

Proposed Regulations

## ● Federal Programs

Resource Conservation and Recovery Act (RCRA)

EPA has proposed listing spent filters, spent desiccants, light ends and filter aids from chlorinated aliphatic hydrocarbon production as a non-specific source of naphthalene-containing hazardous waste (330).

## ● State Water Programs

New York has proposed a surface water quality standard for naphthalene (731).

EEC DirectivesDirective on Drinking Water (533)

The mandatory values for polycyclic aromatic hydrocarbons in surface water treatment categories A1, A2 and A3 used or intended for the abstraction of drinking water are 0.0002 and 0.001 mg/L, respectively. No guideline values are given for any treatment category.

Directive Relating to the Quality of Water Intended for Human Consumption (540)

The maximum admissible concentration for polycyclic aromatic hydrocarbons is 0.2 µg/L.

Directive on Ground Water (538)

Direct discharge into ground water (i.e., without percolation through the ground or subsoil) of organohalogen compounds and substances which may form such compounds in the aquatic environment, substances which possess carcinogenic, mutagenic or teratogenic properties in or via the aquatic environment, and mineral oils and hydrocarbons is prohibited. Appropriate measures deemed necessary to prevent indirect discharge into ground water (i.e., via percolation through ground or subsoil) of these substances shall be taken by member countries.

Directive on Toxic and Dangerous Wastes (542)

Any installation, establishment, or undertaking which produces, holds and/or disposes of certain toxic and dangerous wastes including phenols and phenol compounds; organic-halogen compounds, excluding inert polymeric materials and other substances referred to in this list or covered by other Directives concerning the disposal of toxic and dangerous waste; chlorinated solvents; organic solvents; biocides and phyto-pharmaceutical substances; ethers and aromatic polycyclic compounds (with carcinogenic effects) shall keep a record of the quantity, nature, physical and chemical characteristics and origin of such waste, and of the methods and sites used for disposing of such waste.

## 32.1 MAJOR USES

The production of phthalic anhydride is the main use for naphthalene. It accounts for approximately 60% of U.S. consumption. Twenty percent is used in the production of carbaryl, an insecticide; the remainder is used in the manufacture of tanning agents, moth repellents, surfactants and chemicals such as  $\beta$ -naphthol,  $\alpha$ -naphthol and decahydronaphthalene (440).

## 32.2 ENVIRONMENTAL FATE AND EXPOSURE PATHWAYS

### 32.2.1 Transport in Soil/Ground-water Systems

#### 32.2.1.1 Overview

Naphthalene may move through the soil/ground-water system when present at low concentrations (dissolved in water and sorbed on soil) or as a separate organic phase (resulting from a spill of significant quantities of the chemical). In general, transport pathways of low soil concentrations can be assessed by equilibrium partitioning, as shown in Table 32-1. These calculations predict the partitioning of naphthalene among soils particles, soil water and soil air. The portions of naphthalene associated with the water and air phases of the soil are more mobile than the adsorbed portion.

The estimates for the unsaturated topsoil model indicate that most of the naphthalene (99%) is expected to be sorbed to the soil. Only a small amount (0.5%) will be present in the soil water phase and available to migrate by bulk transport (e.g., the downward movement of infiltrating water), dispersion and diffusion. Very little naphthalene will be in the gaseous phase of the soil (<0.1%).

In saturated, deep soils (containing no soil air and negligible soil organic carbon), a higher fraction of the naphthalene (20%) is expected to be present in the soil-water phase (Table 32-1) and transported with flowing ground water.

#### 32.2.1.2 Sorption on Soils

The mobility of naphthalene in the soil/ground-water system (and its eventual migration into aquifers) is strongly affected by the extent of its sorption on soil particles. In general, sorption on soils is expected to:

- increase with increasing soil organic matter content;
- increase slightly with decreasing temperature;

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TABLE 32-1 (H)

EQUILIBRIUM PARTITIONING CALCULATIONS FOR NAPHTHALENE  
IN MODEL ENVIRONMENTS<sup>a</sup>

Soil Environment	Estimated Percent of Total Mass of Chemical in Each Compartment		
	Soil	Soil-Water	Soil-Air
Unsaturated topsoil <sup>b,c</sup> at 25°C	99.4	0.5	0.03
Saturated deep soil <sup>d</sup>	80.2	19.8	-

- a) Calculations based on Mackay's equilibrium partitioning model (34,35,36); see Introduction for description of model and environmental conditions chosen to represent an unsaturated topsoil and saturated deep soil. Calculated percentages should be considered as rough estimates and used only for general guidance.
- b) Utilized estimated soil sorption coefficient:  $K_{oc} = 962$ .  
(Estimated by Arthur D. Little, Inc.)
- c) Henry's law constant taken as  $4.82 \times 10^{-4}$  atm·m<sup>3</sup>/mol at 25°C (74).
- d) Used sorption coefficient ( $K_p$ ) calculated as a function of  $K_{oc}$  assuming 0.1% organic carbon:  $K_p = 0.001 \times K_{oc}$ .

- increase moderately with increasing salinity of the soil water; and
- decrease moderately with increasing dissolved organic matter content of the soil water.

The available data (10,759,760) indicate that naphthalene sorption onto soils and sediments is a reversible process, and that the kinetics of desorption are slower than the kinetics of adsorption. These observations and the relatively high aqueous solubility of naphthalene suggest that migration with infiltrating water may be an important transport process for naphthalene.

In a field study of the effects of dune soil on the removal and modification of river-borne organics during dune-infiltration (using water from the Rhine River), Piet et al. (226) found increases in the naphthalene concentration after infiltration. While the reason for the increase is not known, and may have been due to some artifact of the study, the results do indicate that naphthalene is easily transported by infiltrating water.

