

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

There are no known natural sources of 2-nitrophenol and 4-nitrophenol in the environment (HSDB 1989). The primary anthropogenic sources of the two compounds in air are probably industrial manufacturers and processors. Manufacturing and processing industries release an estimated total of 33,000 pounds of 2-nitrophenol and 5,500 pounds of 4-nitrophenol in the air (TRI 1989). Very little of these compounds is directly released to surface waters or soil. About 21,500 pounds of 2-nitrophenol and 250 pounds of 4-nitrophenol are disposed of in off-site landfills by the industries. In addition, about 7,000 pounds of 4-nitrophenol are disposed of by underground injection (TRI 1989). The nitrophenols can also be formed in the air as a result of the atmospheric photochemical reactions of several aromatic compounds formed from anthropogenic sources. They are also formed in vehicular exhausts as a result of the thermal reaction of fuel with oxides of nitrogen. 4-Nitrophenol is formed as a degradation product and it is an impurity in parathion formulations (HSDB 1989; Nojima et al. 1976, 1980).

In the air, both photolysis and physical removal processes such as gravitational settling of aerosols and wet deposition by rain and snow will probably determine the fate of 2-nitrophenol and 4-nitrophenol. The atmospheric half-lives of these compounds are not known. In water, both photolysis and biodegradation will be important fate processes. Photolysis will be more important in near-surface water; where attenuation of sunlight is usually minimal. The half-life of the nitrophenols may range between 1 and 8 days in fresh water and may range between 13 and 21 days in sea water. In soils, biodegradation may be the most important fate process for these nitrophenols. In top-soil, the half-life of 4-nitrophenol may be about 1-3 days under aerobic conditions and around 14 days under anaerobic conditions. In subsoils, the half-life of 4-nitrophenol may be about 40 days under aerobic conditions and even slower under anaerobic conditions. The half-life of 2-nitrophenol may be about 12 days under aerobic conditions (Bourquin et al. 1982; Bourquin 1984; EPA 1985; HSDB 1989; Kincannon and Lin 1985; Loekke 1985). However, other studies have found that the rate of disappearance of nitrophenols, both in water and soil, may not be first-order, and evaluation of a biodegradation half-life may not be meaningful (Hoover et al. 1986; Jones and Alexander 1986, 1988; Scow et al. 1986, 1989; Zaidi et al. 1988, 1989). The products of biodegradation have also been studied with pure cultures of microorganisms. Catechol, beta-keto adipic acid, and nitrite have been identified as products of aerobic biodegradation of 2-nitrophenol (Zeyer and Kearney 1984) and 4-nitrocatechol, hydroquinone, gamma-hydroxymuconic semialdehyde, and nitrite from 4-nitrophenol (Raymond and Alexander 1971; Spain et al. 1979). On the other hand, 2-aminophenol and 4-aminophenol have been isolated from anaerobic biodegradation of 2-nitrophenol and 4-nitrophenol, respectively (Adhya et al. 1981; Villanueva 1961).

Monitoring data for the nitrophenols in any environmental medium were limited. The average concentration of 2-nitrophenol in the gas phase during

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seven rainfalls in Portland, Oregon, in 1984 was $0.024 \mu\text{g}/\text{m}^3$. The corresponding concentration in rain water was $0.059 \mu\text{g}/\text{L}$ (Leuenberger et al. 1985). The nitrophenols have been identified in effluents from several industries at a median concentration of less than $10 \mu\text{g}/\text{L}$ (Staples et al. 1985). 4-Nitrophenol was detected in the potable water supply of Ames, Iowa, at a concentration of $0.2 \text{ mg}/\text{L}$. The source of the compound was probably the contamination of well water from coal gas plant wastes (EPA 1980). No other report of detection of either nitrophenol in U.S. drinking waters was found in the literature. The two nitrophenols and their mixture have been detected in 14 NPL waste sites (View 1989). The frequency of these sites within the United States can be seen in Figure 5-1.

