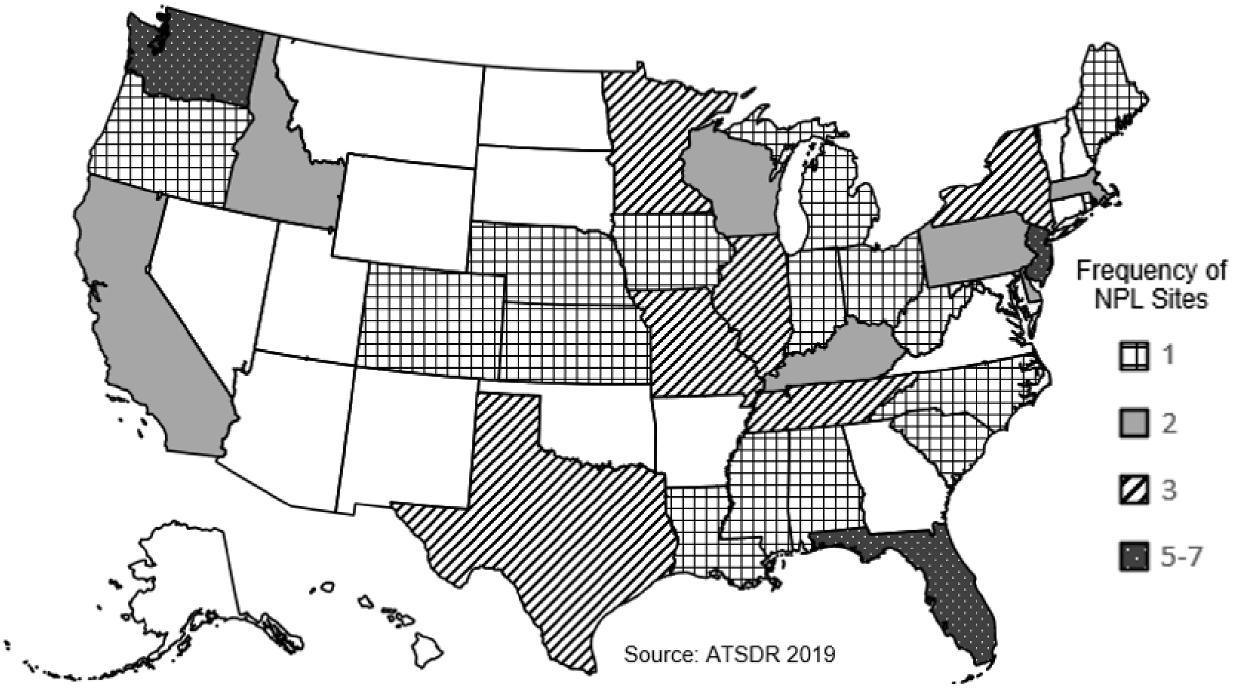
CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

2,4-DNP has been identified in at least 65 of the 1,867 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2019). 2,6-DNP has been identified in at least one of these sites. However, the number of sites in which DNPs have been evaluated is not known. The number of sites in each state is shown in Figure 5-1.

Figure 5-1. Number of NPL Sites with Dinitrophenol Contamination



Source: ATSDR 2019

- The general population could be exposed to DNPs by inhaling contaminated air and ingesting contaminated food and drinking water.

- A daily intake of DNP from air, food, or drinking water has not been estimated, as there are no pertinent data.

- DNPs are used as pH indicators and in the synthesis of dyes, picric acid, picramic acid, wood preservatives, photographic developers, and explosives.

- DNPs are not likely to volatilize appreciably from water or soil. Leaching from soil to groundwater will vary by soil type and degree of DNP adsorption. 2,4-DNP may biodegrade slowly.

DNPs do not occur naturally in the environment; they are released to the environment primarily during their manufacture and use, and from waste disposal sites that contain DNPs (Games and Hites 1977; McLuckey et al. 1985; Patil and Shinde 1988). DNPs also form in the atmosphere from the reaction of benzene with NOx in ambient air (Nojima et al. 1983). Significant removal of DNPs from the atmosphere due to photochemical or other chemical reactions is not likely. Dry and wet deposition of particulate DNPs 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 DNPs in natural waters (EPA 1979a; Lipczynska-Kochany 1992; Tratnyek and Hoigne 1991; Tratnyek et al. 1991). The loss of DNPs from water due to volatilization is negligible (EPA 1979a). Moderate amounts of DNPs are removed from water to sediment due to adsorption (EPA 1979a). Biodegradation may be the most important loss process for DNPs in natural waters (EPA 1979b; 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 DNPs in soil. Biodegradation may be the most significant process for destroying DNPs in soil (Kincannon and Lin 1985; EPA 1989; O’Connor et al. 1990). The loss of DNPs from soil due to volatilization is not significant (Wild and Jones 1992). The mobility of DNPs 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; EPA 1989; O’Connor et al. 1990).

