

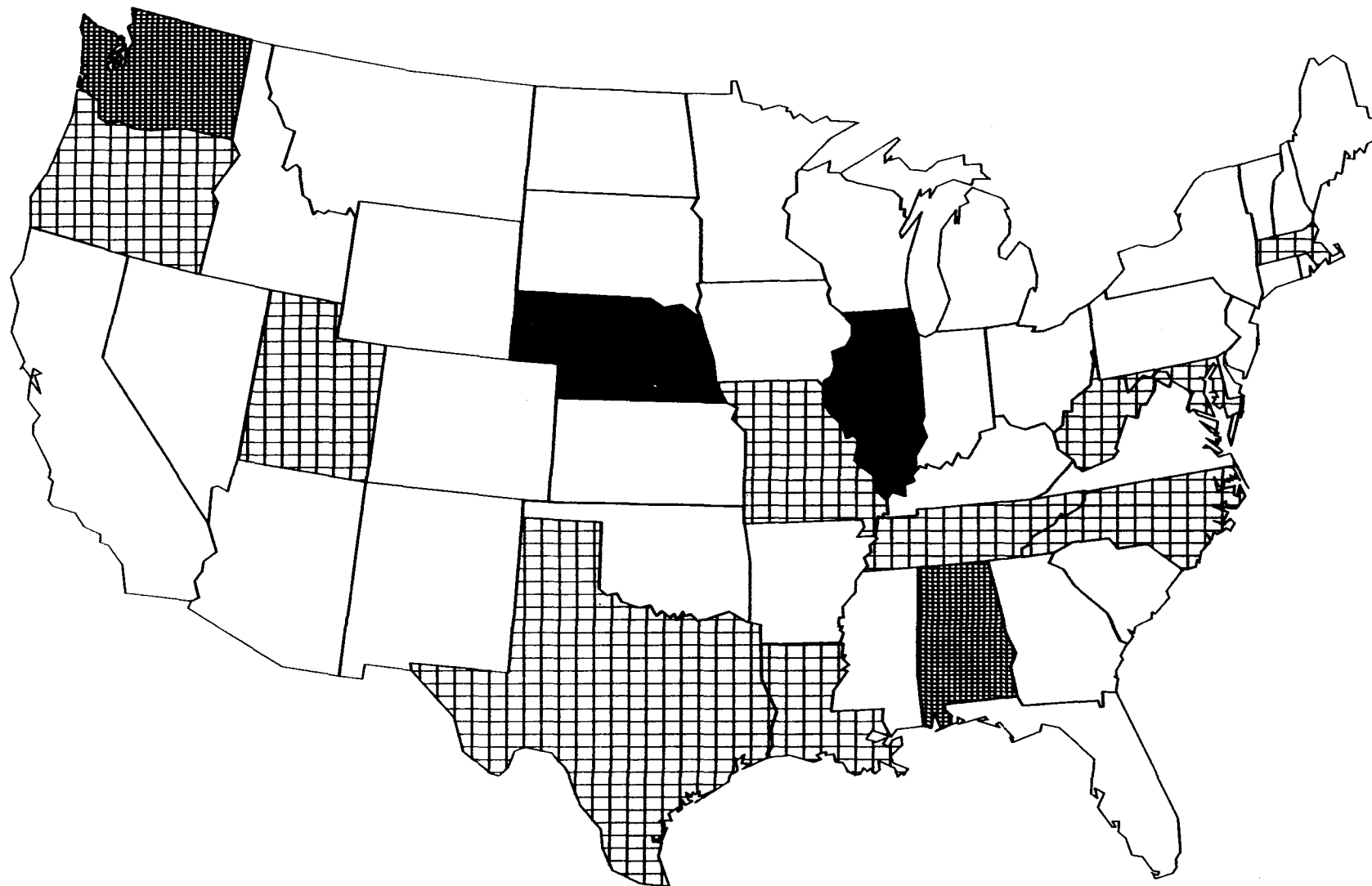
5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

2,4,6-Trinitrotoluene is released to the environment from manufacturing and munitions processing facilities. Upon release to surface waters, 2,4,6-trinitrotoluene undergoes rapid photolysis to a number of products. Biodegradation by microorganisms including bacteria and fungi also occurs in surface waters but at rates much slower than photolysis. 2,4,6-Trinitrotoluene is expected to be transported mainly in the aqueous phase; the compound is not expected to volatilize from surface water to the atmosphere or significantly partition to soils or sediments. Bioconcentration of 2,4,6-trinitrotoluene by plants and aquatic organisms is limited, and biomagnification of the compound in terrestrial and aquatic food chains is not expected. Little information is available on the concentrations of 2,4,6-trinitrotoluene or its degradation products in ambient media. The most important routes of human exposure to the compound, that the general public may be exposed to, appear to be ingestion of contaminated drinking water and dermal contact with contaminated surface water. However, members of the general public may also be exposed to 2,4,6-trinitrotoluene released to the atmosphere as a result of ordnance demilitarization and disposal through incineration and detonation, as well as by ingestion of foods contaminated through uptake of the compound from contaminated soils or deposition of 2,4,6-trinitrotoluene particulates from the atmosphere. Workers may be exposed via inhalation and dermal contact. Workers involved in the manufacture of 2,4,6-trinitrotoluene or the processing of munitions containing the compound may be exposed to high concentrations of 2,4,6-trinitrotoluene through inhalation and dermal contact.