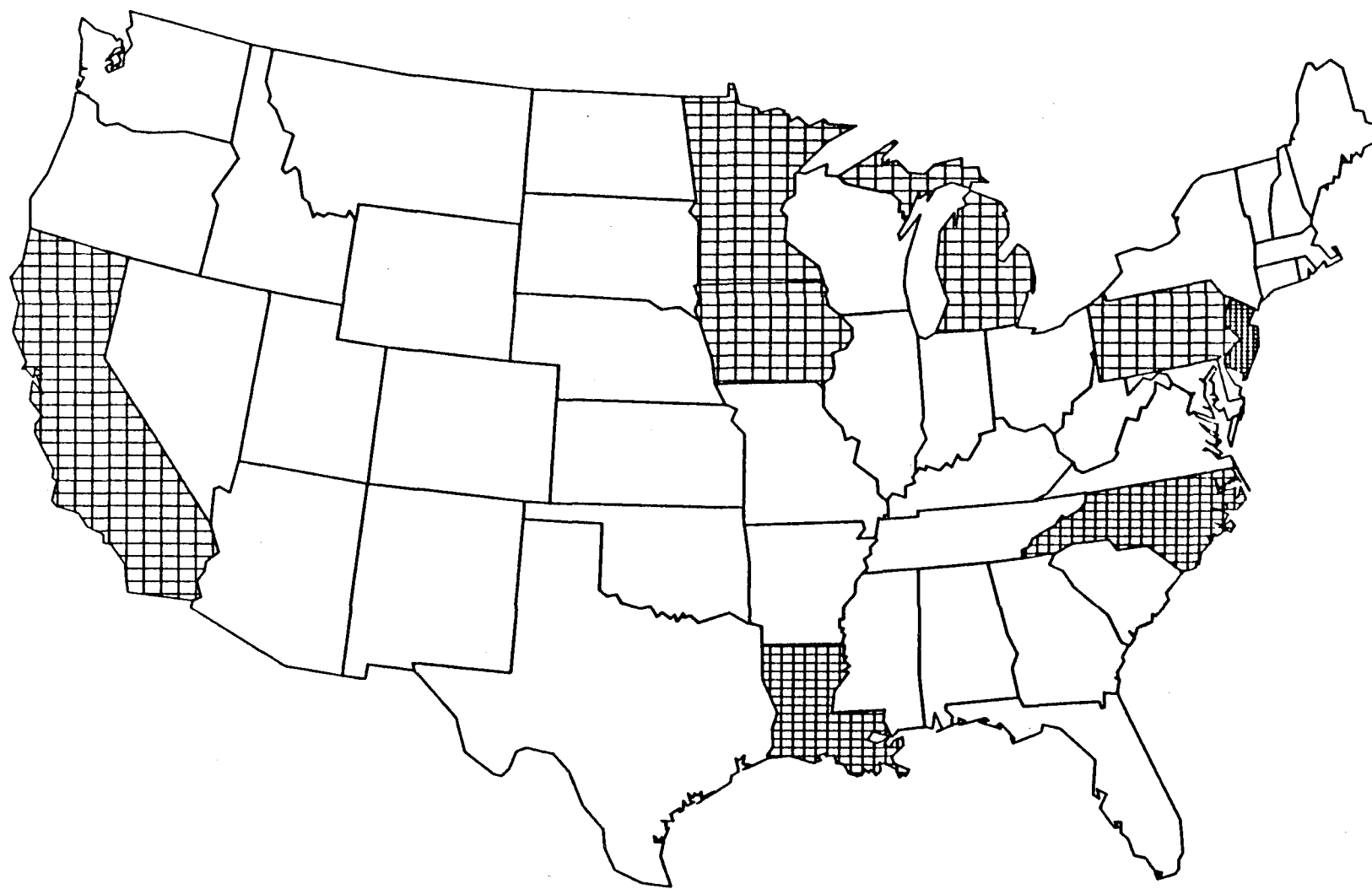
No report on the detection of either nitrophenol in any food was found in the literature. In a Health and Nutrition Survey conducted by the National Center for Health Statistics, 4-nitrophenol (as its glucuronide or sulfate conjugate) was quantifiable in 2.4% of urine samples of the general population, with a geometric mean value of less than $10 \mu\text{g}/\text{L}$. It was speculated that the 4-nitrophenol originated from the pesticides methyl and ethyl parathion (Carey and Kutz 1985; Kutz 1983). Although no experimental data are available, it is likely that people who live near landfills that contain these compounds, applicators of certain pesticides, and those people who consume contaminated drinking water from groundwaters adjacent to parathion-treated farmlands are potentially exposed to doses higher than the background level.

5.2 RELEASES TO THE ENVIRONMENT

5.2.1 Air

There is no evidence of the formation of 2-nitrophenol and 4-nitrophenol from natural sources in the environment (HSDB 1989). The primary anthropogenic sources of the two compounds in air are probably industrial manufacturers and processors. The manufacturing and processing industries release an estimated total of 33,000 pounds of 2-nitrophenol and about 5,500 pounds of 4-nitrophenol in the air (TRI 1989). These facilities and the amount of individual atmospheric emissions are shown in Table 5-1. Monsanto Co. disposes of a large amount (about 175,000 pounds) of 4-nitrophenol and 4,000 pounds of 2-nitrophenol by incinerator/thermal processes (TRI 1989). It should be mentioned that the TRI (1989) release data in these sections are quantities released to the environment in 1987. Since the efficiencies of the incinerator/thermal processes are less than 100%, a small amount of undegraded nitrophenols will be released into the air during these processes. The nitrophenols can also be formed in the air as a result of atmospheric photochemical reactions of nitrobenzene, aromatic hydrocarbons (e.g., benzene and toluene) and bromobenzene primarily formed from anthropogenic sources with nitrogen oxides present in the air (HSDB 1989; Nojima et al. 1976, 1980;

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



FREQUENCY  1 SITE  2 SITES  5 SITES

* Derived from View 1989

TABLE 5-1. Releases to the Environment from Facilities that Manufacture or Process Nitrophenols^a

Facility	Location	Release in lbs							Isomer
		Air	Underground injection	Water	Land	Total environment	POTW transfer	Off-site transfer	
Monsanto Company	Anniston, AL	500	0	0	250	750	250	0	4-NP
Monsanto Company	Sauget, IL	27,000	0	0	0	27,000	120,000	4,000	2-NP
Monsanto Company	Sauget, IL	2,200	0	0	0	2,200	92,000	175,000	4-NP
Monsanto Company	Luling, LA	2,250	6,800	0	0	9,050	0	250	4-NP
Ciba-Geigy Corporation	St. Gabriel, LA	0	0	250	0	250	0	0	2-NP
FMC Corporation - Baltimore Plant	Baltimore, MD	6,149	0	0	0	6,149	7,684	21,553	2-NP
Mallinckrodt, Inc.	St. Louis, MO	0	0	0	0	0	1,200	0	4-NP
Monsanto Company	St. Louis, MO	500	0	0	0	500	90,000	0	4-NP
Kollsman	Merrimack, NH	0	0	0	0	0	0	0	2-NP
Tennessee Eastman Company	Kingsport, TN	2	0	0	0	2	0	0	4-NP

^aDerived from TRI 1989 and release data for 1987

2-NP = 2-nitrophenol

4-NP = 4-nitrophenol

Off-site = waste containing nitrophenols are transferred away from plant site for incineration, land, or other modes of disposal

POTW = publicly owned treatment works

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Rippen et al. 1987). The nitrophenols are released from exhausts of both gasoline- and diesel-powered vehicles (Nojima et al. 1983). 4-Nitrophenol is a degradation product of parathion and is one of the impurities in parathion formulations (HSDB 1989). Therefore, small amounts of 4-nitrophenol may be released in local windblown dusts in areas where these pesticides are used. A quantitative estimate of atmospheric release of 2-nitrophenol and 4-nitrophenol from any of the last three indirect pathways (photochemical formation, vehicular exhaust, parathion use) is not available.

