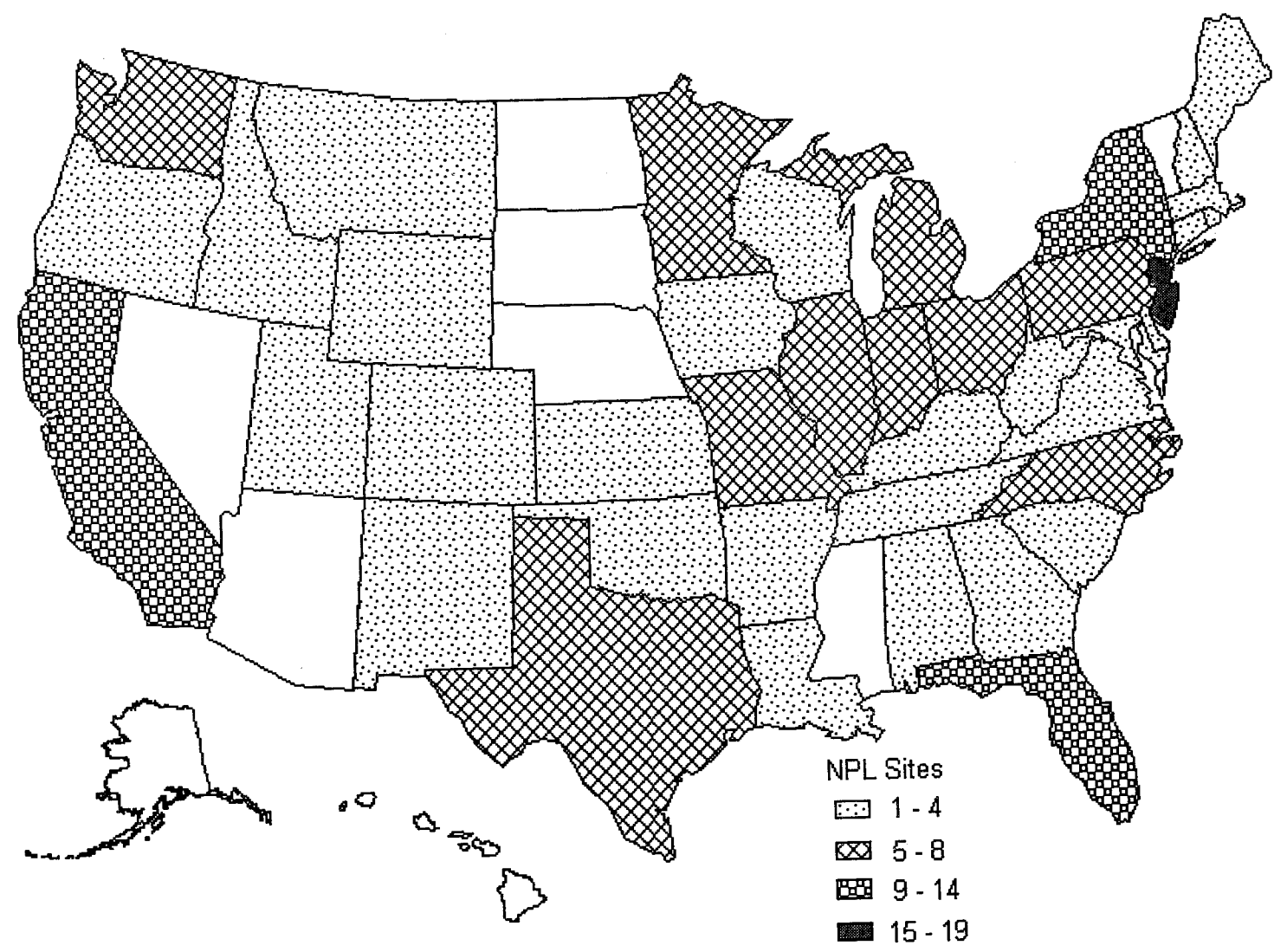## 5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

One or more of the eight chlorophenols discussed in the profile has been identified in at least 171 of the 1,467 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 1998). However, the number of sites evaluated for chlorophenols is not known. The frequency of these sites can be seen in Figure 5-l.

The majority of known environmental releases of chlorophenols were to surface water (Scow et al. 1982). The principal point source of water pollution by chlorophenols is industrial waste discharge; another point discharge is the leaching of chlorophenols from landfills. Chlorophenols enter the atmosphere through volatilization, with mono- and dichlorophenols being the most volatile. The primary nonpoint source pollution of chlorophenols comes from the application of pesticides that are made from chlorophenols and the chlorination of waste water containing phenol.

Once released to the environment, chlorophenols are subject to a series of physical, chemical, and biological transformations. Sorption, volatilization, degradation, and leaching are the primary processes governing their fate and transport. The pH in water and in soil and sediment is a major factor affecting the fate and transport of chlorophenols in these media, since the degree to which the compounds ionize increases with increasing pH. In addition, physiochemical properties of chlorophenols such as water solubility, Henry's law constant, organic carbon sorption coefficient, volatilization rate, and photolysis rate determine transport processes. Important environmental parameters influencing these processes include organic matter content and clay content in soil, sediment, and water, as chlorophenols are in general preferentially adsorbed to these soil constituents. In general, as the number of chlorine molecules increase, there is a reduction in vapor pressure, an increase in boiling point, and a reduction in water solubility of the chlorophenols (Solomon et al. 1994). Therefore, increasing chlorination increases the tendency of these compounds to partition into sediments and lipids and to bioconcentrate. Chlorophenols are subject to abiotic and biotic degradation and transformations. However, compounds containing chlorine in the *meta* positions show greater resistance to microbial attack.