2,4,6-Trinitrotoluene has been identified in at least 20 of the 1,397 hazardous waste sites on the EPA National Priorities List (NPL) (HAZDAT 1994). However, the number of sites evaluated for 2,4,6-trinitrotoluene is not known. The frequency of these sites within the United States can be seen in Figure 5-1.

FIGURE 5-1. FREQUENCY OF NPL SITES WITH 2,4,6-TRINITROTOLUENE CONTAMINATION *



FREQUENCY



1 SITE
3 SITES



2 SITES

*Derived from HazDat 1994

5. POTENTIAL FOR HUMAN EXPOSURE

5.2 RELEASES TO THE ENVIRONMENT**5.2.1 Air**

2,4,6-Trinitrotoluene is released to the ambient atmosphere as a result of open detonation and open burning techniques used in the demilitarization of munitions (Army 1986e) (also see Section 4.4). Gases and particulates are released to the atmosphere as a result of these activities and from the disposal of munitions containing 2,4,6-trinitrotoluene in rotary kiln incinerators. 2,4,6-Trinitrotoluene dusts and vapor are released into indoor air atmospheres in military production and processing facilities during manufacturing of 2,4,6-trinitrotoluene and munitions (Hathaway 1985). Fugitive dusts containing the compound are probably generated at sites with contaminated surface soils (e.g., military installation burning grounds) (Kraus et al. 1985).

5.2.2 Water

2,4,6-Trinitrotoluene has historically been discharged in large quantities in the aqueous effluents of explosives production/manufacturing facilities and ammunition load, assemble, and pack (LAP) plants, from decommissioning activities, and through field use/disposal. Estimates of the loadings of 2,4,6-trinitrotoluene in these effluents vary. Some investigators have reported concentrations of about 120 mg/L in manufacturing facility waste waters and 25 mg/L in loading plant facility effluents (Freeman and Colitti 1982). Others report concentrations of 40-120 mg/L in manufacturing plant effluents, with generally higher concentrations in LAP plant waste waters (Andren et al. 1977b). Concentrations of 0.1-3.4 mg/L have been detected in about 20% of the samples of sellite manufacturing process condensate wastewater collected from a 2,4,6-trinitrotoluene manufacturing facility (Army 1980b; Spangord et al. 1982a).

Estimates of historical 2,4,6-trinitrotoluene releases to surface waters from Army ammunition plants have been developed on the basis of surveys of munitions facilities. Sources include production plants (emissions range from 61 to 210 pounds/day) and LAP plants (1-150 pounds/day). Estimates of average downstream concentrations of 2,4,6-trinitrotoluene in the surface waters receiving these

5. POTENTIAL FOR HUMAN EXPOSURE

effluents are 0.006-0.025 mg/L for production plants and <0.001-0.038 mg/L for LAP plants (Rosenblatt et al. 1973; Small and Rosenblatt 1974). 2,4,6-Trinitrotoluene has been detected in the effluent of the Radford, Virginia, production plant at 101-143 ppm (Nay 1972a).

5.2.3 Soil

2,4,6-Trinitrotoluene is released to soils from spills, disposal of solid waste, open incineration and detonation of ordnances, leaching from inadequately sealed impoundments (e.g., pits, ponds, and lagoons), and demilitarization of munitions (EPA 1989c; Kraus et al. 1985; Army 1986e).

Demilitarization of munitions can result in contamination of surface soils by activities such as open burning and open detonation or landfilling of solid wastes generated during rotary kiln incineration and nondestructive reprocessing of munitions containing 2,4,6-trinitrotoluene (Army 1986e).

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

On the basis of the relatively low vapor pressure (1.99×10^{-4} mmHg at 20°C) and relatively high water solubility (130 mg/L at 20°C) (see Table 3-2) of 2,4,6-trinitrotoluene, the compound is not expected to partition from surface waters to the atmosphere. Limited volatilization from aqueous solutions was found in air stripping tests on raw and neutralized waste water samples, where only 8-10% of the 2,4,6-trinitrotoluene concentration was lost during an 18-day test period (Nay 1972a). Volatilization half-lives of 10,000 days have been estimated for ponds, streams, and lakes (Spanggord et al. 1985). A volatilization half-life of 119 days has been estimated from a model river at 20°C 1 meter deep flowing at the rate of 1 meter/second, with a wind speed of 3 meters/second (HSDB 1994).

On the basis of the measured and estimated values for the soil organic carbon adsorption coefficient (K_{oc}) of 300-1,100, 2,4,6-trinitrotoluene is not expected to significantly partition from surface waters to sediment or strongly sorb to soil particulates (Spanggord et al. 1985). This expected behavior has been confirmed in short-term laboratory adsorption/desorption tests and long-term lysimeter studies. Short-term (24-hour) laboratory batch adsorption/desorption tests were conducted using

