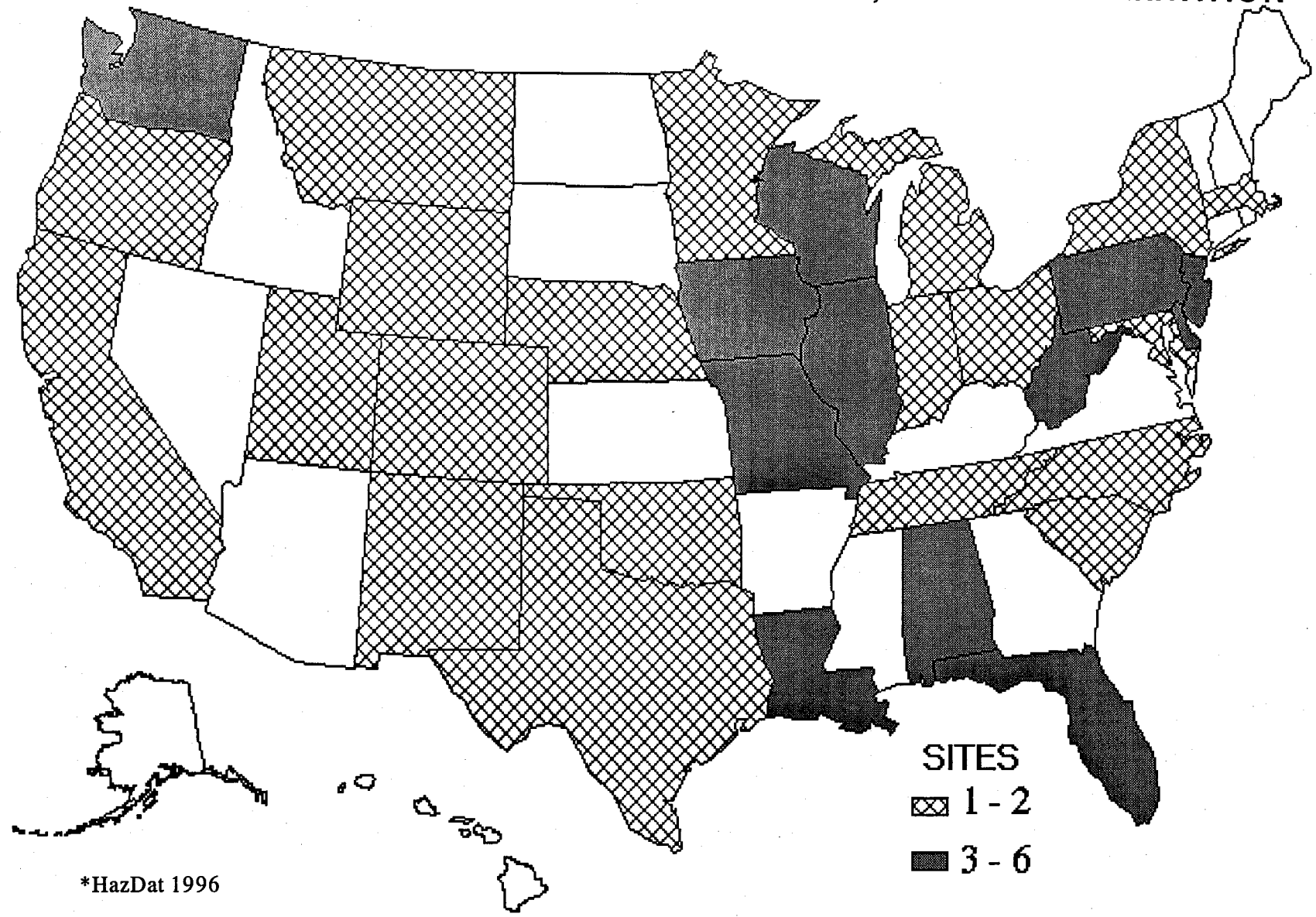# 5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

2,4-DNT and 2,6-DNT have been identified in at least 69 and 53 of the 1,467 current or former EPA National Priorities List (NPL) hazardous waste sites, respectively (HazDat 1998). However, the number of sites evaluated for 2,4-DNT and 2,6-DNT is not known. The frequency of these sites within the United States can be seen in Figures 5-l and 5-2.

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 2,4- and 2,6-DNT have been obtained primarily from the workplace.