The general population may be exposed to chlorophenols through ingestion of chlorinated drinking water and food contaminated with the compounds and inhalation of contaminated air. Exposure to 4-CP could also occur through its use as a root canal packing. Populations with potentially unusually high exposure to

Figure 5-1. Frequency of Sites with Chlorophenols Contamination*

NPL Sites

- ☐ 1 - 4
- ☒ 5 - 8
- ▦ 9 - 14
- ■ 15 - 19

*Source: HazDat 1998

chlorophenols generally include employees of facilities that manufacture or use chlorophenols and their derivatives and those who live in the vicinity of chlorophenol-containing waste disposal sites and waste incinerators.

5.2 RELEASES TO THE ENVIRONMENT

5.2.1 Air

According to the Toxic Chemical Release Inventory, in 1996, releases of chlorophenols to the air from three large processing facilities were 2148 kg (4,775 pounds) (TRI96 1998). Table 5-l lists amounts released from these facilities. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

Both monochlorophenols and 2,4-DCP are volatile, and volatilization may be the major dispersal mechanism of these chemicals into the atmosphere. Trichlorophenols and tetrachlorophenols are slightly volatile. However, only a small fraction (approximately 5%) of chlorophenols (based on 2-CP, 2,4-DCP, and 2,4,6- TCP) are emitted to the atmosphere (Scow et al. 1982). These releases are primarily in vapor form and are principally associated with chlorophenol production and its use in the manufacture of end-use products (Scow et al. 1982).

Releases of chlorophenols to the atmosphere may also occur through the incineration of chlorinated wastes. 2,4-DCP has been detected in atmospheric emissions from the combustion of municipal solid waste, hazardous waste, coal, wood, and 2,4-DCP-based herbicides (Gomez et al. 1988; Junk et al. 1986; Oberg et al. 1989; Paasivirta et al. 1985). Trichlorophenols have been detected in flue gas condensates and fly ash from municipal incinerators (Viau et al. 1984). Di-, tri- and tetrachlorophenols have also been detected in fly ash from wood, oil, and coal-fired power plants at concentrations in the ng/g level (Paasivirta et al. 1985).

Chlorophenols have been detected in air samples collected at 2 of the 1,467 current or former NPL hazardous waste sites (HazDat 1998).

Table 5-1. Releases to the Environment from Facilities that Manufacture or Process Chlorophenols

State[b]	Facilities	Air[c]	Water	Land	Total of reported amounts released in pounds per year[a]			
					Underground Injection	POTW Transfer	Off-site Waste Transfer	Total Environment[d]
KS	1	4,265	0	0	40,154	0	7,500	51,919
MI	1	10	13	0	0	0	0	23
TX	1	500	0	0	73,400	0	4,158	78,058

Source: TRIS96 1998

[a]Data in TRI are maximum amounts released by each facility

[b]Post office state abbreviations used

[c]The sum of fugitive and stack releases are included in releases to air by a given facility

[d]The sum of all releases of the chemical to air, land, and water, and underground injection wells; and transfers off-site by a given facility

POTW = publicly-owned treatment works

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5.2.2 Water

According to the Toxic Chemical Release Inventory, in 1996, releases of chlorophenols to the water from three large processing facilities were 6 kg (13 pounds) (TR196 1998). There were no releases of chlorophenols into publicly owned treatment works (POTWs) in 1996 (TR196 1998). Table 5-l lists amounts released from these facilities. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

The majority (85%) of known environmental releases of three chlorophenols (2-CP, 2,4-DCP, and 2,4,6-TCP) were to surface water (Scow et al. 1982). The estimated 1977 water emissions of 2,4-DCP were 741,000 pounds from U.S. production facilities (Scow et al. 1982). Industrial waste discharge is a major point source of water pollution by mono- and dichlorophenols (Krijgsheld and Van der Gen 1986). Monochlorophenol concentrations of between 10-20 µg/L have been released in waste water produced during the manufacture of specialty chemicals (Buikema et al. 1979; Hites et al. 1979), and 5.3 µg/L of 4-CP was detected in a bleaching effluent released to surface water from a straw mill (Folke and Lindgaard-Jorgensen 1985). 2,4-DCP or 2,4,6-TCP were also detected in effluents discharged from industries that manufacture iron and steel, electrical components, photographic equipment/supplies, pharmaceuticals, and organic chemicals/plastics and from paper pulp and paperboard mills (EPA 1981; Paasivirta et al. 1985). Oikari et al. (1985) reported that concentrations of 2,4,6-TCP and 2,3,4,6-TeCP were higher downstream from a pulp and paper mill than upstream from the facility. Free chlorophenols were still present in water 11 km downstream from the mill. However, the release of chlorophenols to water from pulp bleaching mills is being reduced as the use of elemental chlorine for bleaching is being phased out in favor of the use of chlorine dioxide (Solomon et al. 1994). Compared to chlorine, chlorine dioxide bleaching results in the production of fewer chlorophenols, and the chlorophenols that are produced contain fewer chlorine molecules.

Other sources of discharge of chlorophenols into aquatic systems include sewage treatment plants and drinking water treatment, which can result in the chlorination of phenol. In a study of 40 Canadian potable water treatment facilities, 4-CP, 2,4-DCP, and 2,4,6-TCP are the three halogenated phenols found most frequently in samples taken from chlorinated water supplies (Sithole and Williams 1986). The frequency of detection ranged from 1 to 12 out of 40 samples. Mean values were <7 Ng/L and the maximum values <130 Ng/L. 2-CP has also been detected in treated drinking water in the Netherlands (1 µg/L) (Buikema et al.

1979). The maximum monochlorophenol concentrations measured in river water range from 2-6 μg/L (Krijgsheld and van der Gen 1986).

