

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Dinitrophenols are released to the environment primarily during their manufacture and use, and from waste disposal sites that contain dinitrophenols (Games and Hites 1977; HSDB 1994; McLuckey et al. 1985; Patil and Shinde 1988). Dinitrophenols also form in the atmosphere from the reaction of benzene with NO_x in ambient air (Nojima et al. 1983). Significant removal of dinitrophenols from the atmosphere due to photochemical or other chemical reactions is not likely. Dry and wet deposition of particulate dinitrophenols are the two significant removal processes in the air (Alber et al. 1989; Capel et al. 1991; Levsen et al. 1990). Neither photochemical nor other chemical processes have been identified that are significant for the transformation/degradation of dinitrophenols in natural waters (Callahan et al. 1979; Lipczynska-Kochany 1992; Tratnyek and Hoigne 1991; Tratnyek et al. 1991). The loss of dinitrophenols from water due to volatilization is negligible (Callahan et al. 1979). Moderate amounts of dinitrophenols are removed from water to sediment due to adsorption (Callahan et al. 1979). Biodegradation may be the most important loss process for dinitrophenols in natural waters (Barth and Bunch 1979; Chambers et al. 1963; Games and Hites 1977; Tabak et al. 1981a, 1981b). As in water, no chemical process has been identified that would be significant for transformation/degradation of dinitrophenols in soil. Biodegradation may be the most significant process for destroying dinitrophenols in soil (Kincannon and Lin 1985; Loehr 1989; O'Connor et al. 1990). The loss of dinitrophenols from soil due to volatilization is not significant (Wild and Jones 1992). The mobility of dinitrophenols in soils decreases with increase in acidity, clay, and organic matter content, but the mobility in soil will increase as the basicity of soil-water increases because the ionized form is more water soluble and moves faster through soil (Kaufman 1976). 2,4-DNP has been measured in groundwater from waste disposal sites (ATSDR 1988; Plumb 1991), indicating the possibility that these compounds leach from soil. Depending on the nature of soil and climatic conditions, the residence time of 2,4-DNP in soil has been determined to be <8-120 days (Kincannon and Lin 1985; Loehr 1989; O'Connor et al. 1990).

Other than in workplace air, dinitrophenols have not been measured in ambient air in the United States, but have been found in other countries. Dinitrophenols at a maximum concentration of 3.2 mg/L have been detected in effluent from a dye-manufacturing plant (Games and Hites 1977), but no monitoring data for drinking water in the United States are available. Dinitrophenols have been

identified in 61 of the 1,408 waste sites on the NPL (HazDat 1994). The frequency of these sites within the United States is shown in Figure 5-1. The maximum detected 2,4-DNP concentration in groundwater from a Superfund site was 30.6 mg/L in Minnesota (ATSDR 1988). No data are available on the levels of dinitrophenols in food or total diet samples in the United States. Within the overall population, occupational groups (Gisclard and Woodward 1946) and people who live near hazardous waste sites that contain these pollutants are more likely to be exposed to higher concentrations of dinitrophenols than the rest of the general population; however, the extent of such exposures for residents around waste sites has not been documented.