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

The relatively low log octanol-water partition coefficients of the DNT isomers (1.98 and 1.72 for 2,4-DNT and 2,6-DNT, respectively) predict that DNT released to the environment would not bioaccumulate. However, the log octanol-water partition coefficients are sufficiently large to indicate adsorption to soil organic matter. The bioavailability and potential toxicity of soil- and sediment-bound products are also unknown. DNT is degraded by oxidation, photolysis, and biotransformation in water or soil, but a variety of degradation products, about which very little is known, is formed. DNT may bind to clays and clay colloids and facilitate its oxidation. It is otherwise expected to be stable in water because it is not hydrolyzed. The relatively low volatility and high solubility of DNT indicates that it will tend to remain in water for long periods of time, unless acted upon by light, oxygen, or biota. As a result, DNT can be transported to groundwater or surface waters.

FIGURE 5-1. FREQUENCY OF NPL SITES WITH 2,4-DNT CONTAMINATION*

SITES
- ⊠ 1 - 2
- ■ 3 - 6

*HazDat 1996

FIGURE 5-2. FREQUENCY OF NPL SITES WITH 2,6-DNT CONTAMINATION*

SITES
1 - 2
3 - 5

*HazDat 1996
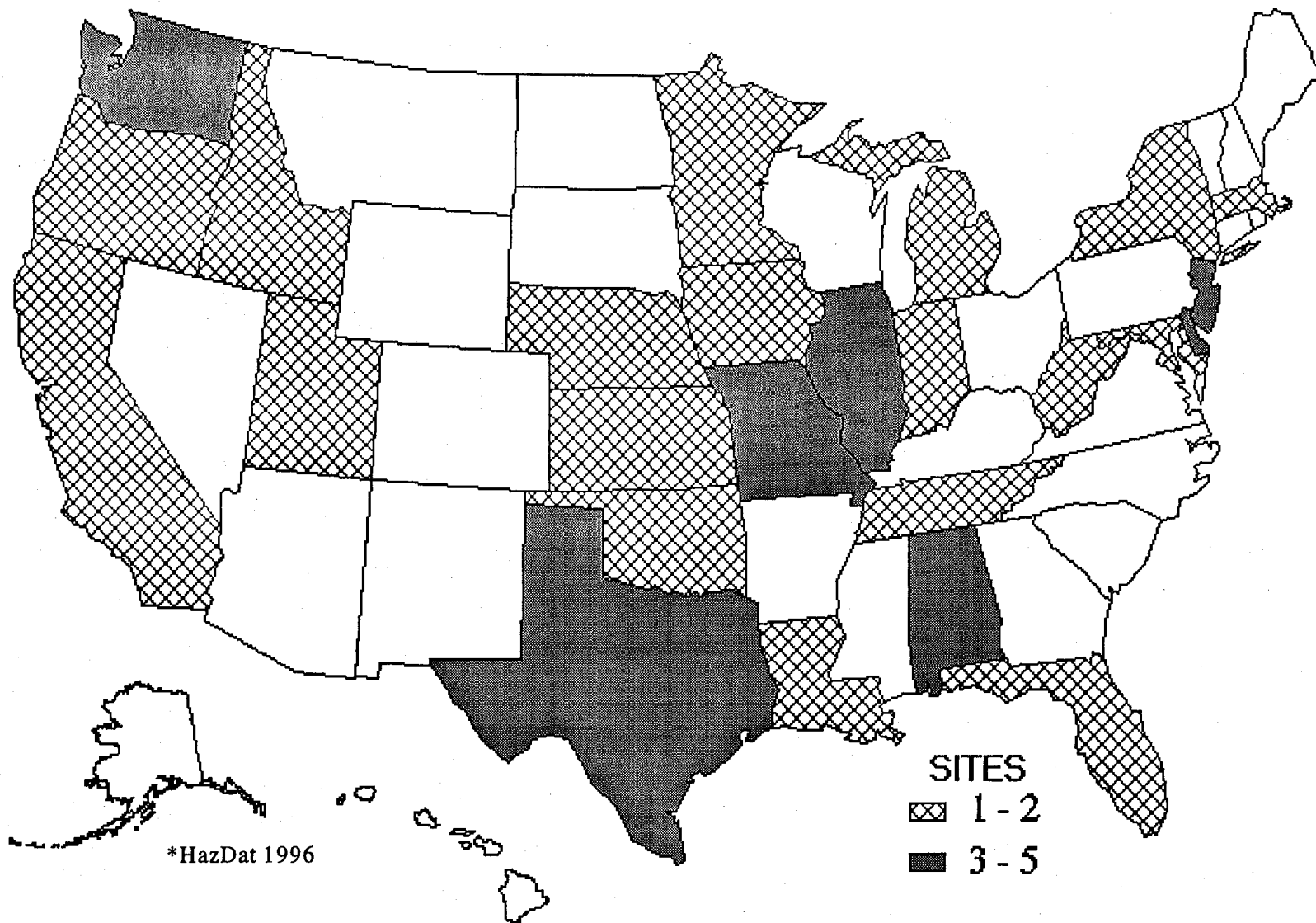
5. POTENTIAL FOR HUMAN EXPOSURE

Studies of occupational exposures to DNT indicate that inhalation and dermal contact can result in absorption of DNT into the body. However, inhalation and dermal contact are less likely to be critical environmental exposure pathways for the general population. Individuals exposed outside the workplace would be more likely to ingest DNT via contaminated drinking water and food.