Other than in workplace air, information on DNPs in ambient air in the United States was not located; however, DNPs have been detected in air in other countries (see Section 5.5.1). DNPs were detected in effluent from a dye-manufacturing plant at a maximum concentration of 3.2 mg/L (Games and Hites 1977), but no monitoring data for drinking water in the United States are available. 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 DNPs in food or total diet samples in the United States. Within the overall population, workers at facilities producing or using DNPs are likely to be exposed to higher concentrations of DNPs than the rest of the general population. It is possible that people who live near hazardous waste sites that contain these pollutants may also have higher exposures; however, the extent of such exposures for residents around waste sites has not been documented.

5.2 PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.2.1 Production

The production volume of 2,4-DNP is Confidential Business Information (CBI) (EPA 1991). Therefore, information on the annual production volumes of 2,4-DNP in the United States in recent years has not been published, although the production volumes are substantial (EPA 1991). The most recent information on production volumes based on non-confidential information lists the production range of 10,000–500,000 pounds for 2002 (NLM 2020). Older data, providing historical data on production, indicate that production volume has substantially decreased. For example, NLM (2020) lists the range for production volume in 1986 as >1–10 million pounds. In 1977, the production volume for 2,4-DNP was <1,000 pounds by Alpine Laboratories, Inc., in Bay Minette, Alabama. Production volumes in 1977 for two alternate production sites (Mobay Chemical Corp. in Charleston, South Carolina, and Martin Marietta Corp. in Charlotte, North Carolina) and one plant, whose name remains confidential, were not reported (TSCAPP 1993). According to data from the U.S. International Trade Commission publication on U.S. production and sales of synthetic organic chemicals (USITC 1970), 863,000 pounds of 2,4-DNP were produced in 1968. One chemical company, Sandoz Chemicals Corp., in Charlotte, North Carolina, was listed as a domestic manufacturer of 2,4-DNP in 1992 (SRI 1994) and its yearly production volume was in the range 0.1–1.0 million pounds.

Table 5-1 reports data from 2018 on the number of facilities in each state that manufacture and process 2,4-DNP and the range of maximum amounts of 2,4-DNP stored on-site. The data reported in Table 5-1 are derived from the Toxics Release Inventory (TRI) of EPA (TRI18 2020). The TRI data should be used with caution since only certain types of facilities were required to report. Thus, this is not an exhaustive list. Neither production sites nor volumes for any of the other DNP isomers were located in the available literature.

Table 5-1. Facilities that Produce, Process, or Use 2,4-Dinitrophenol

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
KY	1	1,000	9,999	12
LA	2	100	9,999	1, 5, 13

Table 5-1. Facilities that Produce, Process, or Use 2,4-Dinitrophenol

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
MS	1	1,000	9,999	1, 5, 13
TX	2	0	9,999	1, 5, 12

[a] Post office state abbreviations used.
[b] Amounts on site reported by facilities in each state.
[c] Activities/Uses:

1. Produce
2. Import
3. Onsite use/processing
4. Sale/Distribution
5. Byproduct
6. Impurity
7. Reactant
8. Formulation Component
9. Article Component
10. Repackaging
11. Chemical Processing Aid
12. Manufacturing Aid
13. Ancillary/Other Uses
14. Process Impurity

Source: TRI18 2020 (Data are from 2018)

The commercial DNP mixture is produced by heating phenol with dilute sulfuric acid, cooling the product, and then nitrating while keeping the temperature below 50°C, or by nitrating with a mixed acid under careful temperature control (Sax and Lewis 1987). 2,3-, 2,5-, and 3,4-DNP are prepared by nitration of m-nitrophenol. 3,5-DNP is prepared by the replacement of one nitro group by methoxyl in 1,3,5-trinitrobenzene and demethylation of the dinitroanisole by anhydrous aluminum chloride. 2,6-DNP is prepared by sulfonation and nitration of o-nitrophenol (Harvey 1959). 2,6-DNP is also produced as a byproduct in the synthesis of 2,4-DNP by way of 2,4-dinitrochlorobenzene. Heating with 6% aqueous sodium hydroxide at 95–100°C for 4 hours hydrolyzes 2,4-dinitrochlorobenzene. 2,4-DNP in the hydrolyzed product is precipitated by adding acid; the precipitate is removed by filtration. The residue is washed to remove added acid and the more soluble 2,6-DNP (Booth 1991).