5. POTENTIAL FOR HUMAN EXPOSURE

uncontaminated surface soils collected from 13 Army ammunition plants. Limited 2,4,6-trinitrotoluene adsorption was found in these tests. The average adsorption coefficient (K_d) for all soils tested was 4, which indicates limited sorption potential. Adsorption was found to be consistently lower under oxidized conditions than under reduced conditions. Almost all of the 2,4,6-trinitrotoluene adsorbed was desorbed upon multiple extraction of the test soils. The pH of the soils exerted no effect on 2,4,6-trinitrotoluene adsorption/desorption or transformation. Transformation products (4-ADNT and 2-ADNT) were detected under both oxidized and reduced conditions (Pennington and Patrick 1990). In long-term lysimeter studies, ring-labeled ^{14}C -2,4,6-trinitrotoluene was added to the top 3 inches of soils in columns (2 feet long and 2 inches in diameter). Four soil types were used, ranging in texture from fine to coarse. The lysimeters were regularly irrigated during the 6-month test period, and column leachate samples were taken every 2 weeks. At the end of the test period, the soil columns were sectioned for analysis. 2,4,6-Trinitrotoluene and its transformation products were retained in the test soil columns. Neither 2,4,6-trinitrotoluene nor its typical biodegradation products were detected in the leachate samples. Analysis of the leachate samples with high ^{14}C activity indicated the presence of only highly polar, nonvolatile products. These products could not be separated or identified. However, two transformation products were identified in the soil columns: 2-ADNT and 4-ADNT. The concentration of these products in the soil columns ranged from 0.01% to 6% of the radiolabelled 2,4,6-trinitrotoluene added to the columns (Kayser and Burlinson 1988).

In other mobility tests with sediments, ring-labeled ^{14}C -2,4,6-trinitrotoluene was added to unsterilized sediments collected from two farm ponds in Syracuse, New York and from the Holston River in Kingsport Tennessee, upstream from an Army Ammunition Plant site. 2,4,6-Trinitrotoluene was not extensively sorbed in short-term (24 hour) tests, partition coefficients varied with pH and temperature. Desorption of 2,4,6-trinitrotoluene or its breakdown products proceeded slowly; steady state conditions were reached after 92 hours in only 1 sediment (Army 1980b).

The log octanol/water partition coefficient (K_{ow}) values of 2.2-2.7 (see Table 3-2) suggest that the compound will not bioconcentrate to high levels (i.e., concentrations $\geq 1,000$ times media concentrations) in the tissues of exposed plants and animals or biomagnify in terrestrial or aquatic food chains (Spanggord et al. 1985). Limited bioconcentration was demonstrated in aquatic bioassays with

5. POTENTIAL FOR HUMAN EXPOSURE

water fleas (*Daphnia magna*), worms (*Lumbriculus variegatus*), algae (*Selenastrum capricornutum*), and bluegill sunfish (*Lepomis macrochirus*). Bioconcentration factors (BCFs) in 96-hour static tests were found to be 209 for the water flea, 202 for the worms, 453 for algae, 9.5 for fish muscle, and 338 for fish viscera (Liu et al. 1983b).

Bioconcentration of 2,4,6-trinitrotoluene by yellow nutsedge was studied in hydroponic cultures containing 5, 10, and 20 mg/L 2,4,6-trinitrotoluene. After a 42-day exposure period, the rhizomes, roots, tubers, and leaves of the plants were analyzed for 2,4,6-trinitrotoluene and metabolites. 2,4,6-Trinitrotoluene and its metabolites, 4-ADNT and 2-ADNT, were taken up and translocated throughout the plants, although the highest concentrations were found in the roots. Concentrations of 2,4,6-trinitrotoluene and metabolites in plant tissues generally increased with increasing 2,4,6-trinitrotoluene concentrations in the growth medium. At the 20-mg/L treatment level, the concentrations in plant roots were 714 mg/kg, 614 mg/kg, and 2,180 mg/kg for 2,4,6-trinitrotoluene, 2-ADNT, and 4-ADNT, respectively (Palazzo and Leggett 1986).

5.3.2 Transformation and Degradation

5.3.2.1 Air

No information was found on the transformation of 2,4,6-trinitrotoluene in the atmosphere. However, 2,4,6-trinitrotoluene released to the atmosphere should undergo direct photolysis, as it does in surface water. Estimates of the photolytic half-life of the compound in air range from 3.7 to 11.3 hours; these estimates are based on the rate of photolysis of the compound in distilled water. Estimates of the photooxidation half-life of the compound in the atmosphere range from 18.4 to 184 days. These estimates are based on the estimated rate constant for reaction with hydroxyl radicals in the atmosphere (Howard et al. 1991).

5. POTENTIAL FOR HUMAN EXPOSURE

5.3.2.2 Water

2,4,6-Trinitrotoluene does not undergo hydrolysis, as demonstrated by the stability of the compound in sea water after 108 days at room temperature (Hoffsommer and Rosen 1973).