5.2.2 Water

The estimated total direct industrial releases of 2-nitrophenol and 4-nitrophenol in U.S. surface waters are 250 and 0 pounds, respectively (TRI 1989). The facilities that emit and the amount of individual emissions in water are shown in Table 5-1. Much larger amounts of the two compounds from direct manufacturing and processing industries are released into publicly owned treatment works (POTWs). The releases of 2-nitrophenol and 4-nitrophenol to POTWs have been estimated to be 128,000 pounds and 184,000 pounds, respectively (see Table 5-1). The parathion formulations contain small amounts of 4-nitrophenol as impurities, and the hydrolysis and biodegradation of the pesticide can produce 4-nitrophenol (Gomaa and Faust 1972). Therefore, application of the pesticide formulations may release 4-nitrophenol into surface water as a result of runoff from land. Small amounts of 4-nitrophenol conjugates are excreted in the urine of people exposed to parathion formulations (Carey and Kutz 1985; Kutz 1983). This could be a minor route of entry of 4-nitrophenol into POTWs. Effluents from the textile industry may also release both 2-nitrophenol and 4-nitrophenol into surface water and POTWs (EPA 1981). In addition, the two nitrophenols were found in treated waste waters from the following industries: iron and steel manufacturing (nitrophenols formed during the coke making process); foundries (nitrophenols formed during the coke making process); pharmaceutical manufacturing; rubber processing; and electrical/electronic components production (EPA 1981).

5.2.3 Soil

It is estimated that only a small amount (250 pounds) of 4-nitrophenol and no 2-nitrophenol is discharged directly to on-site land from facilities in the United States that manufacture or process these chemicals (TRI 1989). However, about 21,500 pounds of 2-nitrophenol and 250 pounds of 4-nitrophenol are disposed of in off-site landfills by these industries (TRI 1989) (see Table 5-1). In addition, about 7,000 pounds of 4-nitrophenol is disposed of by underground injection (see Table 5-1). Therefore, manufacturing and processing industries are sources of the nitrophenols in soils and may cause groundwater contamination near the disposal sites. As has been discussed in Section 5.2.2, the application of parathion formulations to foliage could be an additional source of 4-nitrophenol in soil. Atmospheric to terrestrial transfer, primarily through rainwater and snow, will be secondary sources of

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the nitrophenols in water and soil (Luenberger et al. 1988). Deposition of vehicular exhaust on roadways is another source of nitrophenols in soil. No quantitative estimate of the amounts of the two nitrophenols released into soil from the latter three sources is available.

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

The fate and distribution of 4-nitrophenol in different environmental compartments were assessed with a nonsteady-state equilibrium model (Yoshida et al. 1983). The model predicted the following distribution: air, 0.0006%; water, 94.6%; soil, 0.95%; sediment, 4.44%; and biota, 0.00009%. Therefore, only a very small fraction of this compound released from various sources is expected to remain in the air. The atmospheric concentration of 2-nitrophenol is expected to be higher than the 4-isomer because it has a Henry's law constant value that is four orders of magnitude higher (see Table 3-2). Based on the 4-nitrophenol data given by Yoshida et al. (1983), the fraction in air is still expected to be small for 2-nitrophenol.

The partitioning of a chemical from the atmosphere to land and water depends on its physical state and physico-chemical properties. For example, gravitational settling may be more important than other transport processes for partitioning of suspended particulate matters from air to land and water, whereas wet deposition via rainwater or snow may be more important for chemicals that exist in the vapor phase in air. From the vapor pressure data (see Table 3-2), both these chemicals are expected to be present predominantly in the vapor phase in the atmosphere (Eisenreich et al. 1981), although they have been detected in particulates collected over Yokohama, Japan (Nojima et al. 1983). Because of their significant water solubilities (see Table 3-2) and expected existence in the vapor phase, partitioning of these chemicals from air to surface waters and land via wet deposition is expected to occur. The detection of both these nitrophenols in rainwater by a few authors (Luenberger et al. 1988; Rippen et al. 1987) supports this partitioning mechanism.

The intramedia transport of the two compounds from their points of emission to locations farther away in the air will depend on the lifetime of the compounds in air. Because of their significantly long half-life (days) in the air (Section 5.3.2), these compounds are expected to undergo atmospheric transport from polluted areas to less polluted or pristine areas. However, there is no experimental evidence to confirm the long-range transport of the nitrophenols.

The partitioning of 2-nitrophenol and 4-nitrophenol from water to air and different aquatic phases will depend on its volatility from water to air and its distribution between water, sediment, and biota. Experimental volatilization rates for either of the compounds from water are unavailable.