5.2.2 Import/Export

During 1985, 102,000 pounds of 2,4-DNP were imported into the United States (NLM 2020); no information on export of 2,4-DNP from the United States was located, nor were more recent import data. Neither import nor export data for any of the other DNP isomers were located in the available literature.

5.2.3 Use

DNP (commercial mixture of the 2,3- and 2,6- isomers, but mostly the 2,4- isomer) is used in the synthesis of dyes, picric acid, picramic acid, wood preservatives, diaminophenol dihydrochloride (a photographic developer), and explosives, and as a pH indicator. In the 1930s, 2,4-DNP was prescribed by physicians as a weight-reducing agent; however, the FDA has never approved 2,4-DNP as a pharmaceutical agent (FDA 2016). In 1938, the FDA declared DNP to be extremely dangerous and not fit for human consumption, and use of 2,4-DNP was discontinued due to serious adverse health effects, including fatality (Bartlett et al. 2010; FDA 2020a; NLM 2020). In recent years, however, DNP has been sold illegally for this purpose by unregulated sources via the internet. 2,5-DNP is used in the manufacture of dyes, organic chemicals, and as a pH indicator. DNPs are also used in the manufacture of styrene as inhibitors in the purification stills to reduce polymerization (Coulter et al. 1969; Budavari et al. 1989; Sax and Lewis 1987).

5.2.4 Disposal

2,4-DNP has been identified as a hazardous waste by EPA, and disposal of this waste is regulated under the Federal Resource Conservation and Recovery Act (RCRA). Specific information regarding federal regulations on 2,4-DNP disposal on land, in municipal solid waste landfills, and in incinerators is available in the Code of Federal Regulations (EPA 1990, 1992, 1993).

A method that utilizes the classical Fenton reaction (reaction with ferrous chloride and hydrogen peroxide) has been suggested for the treatment of phenolics in waste waters (Lipczynska-Kochany 1991; Vella and Munder 1993). At a nitrophenol to ferrous chloride concentration ratio of 1:3 and in the presence of excess hydrogen peroxide (nitrophenol/hydrogen peroxide ratio=1:18), >90% of nitrophenol was destroyed in <7 hours and no aromatic degradation products were detected (Lipczynska-Kochany 1991). However, the Fenton’s system is very susceptible to inhibitors and hydroxyl radical scavengers (e.g., phosphate and carbonate) (Vella and Munder 1993). Alternative treatment methods for the reduction of nitrophenol concentrations in waste water include activated carbon treatment and biological treatment methods (Vella and Munder 1993). Ultimate disposal of DNP isomers can be accomplished in an incinerator equipped with an acid scrubber for removing oxides of nitrogen (NOx). EPA suggests rotary kiln and fluidized bed incineration as methods for disposal of DNP. Because DNP has been used as a pesticide, the disposal of containers that contained DNP is required by EPA. Combustible containers from organic or many metalloorganic pesticides may be disposed of in pesticide incinerators or in specified landfill sites.

5.3 RELEASES TO THE ENVIRONMENT

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

5.3.1 Air

Estimated releases of 114 pounds (~0.05 metric tons) of DNPs to the atmosphere, from five domestic manufacturing and processing facilities in 2018, accounted for <1% of the estimated total environmental releases from facilities required to report to the TRI (TRI18 2020). These releases are summarized in Table 5-2.

Releases of 2,4- and 2,6-DNPs in air may occur through automobile exhaust (Nojima et al. 1983). Photochemical reactions of benzene with nitrogen oxides in air also produce DNP in the atmosphere (Nojima et al. 1983). DNPs have been detected in emissions from hazardous waste combustion (James et al. 1984). DNPs may be present in the aerosol or vapor phase near hazardous waste disposal sites.