Photolysis of 2,4,6-trinitrotoluene in aqueous solutions is a well-known phenomenon, which is responsible for the development of “pink water,” and is probably the most important fate process for 2,4,6-trinitrotoluene in aqueous systems. For example, the estimated half-life of 2,4,6-trinitrotoluene in surface waters is 0.16-1.28 hours, based on the rate of photolysis and photooxidation in sunlit natural waters (Howard et al. 1991). The rate of photolysis of 2,4,6-trinitrotoluene in natural surface waters has been found to be much greater than that of the compound in pure water. Phototransformation of 2,4,6-trinitrotoluene in surface waters occurs via direct and indirect photolysis. Direct photolysis of the compound is rapid; the estimated half-life varies from 14 to 84 hours, depending on season and latitude. These rates are increased in natural waters through the influence of humic acids on indirect photolysis. In sunlit natural waters, 2,4,6-trinitrotoluene photolysis proceeds at rates 10-100 times more rapid than those found in distilled water, with half-lives in some natural waters of less than 0.5 hour. Phototransformation in natural surface waters may be accelerated because of the complexation of 2,4,6-trinitrotoluene and natural organics, or by an indirect mechanism by which light absorbed by natural organic constituents is transferred to 2,4,6-trinitrotoluene, or by the chemical trapping by humic acids of the reactive intermediate phototransformation products (Mabey et al. 1983; Spanggard et al. 1985; Zepp et al. 1984). In laboratory studies using distilled water, the rate of transformation increases over time, since photolysis is also promoted by the presence of photodecomposition products in the medium. The pH of the surface water has been found to exhibit a small influence on the rate of transformation only in surface waters that contain few natural organic constituents. 2,4,6-Trinitrotoluene may be more persistent in deep quiescent water bodies or other water systems where sunlight is attenuated. A number of 2,4,6-trinitrotoluene photodecomposition products have been identified, including dinitroanthrils, trinitrobenzaldehyde, trinitrobenzyl alcohol, trinitrobenzene, nitroanilines, condensed azo and azoxy derivatives, and 1,3,5-trinitrobenzene (Burlinson 1980; Mabey et al. 1983). Recently a deep red-brown 2,4,6-trinitrotoluene degradation product of *Mycobacterium* grown in aerobic conditions has been identified (Vorbeck et al. 1994). This

5. POTENTIAL FOR HUMAN EXPOSURE

type of compound (a hydride-Meisenheimer complex) may be the type of chemical causing “pink water.”

2,4,6-Trinitrotoluene is also transformed in surface waters by microbial metabolism, although this process occurs more slowly than photolysis. For example, the estimated biodegradation half-life of 2,4,6-trinitrotoluene in surface water, under both aerobic and anaerobic conditions, is 1-6 months. This estimate is based on aerobic river die-away test data with unacclimated microorganisms (Howard et al. 1991). The relative slowness of microbial degradation may be due in part to the enhanced toxicity of 2,4,6-trinitrotoluene to aquatic organisms in the presence of the near-ultraviolet component of sunlight (Johnson et al. 1994a). Examples of biotransformation of the compound in aqueous systems include the white rot fungus *Phanerochaete chrysosporium*, which was found to degrade ringlabeled ^{14}C -2,4,6-trinitrotoluene. Within 12 days, 35% of the labeled 2,4,6-trinitrotoluene added to the solution was recovered as $^{14}\text{CO}_2$ (Fernando et al. 1990).

Pseudomonad bacteria (*Pseudomonas* sp.) have been found to reduce 2,4,6-trinitrotoluene under aerobic conditions in laboratory studies to monoaminodinitrotoluenes and a diaminomononitrotoluene (Schackmann and Muller 1991). Pseudomonads isolated from mud and water samples collected at the U.S. Naval Ammunition Depot at McAlester, Oklahoma, have also been found to be capable of biotransforming 2,4,6-trinitrotoluene in laboratory studies. 2,4,6-Trinitrotoluene degraded most rapidly in cultures supplemented with yeast extract. In the most active isolate, complete dissimilation was found within 24 hours. Degradation products identified include 2,2',6,6'-tetranitro-4,4'-azoxytoluene; 9,4',6,6'-tetranitro-2,2'-azoxytoluene; 2-amino-4,6-dinitrotoluene; 4-hydroxylamino-2,6-dinitrotoluene; and nitrodiaminotoluene (Won et al. 1974). Pseudomonads isolated from Narragansett Bay, sediments, raw sewage, and boiler plant effluents were able to utilize ring labeled ^{14}C -2,4,6-trinitrotoluene as a sole carbon source in laboratory degradation studies. The amount of 2,4,6-trinitrotoluene transformation varied with the concentration of the test compound in the medium. 2,2',6,6'-Tetranitro-4,4'-azoxytoluene was the only transformation product identified. Nitrite was found in the test medium, which suggests that the transformation proceeded via removal of the nitro groups from the aromatic ring. The recovery of 0.8-1.2% of the label in the form of $^{14}\text{CO}_2$ suggests a mechanism that includes cleavage of the aromatic ring (Traxler et al. 1974).

5. POTENTIAL FOR HUMAN EXPOSURE

Microbial inocula isolated from sewage treatment plant effluents, waste water from a 2,4,6-trinitrotoluene ordnance loading facility, soil suspension, pond water, and aquarium water were found to be capable of degrading 2,4,6-trinitrotoluene in the presence of yeast extract in shake flask cultures at 38°C over 6 days. 2,4,6-Trinitrotoluene concentrations were reduced from the initial loading of 100 mg/L to 0-6 mg/L over the 6-day incubation period. Transformation did not occur in cultures containing only 2,4,6-trinitrotoluene and mineral salts. Microbial inocula isolated from raw sewage were not effective in transforming 2,4,6-trinitrotoluene; however, inocula isolated from sewage sludge digester liquor (supernatant) reduced 2,4,6-trinitrotoluene concentrations by 64% over the test period. 2,4,6-Trinitrotoluene was also degraded in tests with a pure culture of *Pseudomonas aeruginosa* when glucose and supplemental nitrogen in the form of mineral salts were added to the culture medium (Osmon and Klausmeier 1973).

Sediments from Army ammunition plants containing mixtures of explosives, including 2,4,6-trinitrotoluene, have been composted in field trials to reduce their explosives content. For example, sediment from a Louisiana Army Ammunition Plant containing mixed explosives, including 56,800 mg/kg 2,4,6-trinitrotoluene, was added to a compost mix containing straw/horse manure, alfalfa, and horse feed. The temperature inside the pile reached 55°C. After 22 weeks, the total explosives content of the compost was reduced by 99% (Williams et al. 1989).

