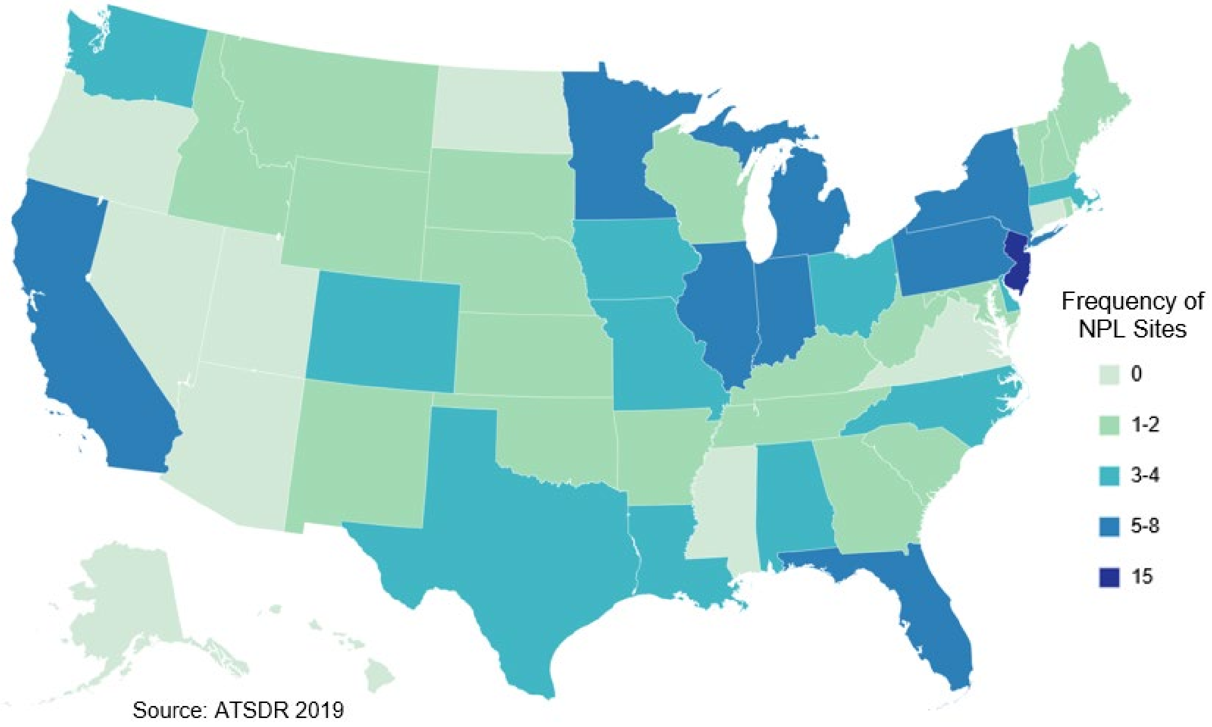
CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Nitrophenols have been identified in at least 135 of the 1,867 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2019). However, the number of sites in which nitrophenols 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 2-Nitrophenol, 3-Nitrophenol, and/or 4-Nitrophenol Contamination



Source: ATSDR 2019

- Nitrophenols are used as intermediates to produce dyes, pigments, pharmaceuticals, rubber chemicals, lumber preservatives, photographic chemicals, pesticides, and fungicides.

- There is no evidence of nitrophenols being released from natural sources. Releases to the environment are primarily from manufacturing and processing industries as well as vehicle exhaust.

- Photolysis, settling, and wet deposition are important fate processes of nitrophenols in air. Nitrophenols are expected to biodegrade in both water and soil.

- Monitoring data for nitrophenols in U.S. air are limited. Levels in water and soil vary widely.
- The general population may be exposed to nitrophenols via inhalation of ambient air or the ingestion of contaminated drinking water.
- Populations with potentially high exposure include workers involved in the manufacture or use of nitrophenols, applicators of certain pesticides that metabolize to 4-nitrophenol, and people who live near landfill sites or agricultural areas that contain pesticides that metabolize to 4-nitrophenol.

There are no known natural sources of nitrophenols in the environment. Nitrophenols can be formed in the air following atmospheric photochemical reactions of several aromatic compounds formed from anthropogenic sources. They are also formed in vehicular exhausts following the thermal reaction of fuel with oxides of nitrogen. 4-Nitrophenol is also formed as a metabolite of certain organophosphate insecticides, including methyl parathion (Li and Kannan 2018; Li et al. 2019). Methyl parathion can be degraded to 4-nitrohenol by hydrolysis or photocatalysis. 2-, 3-, and 4-nitrophenol can also be formed in the atmosphere following photochemical reactions of nitrobenzene, aromatic hydrocarbons, and bromobenzene (Nojima et al. 1976, 1980; Rippen et al. 1987). 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 nitrophenols. The atmospheric half-lives of these compounds are estimated to be 3–18 days (NLM 2022a, 2022b, 2022c). 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 these nitrophenols may range between one and eight days in fresh water and may range between 13 and 139 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 one to three 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 1984; Bourquin et al. 1982; EPA 1985a; Kincannon and Lin 1985; Løkke 1985). 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 (Spain et al. 1979). In addition, 2- and 4-aminophenol have been isolated from anaerobic biodegradation of 2- and 4-nitrophenol, respectively (Adhya et al. 1981; Villanueva 1961). 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; Scow et al. 1989; Zaidi et al. 1988, 1989).