Table 5-2. Releases to the Environment from Facilities that Produce, Process, or Use 2,4-Dinitrophenol[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
KY	1	97	0	0	0	0	97	0	97
LA	2	0	0	0	0	0	0	0	0
MS	1	0	0	0	0	0	0	0	0

Table 5-2. Releases to the Environment from Facilities that Produce, Process, or Use 2,4-Dinitrophenol[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
TX	2	17	0	709,267	0	0	709,267	0	709,284
Total	5	114	0	709,267	0	0	188,429	0	709,381

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

RF = reporting facilities; UI = underground injection

Source: TRI18 2020 (Data are from 2018)

5.3.2 Water

There were no releases of DNPs to surface water from five domestic manufacturing and processing facilities in 2018 required to report to the TRI (TRI18 2020).

DNPs 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 DNPs in surface water are explosives producers (McLuckey et al. 1985), dye-manufacturing plants (Games and Hites 1977), and sewage treatment plants where the influent waters already contain DNPs (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. Small amounts will also enter surface water by wet and dry deposition of atmospheric DNPs (Alber et al. 1989; Bohm et al. 1989; Levsen et al. 1990).

5.3.3 Soil

DNPs may be released in soils in the vicinity of the sites where they are manufactured and used. These releases are summarized in Table 5-2. There were 709,267 pounds (~321 metric tons), which accounted for >99% of the total environmental emissions, were released via underground injection (TRI18 2020). DNPs were also found in the soil of a decommissioned wood preserving facility (EPA 1988b). However, in 2018, there were no releases of DNPs to soil from five domestic manufacturing and processing facilities that are required to report to the TRI (TRI18 2020). Since vehicular exhaust contains DNPs (Nojima et al. 1983), roadside soil might contain these compounds. Small amounts of DNPs will enter soil due to dry and wet deposition of these compounds present in the atmosphere. 2,4-DNP was previously used as an insecticide, acaricide, and fungicide; however, no pesticides containing 2,4-DNP are actively registered in the United States (NLM 2020).

5.4 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. While there are differences in physico-chemical properties (pKa, water solubility, vapor pressure, and other relevant properties) among the isomers, the environmental fate and transport of other DNPs are likely to follow the same general pattern of environmental behavior as that of 2,4-DNP.

5.4.1 Transport and Partitioning

Air. The vapor pressure of 2,4-DNP is 1.49×10^{-5} mm Hg at 18°C (EPA 1981). Organics with vapor pressures of 10^{-4}–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 DNPs. The distance of atmospheric transport of DNPs will depend on atmospheric residence times. The residence time of DNPs, based on the estimated rates of various reactions, is long enough to allow atmospheric transport (see Section 5.3.1). The removal and transport of atmospheric DNPs 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 DNPs have been detected in rain, snow, and fog (Alber et al. 1989; Capel 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 DNPs in the atmosphere have a greater chance to be transported longer distances than DNPs present as aerosols. No monitoring data, however, are available to substantiate long-distance atmospheric transport of DNPs.

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

Water. The partitioning of DNPs from water to suspended solids and sediment due to adsorption would transport these compounds from water to sediment. The sorption of DNPs by soil or sediment would depend on the organic carbon content, clay content, and pH of soil and sediment (EPA 1979a; 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 DNPs 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 DNPs or their metabolites in aquatic organisms were located. Based on bioconcentration factors (BCFs) in the range of 8–24 estimated from octanol/water partition coefficients (EPA 1986b), bioconcentration is not expected to be significant for DNPs in aquatic organisms. In addition, the fact that DNPs 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 $\log \text{BCF} = 1.02 \text{x} \log K_{ow} - 1.82$ 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 4-2), 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.

Takahashi et al. (1994) provided information on the environmental fate of DNPs. Five nitrophenols and two synthetic dyes were ozonated to evaluate: (1) the biodegradability of reaction products from water quality parameters, and (2) the relationship between biodegradability and the behavior of the reaction products and the nitrogen forms. From the comparison of the biodegradability of the target compound, Takahashi et al. (1994) confirmed that the variation of biodegradability was deeply associated with the behavior of the nitrogen forms.

Asman et al. (2005) monitored wet deposition of nitrophenols (including 2,4-DNP) at two sites in Denmark and determined the contributions from regional sources. The authors measured concentrations of selected pesticides and of nitrophenols in rain. Several of the compounds, including 2,4-DNP, could be detected but not quantified. The deposition of 2,4-DNP was up to a factor of 40 higher than that of most of the pesticides tested. Asman et al. (2005) concluded that although these pesticides were not allowed in Denmark, they came in from other places and were transported at least 60–80 km.