2-CP has been detected in the leachate from a municipal landfill, while 2,4-DCP was found in the leachate from an industrial landfill (Brown and Donnelly 1988). 2-CP was detected in the runoff from 1 of 15 cities, while neither 2,4-DCP nor 2,4,6-TCP were detected in the runoff from 3 cities (Cole et al. 1984). Analysis of groundwater taken from 479 waste disposal sites found that 2,4-DCP was detected at 19 sites, 2-CP at 14 sites, and 2,4,5-TCP at 2 sites, while 2,3,4,6-TeCP was not detected at any of the sites (Plumb 1991).

The detection of 2,4,6-TCP in industrially unpolluted surface water in Sweden at concentrations up to 10 ng/L suggests that this compound can be formed by natural chlorination of humic substances (Grimvall et al. 1991). A laboratory investigation (Hodin et al. 1991) reported that the addition of chloroperoxidase from the fungus *Culduriomyces fumugo*, hydrogen peroxide, and potassium chloride to bog water (pH adjusted to 3 with 100 mM phosphate) did result in the production of 2,4,6-TCP. Chloroperoxidase could also chlorinate added phenol to form 2-CP and 4-CP. These results suggest that chloroperoxidase-mediated chlorination of natural organic matter does contribute to the levels of chlorophenols (especially 2,4,6-TCP) that are found in surface water.

Chlorophenols have been detected in groundwater and surface water collected at 98 and 25 of the 1,467 current or former NPL hazardous waste sites, respectively (HazDat 1998).

5.2.3 Soil

According to the Toxic Chemical Release Inventory, in 1996, there were no releases of chlorophenols to soil (TRI96 1998); however, an estimated 5,246 kg (11,658 pounds) are disposed of in off site facilities. In addition, about 51,099 kg (113,554 pounds) are disposed of by underground injection. Therefore, manufacturing and processing industries are sources of release in soils surrounding the disposal sites. Table 5-l lists amounts released from these facilities. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

Releases of chlorophenols to soils may occur through several processes such as disposal of manmade wastes (e.g., landfills), atmospheric deposition, and accidental releases (e.g., spills) (Scow et al. 1982). Smith (1985) has found that the herbicide 2,4-dichlorophenoxyacetic acid can be degraded to 2,4-DCP following

soil application. Unspecified trichloro- and tetrachlorophenols have been identified at sites cornposting yard waste and municipal solid waste (Malloy et al. 1993). The investigators (Malloy et al. 1993) suggested that the source was pentachlorophenol on treated wood in chipped form that had been added as a bulking agent. The use of chlorophenols as a wood preservative (predominantly 2,3,4,6-TeCP) has also resulted in the contamination of soil around sawmills where these compounds were used (Kitunen et al. 1985, 1987; Valo et al. 1984).

Chlorophenols have been detected in soil, sediment, and leachate collected at 65, 31, and 12 of the 1,467 current or former NPL hazardous waste sites, respectively (HazDat 1998).

5.3   ENVIRONMENTAL FATE

5.3.1   Transport and Partitioning

The environmental fate and transport of chlorophenols are controlled by their physical and chemical properties and environmental conditions. As shown in Table 3-2, all chlorophenols are solids at room temperature except 2-CP, which is a liquid. In general, as the number of chlorine molecules increase, there is a reduction in vapor pressure, an increase in boiling point, and a reduction in water solubility (Solomon et al. 1994). Therefore, increasing chlorination increases the tendency of the chlorophenols to partition into sediments and lipids and to bioconcentrate.

The higher vapor pressures of the monochlorophenols suggest that among the chlorophenols, these compounds are most likely to be found in air. Specific data concerning monochlorophenols in air were not identified. The vapor pressures of the chlorophenols suggest that the compounds will not partition from the vapor phase to the particulate phase (Eisenreich et al. 1981). That 2,4-DCP and other chlorophenols do not partition into the particulate phase is supported by the identification of 2,4-DCP, 2,4,5-TCP, 2,4,6-TCP, and 2,3,4,6-TeCP in rain but not on rain filters (Leuenberger et al. 1985). This study indicates that gas scavenging rather than particle scavenging is the more important process for removing chlorophenols from the air (Leuenberger et al. 1985). Estimated rain/air partition coefficients at 8°C are 2.2 x 10^4 for 2,4-DCP and 1.8 x 10^4 for 2,4,5-TCP and 2,4,6-TCP combined (Leuenberger et al. 1985).

The rate of chemical evaporation from an aqueous solution largely depends on a chemicals vapor pressure and water solubility (Henry's law constant). Among the chlorophenols discussed in this profile, 2-CP has

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the highest vapor pressure and, therefore, is mostly likely to evaporate from water (Krijgsheld and Van der Gen 1986). In laboratory studies, evaporation half-lives of 2-CP and 4-CP from water 0.38 cm deep were 1.35-1.6 hours and 12.8-17.4 hours, respectively (Chiou et al. 1980). Since the evaporation rate is inversely related to the depth of water, extrapolation of these data indicates that-2-CP evaporation in water 1 meter deep would require approximately 15 days. The amount of volatilization of 2-CP from fine sandy soil (0.087% organic carbon), applied in spiked municipal waste water, was too small to be directly measured (Piwoni et al. 1986).

Volatilization of 2,4-DCP from water is expected to be slow and, therefore, not a major removal process from surface waters. Using the Henry's law constant, a half-life of 14.8 days was calculated for evaporation from a model river 1 meter deep with a current of 1 meter/second and a wind velocity of 3 meters/second, neglecting adsorption to sediment (Thomas 1982). The biological treatment of waste water containing 2,4-DCP has shown that none of the chemical is removed by stripping (Stover and Kincannon 1983). Volatilization from near-surface soil is also not expected to be a significant removal process.