5.2 RELEASES TO THE ENVIRONMENT

5.2.1 Air

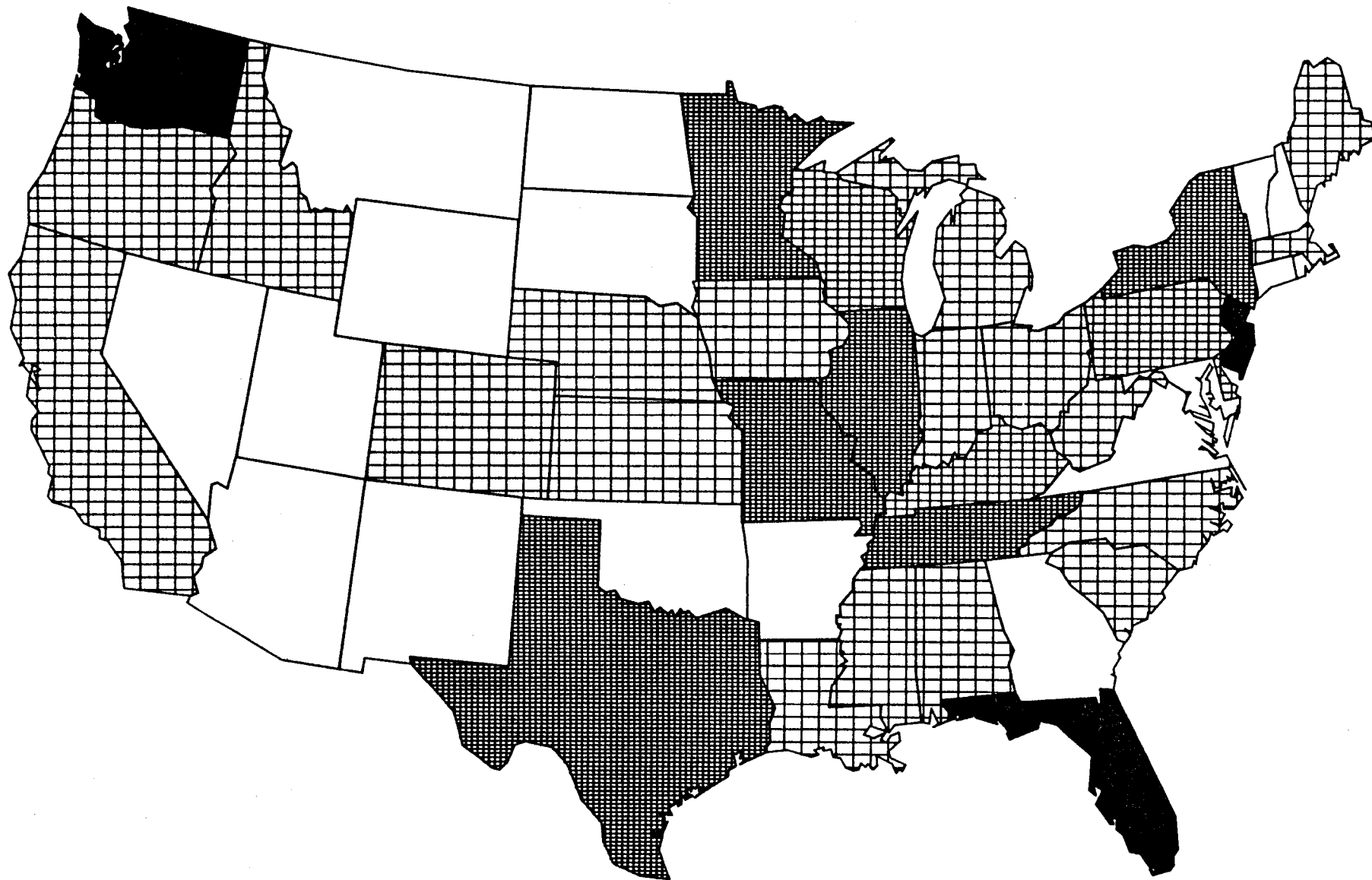
Dinitrophenols are released to the air from manufacturing plants and facilities that use them (HSDB 1994; TRI92 1994). 2,4-DNP releases in air from U.S. facilities that manufactured or processed 2,4-DNP are reported in Table 5-1 (TRI92 1994). According to TRI92 (1994) an estimated 20,312 pounds or 51.6% of the total environmental release was discharged in the air from manufacturing and processing industries in the United States in 1992. The TRI data should be used with caution, since only certain types of facilities were required to report. This is not an exhaustive list. Automobile exhaust is another source of 2,4- and 2,6-DNPs in air (Nojima et al. 1983). 2,4-DNP is also used as an insecticide, acaricide, and fungicide (HSDB 1994). Therefore, application of this type of pesticide could be a source of 2,4-DNP in air. Photochemical reactions of benzene with nitrogen oxides in air also produce dinitrophenols in the atmosphere (Nojima et al. 1983). Dinitrophenols have been detected in emissions from hazardous waste combustion (James et al. 1984).

Dinitrophenols may be present in the aerosol or vapor phase near hazardous waste disposal sites. It has been suggested that the most important origin of dinitrophenols is their formation by photochemical reactions in the atmosphere (Nojima et al. 1983).

5.2.2 Water

Dinitrophenols may be released into surface water from production facilities and by industries that use them. 2,4-DNP has been detected in the waste water from nitrobenzene-manufacturing plants (Patil and Shinde 1988). Other industries or plants that can release dinitrophenols in surface water are

FIGURE 5-1. FREQUENCY OF NPL SITES WITH DINITROPHENOLS CONTAMINATION *



FREQUENCY



1 SITE
2 SITES
3 SITES
5 TO 7 SITES



1 SITE
2 SITES
3 SITES
5 TO 7 SITES

*Derived from HazDat 1994

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

State ^a	City	Facility	Air	Water	Land	Underground injection	Total environment ^b	POTW transfer	Offsite waste transfer
LA	Geismar	BASF Corp.		28			28		
LA	NA	Rubicon Inc.	NA	NA	NA	NA	NA	NA	NA
MS	Pascagoula	First Chemical	3				3		1
NC	Charlotte	Sandoz Chemicals Corp.		100	6		106		6,400
NY	Buffalo	Osmose Wood Preserving Inc.	12				12	5	10
PA	Monessen	Sharon Steel Corp.	8,548				8,548		
PA	Pittsburgh	Shenango Inc.	11,749				11,749		
TX	Beaumont	Du Pont Beaumont Plant				18,925	18,925		
Totals			20,312	128	6	18,953	39,371	5	6,411

Source: TRI92 1994

^aPost Office state abbreviation used

^bThe sum of all releases of the chemical to air, land, water, and underground injection wells by a given facility