Retardation factors, which represent the ratio of the interstitial water velocity to the pollutant velocity in the soil, have been reported for naphthalene. Fu et al. (760) report a retardation coefficient of 23 for naphthalene in soil columns containing approximately 2% organic carbon. Schwarzenbach et al. (77) report the following retardation factors for naphthalene: 16-62 in river sediment (1-2% organic carbon); 2.5-31 in an aquifer close to the river bed (0.1-1% organic carbon); and 1-2.5 in an aquifer far from the river bed (<0.1% organic carbon). These data indicate some retardation (i.e., adsorption) in soils having 1-2% organic carbon, and little or no retardation in deep soils having less than 0.1% organic carbon.

#### 32.2.1.3 Volatilization from Soils

Transport of naphthalene vapors through the air-filled pores of unsaturated soils is a potentially important transport mechanism for near-surface soils. In general, important soil and environmental properties influencing the rate of volatilization include soil porosity, temperature, convection currents and barometric pressure changes; important physicochemical properties include the Henry's law constant, the vapor-soil sorption coefficient, and, to a lesser extent, the vapor phase diffusion coefficient (31).

Volatilization of naphthalene from aqueous solution has been reported to be a significant removal process with rates dependent on current and wind velocities (440). There are no data from laboratory or field tests showing actual soil volatilization rates for naphthalene; sorption of the naphthalene vapors on the soil may slow the vapor phase transport.

The Henry's law constant (H), which provides an indication of a chemical's tendency to volatilize from solution, increases significantly with increasing temperature (28). Moderate increases in H are also observed with increasing salinity due to a decrease in naphthalene's solubility (517).

### 32.2.2 Transformation Processes in Soil/Ground-water Systems

The persistence of naphthalene in soil/ground-water systems is not well documented. In most cases, it should be assumed that the chemical will persist for months to years (or more). Naphthalene that has been released into the air will eventually undergo photochemical oxidation (10).

Naphthalene under normal environmental conditions is not expected to undergo hydrolysis (10). Furthermore, naphthalene is not expected to be susceptible to oxidation or reduction reactions in the soil/ground-water environment. Photolysis of naphthalene in surface soils may occur due to the high absorptivities of the compound in the UV/VIS range; however, no specific data were available.

Naphthalene has been reported to be readily susceptible to aerobic biodegradation after an initial period of acclimation (10,55,519,761). However, the rate and extent of degradation vary considerably depending on environmental conditions. Certain pure and mixed cultures can apparently degrade naphthalene under environmental conditions. Biodegradation in acclimated wastewater treatment plants (e.g., activated sludge) would be expected to be relatively easy based upon the data of Tabak et al. (55). Lee (519) and Herbes (761) have demonstrated biodegradation in aqueous systems located near industrial sources of naphthalene; the highest degradation rates were reported in oil-polluted areas or areas receiving continuous input of naphthalene.

Naphthalene does occur in most soils, and soil microbes have been shown to degrade (aerobic) some PAHs (10). Schwarzenbach et al. (77) report that biological processes were responsible for the "elimination" of naphthalene during infiltration of river water to ground water. However, in most soil/ground-water systems such aerobic degradation would be a minimal importance because of the low concentration of microorganisms (at depth) and the low dissolved oxygen (anaerobic) conditions. No data are available on the possibility of anaerobic biodegradation.

### 32.2.3 Primary Routes of Exposure from Soil/Ground-water Systems

The properties of naphthalene and the above discussion of fate pathways suggest that naphthalene is moderately volatile, moderately adsorbed by soil, and has a moderate potential for bioaccumulation. This compound may volatilize from soil surfaces. That portion not subject of volatilization may migrate to ground water particularly in sandy soils. These fate characteristics suggest several potential exposure pathways.

Inhalation exposures could result from volatilization of naphthalene during drilling or restoration activities. In addition, there is some potential for ground water contamination, particularly in sandy soils. Mitre (83) reported that naphthalene has been found in 12 of the 546 National Priority List (NPL) sites. It was detected at 9 sites in ground water and 4 sites in surface water.

Naphthalene's properties, as well as its presence at NPL sites suggest that it has some potential for movement in soil/ground-water systems. This compound may eventually reach surface waters by this mechanism, suggesting several other exposure pathways:

- Surface water may be used as drinking water supplies, resulting in direct ingestion exposure;
- Aquatic organisms residing in these waters may be consumed, also resulting in ingestion exposure;
- Recreational use of these waters may result in dermal exposure;
- Domestic animals may consume or be dermally exposed to contaminated ground or surface waters; the consumption of meats and poultry could then result in ingestion exposure.

In general, exposures associated with surface water contamination can be expected to be lower than drinking contaminated ground water, partially due to the greater dilution volume for surface waters. In addition, the BCF for naphthalene is not high enough for bioaccumulation to represent a more significant source of exposure than drinking water.

#### 32.2.4 Other Sources of Exposure

Naphthalene is commercially produced and used in part as a moth repellent. This use can result in direct consumer exposure. Estimates of bedroom air concentrations resulting from this use were about 7 ug/m<sup>3</sup>. In addition, naphthalene has been reported in cigarette smoke. Estimated exposures range from 3-300 ug/day, depending on the number of cigarettes smoked (440).

Ambient levels of naphthalene in drinking water and air appear to be generally low or below detection limits, and exposures would not be significant as compared to that resulting from moth ball usage or smoking (440). Brodzinsky and Singh (84) compiled all available atmospheric monitoring data for a number of organics. For naphthalene,

they had data for 106 locations. In urban and suburban locations, the median concentration was 0.94  $\mu\text{g}/\text{m}^3$ . In source-dominated areas, the median concentration was 2.1  $\mu\text{g}/\text{m}^3$ .