5.2 RELEASES TO THE ENVIRONMENT

According to the Toxics Release Inventory (TRI), in 1996, a total of 6,844 pounds (5,080 kg) of 2,4-DNT from 3 large processing facilities and 1,315 pounds (592 kg) 2,6-DNT from 2 large processing facilities were released to the environment (TR196 1998). Tables 5-l and 5-2 list amounts released from these facilities. In addition, an estimated 1,866 pounds (840 kg) of 2,4-DNT and 58 pounds (26 kg) 2,6-DNT were transferred offsite (TR196 1998). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

2,4-DNT and 2,6-DNT have been identified in a variety of environmental media (air, surface water, groundwater, soil, and sediment) collected at 69 and 53 of the 1,467 NPL hazardous waste sites, respectively (HazDat 1998).

5.2.1 Air

According to the Toxics Release Inventory, in 1996, the estimated releases of 4,202 pounds (1,891 kg) 2,4-DNT from 3 large processing facilities and 1,048 pounds (472 kg) 2,6-DNT from 1 large processing facility to air accounted for about 77% of total environmental releases (TR196 1998). Tables 5-l and 5-2 list amounts released from these facilities. The TRI data should be used with caution, however, since only certain types of facilities are required to report. This is not an exhaustive list.

2,4-DNT has been identified in air samples colleced at 1 of the 69 NPL hazardous waste sites, and 2,6-DNT has been identified in air samples colleced at 1 of the 53 NPL hazardous waste sites where they were detected in some environmental media (HazDat 1998).

The DNT isomers have relatively low vapor pressures (2,4-DNT, 5.1×10^{-3} torr [20°C]; 2,6-DNT, 0.018 torr [20°C]) (Maksimov 1968) and quite low Henry's Law constants (2,4-DNT, 4.5×10^{-6} atm-m^3 mol^{-1} [calc., 20°C]; 2,6-DNT, 7.9×10^{-6} atm-m^3 mol^{-1} [calc., 20°C]) (Mabey et al. 1982). As a result, DNT is not

TABLE 5-1.   Releases to the Environment from Facilities that Manufacture or Process 2,4-Dinitrotoluene

			Reported amounts released in pounds per year [a]						
STATE [b]	CITY	FACILITY	AIR [c]	WATER	LAND	UNDER GROUND INJECTION	POTW TRANSFER	OFF-SITE WASTE TRANSFER	TOTAL ENVIRONMENT [d]
MS	PASCAGOULA	FIRST CHEMICAL CORP.	3	0	0	0	0	0	3
VA	RADFORD	U.S. ARMY RADFORD ARMY	5	250	0	0	0	840	1,095
WV	NEW MARTINSVILLE	BAYER CORP.	1,883	99	0	0	0	0	1,982
		TOTALS	1,891	349	0	0	0	840	3,080

Source: TRI96 1998

[a] Data in TRI are maximum amounts released by each facility

[b] Post office state abbreviations used

[c] The sum of fugitive and stack releases are included in releases to air by a given facility

[d] The sum of all releases of the chemical to air, land, and water, and underground injection wells; and transfers off-site by a given facility

POTW = publicly owned treatment works

TABLE 5-2. Releases to the Environment from Facilities that Manufacture or Process 2,6-Dinitrotoluen

			Reported amounts released in pounds per year [a]						
STATE [b]	CITY	FACILITY	AIR [c]	WATER	LAND	UNDERGROUND INJECTION	POTW TRANSFER	OFF-SITE WASTE TRANSFER	TOTAL ENVIRONMENT [d]
WV	NEW MARTINSVILLE	BAYER CORP.	472	94	0	0	0	26	592
		TOTALS	472	94	0	0	0	26	592

Source: TRI96 1998

[a] Data in TRI are maximum amounts released by each facility

[b] Post office state abbreviations used

[c] The sum of fugitive and stack releases are included in releases to air by a given facility

[d] The sum of all releases of the chemical to air, land, and water, and underground injection wells; and transfers off-site by a given facility

POTW = publicly owned treatment works

expected to volatilize from water. However, DNT may be released to or transported in the air as dusts or aerosols or adsorbed to other suspended particles. Exposure to airborne DNT may occur in the workplace. Environmental exposure to DNT in the air may occur if contaminated surface soils are eroded and reentrained.