Monitoring data for nitrophenols in any environmental medium were limited, and recent data are lacking for most mediums. The average concentration of 2-nitrophenol in the gas phase during seven rainfalls in Portland, Oregon in 1984 was 0.024 μg/m^3. The corresponding concentration in rainwater was 0.059 μg/L (Leuenberger et al. 1985). Nitrophenols have been identified in effluents from several industries at a median concentration of less than 10 μg/L (Staples et al. 1985). 4-Nitrophenol was detected in the potable water supply of Ames, Iowa at a concentration of 0.2 mg/L. The source of the compound was likely the contamination of well water from coal gas plant wastes (EPA 1980). Nitrophenols have been detected in 131 NPL waste sites (ATSDR 2019). The frequency of these sites within the United States can be seen in Figure 5-1. No report on the detection of any nitrophenols in any food was found in the literature. The NHANES measured 4-nitrophenol in 90% of urine samples of the general population, with a geometric mean value of 0.64 μg/L (CDC 2020). Although no experimental data are available, it is likely that people who manufacture or use nitrophenols, people who consume contaminated drinking water from groundwaters adjacent to methyl and ethyl parathion-treated farmlands, and people who live near landfill sites containing pesticides that metabolize to nitrophenols are potentially exposed to doses higher than the background level. Farmworkers have been shown to have significantly higher mean creatinine-adjusted concentrations of urinary 4-nitrophenol than the general population (López-Gálvez et al. 2018). Children playing in and around contaminated soil may also be exposed to higher levels of nitrophenols. However, urinary levels of 4-nitrophenol may be due to exposure to methyl parathion and related pesticides (that metabolize to 4-nitrophenol), rather than direct exposure to nitrophenols.

5.2 PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.2.1 Production

Facilities in the United States that produce, process, or use 2- and 4-nitrophenol are presented in Tables 5-1 and 5-2, respectively. 2-Nitrophenol is produced either by the catalytic hydrolysis of 2-nitrochlorobenzene with NaOH or by the reaction of dilute HNO_3 on phenol with subsequent steam distillation for separation from 4-nitrophenol (EPA 1985a; Lewis 2007). 4-Nitrophenol is produced either by the catalytic hydrolysis of 4-nitrochlorobenzene or by the reaction of dilute HNO_3 on phenol and subsequent steam distillation to separate the 4- from the 2- isomer (EPA 1985a; Lewis 2007). 3-Nitrophenol is an impurity in 4-nitrophenol and is produced as a byproduct of synthesis or a degradation product (Wróbel et al. 2000).

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

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
LA	2	100,000	999,999	1, 2, 3, 5, 6, 13

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

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

Source: TRI21 2022 (Data are from 2021)

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

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
LA	1	10,000	99,999	5, 13
OH	1	1,000	9,999	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. Used Processing
4. Sale/Distribution
5. Byproduct
6. Reactant
7. Formulation Component
8. Article Component
9. Repackaging
10. Chemical Processing Aid
11. Manufacture Aid
12. Ancillary
13. Manufacture Impurity
14. Process Impurity

Source: TRI21 2022 (Data are from 2021)

5.2.2 Import/Export

Syngenta Corporation in Greensboro, North Carolina reported receiving imports of 2-nitrophenol totaling 1,201,507 pounds in 2015 (EPA 2016). The U.S. International Trade Commission (US ITC) reported that 5,035 kg (Harmonized Tarriff Schedule [HTS] 29089920) of 4-nitrophenol were imported into the United States for consumption in 2021, with no domestic export data available (US ITC 2022).

5.2.3 Use

Nitrophenol isomers are primarily used as intermediates to produce dyes, pigments, pharmaceuticals, rubber chemicals, lumber preservatives, photographic chemicals, pesticides, and fungicides (EPA 1980; O'Neil 2006). Syngenta Corporation uses 2-nitrophenol to manufacture pesticides, fungicides, and other agricultural chemicals (EPA 2016). 3-Nitrophenol is used as an indicator and to synthesize some dyestuffs and drugs (Bingham et al. 2001; 2006). 4-Nitrophenol is used to darken leather and to manufacture drugs, fungicides, methyl and ethyl parathion insecticides, and dyes (Abdollahi and Mohammadirad 2014).

5.2.4 Disposal

Incineration under controlled conditions (to attain complete combustion) appears to be the best method of disposal for nitrophenols (OHM/TADS 1989). The waste containing nitrophenols can be incinerated with a rotary kiln incinerator at 820–1,600°C, with a residence time of hours. It can also be incinerated in a fluidized bed incinerator at 450–980°C, with a residence time of seconds for liquids and gases. The residence time is longer for solids. Incineration of large quantities may require scrubbers to control the emission of NO gases (EPA 1981b). Biological treatment with powdered activated carbon and activated sludge has been used for liquid wastes (Kincannon and Esfandi 1981). Oxidation by passing air at 275°C through the aqueous waste destroys 99.6% of 4-nitrophenol (Heimbuch and Wilhelmi 1985). A resin absorption (Ambelite XAD-7) method for the removal of 4-nitrophenol has been used for industrial wastewater. A guideline for maximum daily effluent discharge of 2.13 mg of total toxic organics (including both nitrophenols) per liter of wastewater was set for electroplating plants that discharge <10,000 gallons of wastewater per day (EPA 2020a). Similarly, the limitations for daily effluent discharge from electrical and electronic industries is set at 1.37 mg/L of total toxic organics (EPA 2020b).

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

There were no releases of 2-nitrophenol to the atmosphere from domestic manufacturing and processing facilities required to report to the TRI in 2021 (TRI21 2022); see Table 5-3. There was an estimated release of <1 pound of 4-nitrophenol to the atmosphere from domestic manufacturing and processing facilities required to report to the TRI in 2021 (TRI21 2022); see Table 5-4.

Table 5-3. Releases to the Environment from Facilities that Produce, Process, or Use 2-Nitrophenol[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
LA	2	0	121	4,323	0	0	121	4,323	4,444
Total	2	0	121	4,323	0	0	121	4,323	4,444

[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, wastewater 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: TRI21 2022 (Data are from 2021)

Table 5-4. Releases to the Environment from Facilities that Produce, Process, or Use 4-Nitrophenol[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
LA	1	0	0	0	0	0	0	0	0
OH	1	0.034	0	0	0.19	0	0.224	0	0.224
Total	2	0.034	0	0	0.19	0	0.224	0	0.224

[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, wastewater 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: TRI21 2022 (Data are from 2021)

EPA's National Emission Inventory (NEI) database contains information regarding sources that emit criteria air pollutants (CAPs) and their precursors, and hazardous air pollutants (HAPs) for the 50 United States, Washington DC, Puerto Rico, and the U.S. Virgin Islands. Emissions are estimated from multiple sources, including state and local environmental agencies; the TRI database; computer models for on- and off-road emissions; and databases related to EPA's Maximum Achievable Control Technology (MACT) programs to reduce emissions of HAPs. 4-Nitrophenol emissions estimated from the 2017 inventory are summarized in Table 5-5.