### 32.3 HUMAN HEALTH CONSIDERATIONS

#### 32.3.1 Animal Studies

##### 32.3.1.1 Carcinogenicity

Results of two studies on naphthalene carcinogenicity via oral or subcutaneous routes indicate a negative response. The studies however, are inadequate for assessment of carcinogenic risk. In one study, rats were given 10 g of naphthalene over "a period of time." The rats were followed for up to 1000 days; none developed tumors (442). The other study which provided no indications of carcinogenicity was conducted with rats given a subcutaneous injection of 820 mg of naphthalene/rat. None of the 10 rats developed tumors (442). Another experiment indicated a nonstatistically significant increase in lymphosarcoma in rats given 7 subcutaneous injections of 500 mg/kg. However, the naphthalene used contained 10% of an unknown impurity and carbolfuchsin, a known carcinogen, was applied to the injection site prior to administration. A skin-painting study in mice produced lymphocytic leukemia and lung adenoma, but these results are of little significance with respect to naphthalene since benzene, a known carcinogen, was utilized as the vehicle (441).

Neither IARC nor the NTP has categorized naphthalene with regard to its potential carcinogenicity.

##### 32.3.1.2 Mutagenicity

Naphthalene was found to be nonmutagenic in E.coli and various strains of Salmonella typhimurium (443,444). In vitro cell transformation assays were also negative (445).

##### 32.3.1.3 Teratogenicity, Embryotoxicity and Reproductive Effects

Hardin et al. (208) reported no adverse fetal or maternal effects in rats administered 395 mg/kg naphthalene (in corn oil) intraperitoneally on days 1-15 of gestation.

#### 32.3.1.4 Other Toxicologic Effects

##### 32.3.1.4.1 Short-term Toxicity

Ocular toxicity is the most common effect resulting from short-term, high-level exposure to naphthalene in animals. Cataracts and retinopathy were produced in rabbits fed 1000 mg/kg daily for 46 days. Retinal changes were noted as early as day 3 (446). Weanling rats fed a diet of 2% naphthalene for 60 days also developed cataracts (447). Grant (19) reports that nearly all parts of the eye are affected in varying degrees, with the response differing from animal to animal. The mechanism by which cataracts are induced is thought to be due to the formation of reactive metabolites (1,2-dihydroxynaphthalene and 1,2-naphthoquinone) in the eye which combine irreversibly with thiol groups of lens protein (19).

Curiously, direct application of a 10% solution in oil to the eyes or intraperitoneal injection of 500 mg/day for 50 days failed to produce cataracts in rabbits (446). However, lens changes were noted after a 5-day application of 1% dihydrodiol, a naphthalene metabolite (448).

The lung also appears to be a target for naphthalene-induced toxicity, with bronchiolar necrosis being observed in mice after single intraperitoneal doses of 128 mg/kg; the tissue had returned to normal within 7 days (449). Dogs experienced an 83% drop in hemoglobin levels after receiving an oral dose of 1800 mg/kg divided over 5 days (450).

##### 32.3.1.4.2 Chronic Toxicologic Effects

A 90-day feeding study of CD-1 mice revealed no significant ocular or hematological changes. The only significant organ change was a reduction in the spleen weight of females but there was no evidence of immunotoxicity in any treatment group. The dosages ranged from 5.3 to 133 mg/kg/day (451).

#### 32.3.2 Human and Epidemiologic Effects

##### 32.3.2.1 Short-term Toxicologic Effects

Hemolytic anemia is the most severe effect associated with naphthalene exposure and is seen for the most part in individuals with a deficiency of glucose-6-phosphate dehydrogenase (G6PD). G6PD-deficiency causes a decrease in the levels of reduced glutathione (GSH) in red blood cells, leading to denaturation of hemoglobin and subsequent changes in the red blood cells. G6PD-deficiency is most prevalent in blacks, Orientals and individuals of Jewish ancestry, making

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them more susceptible to these effects (54). All newborn infants (1-2 weeks old) are also susceptible to the possible hemolytic effects of naphthalene due to the reduced activity of enzyme systems normally found in all newborn infants.

The lethal ingested dose of naphthalene in non-sensitive adults ranges between 5 and 15 g (17). Ingestion of 6 g has been survived but 2 g ingested over a day killed a child (452,453). Initial symptoms of ingestion include eye irritation, headache, abdominal pain and nausea which may progress to jaundice and renal tubular blockade. Hematologic features include dramatic decreases in hemoglobin, hematocrit and red cell count (46). Greater damage occurs when naphthalene is ingested in combination with fats which facilitate absorption and subsequent systemic effects of naphthalene.

Naphthalene is irritating to the skin upon direct contact and a small percentage of the population may be hypersensitive to it. In one case, an individual developed a case of exfoliative dermatitis. A patch test for naphthalene proved positive. When naphthalene exposure was discontinued, the skin condition cleared rapidly and did not recur in a 3-year follow-up period (454). Clothing impregnated with naphthalene has caused skin rashes and systemic poisoning in infants. Effects may have been enhanced by the application of baby oil to the infants' skin, thus increasing the absorption of the highly lipid-soluble naphthalene (455,56).

Naphthalene vapor causes eye irritation at 15 ppm. Eye contact with the solid may result in conjunctivitis, corneal injury and diminished visual acuity (46).

There is one report of transplacental naphthalene poisoning but no details are available (456).

#### 32.3.2.2 Chronic Toxicologic Effects

In the general population, 50 cases of severe chronic effects have been reported from repeated ingestion of a mixture of naphthalene and isopropyl alcohol. The symptoms resembled those of ethanol intoxication and included tremors, restlessness and hallucinations. The effects subsided in a few days (457).

Repeated inhalation of vapors may produce malaise, headache and vomiting (12). In a study of 21 workers exposed to high concentrations of vapors for 5 years, 8 developed peripheral lens opacities (446). In other studies, no eye abnormalities occurred in workers exposed to naphthalene for several years (46).

In a single case report, aplastic anemia was found in a 68-year-old black woman who had been exposed to moth-proofing compounds for a period of 39 years. It was estimated that she was exposed to 184 ppm of naphthalene and 1400 ppm of 1,4-dichlorobenzene. No other cases of aplastic anemia have been attributed to either of these chemicals alone or in combination (458).