The Henry's law constants for 2,4,5-TCP (0.0039) and 2,4,6-TCP (0.0043) are similar to 2,4-DCP (0.0033). Therefore, the volatilization of these trichlorophenols should be similar to that of 2,4-DCP. In 2-hour laboratory studies, the volatilization rates of 2,4,6-TCP from water and three soil types were determined by Kilzer et al. (1979). These rates, expressed as the percentage of applied compound per milliliter of water evaporated from humus, loam, sand, and water, were 0.15, 0.73, 1.05, and 1.4%, respectively, in the first hour after the addition of 50 ppb 2,4,6-TCP. Similar rates were reported during the second hour. In wind tunnel experiments, Sugiura et al. (1984) estimated a half-life of 48 hours for loss of 2,4,6-TCP from water through volatilization. An estimated 58% of 2,4,6-TCP in a nutrient solution in which tomatoes were grown was lost to the air (from photolysis and/or volatilization) over a period of 30 days (Fragiadakis et al. 1981).

Experimental studies examining the volatilization of tetrachlorophenols were not located. Based on lower Henry's law constants and a greater potential to exist as the dissociated compound in the environment, tetrachlorophenols would be less likely to volatilize from water and soil than the lower chlorinated chlorophenols .

In addition to vapor pressure and solubility, pK_a and log K_{ow} (octanol water partition coefficients) are other important properties which determine the transport and partitioning of chemicals. The lower chlorophenols have higher pK_a values (7.42-8.49). Therefore, in natural waters these compounds will exist primarily as the

undissociated compounds, and adsorption to sediments at a pH of not more than one unit greater than the pK_a can be predicted based on the organiccontent of the sediments and the octanol/water partition coefficient (Schellenberg et al. 1984). In contrast, the pK_a values of the tetrachlorophenols are lower (5.48-6.96) so that at ambient pH values these compounds are present predominantly in the ionized form, and the adsorption to sediemtns will also be dependant on the ionic strength of the wat (Schellenberg et al. 1984).

In general, a chemical will preferentially partition into organic matter if its log K_{ow} is > 1 (Scow et al. 1982). Log K_{ow}s for the chlorophenols are all > 2 (see Table 3-2); therefore, the chlorophenols will all tend to partition into sediments. Despite this prediction, a modeling study completed by Yoshida et al. (1987) suggests that most of the 2,4,6-TCP released to surface waters would remain in the water rather than absorb to sediments. They estimated that in a river receiving daily inputs of the compounds, 72% would be in the water and 28% in the sediment. In a deep, otherwise unpolluted lake, 84% would be in the water and 16% in the sediment. Laboratory sorption experiements with natural sediments containing up to 10% organic matter have been conducted using 2-CP and 2,4-DCP (Isaacson and Frink 1984). Sediment sorption capacity was extensive (up to 0.3 mmol/g), and up to 90% of the adsorption was irreversible.

Chlorophenols are capable of binding to soil organic matter via covalent bond formation, resulting from biologically or chemically catalyzed reactions. In a batch sorption experiment, the binding of 4-CP to soil requires oxygen and soil bioactivity, indicating a biologically mediated oxidative coupling reaction. The addition of hydrogen peroxide, which may be an oxygen source, caused a 4.4 fold increase in 4-CP binding (Bhandari et al. 1996).

As the number of chlorines on phenols increases, sorption of chlorophenols to organic material in soil increases. For example, at two sawmills in Finland where chlorophenol wood preservative (primarily 2,3,4,6-TeCP) was used, soil was contaminated to a depth of 80 to 100 cm to the same extent as at the surface (Valo et al. 1984). As soil depth increased, the concentration of dichlorophenols increased. The investigators attributed this observation to a greater transport of dichlorophenols through the soil and to the relatively increased degradation of the higher chlorinated phenols. An experimental study that examined the movement of 2-CP and 2,4,5-TCP through two soil types (organic carbon 2.1 mg C/g soil or 1.5 mg C/g soil) found that the relative velocity of the chlorophenol through soil into water was 3.5-4 times greater for 2-CP compared to 2,4,5-TCP (Kjeldsen et al. 1990). The chlorophenols moved slowest in the soil with the greatest organic carbon content.

Chlorophenol groundwater contamination will occur if sufficient quantities of the chemical are present to exceed the sorption capacity of the vadose zone saturated soils (Scow et al. 1982). Contamination is most likely in soils with low organic carbon content or high pH. Once in groundwater, sorption of chlorophenols by the solid aquifer matrix may be estimated based on log K_{ow} and organic carbon content, provided that the organic carbon content exceeds 0.1% and the aquifer pH is not sufficiently high for significant dissociation to occur (Schellenberg et al. 1984; Schwarzenbach and Westall 1985). In a natural gradient tracer test conducted within an unconsolidated aquifer, sorption was not an important factor, compared to dispersion and degradation, in the attenuation of 4-CP concentrations (Sutton and Barker 1985). The authors attributed this finding to the low organic carbon content of the aquifer sand unit, which prevented significant hydrophobic sorption.

The bioaccumulation potential of 2-CP, 4-CP, 2,4-DCP, 2,4,5-TCP, 2,4,6-TCP, and 2,3,4,6-TeCP was reviewed by Loehr and Krishnamoorthy (1988). Based on bioconcentration values and log octanol/water partition coefficients, they concluded that all chlorophenols studied had the potential for accumulation in aquatic organisms. Logs of bioconcentration factors ranged from 0.81-2.33 for 2-CP, 1.79-3.28 for 2,4,5-TCP, and 1.95-2.3 for 2,3,4,6-TeCP. Values of bioconcentration factors for 4-CP, 2,4-DCP, and 2,4,6-TCP were predicted mathematically (Veith et al. 1980).

Research on biomagnification of chemical residues within the aquatic food chain indicates that the potential for residue accumulation by fish through food chains is relatively insignificant (<10%) for most compounds when compared to the tissue residues resulting from the bioconcentration process (i.e., direct uptake from water) (Barrows et al. 1980). These data suggest that only those chemicals that are relatively persistent in fish tissues appear to have any potential for significant transfer through food chains (Barrows et al. 1980). A very short tissue half-life of <l day was measured after bluegill sunfish exposure to 2-CP was terminated (Veith et al. 1980). Therefore, due to their relatively low bioconcentration factors (<1,000) and short biological half-lives (<7 days), monochlorophenols will probably not biomagnify within aquatic food chains (Barrows et al. 1980). Data regarding the biomagnification of the higher chlorophenols were not located.