Sediment and Soil. The possibility of transport of DNPs 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 DNPs from soil to groundwater also may occur via leaching. The amount of DNP leached depends on the DNP 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 pHs (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 DNPs is high in such soils. Conversely, the leaching of DNPs 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. DNPs have been detected in agricultural watersheds (Wegman and Wammes 1983). This indicates that transport of DNPs to adjacent surface water or land occurs via runoff or as a result of hydrogeological movement of groundwater to surface water from fields where DNPs have been used as pesticides, or other pesticides have been applied (DNPs may also originate as impurities in certain pesticides such as Dinoseb). Such movement of DNPs from soils and groundwater in waste sites is also possible.

Some loss of DNPs 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 (WRSIC 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 DNPs undergo metabolism in plants, plant accumulation of DNPs 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 DNPs (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.

5.4.2 Transformation and Degradation

Air. The reactions of DNPs with hydroxyl and nitrate radicals may be important in determining the residence times of DNPs 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 DNPs 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} cm^3/molecule-second. Based on an average ambient atmospheric concentration of hydroxyl radicals of 5×10^5 radicals/cm^3 (Atkinson 1988), the estimated half-life for the reaction is 28 days. Since DNPs 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 DNPs 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.

Water. The estimated rate constants for the reaction of 2,4-DNP with singlet oxygen ($^1O_2$) and peroxy radicals (RO_2) are 3×10^4/molar-hour and 5×10^5/molar-hour, respectively (EPA 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 (EPA 1979a), 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 19SS), adapted sediment from rivers or waste lagoons (EPA 1979b; 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 (≈10–20 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 concentrations ≤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.

Sediment and Soil. No study was located that reported the abiotic degradation/transformation of DNPs 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; WRSIC 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 DNPs in soils. Both aerobic and anaerobic degradation of DNPs 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 DNP 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 DNPs 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 DNPs for the aerobic biodegradation of soil may vary from 8 to 120 days (Kincannon and Lin 1985; EPA 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 (DOE 1986).

5.5 LEVELS IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to DNPs depends, in part, on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of DNPs in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on DNP 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.

Table 5-3 shows the lowest limits of detection that are achieved by analytical analysis in environmental media. No monitoring data were identified for DNPs in air (see Section 5.5.1). 2,4-DNP was not detected in groundwater or surface water (see Section 5.5.2). Data on other DNP isomers were not available.

Table 5-3. Lowest Limit of Detection Based on Standards[a]

Media	Detection limit	Isomer	Reference
Air	~0.05 mg/kg in particulate matter	2,4- and 2,6-DNP	Nojima et al. 1983
Drinking water	0.005 μg/L	2,4-DNP	Schultz 1983
Surface water and groundwater	13 μg/L	2,4-DNP	EPA 1986c
Soil	0.05 mg/kg	2,3-, 2,5-, 2,6-DNP	Wegman and Wammes 1983
	0.01 mg/kg	2,4- and 3,5-DNP	

Table 5-3. Lowest Limit of Detection Based on Standards[a]

Media	Detection limit	Isomer	Reference
Sediment	0.05 mg/kg	2,3-, 2,5-, 2,6-DNP	Wegman and Wammes 1983
	0.01 mg/kg	2,4- and 3,5-DNP	
Serum and plasma	<0.05 mg/L	2,4-DNP	Robert and Hagardom 1983

[a]Detection limits based on using appropriate preparation and analytics. These limits may not be possible in all situations.

Detections of 2,4-DNP in water and soil at NPL sites are summarized in Table 5-4; there were no detections of other isomers at NPL sites.

Table 5-4. 2,4-Dinitrophenol Levels in Water, Soil, and Air of National Priorities List (NPL) Sites

Medium	Median[a]	Geometric mean[a]	Geometric standard deviation[a]	Number of quantitative measurements	NPL sites
Water (ppb)	400	260	33	5	5
Soil (ppb)	460,000	190,000	20	8	7
Air (ppbv)			No data		

[a]Concentrations found in ATSDR site documents from 1981 to 2019 for 1,867 NPL sites (ATSDR 2019). Maximum concentrations were abstracted for types of environmental media for which exposure is likely. Pathways do not necessarily involve exposure or levels of concern.