2,4,6-Trinitrotoluene has been reported to persist in groundwater for long periods of time by Rosenblatt (1980). However, other estimates of the half-life of the compound in groundwater range from 1 to 12 months, based on estimated unacclimated aqueous anaerobic and aerobic biodegradation (Howard et al. 1991).

5.3.2.3 Soil

Solid chunks of 2,4,6-trinitrotoluene buried in soil or exposed on the soil surface can persist for many years (Rosenblatt 1980). In smaller amounts, 2,4,6-trinitrotoluene may undergo photolysis in surface soils to trinitrobenzene and trinitrobenzaldehyde (Ryon et al. 1984).

5. POTENTIAL FOR HUMAN EXPOSURE

The transformation of 2,4,6-trinitrotoluene in soils has been found to be influenced by a number of environmental factors. In a study using ring-labeled ^{14}C -2,4,6-trinitrotoluene, the effects of soil organic matter content, 2,4,6-trinitrotoluene concentration, oxygen concentration, moisture content, temperature, incubation period, and microbial activity on 2,4,6-trinitrotoluene transformation in soil were examined. The soil pH was maintained at 6.5 throughout the test. In samples collected for analysis after 6 months and 11 months incubation, biological transformation was highest in soils containing the lowest concentration of 2,4,6-trinitrotoluene (0.1%) and lowest in soils containing the highest starting concentration of 2,4,6-trinitrotoluene (10%). The highest concentrations of degradation products were recovered from the soils receiving the lowest 2,4,6-trinitrotoluene loadings. Degradation products identified included 2-amino-4,6-dinitrotoluene, 4-amino-2,6-dinitrotoluene, and diamines. As biotransformation increased, the amount of unextractable radioactive residue increased, suggesting that the metabolites of 2,4,6-trinitrotoluene exhibited stronger sorption to soils than the parent compound. Degradation decreased in sterilized soils. Of the environmental parameters evaluated in this study, the initial 2,4,6-trinitrotoluene concentration and the soil moisture level had the most influence on the rate of 2,4,6-trinitrotoluene transformation. The presence or absence of microbial activity and incubation temperature had less effect, and the remaining variables had no effect on 2,4,6-trinitrotoluene transformation (Army 1985a).

The white rot fungus *Phanerochaete chrysosporium* was found to degrade ring labeled ^{14}C -2,4,6-trinitrotoluene sorbed to soils. After 30 days incubation, 6.3% of the sorbed 2,4,6-trinitrotoluene was recovered as $^{14}\text{CO}_2$. An additional 63.6% of the radioactivity was recovered in acetonitrile extracts, and 25.2% was unextractable. In the acetonitrile extract, only 2.2% of the radiolabel was in the form of undegraded 2,4,6-trinitrotoluene (Fernando et al. 1990).

In the same study, soil cultures containing 10,000-mg/kg loadings of ring-labeled ^{14}C -2,4,6-trinitrotoluene were extracted after 30-, 60-, and 90-day incubation periods and mass balances were calculated. The 90-day mass balance indicated that 18.4% of the radioactivity was recovered as $^{14}\text{CO}_2$, 62.6% in the form of metabolites present in the acetonitrile extract fraction, and 11.5% was bound to the soil/fungal matrix. The concentration of residual undegraded 2,4,6-trinitrotoluene in the 90-day acetonitrile extract was 14.9%, versus the >99% activity in the control samples (Fernando et al. 1990).

5. POTENTIAL FOR HUMAN EXPOSURE

In screening studies of 190 species of fungi from 98 genera, 183 species were found to be able to transform 2,4,6-trinitrotoluene in 5-day shake culture tests. Transformation products included 4-amino-2,6-dinitrotoluene, 4-hydroxylamino-2,6-dinitrotoluene, and 4,4'-azoxy-2,2',6,6'-tetranitrotoluene. None of the test organisms exhibited an ability to cleave the aromatic ring of 2,4,6-trinitrotoluene (Parrish 1977). A sulfate-reducing bacterium, *Desulfovibrio*, has been isolated that degrades 2,4,6-trinitrotoluene. However, this isolate also does not degrade 2,4,6-trinitrotoluene all the way to carbon dioxide (Boopathy and Kulpa 1992).

Composting of 2,4,6-trinitrotoluene in soils has been examined in laboratory scale and large-scale tests. In laboratory tests with ring labeled ^{14}C -2,4,6-trinitrotoluene, rapid biotransformation was found, with initial average activity levels of 93.5% reduced to 46.6% and 16.6% after 3 weeks and 6 weeks, respectively. No degradation products were detected in samples collected after 3 weeks. Minor amounts (i.e., less than 2%) were detected in samples collected at 6 weeks. The degradation products included 2-amino-4,6-dinitrotoluene, 4-amino-2,6-dinitrotoluene, 2,6-diamino-4-nitrotoluene, and 2,2',6,6'-tetranitro-4,4'-azoxytoluene. The decrease in ^{14}C -2,4,6-trinitrotoluene concentration was found to be correlated with a reduction in the solvent extractable activity and a significant increase in the compost-bound radioactivity. This finding suggests that 2,4,6-trinitrotoluene was transformed into more polar metabolites. Similar results were found in the large scale greenhouse trials, where 2,4,6-trinitrotoluene concentrations decreased from 19,041 $\mu\text{g/g}$ to less than 17 $\mu\text{g/g}$ after 3 weeks. 2,4,6-Trinitrotoluene was not detected in leachate samples from fresh compost piles. After 3 weeks, the leachate was found to contain 6% of the radiolabel. The mechanism for the rapid transformation of 2,4,6-trinitrotoluene in these systems is unclear; however, there is no evidence to suggest that transformation proceeds via cleavage of the benzene ring (Isbister et al. 1984). In field studies of aerated static piles, the effects of temperature on composting were examined. Under thermophilic conditions, extractable 2,4,6-trinitrotoluene was reduced from 11,840 $\mu\text{g/g}$ to 3 $\mu\text{g/g}$, while under mesophilic conditions, 2,4,6-trinitrotoluene was reduced from 11,190 $\mu\text{g/g}$ to 50 $\mu\text{g/g}$ (Williams et al. 1992).