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

5.2.2 Water

According to the Toxics Release Inventory, in 1996, the estimated releases of 2,4-DNT and 2,6-DNT of 776 pounds (349 kg) from 2 large processing facilities and 209 pounds (94 kg) from 1 large processing facility, respectively, to water accounted for about 12% of total environmental releases (TRI96 1998). Tables 5-l and 5-2 list amounts released from these facilities. The TRI data should be used with caution, however, since only certain types of facilities are required to report. This is not an exhaustive list.

2,4-DNT has been identified in surface water at 19 of 69 NPL hazardous waste sites, and in groundwater at 54 of 69 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1998). 2,6-DNT has been identified in surface water at 18 of 53 NPL hazardous waste sites, and in groundwater at 32 of 53 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1998).

The occurrence of DNT 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). DNT occurs 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 DNT in waste waters from other manufacturing uses (e.g., polyurethane forms) has not been reported. The frequency of detection of DNT 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 DNT, and the median of positive samples was less than 10 μg/L. The presence of DNT was not detected in samples of sediment or biota.

5. POTENTIAL FOR HUMAN EXPOSURE

The water solubility of 2,4- and 2,6-DNT (270 ppm and 180 ppm, respectively) (Mabey et al. 1982) is sufficient to permit transport in surface or groundwaters. Thus, releases to water are very important sources of potential human exposure. Prior to introduction of discharge controls, washings from munitions manufacturing and demilitarization facilities could produce thousands of gallons of contaminated effluent per day at a single facility. Moreover, water contamination may persist. For example, an old effluent lagoon contained detectable quantities of DNT about 12 years after use had been discontinued (Jenkins et al. 1986).

Hashimoto et al. (1982) reported the release of as much as 150 kg/day of DNT isomers in the effluent from a single coastal industrial drain in Dokai Bay, Japan, with a daily average release of 76 kg/day over 7 months. However, DNT concentrations in the bay decreased with distance from the site more rapidly than predicted by simple dilution and tidal action. The salting-out effect of sea water on nitroaromatic compounds was probably responsible for this effect (Hashimoto et al. 1984).

5.2.3 Soil

According to the Toxics Release Inventory, in 1996, there were no reported releases of 2,4-DNT or 2,6-DNT to soil (TR196 1998). The TRI data should be used with caution, however, since only certain types of facilities are required to report. This is not an exhaustive list

2,4-DNT has been identified in soil at 35 of 69 NPL hazardous waste sites, and in sediment at 16 of 69 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1998). 2,6-DNT has been identified in soil at 20 of 53 NPL hazardous waste sites, and in sediment at 9 of 53 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1998).

No information on releases of DNT to soil were located. The extensive use of DNT as an intermediate in the synthesis of toluenediisocyanate and polyurethane foam is not a reported source of releases to soil.

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

The water solubilities of DNT are moderate (Callahan et al. 1979), and the octanol-water partition coefficients are low (Mabey et al. 1982). As a result, there is a potential for transport of DNT by surface or

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groundwater. Spanggord et al. (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. Mabey et al. (1982) calculated sediment-water partitioning coefficients of 45 and 92 for 2,4-DNT and 2,6-DNT, respectively. Depending on the nature of the sediment load, the total concentration of DNT carried in the soil and water column could be high. DNT in buried munitions wastes could potentially be released to groundwater or transported as contaminated soil and sediment.

The expected bioaccumulation of DNT in animal tissues is negligible. The low octanol-water partition coefficients do not indicate a concern for biological lipid accumulation (Trabalka and Garten 1982). Values of K_{ow} lower than 2.5 for nonionized organic chemicals predict bioconcentration solely dependent on the magnitude of exposure. The log K_{ow} values for 2,4-DNT and 2,6-DNT are 1.98-2.01 and 2.05-2.28, respectively (Callahan et al. 1979; Mabey et al. 1982), indicating that bioaccumulation is not likely to occur.

Direct measurement of plant uptake of DNT 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; Nolt 1988) suggests that 2,4- and 2,6-DNT would be readily taken up by plants. However, plant uptake of related nitroaromatic compounds such as 2,4,6-TNT and its byproduct 4-amino-2,6-DNT has 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 (Cataldo et al. 1989).

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 DNT is so dependent on environmental conditions and the presence of effective microorganisms, the protective view that DNT is of heavy concern for persistence in water, plant uptake, and leaching to graundwater may be warranted. The lack of concern for bioaccumulation, multimedia/multispecies action, and atmospheric action also appears to be justified.