5.5.1 Air

No monitoring data reporting ambient, indoor, or occupational air levels of DNPs in the United States were located. Air monitoring data from foreign countries report air concentrations ranging from 0.01 to 53.5 ng/m^3 (Delhomme et al. 2010; Nojima et al. 1983). A review of vapor intrusion data from ATSDR public health assessments completed between 1994 and 2009 did not identify any sites with detected levels of DNPs in groundwater, soil gas, or air (Burk and Zarus 2013). Since DNP is solid at typical ambient conditions, vapor intrusion is not expected to be of concern.

5.5.2 Water

No monitoring data regarding the concentrations of DNPs in U.S. drinking water were located. 2,4-DNP was not detected in over 1,300 surface water samples collected in 2016–2020 from all across the United

States (NWQMC 2020). In a study completed in 2013 by the Oregon Department of Environmental Quality, 2,4-DNP was not detected at or above the lower reporting limit of 209–250 ppt (NWQMC 2020). Recent groundwater testing reports indicate that 2,4-DNP has not been detected at or above reporting limits of 0.5–50 ppb in over 1,000 samples collected across the United States (NWQMC 2020). Foreign monitoring data for rain water reported 2,4-DNP concentrations ranging from <1.0 to 0.367 μg/L (Quaghebeur et al. 2004; Schussler and Nitschke 2001). The ranges of DNP (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). 2,4-DNP was not detected in storm water or wastewater treatment effluent samples collected by the Oregon Department of Environmental Quality in 2010 and 2015, respectively (NWQMC 2020).

5.5.3 Sediment and Soil

As with other media, monitoring results were located only for the 2,4-DNP isomer. 2,4-DNP was not detected at or above quantification (2.1–7,000 μg/kg) or lower reporting limits (26–990 μg/kg) in approximately 3,000 sediment samples collected across the United States from 2010 to 2020 (NWQMC 2020). In surface and subsurface soil samples collected from Bainbridge Island, Seattle, Washington, 2,4-DNP was not detected (NWQMC 2020). 2,4-DNP was also not detected in approximately 350 soil samples collected from other sites in the United States (NWQMC 2020). At superfund sites in Alaska, Colorado, and Utah, 2,4-DNP was not detected in soil samples (NWQMC 2020). Soil samples collected post-Katrina in 2005 and 2006 also did not contain 2,4-DNP (NWQMC 2020).

5.5.4 Other Media

Despite 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.

5.6 GENERAL POPULATION EXPOSURE

The general population could be exposed to DNPs by inhaling contaminated air and ingesting contaminated food and drinking water. The concentration of DNPs in urban air is expected to 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. Although the use of 2,4-DNP in diet pills is no longer legal, the availability of this product from unregulated internet sources may lead to exposure of the general population. The general population may be dermally exposed to 2,4-DNP from using wood treated with 2,4-DNP. The occurrence of this exposure, however, has not been verified. ATSDR's three-compartment Shower and Household Water-Use Exposure (SHOWER) model predicts air concentrations in the shower stall, bathroom, and main house throughout the day for households with up to eight members; the model is a desktop application that is available by sending a request to showermodel@cdc.gov. Using concentrations in water and human activity patterns, the model estimates a daily TWA exposure concentration from breathing indoor air. Inhalation exposure from bathing in 2,4-DNP contaminated water cannot be estimated using the model because volatilization factors are not available for 2,4-DNP. The model can also estimate a dermal dose from skin contact while bathing and washing hands if the 2,4-DNP concentration in water is known.

Occupational exposure to 2,4-DNP may occur in the chemical manufacturing industry and munitions manufacturing industry. 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 ≥40 mg/m^3 (Gisclard and Woodward 1946). Occupational exposures to DNPs would also occur in picramide manufacturing, dye manufacturing, the photographic industry, and wood treatment facilities. Studies establishing occupational exposure to DNPs 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 DNPs or any other chemical.

2,4-DNP and 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 or in a suicide attempt). 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 to 2,4-DNP-contaminated dust and vapor 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 4 mg/kg body weight/day (Davidson and Shapiro 1934).

5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Within the general population, workers in facilities using DNPs have potentially high exposures to DNPs. Persons who reside with, or otherwise come into regular contact with persons who work with DNPs or obtain 2,4-DNP illegally may have potentially high exposures.

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 formed by photochemical reactions than populations of less polluted areas. It is possible that people who live near hazardous waste sites that contain these pollutants may also have higher exposures from inhaling contaminated air or ingesting contaminated groundwater; however, the extent of such exposures for residents around waste sites has not been documented.