Isensee and Jones (1971) studied the uptake of 2,4-DCP from solution and soil by oats and soybeans. The compound was taken up by the plants, with the concentrations decreasing as the plants matured. At maturity, 2,4-DCP in oat seeds was below detection (<0.001 μg/g) and in soybeans was 0.003 μg/g. Data regarding the uptake of other chlorophenols by plants were not located.

The bioaccumulation of 2,3,4,6-TeCP was examined in earthworms *(Lumbricus rubellus* and *Aporrectodea caliginosa tuberculata)* at a sawmill that had been closed 28 years before sampling (Haimi et al. 1992). At a distance of 5 meters from the dipping basin, 2,3,4,6-TeCP concentrations were 430 and 1,980 μg/g fat in *Lumbricuss* and *Aporrectodea,* respectively, while soil concentrations were 336 μg/g dry soil. The difference between the two species was attributed to greater ingestion of contaminated soil by *Aporrectodea.* Additional data regarding bioaccumulation of chlorophenols in terrestrial organisms was not identified. It is not known whether 2,3,4,6-TeCP biomagnifies up the terrestrial food chain. Based on physical properties (i.e., greatest log octanol water partition coefficient), the tetrachlorophenols, rather than lower chlorinated phenols, would have the greatest potential to biomagnify.

5.3.2 Transformation and Degradation

5.3.2.1 Air

Limited data on the environmental transformations of atmospheric chlorophenols are available. Although chlorophenols absorb primarily in deep ultraviolet, some absorption in the solar visible spectrum is possible because of the overlap between this spectrum and the ultraviolet spectrum (Bunce and Nakai 1989). Bunce and Nakai (1989) found that photolysis and hydroxyl (OH) radical attack were complementary processes for 4 of the chlorophenols. As indicated below, a greater percentage of 2-CP and 4-CP were degraded by hydroxyl attack compared to photolysis, while with increasing chlorination, photolytic degradation increased and hydroxyl attack decreased. Tetrachlorophenols were not tested in this study.

Chlorophenol	Photolytic degradation (% per hour)	Hydroxyl Radical Attack (% per hour)
2-CP	0.024	41
4-CP	0.022	41
2,4-DCP	0.11	11
2,4,5-TCP	2.3	8

5.3.2.2   Water

Both direct photolysis and the reaction of chlorophenols with hydroxyl radicals and singlet oxygen produced by ultraviolet radiation may be important processes of chlorophenol degradation near the water surface. Photolysis of monochlorophenols in water results in dechlorination, with the position of the chlorine on the ring strongly influencing the transformation (Boule 1982). In the molecular form, 2-chlorophenol is

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converted into pyrocatechol. However, in the anionic form, it is reduced in a cyclopentadienic acid and dimerizes. For 3-chlorophenol, the photochemical product is resorcinol regardless of the pH. For 4-chlorophenol, hydroquinone is formed along with polyphenolic oligomers (Boule 1982). The photolysis rates of 2-CP in natural waters depends on pH, season, and dissolved organic material (Kawaguchi 1992a, 1992b). In all cases the reaction rate is first order. Based on empirical data, these investigators proposed that direct photolysis of 2-CP may only occur in natural waters at pH between 7 and 9. Indirect photolysis in lake waters was only significant in summer months; in sea waters, indirect photolysis has a more significant role in the spring and fall. Kawaguchi et al. (1992a, 1992b) also found that the dissolved organic matter in pond water does not contribute to indirect photolysis as significantly as a humic acid solution.

The photocatalytic degradation process with titanium dioxide particles has been shown to be feasible for achieving a high degree of removal of 2-chlorophenol in water (Ku et al. 1996), with almost complete disappearance in only a few hours of illumination time. However, the demineralization of reaction intermediates requires a longer time, and was found to be more effective for acidic solutions. Increasing the light intensity would significantly increase the decomposition rate of 2-chlorophenol at pH 3, but not pH 11. The higher removals at acidic conditions may be due to the increased amounts of undissociated 2-chlorophenol species adsorbed on the TiO_2 surface; the TiO_2 acting as a catalyst in the photochemical degradation.

The reaction of hydroxyl radicals with monochloro- and dichlorophenols was studied by Kochany and Bolton (1991) using spin trapping with electron paramagnetic resonance detection of spin adducts. The reaction rate of 4-CP ($3.2/10^{10}$ $M^{-1}s^{-1}$) and 2,4-DCP ($3.8/10^{10}$ $M^{-1}s^{-1}$) with hydroxyl radicals was greater than the reaction rate of 2-CP ($1.92/10^{10}$ $M^{-1}s^{-1}$). The observation that chlorophenols with *meta*-substitution have even slower reaction rates ($1.04/10^{10}$ $M^{-1}s^{-1}$ for 3-CP, $0.9/10^{10}$ $M^{-1}s^{-1}$ for 3,5-DCP) indicates that for the monochloro- and dichlorophenols, the location of chlorine rather than the number of chlorines is more important in determining the reaction rate. Higher chlorinated phenols were not examined in this study. Chlorophenols may also be removed via reaction with photochemically produced singlet oxygen in natural waters. The estimated half-life for the reaction of 2,4-DCP at pH 7 and 2,4,6-TCP with singlet oxygen at pH 5.5 under midday sun (assuming a singlet oxygen concentration of $4x10^{-14}$) using experimentally determined rate constants is 62 hours (Scully and Hoigne 1987). The rate of reaction of singlet oxygen with 2,4-DCP and 2,4,6-TCP increased significantly as the solution pH was raised from 5.5 to 9 (Scully and Hoigne 1987). This observation is consistent with a study by Tratnyek and Hoigne (1991) who found that the reaction of phenolate ions with singlet oxygen was about one order of magnitude greater than the reaction of the undissociated chlorophenol. The compounds examined in this

study were 2-CP, 4-CP, 2,4-DCP, and 2,4,6-TCP. Although tetrachlorophenols are most likely to exist as ions in natural waters, it is not known whether the ions react more readily with singlet oxygen than do the undissociated tetrachlorophenol compounds.