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5.3.2 Transformation and Degradation

5.3.2.1 Air

Based on its rapid photolysis in water, DNT is presumed to be subject to oxidation of its methyl group, decarboxylation, ring oxidation, and/or nitroreduction in air and sunlight. Indirect photolysis must be considered as well. Although the literature implies that these routes lead to destruction of DNT, no experimental measurements were located in the available studies.

5.3.2.2 Water

DNT 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 (Andrews and Osmon 1977; Bausum et al. 1992; Bradley et al. 1995; Freedman et al. 1996; Ho 1986; Noguera and Freedman 1996; Roth and Murphy 1979). Ho (1986) studied photooxidation of 2,4-DNT in aqueous solution in the presence of hydrogen peroxide and suggested that the degradation pathway of 2,4-DNT was, although it includes other intermediates, as follows: 2,4-DNT -- 1,3-dinitrobenzene - hydroxynitrobenzene derivatives + carboxylic acids – CO_2 H_2O, and HNO_3. Oxidation of aqueous DNT with hydrogen peroxide or UV irradiation alone was very slow, and elimination was not complete. Dillert et al. (1995) reported that degradations of DNT and several other nitroaromatics were accelerated in irradiated TiO_2, suspensions and that the degradation rates were dependent on time, solution pH, and light intensity. At given temperature, pH, and photo intensity, degradation rates were shown in the order of 2-nitrotoluene > nitrobenzene > DNT > 1,3-dinitrobenzene > TNT > trinitrobenzene, and the degradations followed first order kinetics. There was very little influence on degradation rates by changes in pH (Dillert et al. 1995; Kumar and Davis 1997).

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 DNT in waste water have spurred considerable study of the abiotic and biotic fate of 2,4- and 2,6-DNT. Spanggord et al. (1980) reported that the half-lives of DNT in 3 sunlit natural waters were 3-10 hours, whereas the photolysis half-life in distilled water was 43 hours. Simmons

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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. Since the calculated rates of oxidation are less by a factor of about 10^{-5}, photolysis is probably the major route of degradation of DNT in oxygenated waters.

DNT may be also degraded by ozonation and chlorination. Lee and Hunter (1985) reported that both ozone and chlorine produced less than 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.

In the absence of sunlight and oxygen, any losses of DNT would apparently be dependent on biodegradation. Spanggord et al. (1980) observed biodegradation in an aerobic environment, with a half-life of less than 1 hour. Under anaerobic conditions, the half-life of 2,6-DNT in non-acclimated sewage is found to be 28 days, with no loss of the compound under aerobic conditions during the same period (Hallas and Alexander 1983). Similarly, Liu et al. (1984) reported no loss of 2,4-DNT in aerobic municipal activated sludge to which benzene was added as a carbon source for bacterial growth, but complete biotransformation of 2,4-DNT within 14 days under anaerobiosis. 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 DNT from microorganisms taken from areas that are frequently exposed to DNT (Bausum et al. 1992; Bradley et al. 1995; 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 DNT was shown to be converted to CO_2 with 2,4-DNT conversion occurring at a greater rate than that of 2,6-DNT; concentrations

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ranged from 0.004 to 10.0 ppm (Bausum et al. 1992). The rate of mineralization to CO_2 was concentration
dependant and increased with increasing concentration.

In the Bradley et al. (1995) study, a culture of microorganisms taken from aquifer sediments at an
explosivescontaminated site was observed to be capable of removing added 2,4- and 2,6-DNT. The removal rate
of 2,4-DNT after 70 days was greater than 99% after application of 100 µM of 2,4-DNT. Removal of 2,6-DNT
at the same concentration was less efficient, with 60% of the compound being removed after 70 days.
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 mg/L and 142 mg/L,
respectively. Ethanol and ether were chosen because they are often found in munitions manufacturing
wastewater 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 DNT was mineralized to a significant degree.

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 (DAT) (Cheng et al.
1996). During the biotransformation, two intermediates were formed: 2-amino-4-nitrotoluene and 4-amino-
2-nitrotoluene. 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 DNT, the other with activated
sludge that was not routinely exposed to nitroaromatic compounds. The acclimated culture consumed DNT
twice as fast as the unacclimated culture, with reduction of DNT to aminonitrtoluenes as the initial pathway.
The principal metabolites identified in the acclimated culture were 6-nitroindazole, 2-nitrotoluene,
4 nitrotoluene, as well as products from acetylation at the pm-u position (4-acetamide-2-nitrotoluene and
4 acetamidetoluene). Reduction of aminonitrotoluenes to 2,4-diaminotoluene also occurred, and its
subsequent disappearance results in accumulation of significant amount of nonfilterable material in both
cultures. The soluble metabolites formed from the unacclimated culture were more hydrophilic. Initial

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characterization of the highly hydrophilic metabolites indicated approximately equal amounts of negativelycharged and neutral compounds.