Mixed microbial cultures isolated from two soils, one from a wooded area near a 2,4,6-trinitrotoluene loading facility and one from a greenhouse located 30 miles away, were tested for their ability to

5. POTENTIAL FOR HUMAN EXPOSURE

degrade 2,4,6-trinitrotoluene. Both soils contained microbes capable of transforming 2,4,6-trinitrotoluene, added at a concentration of 100 mg/L, in the presence of yeast extract and glucose. Over the test period, 2,4,6-trinitrotoluene degradation was greater in the inoculum isolated from the soil near the 2,4,6-trinitrotoluene loading facility (36%) than for the remote soil (14%). Most of the microorganisms exhibiting 2,4,6-trinitrotoluene activity appeared to be pseudomonads (Osmon and Klausmeier 1973).

The estimated half-life of 2,4,6-trinitrotoluene in soils ranges from 1 to 6 months. This estimate was made on the basis of the estimated unacclimated aqueous aerobic biodegradation half-life (Howard et al. 1991). In laboratory tests with sandy loam and sandy silt loam soils, the aerobic degradation half-life of the compound was determined to be 5.7-7.7 days (EPA 1989c).

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

Nitroaromatics associated with the manufacture and processing of military munitions have generally not been detected in atmospheric monitoring studies (EPA 1976a).

5.4.2 Water

2,4,6-Trinitrotoluene has been detected in surface water and groundwater samples collected only in the vicinity of munitions facilities. For example, the compound has been found in pink water effluents at concentrations of 774-998 ppb in lagoon water (Triegel et al. 1983) and 1-178 mg/L from LAP plants (Patterson et al. 1977).

2,4,6-Trinitrotoluene has been detected in groundwater samples collected in several monitoring studies conducted in the vicinity of munitions facilities. For example, using on-site high-performance liquid chromatography analysis, 2,4,6-trinitrotoluene was detected at concentrations of 320 µg/L at 200 feet downgradient and at 1 µg/L at 1,070 feet downgradient in groundwater samples collected at a demilitarization facility near Hawthorne, Nevada (Goerlitz and Franks 1989). As a result of leachates

5. POTENTIAL FOR HUMAN EXPOSURE

from disposal of solid wastes in cesspools, burning areas, and on-site leaching pits, 2,4,6-trinitrotoluene was detected in groundwater samples collected at the Cornhusker Army Ammunition Plant near Grand Island, Nebraska (Spalding and Fulton 1988).

5.4.3 Soil

2,4,6-Trinitrotoluene has been detected in surface soil samples at an average concentration of 13,000 mg/kg at the U.S. Department of Energy's Weldon Spring site in St. Charles County, Missouri. The chemical plant at the site was used by the U.S. Army to produce 2,4,6-trinitrotoluene explosives in the 1940s (Haroun et al. 1990). At the West Virginia Ordnance Works located in Mason County, West Virginia, 2,4,6-trinitrotoluene and other nitroaromatics have been detected in surface soils at burning sites in concentrations of up to 4% (40,000 mg/kg). Nitroaromatics, principally 2,4,6-trinitrotoluene, were detected at up to 20,000 mg/kg within 5-10 meters of the foundations of processing and refining facilities (Kraus et al. 1985).

At the Lone Star Army Ammunition Plant located in Texarkana, Texas, 2,4,6-trinitrotoluene has been detected at a concentration of about 15% in samples of sludge taken from ponds used as solids settling areas for pink water effluent. 2,4,6-Trinitrotoluene concentrations were highest in surface soil samples (e.g., 18.8 mg/kg at 0.2-0.6 meter depth), with decreasing concentration with increased depth (e.g., <3 mg/kg below 4.5 meters) (Phung and Bulot 1981). Triegel et al. (1983) found 2,4,6-trinitrotoluene at concentrations of 200-56,700 ppm in sludge samples from pink water lagoons, and at 18.9-158 ppm in surface soil samples collected from directly beneath the lagoon.

5.4.4 Other Environmental Media

No information was found on the concentrations of 2,4,6-trinitrotoluene in other media.

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

According to the National Occupational Exposure Survey, a total of 31 workers were estimated to have been exposed to 2,4,6-trinitrotoluene in domestic workplaces in 1980 (NIOSH 1990).