### 32.3.3 Levels of Concern

There are no adequate chronic toxicity or epidemiological studies available for use as a basis for a naphthalene water criterion. The USEPA (355) has, therefore, established that a satisfactory human health criterion for naphthalene cannot be derived at this time.

Both OSHA (298) and the ACGIH (3) have set an occupational exposure limit of 10 ppm (50 mg/m<sup>3</sup>) for naphthalene, based on preventing eye irritation.

### 32.3.4 Hazard Assessment

Evaluation of the potential risks to humans from exposure to naphthalene is hampered by the scarcity of quantitative data on carcinogenic or long-term effects of naphthalene exposure.

The two major effects linked to naphthalene exposure include cataract formation and hemolytic anemia. Information on the production of cataracts is mainly anecdotal. Cataracts have been described in workers exposed to high levels of naphthalene vapor; other studies have noted negative findings. The dose-effect relationship between naphthalene and hemolytic anemia also is not clear. Individuals with relative deficiencies in the enzymes needed to maintain reduced glutathione levels, as well as the fetus and young infants (1-2 weeks old), appear at increased risk to develop hemolytic anemia, which can lead to renal damage.

Studies on the chronic effects of naphthalene have generally been negative. This substance has not been shown to be carcinogenic, teratogenic or mutagenic.

## 32.4 SAMPLING AND ANALYSIS CONSIDERATIONS

Determination of naphthalene concentrations in soil and water requires collection of a representative field sample and laboratory analysis. Care is required to prevent losses during sample collection and storage. Soil and water samples should be collected in amber glass containers; extraction of samples should be completed within 7 days of

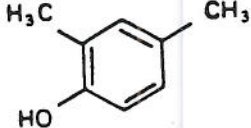
sampling and analysis completed within 14 days. In addition to the targeted samples, quality control samples such as field blanks, duplicates, and spiked matrices may be specified in the recommended methods.

EPA-approved procedures for the analysis of naphthalene, one of the EPA priority pollutants, in aqueous samples include EPA Methods 610, 625, and 1625 (65). Prior to analysis, samples are extracted with methylene chloride as a solvent using a separatory funnel or a continuous liquid-liquid extractor. The semi-volatile constituents in the concentrated extract may be separated by either a high performance liquid chromatographic (HPLC) column (Method 610) or a gas chromatographic (GC) column (Method 610, 625, and 1625); naphthalene is then detected with an ultraviolet detector (Method 610/HPLC), flame ionization detector (Method 610/GC) or a mass spectrometer (Method 625 and 1625).

The EPA procedures recommended for naphthalene analysis in soil and waste samples, Methods 8100, 8250, and 8310 (63), differ from the aqueous procedures primarily in the preparation of the sample extract. Solid samples are extracted using either soxhlet extraction or sonication methods. Neat and diluted organic liquids may be analyzed by direct injection. Method 8100 employs a GC with flame ionization detection for analysis of the naphthalene concentration; Method 8250 uses a GC with mass spectrometric detection and Method 8310 uses an HPLC with ultraviolet detection.

Typical naphthalene detection limits that can be obtained in wastewaters and non-aqueous samples (wastes, soils, etc.) are shown below. The naphthalene detection limit for Method 610/GC was not determined. The actual detection limit achieved in a given analysis will vary with instrument sensitivity and matrix effects.

<u>Aqueous Detection Limit</u>	<u>Non-Aqueous Detection Limit</u>
1.8 µg/L (Method 610/HPLC)	1 µg/g (Method 8010)
1.6 µg/L (Method 625)	1 µg/g (Method 8240)
10 µg/L (Method 1624)	

COMMON SYNONYMS: m-Xylenol 2,4-Xylenol 4,6-Dimethylphenol 1-Hydroxy-2,4-dimethylbenzene	CAS REG. NO.: 105-67-9	FORMULA: $C_8H_{10}O$	AIR W/V CONVERSION FACTORS at 25°C
	NIOSH NO.: ZE5600000		4.98 mg/m <sup>3</sup> ≈ 1 ppm 0.201 ppm ≈ 1 mg/m <sup>3</sup>
	STRUCTURE:		MOLECULAR WEIGHT: 122.16