Table 5-5. 4-Nitrophenol Emissions to the Air Based on 2017 National Emissions Inventory

Emission sector	Pounds emitted
Commercial cooking	32,489.83
Fuel combustion; commercial/institutional; biomass	3.18
Fuel combustion; commercial/institutional; other	0.002
Fuel combustion; electric generation; biomass	12.09

Table 5-5. 4-Nitrophenol Emissions to the Air Based on 2017 National Emissions Inventory

Emission sector	Pounds emitted
Fuel combustion; electric generation; coal	198.35
Fuel combustion; electric generation; natural gas	0.30
Fuel combustion; electric generation; oil	21.44
Fuel combustion; electric generation; other	0.02
Fuel combustion; industrial boilers; internal combustion engines; biomass	59.53
Fuel combustion; industrial boilers; internal combustion engines; coal	217.77
Fuel combustion; industrial boilers; internal combustion engines; natural gas	0.01
Fuel combustion; industrial boilers; internal combustion engines; oil	0.06
Fuel combustion; industrial boilers; internal combustion engines; other	40.91
Industrial processes; cement manufacture	0
Industrial processes; chemical manufacture	0
Industrial Processes - ferrous metals	109.80
Industrial processes; not elsewhere classified	3.61
Industrial processes; non-ferrous metals	0.45
Industrial processes; petroleum refineries	29.37
Industrial processes; pulp and paper	1.62
Industrial processes; storage and transfer	0.11
Miscellaneous non-industrial; not elsewhere classified	1,383.14
Solvent; industrial surface coating and solvent use	0.196
Waste disposal	1,803.45

Source: EPA 2017

There is no evidence of the formation of the nitrophenols from natural sources in the environment. The primary anthropogenic source of the nitrophenol isomers found in air is traffic activity. These nitrophenols are released from exhausts of both gasoline- and diesel-powered vehicles (Inomata et al. 2015, 2016; Lu et al. 2019; Nojima et al. 1983; Rubio et al. 2019). Since the efficiencies of the incinerator/thermal processes are <100%, a small amount of undegraded nitrophenols will be released into the air during these processes. 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 (Nojima et al. 1976, 1980; Rippen et al. 1987). 4-Nitrophenol is a degradation product of some organophosphorus insecticides (Li and Kannan 2018; Li et al. 2019). Therefore, small amounts of 4-nitrophenol may be released in local windblown dusts in areas where these pesticides are used. Li et al. (2020) conducted a study of nitrated phenols and phenolic precursors in the atmosphere in urban Jinan, China. Coal combustion (45%) was the major source for 4-nitrophenol found in samples from winter, whereas in the spring, vehicular exhaust (40%) was the major source. This trend also changed in the summer when secondary formation (41%) of 4-nitrophenol was the key source (Li et al. 2020). 2-Nitrophenol and 4-nitrophenol were not detected in the emissions from the burning of three types of firewood, but 4-nitrophenol was detected at an average concentration of 0.09±0.08 $\mu g/m^3$ in emissions from pellet stoves (Rubio et al. 2019).

5.3.2 Water

Estimated releases of 121 pounds (~0.055 metric tons) of 2-nitrophenol to surface water from 2 domestic manufacturing and processing facilities in 2021, accounted for about 2.7% of the estimated total environmental releases from facilities required to report to the TRI (TRI21 2022). This estimate includes releases to wastewater treatment and publicly owned treatment works (POTWs) (TRI21 2022); see Table 5-3. There were no releases of 4-nitrophenol to surface water from domestic manufacturing and processing facilities required to report to the TRI in 2021 (TRI21 2022); see Table 5-4.

Nitrophenols may form during water decontamination processes when nitrate and nitrite are present (Dzengel et al. 1999; Vione et al. 2001). Effluents from the textile industry may also release both 2- and 4-nitrophenol into surface water and publicly owned treatment works (POTWs) (EPA 1981a). In addition, 2- and 4-nitrophenol were found in treated wastewaters 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 1981b).

5.3.3 Soil

There were no releases of 2-nitrophenol to the soil. However, 4,323 pounds (~1.96 metric tons) of 2-nitrophenol, accounting for about 97% of the total environmental emissions, were released via underground injection (TRI21 2022); see Table 5-3. There was an estimated release of <1 pound of 4-nitrophenol to soil from domestic manufacturing and processing facilities required to report to the TRI in 2021 (TRI21 2022); see Table 5-4.

Manufacturing and processing industries are sources of nitrophenols in soils and may cause groundwater contamination near the disposal sites. 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 nitrophenols in water and soil (Harrison et al. 2005; Leuenberger et al. 1988). Deposition of vehicular exhaust on roadways is another source of nitrophenols in soil. No quantitative estimate of the amounts of 2- or 4-nitrophenol released into soil from the latter three sources is available.

5.4 ENVIRONMENTAL FATE

5.4.1 Transport and Partitioning

Air. The fate and distribution of 4-nitrophenol in different environmental compartments were assessed with a non-steady-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 3- and 4-nitrophenol because it has a much higher Henry's law constant and vapor pressure than the other isomers. The partitioning of a chemical from the atmosphere to land and water depends on its physical state and physico-chemical properties such as the vapor pressure. In general, compounds with higher vapor pressures such as 2-nitrophenol tend to partition to the vapor phase, while substances with vapor pressures lower than $1\text{x}10^{-4}$ mm Hg tend to partition more to the particulate phase in the atmosphere. In a study of the phase distribution of nitrophenols in the ambient air of Rome, Italy, it was determined that 4-nitrophenol was predominantly detected in the particulate phase (82% particulate phase and 18% vapor phase), while 2-nitrophenol was predominantly in the vapor phase (Cecinato et al. 2005). The intra-media 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. These compounds are likely to undergo atmospheric transport from polluted areas to less polluted or pristine areas (Rippen et al. 1987). However, there is no experimental evidence to confirm the long-range transport of these nitrophenols.