Hwang et al. (1986) studied the photolysis and microbial degradation of 4-CP, 2,4-DCP, and 2,4,5-TCP in both estuarine and distilled water. Photolysis was the primary transformation process for 2,4-DCP and 2,4,5-TCP, with the rate of photolysis decreased in the order 2,4,5-TCP, 2,4-DCP, and 4-CP. The rate of photolysis of 2,4-DCP was greater in estuarine compared to distilled water, suggesting a photosensitized reaction, The type of water had no effect on the photolysis of 4-CP and 2,4,5-TCP. Unlike the polychlorinated phenols, microbial degradation was the primary transformation process for 4-CP (Hwang et al. 1986).

There are numerous studies regarding the microbial degradation of chlorophenols in water and sediments (Abrahamsson and Klick 1991; Aly and Faust 1964; Banerjee et al. 1984; Genther et al. 1989; Hwang et al. 1986; Vaishnav and Korthals 1988), as well as numerous studies concerning the degradation of these compounds by sludge (Armenante et al. 1992; Battersby and Wilson 1989; Boyd and Shelton 1984; Liu and Pacepavicius 1990; Tabak et al. 1981). Although as a group chlorophenols are poorly biodegradable and persistent in the environment, several studies have shown that aerobic degradation of chlorophenol congeners is possible (Steiert et al. 1988; Armenante et al. 1992). The aerobic degradation of chlorphenols by microorganisms requires the participation of the enzyme's oxygenases to incorporate atmospheric oxygen into their substrates. For fission of the benzene nucleus, the ring is usually first dihydroxylated by an oxygenase such that two hydroxyl groups are situated either *ortho* or *para* to one another on the ring (Steiert and Crawford 1985). Subsequent ring fission occurs through another oxygenase-catalyzed reaction involving the insertion of dioxygen into the aromatic nucleus. The crucial step in the biodegradation of chlorophenols is the removal of the chlorine substituents. For the catabolism of the lesser substituted phenols (mono- and dichlorophenols), dioxygenase from chlorophenol-degrading bacteria usually opens the dihydroxylated aromatic ring before dechlorination takes place (Steiert and Crawford 1985). With more highly substituted phenols, some of the chlorosubstituents must be removed before ring cleavage since the halogen atoms deactivate the aromatic nucleus to electrophilic attack by dioxygenases.

It has been reported that 4-CP can be partially or completely degraded by several aerobic bacteria such as *Pseudomonas* sp. B13 (Knackmuss 1978) and *Azobactirium sp*. GPl (Wieser 1997). The catabolic degradation routes for mono- or dichlorophenols are known to be *meta*- and modified *ortho*-pathways (Bae et al. 1996). In these pathways, 4-CP is hydroxylated to 4-chlorocatechol which then undergoes intradiol

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cleavage before the chloro-substituent is removed. In addition, 4-CP degradation by *Azobactirium ureufaciens* CPR706 was reported via a pathway in which the chloro-substituent of 4-CP was replaced with an incoming hydroxyl group to form hydroquinone (Bae et al. 1996). After 4-CP degradation was completed, the accumulated hydroquinone disappeared from the medium via ring fission forming the 4-hydroxymuconic semialdehyde intermediate. The general observation of these studies is that compounds with a chlorine in the *meta-* and/or *para-* position are the most resistant to degradation (Abrahamsson and Klick 1991). In addition, if the bacteria have not been cultured in the presence of a chlorophenol, they require an adaption period before the compounds can be degraded. For example, degradation of 2,4-DCP was observed in natural water collected from a river following lag times of 2.5 and 8.3 days for 2 separate collections (Banerjee et al. 1984). The rates of degradation of 4-CP, 2,4-CP, and 2,3,4,5-TeCP in river water were 6.5×10^{-6}, 2.3×10^{-6}, and 1.4×10^{-7} moles/hour, respectively (Banerjee et al. 1984). A study by Liu and Pacepavicius (1990) indicates that the position, rather than the number of chlorine atoms, is more important in determining the biodegradation of chlorophenols. The biodegradation of chlorophenols was studied in both aerobic and anaerobic systems using a pentachlorophenol-degrading bacterial culture. The results, shown in Table 5-2, indicate lag time to degradation, and half-life tended to be shorter for compounds with a chlorine in the 4 position and longer for compounds with a chlorine at the 5 position. Anaerobic degradation of the chlorophenols required a longer lag time and the half-lives were longer.

Reductive dehalogenation of chlorinated aromatic compounds whereby chlorines are being replaced by hydrogens occurs extensively under anaerobic conditions (Steiert and Crawford 1985). Anaerobic dehalogenation of 2-chlorophenol, a common intermediate of polychlorophenol degradation, by mixed cultures was reported (Theme1 et al. 1996). Acetate was found to be the major end product, with phenol and benzoate as intermediate products, but CO, was not found to be an end product.

A study of anaerobic degradation of chlorophenols in waste water in an upflow anaerobic sludge blanket reactor indicated that the higher chlorophenols were converted to lower chlorinated compounds via reductive dechlorination reactions (Woods et al. 1989). The rate of these reactions was dependent on the position of the chlorine; chlorines adjacent to the hydroxyl group were preferentially removed, and *meta* chlorines were removed following acclimation, with no evidence for the removal of *para* chlorines. Woods et al. (1989) also found no evidence for the dechlorination of monochlorophenols in this system.