NA = not available

POTW = Publicly Owned Treatment Works

explosives producers (McLuckey et al. 1985), dye-manufacturing plants (Games and Hites 1977), and sewage treatment plants where the influent waters already contain dinitrophenols (DeWalle et al. 1982). Since 2,4-DNP is also used to produce picric acid, picramide, and photographic developer (diaminophenol hydrochloride), and in preserving wood (Hawley 1981), waste waters or land runoffs from these industries may release 2,4-DNP to surface water. The releases of 2,4-DNP to water from facilities that manufactured and processed 2,4-DNP in the United States during 1992 are reported in Table 5-1 (TRI92 1994). According to TRI92 (TRI92 1994), an estimated 128 pounds, amounting to 0.3% of the total release, was discharged to water from manufacturing and processing facilities in the United States in 1992. 2,4-DNP is also used as an insecticide, acaricide, and fungicide (HSDB 1994). Therefore, application of this pesticide would be a source of 2,4-DNP in water. Dinitrophenols will also be released into groundwater from hazardous waste sites containing insecticides or pesticides, such as Dinoseb, which may contain dinitrophenols as impurities (ATSDR 1988; Overcash et al. 1982; Plumb 1991). Small amounts will also enter surface water by wet and dry deposition of atmospheric dinitrophenols (Alber et al. 1989; Bihm et al. 1989; Levsen et al. 1990).

5.2.3 Soil

Dinitrophenols may be released in soils in the vicinity of the sites where they are manufactured and used. Dinitrophenols were found in the soil of a decommissioned wood preserving facility (EPA 1988a). The release of 2,4-DNP to land from facilities that manufactured or processed the compound in the United States in 1992 is reported in Table 5-1 (TRI92 1994). According to TRI92 (1994), an estimated 18,925 pounds were injected underground, and 6 pounds were released to soil, for a combined land release of 48.1% of the total environmental release. Dinitrophenols will be found in soils of hazardous waste sites where wastes containing these compounds are disposed (HazDat 1994). 2,4-DNP is also used as an insecticide, acaricide, and fungicide (HSDB 1994). Therefore, application of this pesticide would be a source of 2,4-DNP in soil. Since vehicular exhaust contains dinitrophenols (Nojima et al. 1983), roadside soil might contain these compounds. Small amounts of dinitrophenols will enter soil due to dry and wet deposition of these compounds present in the atmosphere.

5.3 ENVIRONMENTAL FATE

Very little data regarding the fate and transport of 2,3-, 2,5-, 2,6-, 3,4-, or 3,5-DNP in the environment were located in the literature; however, more data are available for 2,4-DNP. Although, depending on

physico-chemical properties (pK_a , water solubility, vapor pressure and other relevant properties) there will be differences, the environmental fate and transport of other dinitrophenols are likely to follow the same general pattern of environmental behavior as that of 2,4-DNP.

5.3.1 Transport and Partitioning

The vapor pressure of 2,4-DNP is 1.49×10^{-5} mm Hg at 18 °C (Mabey et al. 1981). Organics with vapor pressures of 10^{-4} to 10^{-8} mm Hg at ambient temperature should exist partly in the vapor and partly in the particulate phase in the atmosphere (Eisenreich et al. 1981). Nitrophenols were detected experimentally in the particulate phase in air (Nojima et al. 1983), although the method used to collect atmospheric particulate matter was not suitable for collecting vapor-phase dinitrophenols. The distance of atmospheric transport of dinitrophenols will depend on atmospheric residence times. The residence time of dinitrophenols, based on the estimated rates of various reactions, is long enough to allow atmospheric transport (see Section 5.3.2.1). The removal and transport of atmospheric dinitrophenols to land and water by physical processes, such as wet and dry deposition, will depend on the physical states of these compounds in the atmosphere. Since dinitrophenols have been detected in rain, snow, and fog (Alber et al. 1989; Cape1 et al. 1991; Levsen et al. 1990), at least partial removal of these compounds occurs by physical processes. Because of faster rates of travel, unreacted vapor-phase dinitrophenols in the atmosphere have a greater chance to be transported longer distances than dinitrophenols present as aerosols. No monitoring data, however, are available to substantiate long-distance atmospheric transport of dinitrophenols.

Based on its vapor pressure, water solubility, and presence predominantly in ionic forms in most natural waters ($pK_a = 4.09$ for 2,4-DNP), Callahan et al. (1979) concluded that the volatilization of these compounds from water to air is not significant.

The partitioning of dinitrophenols from water to suspended solids and sediment due to adsorption would transport these compounds from water to sediment. The sorption of dinitrophenols by soil or sediment would depend on the organic carbon content, clay content, and pH of soil and sediment (Callahan et al. 1979; Kaufman 1976). An increase in clay and organic carbon content and a decrease in pH (thereby increasing the concentration of the un-ionized form) would increase the amount sorbed. Therefore, the sorption and subsequent transport of dinitrophenols from water to suspended solids and

sediment would be significant in natural waters that are acidic and/or have high organic matter and clay content.

No experimental data on the bioconcentration potential for dinitrophenols or their metabolites in aquatic organisms were located. Based on bioconcentration factors in the range of 8-24 estimated from octanol/water partition coefficients (EPA 1986a), bioconcentration is not expected to be significant for dinitrophenols in aquatic organisms. In addition, the fact that dinitrophenols exist predominantly in ionic forms in most natural waters (pH 5-9) further indicates that bioconcentration is not significant (bioconcentration is usually significant for hydrophobic and non-ionic compounds). Using the equation $\log BCF = 1.02 \times \log K_{ow} - 1.82$ to correct the BCF due to ionization in water (McCarty et al. 1993) and a value of 1.54 for $\log K_{ow}$ (see Table 3-2), the BCF of 2,4-DNP in fish can be estimated to be 0.56. Therefore, the concentration of 2,4-DNP in fish may be even lower than its concentration in water.