Water. Because of their significant water solubilities, partitioning of these chemicals from air to surface waters and land via wet deposition is expected to occur. The detection of both 2- and 4-nitrophenol in rainwater in a few studies (Harrison et al. 2005; Leuenberger et al. 1988; Rippen et al. 1987) supports this partitioning mechanism. Experimental volatilization rates for nitrophenols from water are unavailable.

The modeling data based on non-steady-state equilibrium predict that volatilization of 4-nitrophenol will be insignificant (Yoshida et al. 1983). The Henry's law constant values are 1.3×10^{-5} atm-m^3/mol at 20°C for 2-nitrophenol and 1.28×10^{-8} atm-m^3/mol at 20°C for 4-nitrophenol (Tremp et al. 1993), suggesting that only 2-nitrophenol may volatilize from water; however, the dissociation constant (pKa) values of the two compounds (7.23 for 2-nitrophenol and 7.15 for 4-nitrophenol) indicate that significant fractions of these nitrophenols will exist in partially anionic form in the environment (NLM 2022a, 2022b, 2022c). Since ionic species do not volatilize significantly from water, the ionization may further limit volatilization (NLM 2022a, 2022b, 2022c). The partitioning of nitrophenols between water and sediment is also expected to depend on the pH of the water. Under acidic conditions, the nitrophenols are expected to exist as the fully protonated species, which have a greater tendency to partition to the sediment compartment as opposed to the conjugate base (anionic form).

Sediment and Soil. Based on the vapor pressure and Henry's Law constants of these substances, volatilization of 3-, and 4-nitrophenol from soils is expected to be low. Since both the vapor pressure and Henry's Law constant of 2-nitrophenol are much larger than the other two isomers, 2-nitrophenol is expected to have greater volatilization potential; however, all three substances may partially exist in ionic form depending upon the pH of the soil, and the anionic species will not be volatile. 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 possible for 2-nitrophenol. In the same terrestrial ecosystem study, 35.7 and 12.7% of the applied radioactivities were recovered in plants where 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 possible metabolism in plants.

The adsorption of the nitrophenols is also pH-dependent since anions tend to have higher mobility and greater leaching potential in soils as compared to the fully protonated neutral species. The measured log K_{oc} values for 2- and 4-nitrophenol in a clay loam soil of 5.1% organic matter content and a pH of 5.7 were 2.06 and 1.71, respectively (Boyd 1982). Other studies 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. Therefore, in the absence of significant degradation, nitrophenols may leach from soil and may be found in the leachate of landfills.

Other Media. 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 oromelas*) 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 studies 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, the bioconcentration potential of the nitrophenols is low, and evidence for biomagnification is lacking (Loehr and Krishnamoorthy 1988).

5.4.2 Transformation and Degradation

Air. The two processes that are likely to degrade nitrophenols in air are direct photolysis and reactions with atmospheric oxidants such as hydroxyl 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 >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 nitrophenols are available. The rate constant for the gas-phase reaction of 2-nitrophenol with OH radicals is 9.0×10^{-13} cm^3 -molecule/second at 21°C (Atkinson 1986) and 8.95×10^{-13} cm^3 -molecule/second at 27°C for 4-nitrophenol (Güsten 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 1986), the atmospheric half-life of 4-nitrophenol due to this reaction is an estimated 18 days

Water. Chemical oxidation reactions of 2- and 4-nitrophenol by singlet oxygen and alkyl peroxy radicals formed from sunlight-induced photochemical reactions in water are too slow to be significant (EPA 1985a; Scully and Hoigné 1987). OH radicals in water attack 2- 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-nitro1,2-dihydroxybenzene) (Suarez et al. 1970). 4-Nitrophenol photo-reacts quite rapidly in water in the presence of nitrate or nitrite (EPA 1985a). This is not surprising, since nitrate and nitrite in water produce elevated concentrations of hydroxyl radicals when irradiated by sunlight. The irradiation of 4-nitrophenol in neutral or acidic aqueous solution in the presence of air at a wavelength of 365 nm produced primarily hydroquinone and HNO_2, together with small amounts of benzoquinone and 4-nitrocatechol (Hustert et al. 1981; Kotzias et al. 1986). Other studies have determined the photo-transformation quantum yield to be in the range 3.3×10^{-6}–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 1985a). Hustert et al. (1981), determined the aquatic photolytic half-lives of 4-nitrophenol as 5.7 days at pH 5, 6.7 days at pH 7, and 13.7 days at pH 9. The phototransformation of 4-nitrophenol in snow and ice has shown the production of hydroquinone, benzoquinone, and 4-nitrosophenol (Klán and Holoubek 2002)

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; Freitag et al. 1982; Gerike and Fischer 1979; Jones and Alexander 1986; Kool 1984; Korte and Klein 1982; McCormick et al. 1976; Means and Anderson 1981; Neujahr et al. 1974; Patterson and Kodukala 1981; Pitter 1976; Rott et al. 1982; Sudhakar 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 studies 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 and Van Veld 1983; Spain et al. 1980, 1984). The half-life of biodegradation in natural water (parent compound disappearance) reported or estimated from experimental results are as follows: about 3.5 days in water from the Escambia River in Florida (Bourquin 1984; Bourquin et al. 1982) and a mean of 3.2 days for water collected from five ponds and one river in Georgia (Paris et al. 1983; Vaishnav and Korthals 1988). Ingerslev and Nyholm (2000) measured biodegradation of 4-nitrophenol using a shake flask method and found a 0–5-day lag period and a 14–36-day half-life in river water with a bacterial count of 1,950–16,000 bacteria/mL. In lake water, the lag period was 0–7 days, and the half-life was 32–530 days with a bacterial count of 1,100–2,700. In coastal seawater, the lag time was 3 days, and the half-life was 21 days with a high bacterial count of 13,000 bacteria/mL. In offshore seawater, 4-nitrophenol had a lag period of 93–96 days and a half-life of 139 days with a low bacterial count of 100 bacteria/mL (Ingerslev and Nyholm 2000).