4-chlorophenol was demonstrated to be quickly removed from formulated waste water catalyzed by horseradish peroxidase (Zhang et al. 1997) to form radicals or quinones, which might be subsequently

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TABLE 5-2. Aerobic and Anaerobic Biodegradation of Chlorophenols by Pentachlorophenol Adapted Bacteria[a]

Compound	Lag time (hours)		Half-life (hours)	
	Aerobic	Anaerobic	Aerobic	Anaerobic
2-CP	25	250	140	475
4-CP	25	51	88	84
2,4-DCP	0	310	125	430
2,4,5-TCP	300	nd[b]	380	nd[b]
2,4,6-TCP	0	300	120	470
2,3,4,5-TeCP	50	500	165	510
2,3,5,6-TeCP	nd[b]	nd[b]	nd[b]	nd[b]

[a]Data from Liu and Pacepavicius 1990
[b]nd = not degraded after 700 hours of incubation

polymerized to form less soluble large molecules and precipitated from aqueous phase. The flocculant might increase the removal percentage of the pollutant through enhancing the sedimentation of the reaction products The optimum pH for the removal efficiency of chlorophenol was 9.0. The analytical method would, thus, have to quantify both salt and acid forms of the chlorophenol.

5.3.2.3 Sediment and Soil

Chlorophenol isomers undergo biodegradation in soils under aerobic conditions. Aerobic microorganisms that can degrade chlorophenols have been isolated from soil bacterial cultures. *Pseudomonas picketti* DTP0602, which used 2,4,6-TCP as the sole source of carbon and energy, was isolated from mixed cultures of soil bacterial populations that had been acclimatized to 2,4,6-TCP (Kiyohara et al. 1992). This bacterial species dechlorinates the chlorine atom at position 4 of various CPs to yield their corresponding hydroquinones and may involve oxygenation. Two different enzyme systems for hydroxylation at the *ortho* and *para* positions of the phenol ring may be present in this bacterial species. The *para*-hydroxylation system, which may use a monooxygnease, possibly involves the dechlorination of a 4-position chlorine atom of CPs. 2,4,6-Trichlorophenol-4-monooxygenase, a dehalogenating enzyme, was also isolated from TCP-degrading soil bacterium *Azotobacter* sp., strain GPl (Wieser et al. 1997). NADH, flavin adenine dinucleotide, and O_2 are required as cofactors. 2,6-dichlorohydroquinone and Cl^- ions were identified as reaction products. TCP was the best substrate for this enzyme. However, the majority of other chlorophenols converted by the enzyme bear a chloro substituent in the 4-position. 2,6-dichlorophenol, also accepted as a substrate, was hydroxylated in the 4-position to 2,6-dichlorohydroquinone in a nondehalogenating reaction. It was also reported that the addition to the culture medium of a vitamin solution containing biotin, folk acid, pyridoxine hydrochloride, riboflavin, thiamine hydrochloride, niacin, pantothenic acid, cyanocobalamin, p-aminobenzoic acid, and thioctic acid can increase the aerobic degradation and dechlorination of 2-CP and 4-CP by *Pseudomonas picketti* strain LDl culture by 1l-16% (Kafkewitz et al. 1996).

The extent and rate of biodegradation depend on numerous factors, including soil pH, organic carbon content, biomass, and the chlorophenol isomer and its concentration. In neutral clay-loam soil at 20°C under aerobic conditions, 2-CP was degraded the fastest (Baker and Mayfield 1980). Decomposition rates were as follows: 100% of the 2-CP in 1.5 days, 95% of the 2,4,6-TCP in 3 days, 83% of the 4-CP in 20 days, 81% of the 2,4-DCP in 40 days, and 72 and 31% of the 2,4,5-TCP and 2,3,4,5-TeCP, respectively, in 160 days (Baker and Mayfield 1980). Dasappa and Loehr (1991) examined the loss of 2-CP, 4-CP, 2,4 DCP, and 2,4,6-TCP from a laboratory soil microcosm. The loss from soil and the water soluble fraction were examined at two

concentrations for each compound. The loss of chlorophenols from the water soluble fraction was about 1.5 times greater than the loss from soil, and chemical loss was slower at higher initial concentrations. Mineralization of 2,4,5-TCP in soil not previously exposed to chloroorganics has been reported (Matus et al. 1996). The observation of 2,3,4,6-TeCP in soil (157-338 μg/g dry soil) at a sawmill 28 years after it closed provides evidence that this compound can persist in soil. Soil concentrations of 2,3,4,6-TeCP when the mill was closed were not stated. In general, degradation or complete mineralization to carbon dioxide (CO_2) is greater in soils with low organic carbon content (Kjeldsen et al. 1990), slightly alkaline pH (Balfanz and Rehm 1991), increased temperatures (Baker and Mayfield 1980; Baker et al. 1980; Balfanz and Rehm 1991), and increased inoculum concentrations (Balfanz and Rehm 1991).

Microbial degradation of chlorophenols in soil under anaerobic conditions has not been observed consistently. For 2-CP, 4-CP, 2,4-DCP, 2,4,5-TCP, 2,4,6-TCP, and 2,3,4,5-TeCP, no statistically significant differences in degradation rates between nonsterile and sterile clay loam soils occurred when both soil samples were incubated under anaerobic conditions (Baker and Mayfield 1980).

In a study of the degradation of halogenated phenols in anoxic marine sediments, the main degradation pathway was progressive dehalogenation with ortho > para > meta. Sediments which had been exposed to effluent water from a paper and pulp mill showed a higher dehalogenation potential (Abrahamsson and Klick 1991).