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The modeling data based on nonsteady-state equilibrium predict that volatilization of 4-nitrophenol will be insignificant (Yoshida et al. 1983). The Henry's law constant (H) values for these two compounds (see Table 3-2) and the volatility characteristics associated with various H values (Thomas 1982) can be used to predict that volatilization from water will not be important. The dissociation constant (pKa) values of the two compounds (see Table 3-2) indicate that significant fractions of these nitrophenols will be dissociated at pHs above 6. Since ionic species do not volatilize significantly from water, the ionization may further limit volatilization.

The partitioning of the nitrophenols between water and sediment is expected to depend on the pH of the water. Two sorption mechanisms may be operating: one is the normal hydrophobic sorption common to hydrophobic organic compounds, and which can be correlated with organic carbon content of sediments. The other is chemical bonding (probably hydrogen bonding) between the sediment and the chemical (Boyd 1982; Isaacson 1985). The fact that sorption of 4-nitrophenol was correlated with iron oxide, clay, and silt contents of soils (Artiola-Fortuny and Fuller 1982) confirms these hypotheses. The log K_{oc} values of 2.06-2.42 (see Table 3-2) can be used to predict that the two nitrophenols would not be sorbed appreciably to sediments. On the basis of the K_{oc} value, the nonsteady-state equilibrium model (Yoshida et al. 1983) predicts that only 4.4% of 4-nitrophenol will remain in sediment, compared to 94.6% in water. The sorption will be higher for sediments with high organic content, iron oxide and montmorillonite or other clay minerals. Experimental data with an estuarine sediment show that, once 4-nitrophenol is sorbed to reduced estuarine sediment, the desorption of the compound from sediment back to the water column will be insignificant (Siragusa and Delaune 1986).

The bioconcentration factor (BCF) (wet-weight basis) for 4-nitrophenol in a species of green algae (Chlorella fusca) was 30 (Geyer et al. 1984). In golden orfe fish (Leuciscus idus melanotus), the whole-body BCF after 3 days of exposure was 57 (Freitag et al. 1982). With ^{14}C radiolabeled test compound, the mean plateau whole-body ^{14}C BCF for 4-nitrophenol in the fathead minnow (Pimephales promelas) was 180. Only 2.7% of the tissue contained the parent compound after 28 days of depuration, and the compound was eliminated with a mean depuration half-life of 150 hours. 4-Aminophenol was identified as a metabolite (Call et al. 1980). Other authors have estimated a BCF of 126 for 4-nitrophenol from its octanol/water partition coefficient and various regression equations (Isnard and Lambert 1988; Schueuermann and Klein 1988). Based on available BCFs, 4-nitrophenol would biomagnify from lower to higher trophic levels in both aquatic and terrestrial organisms (Loehr and Krishnamoorthy 1988).

The transport and partitioning of nitrophenols in soils will depend on their sorption and volatilization characteristics. The sorption characteristics will be similar to those described in sediments. The measured log K_{oc} values for 2-nitrophenol and 4-nitrophenol in a clay loam soil of

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5.1% organic matter content and a pH of 5.7 were 2.06 and 1.72, respectively (Boyd 1982). Other authors have reported log K_{oc} values in the range 2.18-2.42 for 4-nitrophenol (Hodson and Williams 1988). These K_{oc} values indicate that nitrophenols will not strongly adsorb to soils. Although sorption of 4-nitrophenol to soil is weak, the sorption increases with the hydrogen bonding capacity of soils/sediments (Artiola-Fortuny and Fuller 1982; Isaacson 1985). Therefore, in the absence of significant degradation, nitrophenols may leach from soil and may be found in the leachate of landfills.

In a laboratory study in which a test system was constructed to simulate a typical terrestrial ecosystem in terms of air flow (over soil), percolating water (through soil), and vegetation cover, the fate of nitrophenols was studied with radiolabeled compounds added to soil. Of the total radioactivity applied to soils, only 1.6% in the case of 4-nitrophenol and 45.3% in the case of 2-nitrophenol were recovered in the gas phase after 30 days that were not attributable to CO_2 formed from biodegradation or other mineralization processes. Although the portions of the gas phase that were not attributable to CO_2 were not identified (i.e., they could be the nitrophenols or their metabolites other than CO_2), this study indicates that volatilization from soil will be insignificant for 4-nitrophenol but may be significant for 2-nitrophenol. In the same terrestrial ecosystem study, 35.7% and 12.7% of the applied radioactivities were recovered in plants when 4-nitrophenol and 2-nitrophenol, respectively, were used (Figge et al. 1983). This indicates that a significant portion of nitrophenols (or their metabolites) may be transferred from soil to plant. However, this transfer may not indicate bioaccumulation in plants because of the possible metabolism in plants.

5.3.2 Transformation and Degradation

5.3.2.1 Air

The two processes that are likely to degrade nitrophenols in air are direct photolysis and reactions with free radicals in the air. Very few studies are available on photolysis of nitrophenols in the air. When 4-nitrophenol was coated on silica gel and irradiated with an ultraviolet (UV) lamp of wavelengths greater than 290 nm in the presence of an air current, 39% of the starting material photomineralized to CO_2 after 17 hours (Freitag et al. 1982; Korte and Klein 1982). No experimental data on the vapor-phase photolysis of the nitrophenols are available. Photolysis experiments in water (Section 5.3.2.2) can be used to predict that photolysis of the nitrophenols in air will be a significant degradation process.

The rate constant for the gas-phase reaction of 2-nitrophenol with OH radicals is 9.0×10^{-13} cm^3 -molecule/sec at 21°C (Atkinson 1985) and 8.95×10^{-13} cm^3 -molecule/sec at 27°C (Gusten et al. 1984). Assuming that a 24-hour average concentration of OH radicals in a normal atmosphere is 5×10^5 radicals/ cm^3 (Atkinson 1985), the atmospheric half-life of 4-nitrophenol

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due to this reaction is an estimated 18 days, and the reaction may not be an important fate determining process in the atmosphere.