Biotransformation of DNT by a *Pseudomonas aeruginosa* strain, which was isolated from a propellant wastewater treatment plant, was observed under both aerobic and anoxic conditions (Noguera and Freedman 1996). The biotransformation was mainly reductive under both of these conditions. The primary breakdown products were 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, Zacetamide-4-nitrotoluene, 4-acetamide-2-aminotoluene, and 2,4-diacetamidetoluene.

5.3.2.3 Sediment and Soil

Little information was located regarding transformation of DNT in 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).

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to 2,4-DNT and 2,6-DNT depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. In reviewing data on 2,4-DNT and 2,6-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.

5.4.1 Air

Measurements of DNT in ambient air were not located. In an occupational environment, Ahrenholz (1980) measured breathing zone air concentrations of Tg-DNT that ranged from undetected to 23 $\mu g/m^3$ (timeweighted average [TWA]). Tg-DNT concentrations in the area air samples ranged from undetected to 420

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$\mu g/m^3$ (TWA). Ahrenholz and Meyer (1982) reported that area air samples in a manufacturing facility contained TWA concentrations of Tg-DNT that ranged from undetected to 890 $\mu g/m^3$. Levine et al. (1985b) also measured personal air samples of 2,4-DNT at 10-440 $\mu g/m^3$ and 2,4- and 2,6-DNT at 50-590 $\mu g/m^3$ in the workplace.

5.4.2 Water

As priority pollutants, 2,4- and 2,6-DNT are monitored routinely in U.S. waters, but both the number of positive samples (1.1 - 1.6%) and the mean value (<10 $\mu g/L$) of those samples indicate that release of the compounds to water is neither widespread nor very great. No residues of 2,4- or 2,6-DNT were reported in sediments or biota (Staples et al. 1985). Residues of 2,4-DNT were detected in the groundwater of 1.5% of 800-900 hazardous waste sites (CLPSD 1988). The geometric mean concentration in groundwater was 58 $\mu g/L$. In surface waters, 2,4-DNT was detected at 1.0% of hazardous waste sites at a geometric mean concentration of 104 $\mu g/L$. In surface waters of the river Elbe in Germany, concentrations of 2,4-DNT ranged from 0.1 to 1.3 $\mu g/L$, while concentrations of 2,6-DNT ranged from 0.08 to 0.5 $\mu g/L$ (Feltes et al. 1990). Sohr et al. (1995) reported 2,4-DNT and 2,6-DNT concentrations of 0.7 $\mu g/L$ and 3.1 $\mu g/L$, respectively, at contaminated warfare sites in Germany. Other less contaminated sites contained 28 ng/L 2,4-DNT and 19 ng/L 2,6-DNT (Sohr et al. 1995).

Residues of 2,6-DNT were detected in the groundwater of 1.0% of waste sites at a geometric mean concentration of 18 $\mu g/L$. 2,6-DNT was detected in the surface water of only 0.3% of the waste sites (CLPSD 1988).

5.4.3 Sediment and Soil

Hoke et al. (1993) reported that only low concentrations of 2,4-DNT and 2,6-DNT were detected in sediment of the Great Calumet River-Indian Harbor. Concentrations of 2,4-DNT in sediments ranged from the detection limit of 0.01 $\mu g/L$ to 0.07 $\mu g/L$. 2,4-DNT concentrations in sediment pore water ranged from 0.1 $\mu g/L$ to 1.7 $\mu g/L$. 2,6-DNT was not detected in sediment samples (LOD = 0.01 l.$\mu g/L$) and subsequently was not analyzed for in sediment pore water.

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Concentrations ranging from less than 0.1 mg/kg (detection limit) to 117 mg/kg of 2,4-DNT were found at the Joliet Army Ammunition Plant, in Joliet, IL, an NPL site. 2,6-DNT was detected on this site at concentrations ranging from less than 0.1 mg/kg to 8 mg/kg (Simini et al. 1995).

5.4.4 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). DNT was not detected in fish from Great Lakes harbors and tributaries in Ohio and Wisconsin (DeVault 1985).

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Sources of exposure to DNT for the general population include processing facilities that manufacture or process DNT, as well as hazardous waste sites that release this chemical. There are 3 large processing facilities that release a total of 3,080 kg of 2,4- and 2,6-DNT to the environment annually (TR196 1998), and 2,4- and 2,6-DNT has been found in at least 69 and 53 waste sites, respectively (HazDat 1998). The general population may be exposed to DNT via inhalation, dermal contact, and incidental ingestion pathways. Occupational exposure to DNT 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 pathways will also involve inhalation, dermal contact, and incidental ingestion.