The possibility of transport of dinitrophenols from soil to air via volatilization needs examination. Based on its low volatility and reasonably high water solubility, Wild and Jones (1992) concluded that 2,4-DNP would not volatilize from most soils. Although the possibility of volatilization of phenolic compounds in soil via co-distillation with water has been suggested (Kaufman 1976) and release to air via aerosol formation is possible, no volatilization of 2,4-DNP was observed in 21 days from soil columns (Kincannon and Lin 1985). The transport of dinitrophenols from soil to groundwater also may occur via leaching. The amount of DNP leached depends on the dinitrophenol adsorption capability of soils. Adsorption of phenols in soil increases with a decrease in pH and an increase in organic carbon, goethite (one of the most common iron oxides in soil), and clay content (Hudson-Baruth and Seitz 1986; Kaufman 1976; O'Connor et al. 1990; Shea et al. 1983; Stone et al. 1993). In soils containing goethite, 2,4-DNP adsorption is due to surface complex formation at protonated mineral surfaces (Stone et al. 1993). The adsorption of 2,4-DNP on goethite was shown to be maximum near pH 4.5 and negligible at neutral and alkaline pH (Stone et al. 1993). The adsorption of 2,4-DNP in calcareous soils low in organic carbon, goethite and clay content was low at a pH >7 (Hudson-Baruth and Seitz 1986; O'Connor et al. 1990). The leaching of dinitrophenols is high in such soils. Conversely, the leaching of dinitrophenols from soils will decrease when the organic carbon, clay or goethite content of soil increases and the pH of soil-water attains a pH of <6. The transport of DNP from soil to adjacent land or surface water may occur as a result of lateral movement via runoff and/or hydrogeological movement of contaminated groundwater to surface water. Dinitrophenols have

been detected in agricultural watersheds (Wegman and Wammes 1983). This indicates that transport of dinitrophenols to adjacent surface water or land occurs via runoff or as a result of hydrogeological movement of groundwater to surface water from fields where dinitrophenols have been used as pesticides, or other pesticides have been applied (dinitrophenols may also originate as impurities in certain pesticides such as Dinoseb). Such movement of dinitrophenols from soils and groundwater in waste sites is also possible.

Some loss of dinitrophenols from soil could also occur by plant uptake. High concentrations of these compounds are toxic to the growth and development of plants, especially at lower pH (Overcash et al. 1982). At concentrations likely to cause maximum bioaccumulation (10 mg/kg), the bioaccumulation factor (concentration in plant over concentration in soil) in lettuce, carrot (tops, peels, and root), hot pepper foliage, and fruits was <0.01 at a soil pH of 6.7-7.2 (O'Connor et al. 1990). Since dinitrophenols undergo metabolism in plants, plant accumulation of dinitrophenols due to uptake would not be significant (O'Connor et al. 1990). The uptake and translocation could be significant in soil with low pH where the concentration of non-ionized dinitrophenols (more readily adsorbed than the ionized form) are higher (Shea et al. 1983). Since the concentration of the non-ionized form is only $<0.25\%$ of total DNP at pH 6.7 (O'Connor et al. 1990), the soil pH has to be considerably lower for uptake to be significant in plants.

5.3.2 Transformation and Degradation

5.3.2.1 Air

The reactions of dinitrophenols with hydroxyl and nitrate radicals may be important in determining the residence times of dinitrophenols in the atmosphere (Atkinson et al. 1992). However, the products of these reactions have not been identified. No kinetic data are available for the atmospheric reactions of dinitrophenols with these species. Using the method of Atkinson (1988), the estimated rate constant for the reaction of vapor-phase 2,4-DNP with hydroxyl radicals is 5.76×10^{-13} cm³/molecule-second. Based on an average ambient atmospheric concentration of hydroxyl radicals of 5×10^5 radicals/cm³ (Atkinson 1988), the estimated half-life for the reaction is 28 days. Since dinitrophenols are expected to be present partly in the particulate phase in the air, the reaction rate is expected to be even slower than the estimated value for the gas phase reaction. Grosjean (1985) has concluded that the atmospheric reaction of chemically related 4-methyl-2-nitrophenol with nitrate radicals was not of

major significance. By structural analogy, the reaction of nitrate radicals with 2,4-DNP is not likely to be significant, and the loss of dinitrophenols in the air due to chemical reactions should not be a significant environmental fate process. The overall atmospheric half-life (due to all chemical and physical processes) of 2,4-DNP remains unknown.