5.3.2.2 Water

Chemical oxidation reactions of the two nitrophenols by singlet oxygen and alkyl peroxy radicals formed as a result of sunlight-induced photochemical reactions in water are too slow to be significant (EPA 1985; Scully and Hoigne 1987). OH radicals in water attack 2-nitrophenol and 4-nitrophenol at the 2- and 4-carbon positions, resulting in the formation of a variety of products including 1,4-benzoquinone, 1,4-dihydroxybenzene and 4-nitrocatechol (4-nitro-1,2-dihydroxybenzene) (Suarez et al. 1970). 4-Nitrophenol photoreacts quite rapidly in water in the presence of nitrate or nitrite (EPA 1985). This is not surprising, since nitrate and nitrite in water produce elevated concentrations of OH when irradiated by sunlight.

The photolytic behavior of nitrophenols in water is well studied. The irradiation of 4-nitrophenol in neutral or acidic aqueous solution in the presence of air at wavelength 365 nm produced primarily hydroquinone and HNO₂, together with small amounts of benzoquinone and 4-nitrocatechol (HSDB 1989). Other authors have determined the phototransformation quantum yield to be in the range 3.3×10^{-6} to 8.3×10^{-6} at pH 9.0 (ECETOC 1984; Lemaire et al. 1985). From the quantum yield data, the half-life of 4-nitrophenol in near-surface water was an estimated 27.5 hours at pH 5.5 under sunlight conditions equivalent to noontime, summer conditions in Chicago (EPA 1985). Hustert et al. (1981), on the other hand, used the EPA test procedure and determined the photolytic half-lives of 5.7 days at pH 5, 6.7 days at pH 7, and 13.7 days at pH 9.

The biodegradability of nitrophenols in water has been studied extensively with pure cultures of microorganisms, mixed microorganisms and standardized screening test methods (Blok et al. 1985; Boatman et al. 1986; Chambers et al. 1963; Frietag et al. 1982; Gerike and Fischer 1979; Jones and Alexander 1986; Kitano 1978; Kool 1984; Korte and Klein 1982; McCormick et al. 1976; Means and Anderson 1981; Neujahr and Varga 1970; Neujahr et al. 1974; Patterson and Kodukala 1981; Pitter 1976; Rott et al. 1982; Sudhakar-Barik et al. 1976; Tabak et al. 1981; Wilderer 1981; Zaidi et al. 1988). Depending on test conditions, the results from these tests vary considerably, some predicting that 4-nitrophenol is not easily biodegradable and others predicting easy biodegradability. It has been established that the nitrophenols have a lag period before the onset of biodegradation (Haller 1978).

Several authors have used natural waters to study the aerobic biodegradability of 4-nitrophenol and concluded that, after a few days of adaptation, it will rapidly biodegrade in many of these waters (Bourquin et al. 1982; Spain et al. 1980; Spain and Van Veld 1983; Spain et al. 1984). The half-life of biodegradation in natural water (parent compound disappearance)

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reported or estimated from experimental results are as follows: about 3.5 days in a river (Bourquin et al. 1982; Bourquin 1984); a mean of 3.2 days for five pond and river waters (Vaishnav and Korhals 1988); and a mean of less than 1 day for five pond and river waters based on the concentration of degrader microorganisms of 10^{+6} organisms/ml (Paris et al. 1983). Compared to these fresh waters, the half-life of 4-nitrophenol in sea water may be longer, and the experimental half-life may range between 13 and 21 days (Bourquin et al. 1982; Bourquin 1984; Van Veld and Spain 1983). The rate and extent of degradation of 4-nitrophenol in natural water also depend on the initial concentration of the substance, the nature and concentration of nutrients, the activities of the organisms, and the presence or absence of predators or inhibitors of degrader organisms (Hoover et al. 1986; Jones and Alexander 1988; Rubin and Alexander 1983; Rubin et al. 1982; Subba-Rao et al. 1982; Wiggins and Alexander 1988; Zaidi et al. 1989). Other investigators have found that the rate of biodegradation of nitrophenols may follow complex kinetics and the derivation of a half-life based on simple first-order kinetics in such cases would not be appropriate (Jones and Alexander 1986, 1988; Zaidi et al. 1988).

Biodegradation studies of the two nitrophenols with digested sludge under methanogenic conditions have shown that the compounds are not easily biodegraded and that 4-nitrophenol at high concentration is inhibitory to methanogenic microorganisms (Battersby and Wilson 1989; Horowitz et al. 1982). The anaerobic biodegradation of 4-nitrophenol in bottom sediments of lakes and rivers is also a slow process (Siragusa and DeLaune 1986). However, in anaerobic screening tests using digester sludge inocula, 4-nitrophenol completely disappeared in 1 week in one study (Boyd et al. 1983), and over 75% mineralized in 56 days in another (Shelton and Tiedje 1984). Under anaerobic conditions in two flooded soils, over 50% degradation of 2-nitrophenol and 4-nitrophenol was observed in 10 days (Sudhakar-Barik and Sethunathan 1978).