5. POTENTIAL FOR HUMAN EXPOSURE

Workers involved in the production of munitions can be exposed to 2,4,6-trinitrotoluene during the manufacture of the compound and during its use to fill artillery shells, mines, and other explosive armaments. Historically, more workers have been involved in shell loading than in the manufacture of 2,4,6-trinitrotoluene. Workers are potentially exposed via inhalation of dust and vapors, and through dermal absorption of dust. Exposure to 2,4,6-trinitrotoluene vapors is possible when the compound is melted and poured into shells. Dust exposure is possible in tilling operations using 2,4,6-trinitrotoluene powder, loading of melt kettles, drilling for fuse placement, removal of excess solidified 2,4,6-trinitrotoluene from shells, and recycling excess 2,4,6-trinitrotoluene. Protection only against inhalation of dust or vapors may still result in potentially significant systemic exposure to 2,4,6-trinitrotoluene if skin exposure occurs, since dermal absorption is rapid and accounts for a significant portion of total exposure (Hathaway 1985).

A study by the U.S. Army Environmental Hygiene Agency examined 533 workers exposed to 2,4,6-trinitrotoluene in manufacturing and munitions processing operations. The 8-hour time-weighted average concentration of 2,4,6-trinitrotoluene ranged from less than 0.01 mg/m³ to 1.84 mg/m³; concentrations of greater than 0.5 mg/m³ were experienced by only 12.2% of the workers (Buck and Wilson 1975).

Diazo-positive metabolites and mutagenic activity of metabolites in the urine of workers have been used as indicators of exposure to nitro-aromatic and nitro-amino aromatic compounds, including 2,4,6-trinitrotoluene. In two studies conducted at a 2,4,6-trinitrotoluene manufacturing plant, urine samples were collected from groups of 32 and 50 individuals with variable exposure to 2,4,6-trinitrotoluene. Samples were collected at the end of a workshift and after a holiday or weekend. The workers were divided into three exposure categories: (1) no or low 2,4,6-trinitrotoluene exposure (e.g., laboratories, controlling departments, individuals with no 2,4,6-trinitrotoluene contact during the work shift preceding sampling); (2) medium 2,4,6-trinitrotoluene exposure (e.g., assembling grenades, octal-hexotol foundry, test foundry); and (3) high 2,4,6-trinitrotoluene exposure (e.g., trotyl foundry, sieve house). 2,4,6-Trinitrotoluene concentrations (vapor and dust) in breathing zone samples collected at workstations for each category were: (1) no detectable concentrations; (2) less than 0.3 mg/m³; and (3) 0.3-0.5 or 0.6 mg/m³. The concentration of diazo-positive metabolites and mutagenic metabolites in the urine samples was significantly higher in samples collected at the end of the work shift than in

5. POTENTIAL FOR HUMAN EXPOSURE

samples collected after a holiday or a weekend for all three exposure categories, with the largest mean differences found in the highest exposure groups (Ahlborg et al. 1988a, 1988b).

Given the restricted production and use of 2,4,6-trinitrotoluene, exposure of members of the general population to the compound would probably be limited to populations living in the vicinity of hazardous waste sites or military munitions facilities. These individuals may be exposed to 2,4,6-trinitrotoluene through contact with contaminated environmental media, particularly groundwater. For example, using the multimedia screening model GEOTOX coupled with an exposure pathway model, McKone and Layton (1986b) identified consumption of contaminated water and ingestion of contaminated fruits and vegetables as the potentially most important exposure pathways for populations living near sites where 2,4,6-trinitrotoluene was released to surface soils. The investigation examined the relative importance of the following seven routes of exposure: (1) inhalation; (2) water consumption; (3) fruit and vegetable ingestion; (4) meat and dairy ingestion; (5) fish ingestion; (6) soil ingestion; and (7) dermal absorption. The least important of these pathways, according to the modeling exercise, were inhalation, soil ingestion, and dermal absorption.

As part of the baseline risk evaluation prepared for the remedial investigation of the U.S. Department of Energy's Weldon Spring Site located in Charles County, Missouri, dermal contact with and ingestion of contaminated surface soils, and inhalation of fugitive dust particulates were identified as the most important potential routes of exposure to 2,4,6-trinitrotoluene for workers involved in remedial actions at the site and for the general public. 2,4,6-Trinitrotoluene was detected in surface soils at the site in concentrations of up to 13,000 mg/kg. Modeling estimates of 2,4,6-trinitrotoluene concentrations in ambient air, resulting from the generation of fugitive dust, were 5×10^{-4} mg/m³ and 1×10^{-4} mg/m³ for total particulates and respirable particulates, respectively (Haroun et al. 1990).

Water quality criteria for the protection of human health from exposure to 2,4,6-trinitrotoluene of 44.25 µg/L (Dacre 1980) and 134.96 µg/L (Army 1987d) have been recommended; the latter value is based on a calculated acceptable daily intake of 0.28 mg/day.

5. POTENTIAL FOR HUMAN EXPOSURE

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Workers involved in the manufacture of 2,4,6-trinitrotoluene and the processing of munitions containing the compound may be exposed to high concentrations of 2,4,6-trinitrotoluene in the workplace. Populations living near military munitions facilities or hazardous waste sites may also be exposed to high concentrations of 2,4,6-trinitrotoluene through contact with contaminated media.

5.7 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 2,4,6-trinitrotoluene 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 2,4,6-trinitrotoluene.

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 or eliminate 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 may be proposed.

5.7.1 Identification of Data Needs

Physical and Chemical Properties. The physical and chemical properties of 2,4,6-trinitrotoluene are sufficiently well defined to permit an assessment of the environmental fate of the compound to be made.