5.3.2.2 Water

The estimated rate constants for the reaction of 2,4-DNP with singlet oxygen ($^1\text{O}_2$) and peroxy radicals (RO_2) are 3×10^4 /molar-hour and 5×10^5 /molar-hour, respectively (Mabey et al. 1981). The reaction of hydroperoxy radicals (HO_2) with 2,4-DNP produces a ring hydroxylated product (Lipczynska-Kochany 1992). Based on an assumption that the concentrations of singlet oxygen and peroxy radicals in typical eutrophic waters are 10^{-12} and 10^{-9} molar, respectively (Mill and Mabey 1985) these reactions would not be significant. The experimental value for the rate constant for 2,4-DNP's reaction with singlet oxygen is 4.05×10^5 /molar-second (Tratnyek and Hoigne 1991; Tratnyek et al. 1991). Based on an estimated average singlet oxygen concentration of 4×10^{-14} molar in typical eutrophic fresh water (Tratnyek and Hoigne 1991) and the experimental reaction rate constant, this reaction still would not be important in water (half-life of ≈ 500 days). Although it has been speculated that 2,4-DNP may hydrolyze while adsorbed to clay in water in a manner analogous to mono-nitrophenols (Callahan et al. 1979), no experimental evidence exists of such a reaction in natural water.

The direct photolysis of 2,4-DNP in water is too slow to be an important environmental fate process (Lipczynska-Kochany 1992). 2,4-DNP may be photoreduced to 2-amino-4-nitrophenol in the presence of ascorbic acid or ferrous ions, and the reaction is sensitized by chlorophyll (Massini and Voorn 1967). The possibility of such photoreduction exists in natural water in which the suspended reducing matter may act as a reducing agent and humic substances or algae may serve as a sensitizer.

2,4-DNP is biodegraded by several pure cultures of microorganisms, such as *Pseudomonas sp.* (Bruhn et al. 1987; Sudhakar-Barik et al. 1976), *Scenedesmus obliquus* (Klekner and Kosaric 1992), *Haloanaerobium praevalens*, *Sporohalobacter marismortui* (Oren et al. 1991), *Fusarium oxysporum* (Madhosingh 1961) two strains of *Rhodococcus sp.* (Lenke et al. 1992; Schmidt et al. 1992), *Janthinobacterium sp.* (Gier et al. 1989; Hess et al. 1990; Schmidt et al. 1992), *Corynebacterium simplex* (Gundersen and Jensen 1956; Jensen and Gundersen 1955) a gram-positive bacterium (Suwa et al. 1992), and a filamentous bacterium (Schmidt et al. 1992) isolated from soil, water, and sediment.

DNP is also anaerobically biodegraded by *Veillonella alkalescens* in the presence of hydrogen (McCormick et al. 1976). A sulfate-reducing bacterium, *Desulfovibrio sp.*, isolated from a continuous anaerobic digester, used 2,4-DNP as sole source of nitrogen but not of carbon and energy for growth (Boopathy and Kulpa 1993). Usually, the pure cultures were able to biodegrade 2,4-DNP after a certain adaptation period and as long as the concentration of 2,4-DNP was below a certain toxic level. The degradation pathway depended on the microorganisms and the conditions of aeration. Typically, with aerobic organisms and aerobic conditions, the biodegradation proceeded by replacement of nitro groups by hydroxyl groups and liberation of nitrite, or by hydroxylation of the aromatic ring positions 3, 5, or 6 (Raymond and Alexander 1971). The biodegradation by anaerobic organisms and under anaerobic conditions proceeded by reduction of nitro groups to amino groups (Madhosingh 1961; McCormick et al. 1976). The bacterium *Desulfovibrio sp.* reduced the nitro groups in 2,4-DNP to amines and reductively deaminated the amino groups, leaving the aromatic ring intact with the formation of phenol (Boopathy and Kulpa 1993). Although these pure culture studies are important for establishing degradative pathways, they do not reflect real environmental situations where mixed microorganisms and different nutritional conditions are present.

Complete or partial biodegradation of 2,4-DNP was observed under aerobic conditions with mixed microorganisms from activated sludge (Kincannon et al. 1983a, 1983b; Patil and Shinde 1989; Pitter 1976), enriched sewage (Brown et al. 1990; Wiggins and Alexander 1955), adapted sediment from rivers or waste lagoons (Barth and Bunch 1979; Chambers et al. 1963; Tabak et al. 1964), settled domestic waste water (Tabak et al. 1981a, 1981b), and aeration lagoons and settling ponds (Games and Hites 1977). Typically, aerobic biodegradation occurred if the concentration of 2,4-DNP was below toxic levels ($\approx 10\text{-}20$ mg/L) and adapted microorganisms were used. The adaptation period is usually short (Tabak et al. 1981b). Ozonation prior to aerobic biodegradation increases the biodegradation rate (Medley and Stover 1983). The biodegradation of 2,4-DNP under methanogenic conditions with anaerobic digester sludge was observed with little or no inhibitory effect at concentration ≤ 20 mg/L (O'Connor and Young 1989). As the concentration of 2,4-DNP increased to >100 mg/L, however, the microorganisms needed an adaptation period of 40-90 days before the commencement of biodegradation (Battersby and Wilson 1989; O'Connor and Young 1989). Controlled chemical oxidation of 2,4-DNP with Fenton's reagent or ozone significantly enhances anaerobic biodegradability by reducing the toxicity of 2,4-DNP to methanogens (Wang 1992). No kinetic data were located that estimated 2,4-DNP's biodegradation rate in natural water. It can be concluded from the above discussions, however, that in natural waters in which the degrader populations are small,

biodegradation of 2,4-DNP will be slow until microorganisms multiply to give a large enough degrader population to cause a detectable degradation.