The rate and extent of degradation of 4-nitrophenol in natural water also depend on the initial concentration of the substance, nature and concentration of nutrients, activities of the organisms, and 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 studies 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 >75% mineralized in 56 days in another study (Shelton and Tiedje 1984). Under anaerobic experimental conditions in two flooded soils, >50% degradation of 2- and 4-nitrophenol was observed in 10 days (Sudhakar and Sethunathan 1978).

Sediment and Soil. Data regarding the chemical degradation of nitrophenols in soils are lacking. Oxides of manganese (+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 pHs. At low pHs, nitrophenols may degrade at an appreciable rate, forming dimeric and polymeric oxidation products, since the dissolution rate of one form of manganese oxide with 4-nitrophenol was $<10^{-9}$ mol/L-minute 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. Several studies support this conclusion. Several pure cultures isolated from soils degraded nitrophenols (EPA 1985a). 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 aquifers 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 (Løkke 1985). From a laboratory microcosm study simulating coastal wetlands, the half-life of 4-nitrophenol was predicted to be 2–3 days (Portier 1985).

5.5 LEVELS IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to nitrophenols depends, in part, on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of nitrophenols 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 nitrophenols 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 5-6 shows the lowest limit of detections that are achieved by analytical analysis in environmental media. An overview summary of the range of concentrations detected in environmental media is presented in Table 5-7.

Table 5-6. Lowest Limit of Detection for Nitrophenols Based on Standards[a]

Media	Isomer	Detection limit	Reference
Municipal and industrial wastewater	2-Nitrophenol	0.45 μg/L	EPA 1984
	4-Nitrophenol	2.4 μg/L	EPA 1984
Drinking water	2-Nitrophenol	0.026 g/L	EPA 2000a
	4-Nitrophenol	0.18 g/L	EPA 2000a
Urine	4-Nitrophenol	0.10 μg/L	CDC 2020
Soil/sediment	2-Nitrophenol	660 μg/kg	EPA 1998
	4-Nitrophenol	330 μg/kg	EPA 1998
Groundwater	2-Nitrophenol	10 μg/L	EPA 1998
	4-Nitrophenol	50 μg/L	EPA 1998
Solid waste	3-Nitrophenol	Not reported	EPA 2007a

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

Table 5-7. Summary of Environmental Levels of Nitrophenols

Media	Low	High	For more information
Outdoor air (ng/m^3)	0.01	17.8	Section 5.5.1
Indoor air (ng/m^3)	0.002	0.003	Section 5.5.1
Surface water (ppb)	0.011	88	Section 5.5.2
Ground water (ppb)	<0.2	250	Section 5.5.2
Drinking water (ppb)	<0.2	871.3	Section 5.5.2
Soil (ppb)	<0.8		Section 5.5.3

Detections of nitrophenols in air, water, and soil at NPL sites are summarized in Table 5-8.

Table 5-8. Nitrophenols 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
2-Nitrophenol					
Water (ppb)	10	12.3	5.50	4	4
Soil (ppb)	2,830	1,980	12.1	5	5
Air (ppbv)			No data		

Table 5-8. Nitrophenols 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
3-Nitrophenol[b]					
Water (ppb)			No data		
Soil (ppb)			No data		
Air (ppbv)			No data		
4-Nitrophenol					
Water (ppb)	16	27.4	11.3	9	7
Soil (ppb)	5,140	6,510	49.8	16	15
Air (ppbv)			No data		
Nitrophenol					
Water (ppb)			No data		
Soil (ppb)	1.60×10^6	43,800	432	2	2
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.

[b] 3-Nitrophenol was found at five NPL sites but no data on levels in water, soil, or air were reported.

5.5.1 Air

Monitoring data for nitrophenols in U.S. air are limited; therefore, monitoring data for these compounds in ambient air are presented from samples obtained both in the United States and other countries. In a study of phenols and nitrophenols in the air in the Strasbourg area of France, 3-nitrophenol was detected at mean concentrations of 0.1 ng/m^3 at urban sites, 0.2 ng/m^3 at suburban sites, and 0.01 ng/m^3 at rural sites (Delhomme et al. 2010). A study performed in 2003 of ambient air in Rome, Italy reported mean concentrations of 2-nitrophenol of 10.4 ng/m^3 in the gas phase and 3.5 ng/m^3 in the particulate phase; by contrast, 4-nitrophenol concentrations were 3.9 ng/m^3 in the gas phase and 17.8 ng/m^3 in the particulate phase (Cecinato et al. 2005). Earlier studies in Italy reported 4-nitrophenol concentrations of 0.94–0.163, 0.87, and 0.42 μg/m^3 in urban, semi-rural, and rural areas, respectively (Belloli et al. 2006). In Central Milano, summer concentrations of 4-nitrophenol were reported as 0.106–0.120 μg/m^3 while 2-nitrophenol concentrations were 0.130–0.177 μg/m^3. Analysis of tunnel air showed 2- and 4-nitrophenol concentrations to be 0.232–1.139 and 0.387–0.993 μg/m^3, respectively (Belloli et al. 2006). Concentrations of 2-nitrophenol (1.09–15.99ng/m^3) and 4-nitrophenol (1.29–3.77 ng/m^3) were detected in the air particulate matter collected in Birmingham, United Kingdom in samples collected in 2007 and