REACTIVITY	Reactions of phenols with non-oxidizing mineral acids or organic peroxides or hydroperoxides typically generate heat. Those with alkali or alkaline earth metals, nitrides, or strong reducing agents may produce heat and flammable gases while reactions with azo or diazo compounds, or hydrazines may evolve heat and other gases. Reactions with oxidizing mineral acids or other strong oxidizers may result in heat generation and fire, while those with isocyanates, epoxides, or polymerizable compounds may result in evolution of heat and violent polymerization reactions. Contact with explosive materials may cause an explosion (511).
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PHYSICO-CHEMICAL DATA	<ul style="list-style-type: none"> <li>● Physical State (at 20°C): crystalline solid (23)</li> <li>● Color: white (23)</li> <li>● Odor: no data ( )</li> <li>● Odor Threshold: 0.4 mg/L (67)</li> <li>● Density (g/ml at 20°C): 0.965 (68)</li> <li>● Freezing/Melting Point (°C): 27 (68)</li> <li>● Boiling Point (°C): 210 (68)</li> <li>● Flash Point (°C): no data ( )</li> <li>● Flammable Limits in Air, % by Volume: no data ( )</li> <li>● Autoignition Temperature (°C): no data ( )</li> <li>● Vapor Pressure (mm Hg at 20°C): 0.067 (ADL estim)</li> <li>● Saturated Concentration in Air (mg/m<sup>3</sup> at 20°C): 450 (ADL estim)</li> <li>● Solubility in Water (mg/L at 20°C): 1480 (ADL estim)</li> <li>● Viscosity (cp at 20°C): no data ( )</li> <li>● Surface Tension (dyne/cm at 20°C): no data ( )</li> <li>● Log (Octanol-Water Partition Coefficient), log K<sub>ow</sub>: 2.30 (29)</li> <li>● Soil Adsorption Coefficient, K<sub>oc</sub>: 96 (652)</li> <li>● Henry's Law Constant (atm·m<sup>3</sup>/mol at 20°C): 6.7 x 10<sup>-6</sup> (ADL estim)</li> <li>● Bioconcentration Factor: 150 (bluegill), 9.5 (estim) (214,659)</li> </ul>
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PERSISTENCE IN THE SOIL- WATER SYSTEM	Fairly mobile in soil-water systems, especially in aqueous phase. Volatilization through air-filled pores is not significant. Chemical is resistant to hydrolysis; it may be easily biodegraded in wastewater treatment plants, but biodegradation in natural environments may be insignificant. Chemical may thus persist for months to years (or more).						
PATHWAYS OF EXPOSURE	The primary pathway of concern from a soil-water system is the migration of 2,4-dimethylphenol to ground-water drinking water supplies. Inhalation is not expected to be a pathway of concern for this compound.						
HEALTH HAZARD DATA	<p><u>Signs and Symptoms of Short-term Human Exposure:</u> No reports of human exposure and associated effects were found.</p> <p><u>Toxicity Based on Animal Studies:</u></p> <table border="0" data-bbox="375 884 1404 989"> <tr> <td>LD<sub>50</sub> (mg/kg)</td> <td>LCLo (mg/m<sup>3</sup>)</td> </tr> <tr> <td>oral [rat] 3200 (47)</td> <td>inhalation -- no data</td> </tr> <tr> <td>skin [rat] 1040 (47)</td> <td></td> </tr> </table> <p>Long-Term Effects: No data Pregnancy/Neonate Data: No data Mutation Data: No data Carcinogenicity Classification: IARC - none assigned; NTP - none assigned</p>	LD <sub>50</sub> (mg/kg)	LCLo (mg/m <sup>3</sup> )	oral [rat] 3200 (47)	inhalation -- no data	skin [rat] 1040 (47)	
LD <sub>50</sub> (mg/kg)	LCLo (mg/m <sup>3</sup> )						
oral [rat] 3200 (47)	inhalation -- no data						
skin [rat] 1040 (47)							
HANDLING PRECAUTIONS	Handle chemical only with adequate ventilation • There are no formal guidelines available for this chemical with respect to respirator use. Use a self-contained breathing apparatus with a full facepiece (or the equivalent) where there is any doubt as to the efficacy of gas masks or cartridge-type respirators • Chemical goggles if there is a probability of eye contact • Appropriate clothing to prevent repeated or prolonged skin contact.						
EMERGENCY FIRST AID TREATMENT (59)	<u>Ingestion:</u> Induce vomiting if victim is conscious; get medical attention • <u>Inhalation:</u> Move victim to fresh air; give artificial respiration if necessary • <u>Skin:</u> Thoroughly wash skin with soap and water • <u>Eye:</u> Irrigate with water.						

## ENVIRONMENTAL AND OCCUPATIONAL STANDARDS AND CRITERIA

AIR EXPOSURE LIMITS:Standards

- OSHA PEL (8-hr TWA): none established
- AFOSH PEL (8-hr TWA): none established

Criteria

- NIOSH IDLH (30-min): none established
- ACGIH TLV<sup>W</sup> (8-hr TWA): none established
- ACGIH STEL (15-min): none established

WATER EXPOSURE LIMITS:Drinking Water Standards

None established

EPA Health Advisories

None established

EPA Ambient Water Quality Criteria (355)

- Human Health
  - Based on ingestion of contaminated water and aquatic organisms, no criterion established due to insufficient data.
  - Based on ingestion of contaminated aquatic organisms only, no criterion established due to insufficient data.
  - Based on organoleptic data only, 400 µg/L.
- Aquatic Life
  - Freshwater species
    - acute toxicity: no criterion, but lowest effect level occurs at 2120 µg/L.
    - chronic toxicity: no criterion established due to insufficient data.
  - Saltwater species
    - acute toxicity: no criterion established due to insufficient data.
    - chronic toxicity: no criterion established due to insufficient data.

## REGULATORY STATUS (as of October 1, 1985)

Promulgated Regulations

## ● Federal Programs

Clean Water Act (CWA)

2,4-Dimethylphenol is designated a hazardous substance under CWA. It has a reportable quantity (RQ) limit of 45.4 kg (347, 556). It is also listed as a toxic pollutant (351). Water quality criteria have not been set due to insufficient data. No effluent limitations specific to this chemical have been set.

Safe Drinking Water Act (SDWA)

In states with an approved Underground Injection Control program, a permit is required for the injection of 2,4-dimethylphenol-containing wastes designated as hazardous under RCRA (295).

Resource Conservation and Recovery Act (RCRA)

2,4-Dimethylphenol is identified as a toxic hazardous waste (U101) and listed as a hazardous waste constituent (328,329). Waste streams from the following industries contain 2,4-dimethylphenol and are listed as specific sources of hazardous waste: wood preservation (creosote and/or pentachlorophenol preserving processes) and coking (operational residues) (326,327).

Comprehensive Environmental Response Compensation and Liability Act (CERCLA)

2,4-Dimethylphenol is designated a hazardous substance under CERCLA. It has a reportable quantity (RQ) limit of 45.4 kg. Reportable quantities have also been issued for RCRA hazardous waste streams containing 2,4-dimethylphenol but these depend upon the concentration of the chemicals present in the waste stream (556).

Hazardous Materials Transportation Act (HMTA)

The Department of Transportation has designated 2,4-dimethylphenol as a hazardous material which is subject to requirements for packaging, labeling and transportation (306).

## ● State Water Programs

California has an action level of 400 ppb for drinking water (731). Illinois has a standard of 0.1 mg/L for general use water and 1 µg/L for finished drinking water (731).

Kentucky has a criterion of 5 µg/L for total phenols (732).

Louisiana has a criterion of 5 µg/L for phenols in the public water supply (731).

Iowa has a maximum level of 0.05 mg/L for phenolic compounds in drinking water (731).