5.3.2.3 Sediment and Soil

No study was located that reported the abiotic degradation/transformation of dinitrophenols in soil. It has been speculated that 2,4-DNP in soil may be reduced to 2-amino-4-nitrophenol by sunlight in the presence of a reductant, such as ferrous ions and a sensitizer, such as chlorophyll (Kaufman 1976; Overcash et al. 1982; Shea et al. 1983). Considering, however, that sunlight would not penetrate below the surface layer of soil, photolysis would not be significant at subsurface levels.

Biodegradation is the most important process for the loss of dinitrophenols in soils. Both aerobic and anaerobic degradation of dinitrophenols by pure cultures of microorganisms isolated from soil have been reported (Schmidt and Gier 1989, 1990; Simpson and Evans 1953; Sudhakar-Barik and Sethunathan 1978). Shea et al. (1983) concluded from isolated culture studies that biodegradation in soil may proceed either by reduction of the nitro group or displacement of a nitro group by a hydroxyl group with the release of nitrite ions. The optimum pH for microbial degradation is near neutrality because of the low rate of sorption of DNP to soils and sediment (increasing bioavailability to microorganisms) and low toxicity of DNP towards microorganisms at this pH (O'Connor et al. 1990). A certain concentration of the degrader population must be reached before the onset of detectable dinitrophenol mineralization. The biodegradation will occur as long as the initial concentrations of DNP in soils and sediments do not exceed the level of ≈ 100 mg/kg. Above this level, DNP may be toxic to the degrader microorganisms (Bartha et al. 1967; Namkoong et al. 1988; Schmidt and Gier 1989). Multiphasic (involving several types of reaction kinetics) mineralization kinetics have been observed for the degradation of dinitrophenols in soils. The presence of a consortium of bacteria in soil is responsible for these multiphasic degradation kinetics (Schmidt and Gier 1990). Depending on the soil (pH, organic matter content), the length of acclimation phase, as well as the initial concentration, the residence time of dinitrophenols for the aerobic biodegradation of soil may vary from 8 to 120 days (Kincannon and Lin 1985; Loehr 1989; O'Connor et al. 1990). 2,4-DNP also undergoes biotransformation in anaerobic soil and sediments. 2,4-DNP disappeared within hours due to reduction of the nitro groups to yield diaminophenol as a result of anaerobic activity (Kohping and Wiegel 1987). In contrast to the fast initial reductive biotransformation, the rate of conversion of 2,4-DNP to methane and carbon dioxide was found to be slow. Slow and partial mineralization of

2,4-DNP at low concentrations (<20 mg/kg) to methane was observed under anaerobic conditions after a suitable adaptation period (Young 1986).

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

No monitoring data reporting the ambient air levels of dinitrophenols in the United States were located. However, the reported concentration ranges of 2,4- and 2,6-DNP in particulate matter in air in Yokohama, Japan, during 5 days were 2.4-12 and 3.0-9.2 µg/g particulates, respectively (Nojima et al. 1983). The detection of 2,4-DNP in urban fog (Richartz et al. 1990), rain, and snow (Alber et al. 1989; Levsen et al. 1990) from European cities, and the detection of both 2,4- and 2,6-DNP in automobile exhaust gas (Nojima et al. 1983) are indirect indications of the presence of these compounds in the air. The maximum concentration of 2,4-DNP in fog from different sites in northeastern Bavaria was 30.4 µg/L (Richartz et al. 1990).

5.4.2 Water

No monitoring data regarding the concentrations of dinitrophenols in U.S. drinking water were located. 2,4-DNP was not detected (unspecified detection limit) in water from lakes Erie and Michigan (The Great Lakes Water Quality Board 1983). In a study of the water quality of the Potomac River, 2,4-DNP was detected at a concentration <10 µg/L in water near Chopawamsic Creek in Quantico, Virginia (Hall et al. 1987). Discharges from two sewage treatment plants upstream may be responsible for the presence of 2,4-DNP. The concentrations of 2,4-DNP in rain and snow in Hanover, Germany, ranged from <0.1 to 4.6 µg/L, with a mean concentration of 1.2 µg/L (Alber et al. 1989; Levsen et al. 1990).

The ranges of dinitrophenol (unspecified isomers) concentrations in raw waste waters and final effluents from a dye-manufacturing plant were 400-3,200 and <1-2,700 µg/L, respectively (Games and Hites 1977). According to STORET, 2,4-DNP was detected in 2% of effluent samples at a detection limit of 10 µg/L and in 0.4% of ambient water samples at a detection limit of 20 µg/L (Staples et al. 1985). The concentration ranges of 2,4- and 2,6-DNP in the water of an agricultural watershed in the Netherlands were <0.1-3.5 and <1.0-1.0 µg/L, respectively (Wegman and Wammes 1983). The

source of dinitrophenols in the water was not specified and the investigators concluded that the reported data need further confirmation by mass spectrometry. 2,4-DNP was qualitatively detected in groundwater from three of three unidentified disposal sites in EPA region 3 (Delaware, Maryland, Pennsylvania, Virginia, and West Virginia) that have been monitored for its presence (Plumb 1991). The maximum detected 2,4-DNP concentration in the groundwater from a Superfund site in Minnesota was 30.6 mg/L (ATSDR 1988). This site was a former wood-preserving facility (post and pole preserving) that probably used 2,4-DNP as a wood preservative. The concentration of 2,4-DNP in the groundwater of a Superfund site in New Jersey was 40 µg/L (EPA 1988b). In a monitoring project for the detection of priority pollutants, 2,4-DNP was not detected (detection limit of 42 µg/L) in urban runoff from 15 cities (Cole et al. 1984).