5.3.2.3 Soil

Data regarding the chemical degradation of nitrophenols in soils are lacking. Oxides of Mn (+3/+4) undergo reductive dissolution by substituted phenols. However, nitrophenols are among the most resistant substituted phenols for this reaction, which will be quite slow at neutral and alkaline PH. At low pHs, the nitrophenols may degrade at an appreciable rate, forming dimeric and polymeric oxidation products, since the dissolution rate of one form of Mn_xO_y with 4-nitrophenol was less than 10^{-9} mol/L-min at a pH of 4.4 (Stone 1987). The significance of this reaction under environmental conditions where the concentration of nitrophenols will be expected to be much lower than that used (10^{-2} M) in the experiment of Stone (1987) is likely to be low. The photolytic reaction of nitrophenols will not be significant beyond the surface layer of soil because light attenuation will reduce the light intensity to insignificant levels. The most important fate determining process for nitrophenols in soils is expected to be biodegradation. A number of studies discussed in the following paragraph support this conclusion.

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Several pure cultures isolated from soils degraded nitrophenols (EPA 1985). As in the case of water, adaptation of soil to 4-nitrophenol was a prerequisite for biodegradation; the presence of a critical number of degrader microorganisms was necessary for the initiation of biodegradation. However, unlike in natural water, the mineralization of low concentrations of 4-nitrophenol proceeds with little or no initial acclimation period (Scow et al. 1986). Addition of specific nutrients from pristine aquifer also resulted in more rapid adaptation (Aelion et al. 1987; Swindoll et al. 1988), and the rate of biodegradation was concentration-dependent (Scow et al. 1986). The biodegradation of 2-nitrophenol by soil microorganisms is comparatively slower than that of 4-nitrophenol (Alexander and Lustigman 1966; Figge et al. 1983). In a study designed to simulate biodegradation of chemicals under natural land disposal conditions, the half-life of 2-nitrophenol in sandy loam soil was estimated to be 12 days under aerobic conditions (Kincannon and Lin 1985). In topsoil, the half-life of 4-nitrophenol was about 1 day under aerobic conditions and 14 days under anaerobic conditions. Addition of certain nutrients reduced the anaerobic half-life of 4-nitrophenol. In subsoils, the half-life of 4-nitrophenol was 40 days under aerobic conditions and even slower under anaerobic conditions (Loecke 1985). From a laboratory microcosm study simulating coastal wetlands, the half-life of 4-nitrophenol was predicted to be 2-3 days (Portier 1985).

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

Monitoring data for nitrophenols in U.S. air are limited. Therefore, monitoring data for these compounds in ambient air, rainwater and vehicular exhausts from both inside and outside of the United States are presented. Nitrophenols were detected but not quantified in the urban air and rainwater of a Japanese city in 1975 (Rippen et al. 1987). Concentrations of 2-nitrophenol (less than 0.05-3.9 $\mu\text{g/g}$) and 4-nitrophenol (5.1-42 $\mu\text{g/g}$) were detected in the air particulate matter collected in a Japanese city in 1982. Under engine idling conditions, the concentrations of 2-nitrophenol and 4-nitrophenol in vehicular exhaust gases were 3.1 ppb (17.9 $\mu\text{g/m}^3$) and less than 0.5 ppb (less than 2.9 $\mu\text{m/m}^3$), respectively, for a gasoline engine (2,600 cc) and 6.4 ppb (37 $\mu\text{g/m}^3$) and 2.5 ppb (14.5 $\mu\text{g/m}^3$), respectively, for a diesel engine (7,000 cc) (Nojima et al. 1983). The average concentration of 2-nitrophenol in the gas phase during seven rainfalls in Portland, Oregon, in 1984 was 0.024 $\mu\text{g/m}^3$. The corresponding concentration in rainwater was 0.059 $\mu\text{g/L}$ (Leuenberger et al. 1985). The concentrations of 2-nitrophenol in air and rainwater at Dubendorf, Switzerland, in 1985 were 0.35 $\mu\text{g/m}^3$ (one rainfall) and 0.1-0.8 $\mu\text{g/L}$ (several rainfalls), respectively (Leuenberger et al. 1988). 2-Nitrophenol was also detected in rainwater at a concentration of 0.031 $\mu\text{g/L}$ in Azusa, California, and at 0.1-1.4 $\mu\text{g/L}$ in different locations in West Germany. 4-Nitrophenol was also detected in rainwater at concentrations of 2-24 $\mu\text{g/L}$ in different locations in West Germany. Extremely high values of

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4-nitrophenol (up to 50 µg/L) have been found in rainwater from a thunderstorm after a hot and sunny period (Rippen et al. 1987).

5.4.2 Water

The nitrophenols have been identified in effluents from several industries. 2-Nitrophenol has been detected in effluents from photographic and electronics industries (Burse and Pellizzari 1982). Nitrophenols (isomer unidentified) at a concentration of 5 mg/L was detected in oil shale retort water (Dobson et al. 1985). Nitrophenols have been identified in effluents from other chemical plants, as well. 4-Nitrophenol has been identified in effluent from a pesticide plant (EPA 1985). Both 2-nitrophenol and 4-nitrophenol were detected in the final effluent from the waste water of a petroleum refining industry (Snider and Manning 1982). Nitrophenols have also been identified in primary and secondary effluents of municipal waste water treatment plants. For example, both nitrophenols were identified in the secondary effluent from a waste water treatment plant in Sauget, Illinois, (Ellis et al. 1982), and 4-nitrophenol was detected in both primary and secondary effluent from a waste water treatment plant in Los Angeles, California, in secondary effluent from a waste water treatment plant in Orange County, California, and in primary effluent from a San Diego, California, waste water treatment plant (Young 1978). Based on data from EPA's STORET database from 1980 to January 1984 (to assure better quality, data from earlier years have been excluded), 2-nitrophenol and 4-nitrophenol have been detected in 1.8% (total samples, 1318) and 3.3% (total samples, 1322) of effluent samples for the respective isomer at various locations in the United States. The median concentrations of both nitrophenols in these samples were less than 10 µg/L (Staples et al. 1985). 4-Nitrophenol was found in stormwater runoffs from four (Long Island, New York; Washington, District of Columbia; Little Rock, Arkansas; and Eugene, Oregon) of 15 cities at concentrations ranging from 1 to 19 µg/L (Cole et al. 1984).