2008 (Özel et al. 2011). Air samples collected during 2010 and 2011 at the University of Santiago, Chile had atmospheric 2-nitrophenol concentrations of 8.3–106 ng/m^3 and 4-nitrophenol concentrations of 40–1,400 ng/m^3 (Rubio et al. 2012). Corresponding dew concentrations were not detected to 237 µg/L, not detected to 147 µg/L, and not detected to 629 µg/L for 2-, 3- and 4-nitrophenol, respectively. 4-Nitrophenol was found in ambient particulates from two sites in the Czech Republic (Kitanovski et al. 2020). Concentrations from 1990 to 2001 in air in other literature ranged from 0.8 to 350 ng/m^3 for 2-nitrophenol and from 1.2 to 300 ng/m^3 for 4-nitrophenol (Harrison et al. 2005). These measurements were mostly reported in Europe. Rudel et al. (2001) reported indoor air concentrations of 4-nitrophenol in four of seven samples at 0.002 to 0.003 µg/m^3, with detection of 0.17–6.82 µg/g dust in all the corresponding dust samples.

Concentrations taken from 1990 to 2001 of 2-nitrophenol in clouds were 0.2–0.3 and 0.059–1.4 µg/L in rain. Concentrations of 4-nitrophenol were 2.2–21 µg/L in clouds, 8.1–40.2 µg/L in fog, <0.01–16 µg/L in rain, and 0.008–0.013 µg/L in snow (Harrison et al. 2005). In the past, rainwater concentrations of 2-nitrophenol ranged from 0.024 to 1.4 µg/m^3. The average concentration of 2-nitrophenol in the gas phase during seven rainfalls in Portland, Oregon in 1984 was 0.024 µg/m^3. The corresponding concentration in rainwater was 0.059 µg/L (Leuenberger et al. 1985). The concentrations of 2-nitrophenol in air and rainwater at Dubendorf, Switzerland, in 1985 were 0.35 µg/m^3 (one rainfall) and 0.1–0.8 µg/L (several rainfalls), respectively (Leuenberger et al. 1988). 2-Nitrophenol was detected in rainwater at a concentration of 0.031 µg/L in Azusa, California, and at 0.1–1.4 µg/L in different locations in West Germany. 4-Nitrophenol was also detected in rainwater at concentrations of 2–24 µg/L in different locations in West Germany. Extremely high values of 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).

5.5.2 Water

Measurements of nitrophenols in water samples are well documented for the EPA's Water Quality Portal (WQP). These data are presented in Table 5-9 and summarized below.

Table 5-9. Summary of Concentrations of Nitrophenols (ppb) Measured in Surface and Groundwater Across the United States

Year range	Average	Maximum	Number of Samples	Percent detected
		Surface water		
2-Nitrophenol				
2000–2004	0.26	0.88	104	53.8%
2005–2009	0.16	0.59	83	32.5%
2010–2014	0.40	1.12	329	10.3%
2015–2019	3.69	5.3	15	73.3%
2020–2022[a]		<0.3	96	0%
4-Nitrophenol				
2000–2004	1.60	4.54	146	71.9%
2005–2009	0.77	3.42	184	50.5%
2010–2014	0.96	9.25	208	37.5%
2015–2019	9.96	27	25	88%
2020–2022[a]	0.28	0.5	73	5.5%
		Groundwater		
2-Nitrophenol				
2000–2004	0.25	0.57	158	6.3%
2005–2009	8.59	40	255	60.4%
2010–2014	4.77	5.0	76	56.6%
2015–2019	0.47	0.47	15	6.7%
2020–2022[a]	ND	ND	ND	ND
4-Nitrophenol				
2000–2004	20.11	49	140	3.6%
2005–2009	44.62	250	443	33.6%
2010–2014	20.0	20.0	47	87.2%
2015–2019		<0.2	14	0%
2020–2022[a]	ND	ND	ND	ND

[a] As of October 11, 2022.

ND = no data reported

Source: WQP 2022

According to the WQP database from 2000 to 2022, 2-nitrophenol has been detected in 19% of 627 samples of surface water samples at concentrations of <0.16–5.3 μg/L. The concentration of 4-nitrophenol ranged from <0.28 to 27 μg/L over the same period in 47% of 636 surface water samples at various locations in the United States. No data were reported for 3-nitrophenol (WQP 2022). Concentrations from 1990 to 2001 in surface waters in other literature ranged from 0.028 to 0.43 μg/L for

2-nitrophenol and from 0.011 to 88 µg/L for 4-nitrophenol (Harrison et al. 2005). These measurements were mostly reported in Europe.

According to the WQP database from 2000 to 2022, 2- and 4-nitrophenol have been detected in 41% (total samples 504) and 30% (total samples 644) of groundwater samples for the respective isomer at various locations in the United States. The concentration of 2-nitrophenol ranged from <0.25 to 40 µg/L and the concentration of 4-nitrophenol ranged from <0.2 to 250 µg/L in these samples (WQP 2022).

Nitrophenols (isomer unidentified) at a concentration of 5 mg/L were detected in oil shale retort water (Dobson et al. 1985). 4-Nitrophenol has been identified in effluent from a pesticide plant (EPA 1985a). Both 2- and 4-nitrophenol were detected in the final effluent from the wastewater of a petroleum industry refinery (Snider and Manning 1982). Nitrophenols have also been identified in primary and secondary effluents of municipal wastewater treatment plants. For example, both nitrophenols were identified in the secondary effluent from a wastewater treatment plant in Sauget, Illinois (Ellis et al. 1982), and 4-nitrophenol was detected in both primary and secondary effluent from a wastewater treatment plant in Los Angeles, California, in secondary effluent from a wastewater treatment plant in Orange County, California, and in primary effluent from a San Diego, California wastewater treatment plant (Young 1978).

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).

In the past, 4-nitrophenol was detected in the potable water supply of Ames, Iowa at a concentration of 0.2 mg/L. 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). To assess drinking water contamination after the 2018 Camp Fire in California, water samples were collected from 10 homes in the burn area around Paradise, California. 2-Nitrophenol was detected in one home at 871.3 µg/L (Solomon et al. 2021).