5.4.3 Sediment and Soil

Dinitrophenols (unspecified isomers) were detected in the soil of a decommissioned wood-preserving facility in the rural community of Dixiana, South Carolina (EPA 1988a).

5.4.4 Other Environmental Media

In spite of the finding that aqueous solutions of 2,4-DNP quickly permeate plant cuticles and probably metabolize fast in plants, this chemical has been detected in conifer needles. Concentrations of 2,4-DNP in the needles collected from different areas and of different ages ranged from <3.7 to 33.1 µg/kg (Hinkel et al. 1989). The concentrations of 2,4-DNP were higher in needles obtained from roadside and urban areas than rural areas. The higher concentrations of 2,4-DNP in air and in soil, caused primarily by automobile exhaust near the roadside and by automobile exhaust and other anthropogenic sources in urban areas, may be responsible for the higher concentrations of 2,4-DNP in pine needles collected from these two areas. 2,4-DNP content was also higher in needles from older trees. Hinkel et al. (1989) explained that this was due to continuous input and accumulation rates exceeding degradation rates.

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The general population could be exposed to dinitrophenols by inhaling contaminated air and ingesting contaminated food and drinking water. The concentration of dinitrophenols in urban air is expected to

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be higher than in rural air due to smog and heavy vehicular traffic. The concentration values for 2,4-DNP in ambient air, drinking water, or food from any location in the United States, let alone typical values, were not located. Since the banning of 2,4-DNP in diet pills, there is no evidence of general population exposure to this compound from any consumer products. The general population may be dermally exposed to 2,4-DNP from using wood treated with 2,4-DNP or other insecticides containing this compound as an impurity. The occurrence of this exposure, however, has not been verified.

The possibility of occupational exposure to 2,4-DNP in the chemical manufacturing industry and munitions manufacturing industry is discussed in Section 2.2.1.1. The level of 2,4-DNP in the air of one workroom area (where the chemical was handled) of an industry in the 1940s that manufactured picric acid was typically $\geq 40 \text{ mg/m}^3$ (Gisclard and Woodward 1946). Occupational exposures to dinitrophenols would also occur in picramide manufacturing, dye manufacturing, the photographic industry, and wood treatment facilities. Studies establishing occupational exposure to dinitrophenols from these industries were not located, however. The National Occupational Exposure Survey (NOES) of 1983 estimated that a total of 130 and 28 workers are potentially exposed to 2,4- and 2,6-DNP, respectively (RTECS 1992). The NOES database does not contain data on the frequency, duration, concentration, or route of exposure of workers to dinitrophenols or any other chemical.

2,4-DNP or its metabolites have not been measured in the tissues and body fluids of humans in the general population who did not deliberately ingest the compound (as a diet pill). 2-Amino-4-nitrophenol, a metabolite of 2,4-DNP, was qualitatively detected (Derrien test) in the urine of workmen in a munitions factory in France following inhalation exposure of dust and vapor of this compound and dermal exposure to this compound (Perkins 1919). In a case of fatal occupational poisoning from inhaling dust and vapor of 2,4-DNP in a U.S. chemical industry, the urine of the worker contained 2.08 g/L of 2,4-DNP and 50 mg/L of the metabolite 2-amino-4-nitrophenol (Gisclard and Woodward 1946). 2,4-DNP and its metabolite, 2-amino-4-nitrophenol, were detected in the urine of a woman who had taken sodium salt of 2,4-DNP as a diet pill at a dose of 3.5 mg/kg body weight/day (Davidson and Shapiro 1934).

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Within the general population, occupational groups mentioned in Section 5.5 and people who live near hazardous waste sites have potentially high exposures to dinitrophenols. People who live in urban areas where vehicular traffic is high and atmospheric inversion is known to occur may be exposed to higher levels of DNP than populations of less polluted areas. The possibility of occupational exposure leading to higher-than-background population exposure to dinitrophenols is discussed in Section 5.4 and 5.5. People who live near hazardous waste sites that contain this chemical may be exposed to higher concentrations of dinitrophenols by inhaling contaminated air or ingesting contaminated groundwater. Children near these waste sites especially may be exposed to DNP at higher levels, because they may ingest or be dermally exposed to contaminated dirt while playing at these sites. The extent of such exposures for residents around waste sites, however, has not been documented.

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 dinitrophenols 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 dinitrophenols.

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.