Studies on occupational exposure to DNT are limited. Levine et al. (1985b) evaluated the 7-hour Time-Weighted Average (TWA) personal exposure of workers to DNT technical grade (Tg-DNT) and measured urinary metabolites of DNT 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. Air exposure concentrations of loaders, who load storage tanks, collect samples, and perform cleaning tasks, averaged 0.32 mg/m^3. Exposure of maintenance mechanics averaged 0.12 mg/m^3, and the exposure of acid-stripper operators was 0.06 mg/m^3. 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 DNT 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. In another study of occupational absorption in an

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explosives manufacturing facility (Woollen et al. 1985), personal airborne exposure to DNT ranged from undetectable to 0.1 mg/m^3. Area samples collected near dusty parts of the process ranged from 0.02 to 2.68 mg/m^3. However, air concentrations could not account for the observed excretion levels of the metabolite 2,4-dinitrobenzoic acid, indicating probable dermal uptake.

Two major studies of occupational exposure to DNT (Levine et al. 1985b; Woollen et al. 1985) reported the following: maximum excretion of metabolites occurred at or after the end of a working shift; excretion was practically complete by the start of the next shift; and rates of 2,4-dimtrobenzoic acid excretion in the urine made a plausible marker of exposure, provided that sampling patterns were adequate to compensate for the wide variation over time, both between individuals and for the same person. In both studies, difficulties in detecting metabolites and frequent occurrence of samples with values near the limits of detection hampered interpretation of actual exposure and disposition. Higher exposures in the study by Levine et al. (1985b) permitted more extensive analysis. The results of both studies indicated that dermal contact and inadvertent ingestion were contributing routes of exposure for male and female workers.

The Occupational Safety and Health Administration (OSHA) established an 8-hour Time-Weighted Average (TWA) Permissible Exposure Limit (PEL) for dinitrotoluene as 1.5 mg/m^3, with skin designation to indicate the potential significant contribution to the overall exposure by the cutaneous route (OSHA 1998). The American Conference of Governmental Industrial Hygienist (ACGIH)'s Threshold Limit Value (TLV) for dinitrotoluene is 0.2 mg/m^3, with skin notation (ACGIH 1998). 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 dinitrotoluene as 1.5 mg/m^3, with skin designation (NIOSH 1997).

5.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans and briefly considers potential pre-conception exposure to germ cells. Differences from adults in susceptibility to hazardous substances are discussed in 2.6 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, and breathe more air per kilogram of body weight, and have a

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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; they put things in their mouths; they may ingest inappropriate things such as dirt or paint chips; they spend more time outdoors. Children also are closer to the ground, and they do not have the judgement of adults in avoiding hazards (NRC 1993).

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

Although DNT can degrade in water by several mechanisms, it has the potential to be transported in surface water or groundwater due to its moderate water solubility. Therefore, children playing in DNT contaminated surface water 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 or municipal water contaminated with DNT 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 DNT is 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 parents' work clothes, skin, hair, tools, or other objects removed from the workplace. No information is available concerning exposure from consumer products because DNT is used mainly for military and industrial purposes.

Although DNT is genotoxic in *in vivo* test systems, it is found to be negative in dominant lethal mutations (Ellis et al. 1979) and spermatocyte DNA repair (Working and Butterworth 1984). There is no evidence that exposure of parental germ cells to the active form of DNT could plausibly occur since DNT does not accumulate in tissue.

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5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In addition to individuals who are occupationally exposed to 2,4-DNT and 2,6-DNT (see Section 5.5), there are several groups within the general population that have potentially high exposures (higher than background levels) to 2,4-DNT and 2,6-DNT. These populations include individuals living in proximity to sites where 2,4-DNT and 2,6-DNT were produced or sites where 2,4-DNT and 2,6-DNT were disposed, and individuals living near one of the NPL hazardous waste sites where 2,4-DNT and 2,6-DNT have been detected in some environmental media (HazDat 1998).

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. 2,4-DNT and 2,6-DNT do not appear to be widespread in the environment, and they were not frequently detected at hazardous waste sites.

5.8 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 2,4- and 2,6-DNT is available. Where adequate information is not available, ATSDR, in conjunction with the 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 2,4- and 2,6-DNT.

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.

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5.8.1 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 DNT is presented in Chapter 3 and the data appear to be adequate (HSDB 1998; Lide 1993). The isomers of DNT have many similar traits, including identical molecular weights), but 2,4-DNT has higher melting and boiling points than 2,6-DNT and a greater solubility in water (HSDB 1998). DNT is generally produced as a technical-grade mixture comprised of 95% 2,4- and 2,6-DNT, and 5% other substances. The other substances are predominantly isomers of DNT not discussed in this profile.