Nevada has a criterion of 1 µg/L for phenolics (as phenol) (732).

New York has a ground water quality standard of 1 µg/L for phenols (731).

North Carolina has a standard of 1  $\mu\text{g}/\text{L}$  for phenolic compounds in drinking water (731).

West Virginia has a criterion of 5  $\mu\text{g}/\text{L}$  for phenolic materials (732).

Other states follow EPA Ambient Water Quality Criteria.

#### Proposed Regulations

- Federal Programs

- Clean Water Act (CWA)

- Effluent guidelines for 2,4-dimethylphenol have been proposed in the organic chemicals, plastics and synthetic fibers category (357).

- State Water Programs

- New York has proposed a surface water standard for total phenols and total unchlorinated phenols (731).

#### EEC Directives

##### Directive on Drinking Water (533)

The mandatory values for phenols in surface water treatment categories A1, A2 and A3 used or intended for abstraction of drinking water are 0.001, and 0.005, and 0.1  $\text{mg}/\text{L}$ , respectively. Guideline values for phenols under treatment categories A2 and A3 are 0.001 and 0.01  $\text{mg}/\text{L}$ , respectively. No guideline value is given for treatment category A1.

##### Directive Relating to the Quality of Water Intended for Human Consumption (540)

The maximum admissible concentration for phenols (phenol index) is 0.5  $\mu\text{g}/\text{L}$ . Excluded from this category are natural phenols which do not react to chlorine. No guideline levels for phenols are given.

##### Directive on Ground Water (538)

Direct and indirect discharge into ground water of substances which have a deleterious effect on the taste and/or odor of ground water, and compounds liable to cause the formation of such substances in ground water and to render it unfit for human consumption shall be subject to prior review so as to limit such discharges.

##### Directive on Bathing Water Quality (534)

Mandatory values for phenols (phenol indices) in bathing water are: (1) no specific odor and (2) concentrations  $< 0.05 \text{ mg}/\text{L}$ . Guideline values for phenols suggest concentrations  $< 0.005 \text{ mg}/\text{L}$ .

##### Directive on Fishing Water Quality (536)

Phenolic compounds in both salmonid and cyprinid waters must not be present in such concentrations that they adversely affect fish flavor.

##### Directive on the Quality Required of Shellfish Waters (537)

The mandatory specifications for substances affecting the taste of shellfish require that their concentrations be lower than that liable to impair the taste of the shellfish.



Directive on the Discharge of Dangerous Substances (535)

Organohalogens, carcinogens or substances which have a deleterious effect on the taste and/or odor of human food derived from aquatic environments cannot be discharged into inland surface waters, territorial waters or internal coastal waters without prior authorization from member countries which issue emission standards. A system of zero-emission applies to discharge of these substances into ground water.

Directive on Ground Water (538)

Direct discharge into ground water (i.e., without percolation through the ground or subsoil) of organohalogen compounds and substances which may form such compounds in the aquatic environment, substances which possess carcinogenic, mutagenic or teratogenic properties in or via the aquatic environment, and mineral oils and hydrocarbons is prohibited.

Appropriate measures deemed necessary to prevent indirect discharge into ground water (i.e., via percolation through ground or subsoil) of these substances shall be taken by member countries.

Directive on Toxic and Dangerous Wastes (542)

Any installation, establishment, or undertaking which produces, holds and/or disposes of certain toxic and dangerous wastes including phenols and phenol compounds; organic-halogen compounds, excluding inert polymeric materials and other substances referred to in this list or covered by other Directives concerning the disposal of toxic and dangerous waste; chlorinated solvents; organic solvents; biocides and phyto-pharmaceutical substances; ethers and aromatic polycyclic compounds (with carcinogenic effects) shall keep a record of the quantity, nature, physical and chemical characteristics and origin of such waste, and of the methods and sites used for disposing of such waste.

Directive on the Classification, Packaging and Labeling of Dangerous Substances (787)

2,4-Dimethylphenol is classified as a toxic substance and is subject to packaging and labeling regulations.

## 22.1 MAJOR USES

The compound, 2,4-dimethylphenol, is a naturally-occurring, substituted phenol derived from the cresol fraction of petroleum or coal tars. It is one of 5 isomers of dimethylphenol. No direct commercial applications presently exist for 2,4-dimethylphenol, but it is used commercially in the manufacture of a wide range of products for industry and agriculture. These include phenolic antioxidants, disinfectants, solvents, pharmaceuticals, insecticides, plasticizers, rubber chemicals, polyphenylene oxide, wetting agents and dyestuffs (214).

## 22.2 ENVIRONMENTAL FATE AND EXPOSURE PATHWAYS

## 22.2.1 Transport in Soil/Ground-water Systems

## 22.2.1.1 Overview

The 2,4-isomer of dimethylphenol may move through the soil/ground-water system when present at low concentrations (dissolved in water and sorbed on soil) or as a separate organic phase (resulting from a spill of significant quantities of the chemical). In general, transport pathways of low soil concentrations can be assessed by estimating equilibrium partitioning as shown in Table 22-1. These calculations predict partitioning of 2,4-dimethylphenol among soil particles, soil water and soil air. The 2,4-dimethylphenol associated with the water and air phases of the soil is more mobile than the adsorbed portion.

The estimates for the unsaturated topsoil model indicate that nearly all of the chemical (95%) would be associated with the soil particles. Most of the remainder (5%) is predicted to be present in the soil-water phase and can thus migrate by bulk transport (e.g., the downward movement of infiltrating water), dispersion and diffusion. For the small portion of 2,4-dimethylphenol in the gaseous phase of the soil (0.0004%), diffusion through the soil-air pores up to the ground surface, and subsequent removal by wind, will be possible.

In saturated, deep soils (containing no soil air and negligible soil organic carbon), a much higher fraction of the 2,4-dimethylphenol (71%) is likely to be present in the soil-water phase (Table 22-1) and transported with flowing ground water.