5.7.1 Identification of Data Needs

Physical and Chemical Properties. More experimental and estimated data on the physical and chemical properties for 2,4-DNP are available than for other dinitrophenols (see Table 3-2). Even in the case of 2,4-DNP, reliable experimental or estimated values are not available for vapor pressure,

Henry's law constant, and $\log K_{oc}$. This is not surprising since dinitrophenols exist predominantly in the ionic forms at $\text{pH} > 6$ with very low vapor pressure. If available, the physical constants are important in predicting the environmental transport of dinitrophenols. Therefore, it would be helpful to develop more reliable data on certain physical properties important in predicting the environmental fate of these compounds.

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 1992, became available in May of 1994. This database is updated yearly and should provide a list of industrial production facilities and emissions.

Since each individual isomer of the dinitrophenols is manufactured by one or two U.S. companies (SRI 1992), the production volumes of dinitrophenols in recent years are considered confidential business information and are not available in open literature. No data were located that would permit comparison in the trend of dinitrophenol production rates in recent years or project future production volume. Similarly, the quantities of dinitrophenols exported from or imported into the United States from other countries in recent years remain unavailable. Dinitrophenols are used in industries to manufacture other products (HSDB 1994; Sax and Lewis 1987). Other than treated woods, very few consumer products are known to contain dinitrophenols. Considering the industrial uses of dinitrophenols, both water and soil are likely to be contaminated with significant quantities (ATSDR 1988; EPA 1988c; Games and Hites 1977; Plumb 1991; Wegman and Wammes 1983). Although some information about the disposal methods for dinitrophenols is available (HSDB 1994), more information about the efficiency of the different methods of destruction would be helpful. It would also be useful if information on the amounts of dinitrophenols disposed by the two principal methods (land disposal and incineration) were available. Specific information regarding federal regulations on disposal of 2,4-DNP in land, in water, and by incineration is available (EPA 1992a, 1992b, 1992c).

Environmental Fate. From the data in the literature, it is difficult to conclude whether dinitrophenols will partition in a particular environmental medium; therefore, it would be useful to study the concentration distribution of these compounds between the water and sediment in a natural body of water. The environmental transport of dinitrophenols from water by volatilization would not be significant (Callahan et al. 1979), but transport of these compounds from soil to groundwater was

observed (ATSDR 1988; Plumb 1991). Although it is known that these compounds degrade slowly via biodegradation in water (Games and Hites 1977) and at a faster rate in soil (Kincannon and Lin 1985; Loehr 1989; O'Connor et al. 1990), it would be helpful to develop more quantitative data on the rate of biodegradation, particularly in natural water. The importance of abiotic processes, particularly photolysis and oxidation (by radicals, such as OH, HO₂, NO₃), in the transformation/degradation of these compounds in the environment needs further evaluation. Whether vapor-phase dinitrophenols undergo long-distance transport in the atmosphere needs further study.

Bioavailability from Environmental Media. Available absorption kinetics of dinitrophenols following ingestion and dermal contact are discussed in Section 2.3. No experimental or estimated data were located that provide information about the bioavailability of dinitrophenols from natural air, water, and soil. The observation that dinitrophenols are found at least partly in the particulate-sorbed state in the air (Nojima et al. 1983) indicates that their bioavailability from air is <100%. The adsorption of dinitrophenols to soil and sediment depends on the nature of soil and sediment (e.g., organic matter and clay content) and the pH of the medium (Callahan et al. 1979; Kaufman 1976). Therefore, the bioavailability of particle-sorbed dinitrophenols due to desorption from soil and sediment containing a high percent of organic matter and clay may be less than that of the free form (unadsorbed) of dinitrophenol. The bioavailability of dinitrophenols from inhaled air particulates with small particle diameters remains unknown.

Food Chain Bioaccumulation. The bioconcentration of dinitrophenols from water to aquatic organisms and from soil to plants is not expected to be important (EPA 1986a; O'Connor et al. 1990). No data were located on the biomagnification potential for dinitrophenols in predators that consume contaminated prey.

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

No monitoring data are available for dinitrophenol levels in ambient air, drinking water, and total diet samples (typical food consumed by a person in the United States) of the general population.

Consequently, daily human intake of these compounds from inhalation and ingestion routes remains unknown. Although the intake of dinitrophenols by the general population is expected to be low, studies that evaluate the daily intake would be useful. Since vehicular exhaust contains dinitrophenols (Nojima et al. 1983), it would be helpful to analyze roadside soil to determine whether such soils contain elevated levels of dinitrophenols.

Exposure Levels in Humans. Only limited data on the levels of 2,4-DNP in human tissue and body fluids are available. Most of these data are quite dated and were obtained using outdated analytical methods (Davidson and Shapiro 1934; Gisclard and Woodward 1946; Perkins 1919). Studies that determine the levels of 2,4-DNP and its major metabolite (2-amino-4-nitrophenol) in the blood and urine of the general population and in people living near hazardous waste sites containing these pollutants would be useful. This information is necessary for assessing the need to conduct health studies on these populations.

Exposure Registries. No exposure registries for dinitrophenols were located. These substances are not currently compounds for which a subregistry has been established in the National Exposure Registry. These substances 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 exposure to this substance.

5.7.2 Ongoing Studies

No ongoing studies were located that would fill the gap in data concerning the fate, transport, and monitoring of dinitrophenols in environmental and biological samples.