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 chemical release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1996, became available in May of 1998. This database is updated yearly and should provide a list of industrial production facilities and emissions. The TRI reported that DNT was produced at 3 sites within the United States (TR196 1998).

USITC statistics on synthetic organic chemical production (USITC 1987) do not describe DNT production. Uses of DNT appear to be well characterized (CMR 1983; HSDB 1998). The most commercially important use of DNT is as a chemical intermediate in the production of toluene diisocyanate, a precursor to polyurethane polymers (HSDB 1998). It has been estimated that 99% of all DNT produced is used for this purpose (CMR 1983). DNT is recognized as a potentially hazardous chemical and is subject to a variety of regulations (see Chapter 7), but disposal practices and restrictions are not adequately documented.

Environmental Fate. The low octanol-water partition coefficients of the DNT isomers predict that DNT released to the environment would not bioaccumulate and would be weakly bound to soil organic matter. The relatively low volatility and high solubility of DNT indicate that it 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). DNT has been found in wastewater and groundwater in and around munitions sites (Jenkins et al. 1986; Spanggord and Suta 1982). The occurrence of DNT in wastewater from other manufacturing uses such as polyurethane forms has not been reported.

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Given the importance of information about the behavior of DNT in the water column, and the extensive range of available information relative to that topic (Gillett 1983; Hashimoto et al. 1982, 1984; Jenkins et al. 1986; Mabey et al. 1982; Spanggord et al. 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 DNT in soil, 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 DNT in environmental media or 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). DNT was not detected in fish from Great Lakes harbors and tributaries in Ohio and Wisconsin (DeVault 1985).

Food Chain Bioaccumulation. Limited information indicates that DNT is not widely distributed in the environment. Residues of DNT have not been observed in fish samples and 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; Mabey et al. 1982; Trabalka and Garten 1982). The expected bioaccumulation of DNT is animal tissues in negligible. The log K_{ow}, values for 2,4- and 2,6-DNT are 1.98-2.01 and 2.05-2.28, respectively (Callahan et al. 1979; Mabey et al. 1982), indicating that bioaccumulation is not likely to occur. The bioavailability and potential toxicity of soil- and sediment-bound products are unknown. Degradation of DNT forms a variety of products, about which very little is known. Additional information would help to confirm or refute indications of low potential for bioaccumulation of DNT in foods.

Exposure Levels in Environmental Media. Reliable monitoring data for the levels of 2,4- and 2,6-DNT in contaminated media at hazardous waste sites are needed so that the information obtained on levels of 2,4- and 2,6-DNT in the environment can be used in combination with the known body burdens of 2,4- and 2,6-DNT 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 DNT has not occurred (Staples et al. 1985). Monitoring for priority pollutants in wastewater, drinking water, and biota has failed to detect

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residues in sediments or biota (Staples et al. 1985). DNT was detected at very low frequencies in drinking water, the number of positive samples ranging from 1.1 - 1.6% and the mean value of those samples reported at less than 10 μg/L. 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). Residues of 2,4-DNT were detected in the groundwater of 1.5% of 800-900 hazardous waste cites (CLPSD 1988). The geometric mean concentration in groundwater was 58 μg/L. In surface waters, 2,4-DNT was detected at 1.0% of hazardous waste sites at a geometric mean concentration of 104 g/L.

Exposure Levels in Humans. This information is necessary for assessing the need to conduct health studies on these populations. 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 DNT and its metabolite levels in blood and urine will be useful to provide an estimate of internal dose of exposure.

Exposures of Children. No exposure and body burden studies have been conducted on children; consequently, it is not known if children differ from adults in their weight-adjusted intake of DNT, or if unique exposure pathways for children exist. Since DNT is 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 DNT has 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 DNT and are occupationally exposed to significant quantities of DNT might potentially be exposed to DNT 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.

Exposure Registries. No exposure registries for DNT (2,4- or 2,6-DNT) were located. Neither of these substances is currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates

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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.

5.8.2 Ongoing Studies

Photochemical reactions of 2,4-DNT in aqueous solutions containing cationic surfactant, nonionic surfactant, a hydrogen donor, or a base are being investigated by C.A. Diehl et al. (1995) at Purdue University.

A project to develop and apply biomarkers of exposure associated with 2,6-DNT is being conducted by Dr. Steve Rappaport at University of North Carolina at Chapel Hill (FEDRIP 1998).

A project to develop an anaerobic biodegradative process for the biodegradation of DNT in aqueous streams is being conducted by D. Munnecke at Environmental Biotechnologies, Inc. in Montara, CA (FEDRIP 1997).