5.5.3 Sediment and Soil

Nitrophenols have been detected in soil and sediment samples taken for EPA’s WQP database from 2000 to 2022. These data are described below and summarized in Table 5-10.

Table 5-10. Summary of Concentrations of Nitrophenols (ppb) Measured in Soil and Sediment Across the United States

Year range	Average	Maximum	Number of samples	Percent detected
		Soil		
2-Nitrophenol				
2000–2022[a]		<0.8	141	0%
4-Nitrophenol				
2000–2022[a]		<10	113	0%
		Sediment		
2-Nitrophenol				
2000–2004	2,391	19,000	14	42.9%
2005–2009	230.4	444	71	9.9%
2010–2014	190.9	380	267	0.7%
2015–2019		<0.3	84	0%
2020–2022[a]	ND	ND	ND	ND
4-Nitrophenol				
2000–2004	5,725	34,000	14	42.9%
2005–2009	286.5	444	314	2.2%
2010–2014	69.2	130	270	0.7%
2015–2019	49.5	188	99	13.1%
2020–2022[a]	ND	ND	ND	ND

[a] As of October 11, 2022.

ND = no data reported

Source: WQP 2022

2-Nitrophenol and 4-nitrophenol were not detected in 141 (detection limit <0.8 μg/kg) and 113 (detection limit <10 μg/kg) soil samples, respectively from 2000 to 2022 (WQP 2022). 2-Nitrophenol and 4-nitrophenol were not detected in 92 soil samples collected from 2000 to 2022 from Superfund sites in the United States. Detection in sediment samples has steadily decreased since 2000. In 2000–2004, 2-nitrophenol and 4-nitrophenol were detected in 6 out of 14 samples (42.9%) at average concentrations of 2,391 and 5,725 μg/kg, respectively. The most recent sampling data (2015–2019) reported that 2-nitrophenol was below the detection limit of 0.3 μg/kg in all 84 samples and 4-nitrophenol was detected in 13 of 99 samples (13.1%) at an average concentration of 49.5 μg/kg. Superfund sites around the United States at a maximum concentration of 25 μg/kg. 3-Nitrophenol was found in one sample from Indiana Water Science Center in 2009 at a concentration of 200 μg/kg. 4-Nitrophenol was found in 12 of 2,448 sediment samples from Superfund sites at an average concentration of 105 μg/kg (WQP 2022).

In the past, the monitoring program conducted by EPA at Love Canal (Niagara Falls, New York) in 1980 qualitatively detected the presence of 2- and 4-nitrophenol in sediment/soil samples (Hauser and Bromberg 1982). The concentration range for 2-nitrophenol in a few unspecified municipal landfill leachates was reportedly 8.6–12.0 mg/L (Brown and Donnelly 1988). 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 (EPA 1985b).

5.5.4 Other Media

No data in the literature demonstrated the presence of nitrophenols in foods. Nitrophenols were not included in the U.S. Food and Drug Administration (FDA) Total Diet Study (FDA 2006). The production of 4-nitrophenol from degradation or metabolism of several pesticides, including parathion (which is no longer used in the United States as of October 2003) (EPA 2000b) and methyl parathion, on plant leaves or in soil may result in the contamination of food crops following application of these pesticides. Hair samples were collected from adults (117) and children (40) living in Grande-Synthe, France in 2017; 4-nitrophenol concentrations results are presented in Table 5-11 (Iglesias-González et al. 2021). Perrone et al. (2014) found that 2- and 4-nitrophenol were present in both particulate matter and gas phase of automotive exhaust. 2-Nitrophenol was found at greater concentrations from diesel engine exhaust (0.32–2.34 µg/km) than gasoline engine exhaust (0.01 µg/km). 4-Nitrophenol showed similar results with concentrations of 0.48–5.04 µg/km for diesel engine exhaust and 0.41–1.30 µg/km for gasoline engine exhaust (Perrone et al. 2014).

Table 5-11. 2017 Hair Monitoring Data for 4-Nitrophenol in 117 Adults and 40 Children

	Positive detections (%)	25% Percentile (pg/mg)	50% Percentile (pg/mg)	75% Percentile (pg/mg)	95% Percentile (pg/mg)	Highest detected Value (pg/mg)
Adults	100	11.9	16.1	19.5	34.9	64.3
Children	100	12.6	17.9	30.4	59.2	310

Source: Iglesias-González et al. 2021

5.6 GENERAL POPULATION EXPOSURE

The general population may be exposed to nitrophenols through the inhalation of ambient air. Although limited air monitoring data are available, low levels (<1 μg/m^3) of 2-nitrophenol are expected to exist in the air. Nitrophenols have not been detected in foods. Whether this is due to a lack of effort directed at monitoring these compounds or because they are present at undetectable levels is not known. Therefore, exposure from food, although plausible, remains to be demonstrated with actual monitoring data. 4-Nitrophenol has been detected in human urine; however, this detection 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 (EPA 2009a). The geometric mean and percentiles of 4-nitrophenol detected in human urine from the National Health and Nutrition Examination Survey (NHANES) are presented in Table 5-12. Li and Kannan (2018) measured the concentrations of metabolites of organophosphate, insecticides, and herbicides from urine samples in eight countries, and the mean concentration of 4-nitrophenol in 35 samples from the United States was 1.6 ng/mL. An Environmental Influences on Child Health Outcomes (ECHO) Program study reported that 4-nitrophenol was 1 of 89 analytes measured in the urine of 171 pregnant women from the United States and Puerto Rico roughly spanning the years 2017–2020. 4-Nitrophenol was detected at 0.1–3.8 ng/mL in 69% (118) of the samples collected (Buckley et al. 2022).