Neither of the nitrophenols was detected in water from Lake Erie and Lake Michigan (Great Lakes Water Quality Board 1983). Based on data from EPA's STORET database since 1980 (to assure better data quality), neither of the nitrophenols was detected in any of the over 800 ambient surface water samples analyzed (Staples et al. 1985). 4-Nitrophenol at a concentration of 0.2 mg/L was detected in the potable water supply of Ames, Iowa. The source of the compound was speculated to be the contamination of well water from the wastes of a coal gas plant after the plant ceased operation around 1930 (EPA 1980). No other detection of either nitrophenol in U.S. drinking waters was reported.

5.4.3 Soil

The monitoring program conducted by EPA at Love Canal (Niagara Falls, New York) in 1980 qualitatively detected the presence of both nitrophenols in sediment/soil samples (Hauser and Bromberg 1982). Brown and Donnelly (1988)

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compiled leachate data from several landfills in the United States. The concentration range for 2-nitrophenol in a few unspecified municipal landfill leachates was reportedly 8.6-12.0 mg/L. The presence of 2-nitrophenol in the leachates suggests that the compound was also present in the soil, although no soil monitoring data were reported. 2-Nitrophenol was detected at a concentration of 76 mg/L in one of 1,131 samples taken from drums, tanks, or other containers from 221 hazardous waste disposal sites in 41 states and one territory (Blackman et al. 1984). The nitrophenols have not been monitored in all of the 1,177 hazardous waste sites listed on the NPL. In the sites monitored so far, the two isomers and their mixture were found at 14 sites (View 1989). Additionally, 2-nitrophenol and 4-nitrophenol were found in 15 and 29 matrices (surface water, groundwater, and soil), respectively, in the Contract Laboratory Statistical Program Database (CLPSD 1988). Note that the Contract Laboratory Program Statistical Database includes data from both NPL and non-NPL sites.

5.4.4 Other Environmental Media

No data in the literature demonstrated the presence of the nitrophenols in foods. The production of 4-nitrophenol from degradation or metabolism of several pesticides, including parathion and fluoridifen, on plant leaves or in soil may result in the contamination of food crops following application of these pesticides. When spinach fields were sprayed with 0.5-1.0 pound (active ingredient) of parathion/acre, the 4-nitrophenol residues 7 days following application of the pesticide at the recommended application rate did not exceed the unsprayed spinach. The source of 4-nitrophenol in unsprayed spinach was not stated. Since the recommendations for parathion application call for harvesting at least 14 days following application, 4-nitrophenol may not be found in harvested spinach (because it was not found in spinach on the 7th day following application) (EPA 1980). As of September 1991, EPA has reached a settlement agreement with registrants of the insecticide to limit the use of parathion to nine field crops (alfalfa, corn, canola, cotton, sorghum, soybeans, sunflower, and wheat) and intends to issue a Notice of Intent to Cancel (NOIC) the field use of parathion in the near future. The EPA decision is based on concerns about unacceptable risks of exposure to agricultural workers, the general public, birds, and aquatic invertebrates (EPA 1991).

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The general population may be exposed to nitrophenols through the inhalation of ambient air and ingestion of contaminated foods and drinking water. Although limited air monitoring data are available, low levels (less than 1 $\mu\text{g}/\text{m}^3$) of 2-nitrophenol are expected to exist in the air. Because of photochemical formation of G-nitrophenol in smog and thermochemical formation of both nitrophenols in vehicular exhausts, the levels are expected to be higher in urban and suburban air than in rural air. Nitrophenols have been detected rarely in drinking water and foods. Whether this is because of a lack of effort directed at monitoring these compounds or because they are

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present at undetectable levels is not known. Therefore, exposure from these two sources, although plausible, remains to be demonstrated with actual monitoring data. The detection of 4-nitrophenol in human urine does not indicate direct exposure to this compound, as exposure to several pesticides can cause excretion of the compound in human urine. 4-Nitrophenol is also a metabolite of nitrobenzene (Piotrowski 1967; Robinson et al. 1951b).

4-Nitrophenol conjugates have been detected in human urine. Based on the analysis of 6,990 samples collected from the general population during 1976-1980 via the National Health and Nutrition Survey II (NHANES II) conducted by the National Center for Health Statistics, 4-nitrophenol was quantifiable in 2.4% of the samples, with a high value of 143 µg/L and a geometric mean value of less than 10 µg/L. 4-Nitrophenol originated in the urine from the pesticides methyl and ethyl parathion (Carey and Kutz 1985; Kutz 1983). Based on concerns about unacceptable risk of exposure, EPA intends to issue a Notice of Intent to Cancel (NOIC) the use of parathion on field crops (EPA 1991).

A National Occupational Exposure Survey (NOES) conducted by NIOSH from 1981 to 1983 estimated that 2,155 workers, including 1,553 female workers, are potentially exposed to 4-nitrophenol in the United States (NIOSH 1989). The NOES database does not contain data on the frequency, duration, concentration or route of exposure of workers to 4-nitrophenol. This survey provides only estimates of the number of workers potentially exposed to 4-nitrophenol in the workplace. No reports of actual measured exposure levels under any occupational situation were found in the literature.