The 2,4-isomer of dimethylphenol is a weak acid ( $pK_a = 10.6$ ) which will dissociate slightly in natural waters with elevated pHs (e.g., 7-9). Under most conditions, however, the chemical will be in its

TABLE 22-1 (I)

EQUILIBRIUM PARTITIONING CALCULATIONS FOR 2,4-DIMETHYLPHENOL  
IN MODEL ENVIRONMENTS<sup>a</sup>

Soil Environment	Estimated Percent of Total Mass of Chemical in Each Compartment		
	Soil	Soil-Water	Soil-Air
Unsaturated topsoil <sup>b,c</sup> at 20°C	94.8	5.1	0.0004
Saturated deep soil <sup>d</sup>	28.7	71.3	-

- a) Calculations based on Mackay's equilibrium partitioning model (34,35,36); see Introduction for description of model and environmental conditions chosen to represent an unsaturated topsoil and saturated deep soil. Calculated percentages should be considered as rough estimates and used only for general guidance.
- b) Utilized estimated soil sorption coefficient:  $K_{oc} = 96$ .  
(Estimated by Arthur D. Little, Inc.)
- c) Henry's law constant taken as  $6.7 \times 10^{-6}$  atm·m<sup>3</sup>/mol at 20°C.  
(Estimated by Arthur D. Little, Inc.)
- d) Used sorption coefficient ( $K_p$ ) calculated as a function of  $K_{oc}$  assuming 0.1% organic carbon:  $K_p = 0.001 \times K_{oc}$ .

neutral, non-ionized form. The phenolic group can form complexes with dissolved metal cations, and this may influence environmental fate and transport in ways not applicable to other non-reacting organic compounds.

#### 22.2.1.2 Sorption on Soils

The mobility of 2,4-dimethylphenol in the soil/ground-water system (and its eventual migration into aquifers) is strongly affected by the extent of its sorption on soil particles. In general, sorption on soils is expected to:

- increase with increasing soil organic matter content;
- increase slightly with decreasing temperature;

- increase moderately with increasing salinity of the soil water; and
- decrease moderately with increasing dissolved organic matter content of the soil water.

Based upon its octanol-water partition coefficient of 200, the soil sorption coefficient ( $K_{oc}$ ) is estimated to be 96. This is a relatively low number indicative of weak sorption to soils. However, this conclusion is based upon the assumption that the chemical acts as a neutral species. As mentioned above, the phenolic group can complex with other cations and any such complexation could significantly alter the sorption properties of the chemical in unpredictable ways.

#### 22.2.1.3 Volatilization from Soils

Transport of 2,4-dimethylphenol vapors through the air-filled pores of unsaturated soils is not expected to be an important transport mechanism because of the chemical's low vapor pressure and relatively high water solubility (which allows it to be carried down with infiltrating water).

#### 22.2.2 Transformation Processes in Soil/Ground-water Systems

The persistence of 2,4-dimethylphenol in soil/ground-water systems has not been studied. In most cases, it should be assumed that the chemical will persist for months to years (or more).

2,4-Dimethylphenol under normal environmental conditions is not expected to undergo hydrolysis (10,33). The possibility of aqueous phase oxidation, catalyzed by certain dissolved metals such as copper or iron, has been raised, but there is no evidence that such reactions occur under normal environmental conditions (10).

2,4-Dimethylphenol is likely to be easily biodegraded in biological wastewater treatment plants based on data reported by Callahan et al. (10) and Takak et al. (55). However, other data indicate that biodegradation in natural environments (e.g., rivers, soil/ground-water systems) may not occur at environmentally-significant rates (10). In most soil/ground-water systems, the concentration of microorganisms capable of biodegrading chemicals such as 2,4-dimethylphenol is very low and drops off sharply with increasing depth. Thus, biodegradation in the soil/ground-water system should be assumed to be of minimal importance except, perhaps, in landfills with active microbiological populations.

### 22.2.3 Primary Routes of Exposure From Soil/Ground-water Systems

The above discussion of fate pathways suggests that the volatility of 2,4-dimethylphenol from aqueous solutions is low, it is weakly adsorbed by soil and has a low potential for bioaccumulation. The portion of the compound not adsorbed will be mobile in ground water.

The potential for ground water contamination is high, particularly in sandy soil. Mitre (83) reported that 2,4-dimethylphenol was found at 3 of the 546 National Priority List (NPL) sites. It was detected at one site in ground water and 3 sites in surface water. There was no available monitoring data for 2,4-dimethylphenol in drinking water supplies. There is, however, a potential for exposure through drinking water ingestion from ground water if supplies are contaminated.

Because 2,4-dimethylphenol has the potential for movement in soil/ground-water systems, this compound may eventually reach surface waters by this mechanism, suggesting several other exposure pathways:

- Surface waters may be used as drinking water supplies, resulting in direct ingestion exposure;
- Aquatic organisms residing in these waters may be consumed, also resulting in ingestion exposures through bioaccumulation;
- Recreational use of these waters may result in dermal exposures;
- Domestic animals may consume or be dermally exposed to contaminated ground or surface waters; the consumption of meats and poultry could then result in ingestion exposures.

In general, exposures associated with surface water contamination can be expected to be lower than exposure from drinking contaminated ground water for two reasons. First, surface waters can provide a greater dilution volume. Secondly, the bioconcentration factor for this compound is expected to be low, suggesting limited bioaccumulation in aquatic organisms or domestic animals.

### 22.2.4 Other Sources of Exposure

There is a lack of data on the occurrence of 2,4-dimethylphenol in finished water supplies or in ambient air. 2,4-Dimethylphenol has been detected in industrial effluents (587). Discharge of contaminated effluents near drinking water intakes in surface water could potentially result in ingestion exposure.