5. POTENTIAL FOR HUMAN EXPOSURE

Production, Import/Export, Use, and Release and Disposal. On the basis of the limited production and specialized use of 2,4,6-trinitrotoluene, the compound is expected to have a fairly low human exposure potential. 2,4,6-Trinitrotoluene is not produced commercially in the United States; production of the compound is limited to military arsenals (HSDB 1990). Data on production volumes are not available because production is limited to military arsenals. In addition, import/export data are not available. The compound is a high explosive used by the military in the production of bombs and grenades. 2,4,6-Trinitrotoluene is released to the environment in liquid and solid wastes generated in the manufacture of the compound and the processing of munitions containing the compound. Media most likely to be contaminated include soils, surface water, and groundwater (Army 1986e). Wastes generated in the manufacture of 2,4,6-trinitrotoluene are characterized as hazardous wastes by EPA. Therefore, EPA regulations for their disposal must be followed. Additional studies of composting techniques in the treatment of 2,4,6-trinitrotoluene wastes would provide useful information in determining the effectiveness of these techniques in waste 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 1988, became available in May of 1990. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

2,4,6-Trinitrotoluene is not subject to TRI reporting requirements. Therefore, release data for the compound are not available in TRI.

Environmental Fate. Upon release to the environment, 2,4,6-trinitrotoluene partitions to and is transported in surface water or groundwater. The compound is not expected to partition significantly to the atmosphere or to soils or sediment (HSDB 1990; Spanggord et al. 1985). 2,4,6-Trinitrotoluene undergoes rapid photolytic breakdown in surface waters to a number of degradation products. The compound also undergoes biotransformation in soils and surface water (Army 1985a; Fernando et al. 1990). Additional information on the persistence of 2,4,6-trinitrotoluene in surface water and groundwater, on the kinetics and characterization of the biodegradation products in soils and surface

5. POTENTIAL FOR HUMAN EXPOSURE

waters, and on the identification of 2,4,6-trinitrotoluene complexes with humic materials would aid in determining the importance of these media with respect to potential human exposure. Since 2,4,6-trinitrotoluene has been found to persist in the soil following disposal, effort should be made to develop remediation technologies to minimize human exposure.

Bioavailability from Environmental Media. Available data from tests with laboratory animals and humans indicates that 2,4,6-trinitrotoluene is absorbed following dermal contact, ingestion, and inhalation (Army 1978a, 1981d; Hassman and Hassmanova 1976; Woollen et al. 1986). Although occupational exposure data indicate that the compound is absorbed via inhalation and dermal contact, little information is available regarding the absorption of 2,4,6-trinitrotoluene from contaminated environmental media. Additional information about uptake of the compound from contaminated environmental media, particularly following dermal contact with and ingestion of soils, would be helpful in identifying the most important routes of human exposure to 2,4,6-trinitrotoluene.

Food Chain Bioaccumulation. 2,4,6-Trinitrotoluene undergoes limited bioconcentration by plants and aquatic organisms (Liu et al. 1983b; Palazzo and Leggett 1986). As a result of its limited persistence in surface soils and surface waters and metabolism by terrestrial and aquatic organisms, the compound is not expected to biomagnify in terrestrial or aquatic food chains. Additional information on food chain bioaccumulation to confirm this predicted biomagnification behavior, particularly with respect to identification of 2,4,6-trinitrotoluene complexes with plant tissues, would be helpful in determining the relative importance of this route of exposure to humans.

Exposure Levels in Environmental Media. 2,4,6-Trinitrotoluene has been detected in soil, surface water, and groundwater samples taken at Army ammunition plants and at other military installations where the compound or munitions have been used or processed (Haroun et al. 1990; Kraus et al. 1985; Patterson et al. 1977; Spalding and Fulton 1988; Triegel et al. 1983). 2,4,6-Trinitrotoluene has not been detected in ambient air samples, in foods, or in ambient surface water or groundwater samples taken outside of military arsenals. The acceptable daily intake of the compound in drinking water has been estimated by the Army to be 0.28 mg/day. Additional information on the concentrations of 2,4,6-trinitrotoluene in environmental media at hazardous waste

5. POTENTIAL FOR HUMAN EXPOSURE

sites and military arsenals, particularly in groundwater, would be helpful in estimating the doses that exposed populations may be receiving as a result of contact with these media.

Exposure Levels in Humans. Diazo-positive and mutagenically active metabolites of 2,4,6-trinitrotoluene have been detected in workers exposed to the compound at military facilities (Ahlborg et al. 1988a, 1988b). Additional information from biological monitoring of populations living in the vicinity of hazardous waste sites or military arsenals would aid in assessing the utility of biomarkers as indicators of human exposure.

Exposure Registries. No exposure registries for 2,4,6-trinitrotoluene were located. This substance is not 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 the epidemiological research needed to assess adverse health outcomes that may be related to the exposure to this substance.

5.7.2 On-going Studies

A study is being conducted at the University of Illinois to examine the effect of the addition of organic amendments to soils contaminated with 2,4,6-trinitrotoluene. The study, which is sponsored by the U.S. Department of Agriculture, is evaluating the use of organic amendments to stabilize and bioremediate soils containing residual explosives.

At the Los Alamos National Laboratory, a study is being conducted on the uptake and biotransformation of explosives, including 2,4,6-trinitrotoluene, by plants.

Remedial investigations and feasibility studies at hazardous waste sites and military arsenals known to be contaminated with 2,4,6-trinitrotoluene should add to the available data base for environmental levels, environmental fate, and human exposure.