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Besides workers involved in the manufacture or use of 2-nitrophenol and 4-nitrophenol and applicators of certain pesticides, members of the general population who live near landfill sites that contain these compounds may be exposed to the compounds at higher than background levels via inhalation. Children playing in and around these landfill sites may be exposed dermally. Another sector of the general population, those in agricultural areas that use parathion and related pesticides for crop protection, may be exposed to 4-nitrophenol at higher than background levels via the consumption of drinking water from groundwater and possibly via the consumption of foods. No experimental data either on background levels of human exposure from any route or evidence of higher than background levels of exposure were found in the literature.

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-nitrophenol and 4-nitrophenol is available. Where

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adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (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-nitrophenol and 4-nitrophenol.

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. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

5.7.1 Data Needs

Physical and Chemical Properties. As can be seen from Table 3-2, the physical and chemical properties of 2-nitrophenol and 4-nitrophenol have been sufficiently characterized to permit estimation of its environmental fate. However, there are considerable variations in the reported values of some of the physical data, such as water solubility and vapor pressure, in the literature. Knowledge of more accurate vapor pressure and water solubility data are important in predicting the volatility of the nitrophenols from water and soil.

Production, Import/Export, Use, and Disposal. No data on the production volume for 2-nitrophenol in the United States were available in the literature. The availability of this data is important because the risk of human exposure to a chemical is often related to its production volume. The import/export data for these chemicals are known (CMR 1987; EPA 1985). The data on usage (CMR 1987; HSDB 1989) indicates that the potential for general population exposure to nitrophenols from consumer products or the environment is low. More detailed site- and medium-specific (e.g., air, water, or soil) release data than given in Table 5-1 are necessary to assess the potential for exposure to these compounds from different sources.

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 Toxic Release Inventory (TRI), which contains this information for 1987, became available in May of 1989. This database is updated yearly and should provide a list of industrial production facilities and emissions.

Although some data are available on the methods of disposal of these compounds (HSDB 1989; OHM/TADS 1989), more data are needed to assess the impact of disposal on the possible levels of human exposure.

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Environmental Fate. Data in the existing literature are sufficient to allow assessment of the environmental fate of 4-nitrophenol in water and soil. Data on 2-nitrophenol are sparse (see Section 5.1). More data are needed to assess the fate of these compounds in air with more confidence. Based on the compounds' photolytic behavior in water (see Section 5.3.2.2), direct photolysis in air is expected to be the primary fate process in air. However, no data were available on the vapor-phase photolysis of the compounds that would permit estimation of their half-lives in the atmosphere. If degradation follows simple kinetics, these half-lives are important since they indicate the degree of persistence of a compound in a certain environmental medium.

Bioavailability from Environmental Media. No information was located regarding absorption of 2-nitrophenol and 4-nitrophenol in humans following inhalation, oral, or dermal exposure. Absorption by the inhalation route in animals could be inferred from the appearance of adverse effects after exposure to 4-nitrophenol dusts. However, oral and/or dermal absorption could also have occurred. Limited data obtained in animals (see Section 2.3.1) indicate that 4-nitrophenol is readily and almost completely absorbed by the oral route when administered by gavage, but no data were available concerning absorption from food or drinking water. Data regarding 2-nitrophenol were not available. An ethanol solution of 4-nitrophenol was not well absorbed when applied to the skin of animals, since most of the dose could be recovered from the application site a week after dosing. It is not known whether 2-nitrophenol can be absorbed through the skin. Knowledge of the compounds' bioavailability will permit estimation of their absorption in a body organ from an environmental medium, in cases where the exposure level is known.

Food Chain Bioaccumulation. Although some data on bioconcentrations of these chemicals in edible aquatic organisms and transfer of the chemicals from soil to edible plants are available (see Section 5.3.1), it has not yet been firmly established whether food chain bioaccumulation occurs. There is also a lack of data on plant-to-animal transfer. Data on the biomagnification of these chemicals in the food chain are scant. Significant food chain bioaccumulation would indicate the possibility of significant human exposure to these chemicals from the consumption of aquatic and terrestrial foods.

Exposure Levels in Environmental Media. Data are not available to establish any ambient level of these compounds in air, drinking water, or foods. Even data on the levels of these compounds under conditions in which they are expected to show elevated values are scarce. Reliable, up-to-date monitoring data for air, drinking water, and foods would allow estimation of the extent of exposure from each of the sources.

Exposure Levels in Humans. The levels of 4-nitrophenol in the urine of the general population are known (Carey and Kutz 1985; Kutz 1983). However, the data are outdated and need to be updated to establish contemporary background levels of this compound in human urine. The levels of

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4-nitrophenol in other body tissues of the general population (although its levels in the plasma of parathion sprayers have been determined) are not known, possibly because of its quick excretion from the body. The level of 2-nitrophenol in any body tissue or fluid has not yet been determined (Piotrowski 1967). No data on the levels of either compound in any body tissue or fluid for populations living near hazardous waste sites are available.

Exposure Registries. No exposure registries for 2-nitrophenol or 4-nitrophenol were located. This compound is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. This compound 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 compound.

5.7.2 On-going Studies

No on-going studies regarding the environmental fate, environmental levels, food chain bioaccumulation, or exposure levels in humans for either 2-nitrophenol or 4-nitrophenol were found in the literature.

As part of the Third National Health and Nutrition Evaluation Survey (NHANES III), the Environmental Health Laboratory Sciences Division of the Center for Environmental Health and Injury Control, Centers for Disease Control, will be analyzing human urine samples for 2-nitrophenol and 4-nitrophenol and other phenolic compounds. These data will give an indication of the frequency of occurrence and background levels of these compounds in the general population.