## 22.3 HUMAN HEALTH CONSIDERATIONS

### 22.3.1 Animal Studies

#### 22.3.1.1 Carcinogenicity

Boutwell and Bosch (588) reported that 2,4-dimethylphenol produced papillomas and carcinomas on the skin of tumor-susceptible female Sutter mice. It should be noted, however, that the 2,4-dimethylphenol was applied as a 10% solution in benzene and that the mice were housed in cages treated with creosote, both known carcinogens. These investigators (588) also evaluated the ability of 2,4-dimethylphenol to promote the appearance of tumors after a single application of the carcinogen, dimethylbenzanthracene. Five milligrams of 2,4-dimethylphenol in benzene applied twice a week elicited a carcinogenic response in 18% of the mice at 23 weeks. Again, the use of benzene as the solvent confounds interpretation of this study.

#### 22.3.1.2 Mutagenicity

No mutagenicity data are available.

#### 22.3.1.3 Teratogenicity, Embryotoxicity and Reproductive Effects

No teratogenicity data are available.

#### 22.3.1.4 Other Toxicologic Effects

##### 22.3.1.4.1 Short-term Toxicity

The effects of acute administration of 2,4-dimethylphenol have been examined in mice, rats and rabbits. Ten percent solutions in oil (unspecified) were administered by intubation to rats and mice. In general, dimethylphenols were less toxic than phenol and methylphenols in mice; 2,4-dimethylphenol was less toxic to rats. The oral LD<sub>50</sub> values for 2,4-dimethylphenol were 809 mg/kg in mice and 3200 mg/kg in rats (214). No appreciable toxic effects were seen in rabbits following doses of 273-425 mg/kg; the route of administration was not specified (213). Topical administration has been shown to be lethal to mice at 5600 mg/kg; an LD<sub>50</sub> value of 1040 mg/kg was recorded for rats (47,213). Tested by application of a drop into rabbit eyes, the 3,5-isomer caused severe and presumably permanent injury (19). No inhalation studies of 2,4-dimethylphenol have been conducted. Other dimethylphenol isomers produce difficult respiration, disturbance of motor coordination and development of spasms with acute inhalation exposures (214).

#### 22.3.1.4.2 Chronic Toxicity

No long-term toxicity studies of 2,4-dimethylphenol have been conducted. However, the 2,6- and 3,4-isomers of dimethylphenol were evaluated in a 10-week study with male rats given oral doses of 29.5 mg/kg 2,6-dimethylphenol or 72.5 mg/kg of 3,4-dimethylphenol. The dosing regimen was not indicated. Animals treated with the 2,6-isomer exhibited a depressed body weight gain and increased organ to body weight ratios for the liver and spleen. Rats treated with the 3,4-isomer exhibited the same effects plus an increase in the organ to body weight ratios for the heart and lungs. Cellular changes in the liver were observed in both groups. No hematological changes were observed (589).

#### 22.3.2 Human and Epidemiologic Studies

No reports of human toxicity were found in the literature. It is unlikely that any segment of the population is exposed to this compound alone. Many workers are exposed by inhalation to commercial degreasing agents which contain methylphenols and dimethylphenols; however, no adverse effects have been reported. Since 2,4-dimethylphenol has been identified in cigarette and marijuana smoke, smokers and those exposed to smoke may be at risk (214).

#### 22.3.3.3 Levels of Concern

The USEPA (355) has not established an ambient water quality criterion for the protection of human health for 2,4-dimethylphenol due to the insufficiency of available data; a criterion of 400 µg/L is suggested by the USEPA on an organoleptic basis (355).

#### 22.3.3.4 Hazard Assessment

Nominally, 2,4-dimethylphenol is a cocarcinogen. Assessment of positive findings in skin-painting and tumor-promotion studies conducted with 2,4-dimethylphenol, however, are confounded by the use of benzene as the vehicle for compound administration and concomitant exposure to creosote. The impact, if any, that these two carcinogens exerted on the test results for 2,4-dimethylphenol is uncertain. The lack of mutagenic, reproductive and long-term exposure data for this compound further complicates an assessment of the human health hazards associated with exposure to 2,4-dimethylphenol. In view of the paucity of available health effects data, an assessment of hazard associated with exposure to 2,4-dimethylphenol cannot be made with any degree of confidence at this time.

## 22.4 SAMPLING AND ANALYSIS CONSIDERATIONS

Determination of 2,4-dimethylphenol concentrations in soil and water requires collection of a representative field sample and laboratory analysis. Care is required to prevent losses during sample collection and storage. Soil and water samples should be collected in glass containers; extraction of samples should be completed within 7 days of sampling and analysis completed within 40 days. In addition to the targeted samples, quality control samples such as field blanks, duplicates, and spiked matrices may be specified in the recommended methods.

EPA-approved procedures for the analysis of 2,4-dimethylphenol, one of the EPA priority pollutants, in aqueous samples include EPA Methods 604, 625, and 1625 (65). Prior to analysis, samples are extracted with methylene chloride as a solvent using a separatory funnel or a continuous liquid-liquid extractor. An aliquot of the concentrated sample extract is injected onto a gas chromatographic (GC) column using a solvent flush technique. The GC column is programmed to separate the semi-volatile organics; 2,4-dimethylphenol is then detected with a flame ionization detector (Method 604) or a mass spectrometer (Methods 625 and 1625).

The EPA procedures recommended for 2,4-dimethylphenol analysis in soil and waste samples, Methods 8040 and 8250 (63), differ from the aqueous procedures primarily in the preparation of the sample extract. Solid samples are extracted using either soxhlet extraction or sonication methods. Neat and diluted organic liquids may be analyzed by direct injection.

Typical 2,4-dimethylphenol detection limits that can be obtained in wastewaters and non-aqueous samples (wastes, soils, etc.) are shown below. The actual detection limit achieved in a given analysis will vary with instrument sensitivity and matrix effects.

<u>Aqueous Detection Limit</u>	<u>Non-Aqueous Detection Limit</u>
0.32 µg/L (Method 604)	1 µg/g (Method 8040)
2.7 µg/L (Method 625)	1 µg/g (Method 8250)
10 µg/l. (Method 1625)	