Table 5-12. Geometric Mean and Selected Percentiles of Urinary 4-Nitrophenol (in μg/L) for the U.S. Population from the National Health and Nutrition Examination Survey (NHANES)

	Survey years	Geometric mean (95% CI)	Selected percentiles				Sample size
			50th	75th	90th	95th	
Total	2011–2012	0.64 (0.57–0.71)	0.63	1.17	2.17	3.31	2,350
	2013–2014	0.64 (0.60–0.69)	0.61	1.18	2.17	3.21	2,584
Age group							
6-11 years	2011–2012	0.61 (0.50–0.75)	0.60	1.21	2.08	2.78	394
	2013–2014	0.84 (0.72-0.98)	0.68	1.66	3.11	4.09	411
12–19 years	2011-2012	0.62 (0.51-0.74)	0.64	1.15	1.85	2.51	376
	2013–2014	0.66 (0.57–0.77)	0.68	1.23	1.82	2.71	415
20+ years	2011–2012	0.64 (0.57–0.72)	0.63	1.18	2.23	3.48	1,580
	2013–2014	0.62 (0.58–0.67)	0.57	1.14	2.07	3.21	1,758

Table 5-12. Geometric Mean and Selected Percentiles of Urinary 4-Nitrophenol (in µg/L) for the U.S. Population from the National Health and Nutrition Examination Survey (NHANES)

	Survey years	Geometric mean (95% CI)	Selected percentiles 50th	75th	90th	95th	Sample size
Sex							
Male	2011–2012	0.67 (0.61–0.74)	0.70	1.24	2.21	3.19	1,190
	2013–2014	0.67 (0.62–0.73)	0.65	1.17	2.02	3.03	1,306
Female	2011–2012	0.60 (0.52–0.70)	0.58	1.13	2.14	3.48	1,160
	2013–2014	0.62 (0.56–0.68)	0.58	1.19	2.32	3.40	1,278
Race/ethnicity							
Mexican American	2011–2012	0.62 (0.52–0.73)	0.68	1.18	1.84	2.51	285
	2013–2014	0.68 (0.58–0.80)	0.67	1.30	2.07	2.64	403
Non-Hispanic Black	2011–2012	0.70 (0.55–0.87)	0.72	1.37	2.34	3.47	642
	2013–2014	0.76 (0.69–0.84)	0.78	1.37	2.49	3.59	576
Non-Hispanic White	2011–2012	0.62 (0.54–0.71)	0.60	1.15	2.13	3.31	752
	2013–2014	0.60 (0.56–0.64)	0.57	1.10	2.03	3.16	986
All Hispanic	2011–2012	0.64 (0.58–0.72)	0.68	1.16	1.98	2.98	546
	2013–2014	0.69 (0.60–0.79)	0.67	1.29	2.17	2.82	637
Asians	2011–2012	0.72 (0.63–0.81)	0.62	1.54	2.84	3.87	325
	2013–2014	0.74 (0.62–0.89)	0.63	1.39	3.16	4.90	284

CI = confidence interval

Source: CDC 2020

A monitoring study of urine from 30 people and their dogs exposed to pesticides revealed the metabolite 4-nitrophenol in 100% of samples, with a geometric mean of 1.76 µg/L for humans and 2.91 µg/L for their dogs (Wise et al. 2022). Fenske et al. (2002) conducted a focus study on children of pesticide applicators, farm workers, agricultural, and a reference group. Children were ≤6 years old living in central Washington State. 4-Nitrophenol is a metabolite of the pesticides chlorpyrifos and parathion used in this area. 4-Nitrophenol was found in 6–8% of urine samples from each group (Fenske et al. 2002). Li et al. (2019) measured pesticide metabolite concentrations in Australian infants and toddlers. There was a significant increase in the concentration of urinary 4-nitrophenol with age, which may suggest that exposure increases because of increased activity and dietary intake (Li et al. 2019).

5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Workers involved in the manufacture or use of nitrophenols and applicators of certain pesticides may be exposed to higher levels of nitrophenols than the general population. The geometric mean creatinine-adjusted concentration for urinary 4-nitrophenol (1.63 µg/g) in 20 migrant farmworkers in Sonora, Mexico was significantly higher than in the general United States population and Mexican American populations (López-Gálvez et al. 2018). Members of the general population who live near landfill sites that contain these compounds may be exposed at higher than background levels via inhalation. Another sector of the general population, those in agricultural areas that use methyl parathion and related pesticides (that metabolize to 4-nitrophenol) for crop protection, may be exposed to 4-nitrophenol at higher than background levels via the consumption of drinking water from contaminated groundwater and possibly via the consumption of foods. Since nitrophenols are released from car exhaust, potentially high exposures could also occur in populations living near heavy traffic, or people who work with or spend time around idling gasoline- or diesel-powered motor vehicles.

Children playing in and around soils containing certain pesticides may be exposed to nitrophenols. 4-Nitrophenol was detected in 96% of urine samples from children aged 2–5 years living in Washington State in 1998 in areas having potentially elevated organophosphorus pesticide exposure (Kissel et al. 2005). The mean concentration of urinary 4-nitrophenol was 11.6 µg/L. Roca et al. (2014) assessed exposure to pesticides in school children aged 6–11 years in agricultural and urban areas of Valencia, Spain with high pesticide use and high concentrations of contemporary pesticides in the air. 4-Nitrophenol was one of the most frequently detected compounds in urine samples, with a detection frequency of 53%. The geometric mean creatinine (Cre)-adjusted urinary level of 4-nitrophenol was 0.96 µg/g Cre. The median concentration of 4-nitrophenol was higher in the urine of children living in agricultural locations (1.11 µg/g Cre) than urban locations (0.4 µg/g Cre). 4-Nitrophenol was one of the most frequently detected biomarkers of pesticide exposure in the urine of lactating mothers in Valencia, Spain at an average concentration of 0.8 ng/mL and detection frequency of 84% (Fernández et al. 2020). Béranger et al. (2018) investigated prenatal exposure to pesticides by measuring pesticides and metabolites in hair strands in mothers living in agricultural areas of northeastern and southwestern France in 2011. 4-Nitrophenol was found at the second highest mean concentration (13.18 pg/mg) of the 140 pesticides and metabolites studied (Béranger et al. 2018).