Another study demonstrated that anaerobic degradation of chlorophenols with an estuarine sediment inoculum was coupled to sulfate reduction, which was the electron sink. The relative rates of degradation were 4-chlorophenol > 3 chlorophenol > 2 chlorophenol, 2,4-dichlorophenol (Haggblom and Young 1990).

5.4   LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

During seven rain events in Portland, Oregon, in 1984, 2,4-DCP was detected in the air in all seven events at an average concentration of 1.5 ng/m^3 (0.23 ppt), combined 2,4,5-TCP and 2,4,6-TCP were detected in 6/7 events at an average concentration of 0.15 ng/m^3 (0.02 ppt), and 2,3,4,6-TeCP was detected in 5/7 events at an average concentration of 0.27 ng/m^3 (0.03 ppt) (Leuenberger et al. 1985). Average concentrations in rain for the seven events were 5.9, 1.1, 1.4, and 20 ng/m^3 (0.89. 0.14,0.17, and 2.1 ppt) for

2,4-DCP, 2,4,5-TCP, 2,4,6-TCP, and 2,3,4,6-TeCP, which were detected in 7/7, 4/7, 5/7, and 7/7 of the events respectively. Additional data regarding ambient levels of chlorophenols in indoor or outdoor air were not identified. However, data on 2-CP levels after the accidental derailment and rupture of a train tanker are available. On the day of the accident, air concentrations ranging from 0.02 to 0.7 mg/m^3 (0.04 to 0.19 ppm) were detected in the immediate vicinity of the spill (Scow et al. 1982). Eighteen days after the spill, air levels were <2 μg/m^3 (<0.5 ppb). No additional data are available regarding air emissions following accidental releases.

5.4.2 Water

Grimvall et al. (1991) measured 2,4,6-TCP in unpolluted surface waters in remote areas of southern Sweden and in pulp bleaching plant recipient waters, Lake Vattern and the Baltic Sea. Concentrations up to 10 ng 2,4,6-TCP/L were found in unpolluted waters, with concentrations of 2,4,6-TCP in Lake Vattern decreasing from 12 ng/L to 1 ng/L with increasing distance from the bleaching plant. 2,4,6-TCP concentrations in the Baltic Sea were <l ng/L. This study suggests that 2,4,6-TCP can be formed by both industrial and natural chlorination of humic substances, an observation that was confirmed in the laboratory (Haimi et al. 1992).

Analysis of chlorophenol concentrations downstream of paper mills along the Rainy River in Canada and northern Minnesota did not identify 2-CP, 4-CP, 2,4,5-TCP, 2,3,5,6-TeCP, or 2,3,4,5-TeCP using methods with detection limits as low as 50 ng/L (Merriman 1988). In water samples from northern Alberta, Canada, 2-CP was not detected (detection limit 0.005 μg/L), while 2,4-DCP concentrations were <0.002-7.1 μg/L, and 2,4,6-TCP concentrations were <0.002-17 μg/L (Morales et al. 1992). 2,4-DCP, 2,4,6-TCP, and 2,3,4,6-TeCP were identified in water samples from at least one of the three sampling stations. A summary of STORET data of priority pollutants in ambient water (Staples 1985) indicated that 2-CP was detected in 0.2% of 814 samples, 2,4-DCP was detected in 0.4% of 876 samples, and unspecified trichlorophenols were detected in 0.1% of 880 samples. Analysis of runoff from 15 United States cities for 2-CP, 2,4-DCP, and 2,4,6-TCP identified only 2-CP, which was found in samples from only one city (Cole et al. 1984).

Chlorophenols are produced during the chlorination of organic material present in industrial and municipal waste waters. Consequently, several investigators have detected these chemicals downstream of waste water discharge points. Maximum surface water concentrations measured in 13 samples downstream from a chlorinated waste water discharge in the Netherlands were (in μg/L) 0.6 for 2-CP, 2.1 for 4-CP, 0.33 for 2,4-DCP, 0.32 for 2,4,5-TCP, 0.74 for 2,4,6-TCP, 0.02 for 2,3,4,5-TeCP, 0.2 for 2,3,4,6-TeCP, and 0.08 for

2,3,5,6-TeCP (Wegman and van de Broek 1983). Maximum monochlorophenol concentrations of between 2 and 6 µg/L have been measured in European rivers (Krijgsheld and van der Gen 1986).

Chlorination of drinking water at treatment plants can result in detectable levels of chlorophenols if the required precursors are available in the raw water (Krijgsheld and van der Gen 1986). In a study of Canadian potable water treatment facilities conducted in the summer, maximum concentrations of 65, 127, 72, and 148 ng/L of 2-CP, 4-CP, 2,4-CP, and 2,4,6-TCP, respectively, were measured, while 2,3,4,5-TeCP was not detected in the water (Sithole and Williams 1986).

5.4.3 Sediment and Soil

Chlorophenols have been detected in groundwater from waste disposal sites indicating that these compounds can leach through soil (Plumb 1991). 2,4-DCP was detected most frequently, followed by 2,4,6-TCP, 2-CP, and 2,4,5-TCP. 2,3,4,6-TeCP was not detected at any of the 479 sites. It was not reported how much of each chlorophenol was disposed at each site, and soil concentrations at the sites were not reported. 2,4-DCP in the concentration range of 3.2-79.7 µg/L, as well as other organic compounds, has been found in groundwater samples taken near an abandoned creosote waste site in Conroe, Texas (Bedient et al. 1984). It is not clear whether soil samples were analyzed for 2,4-DCP, although soil concentrations of other organic compounds were provided. Kitunen et al. (1985) reported soil concentrations (in mg/kg wet weight) of 2.7- 47.4, 2, 4-DCP; 0.8-15.7, 2, 4, 5-TCP; 7.3-1,258.3, 2, 4, 6-TCP; 231-1,776.4, 2, 3, 4,6-TeCP; and 0.9-2.2, 2, 3, 4, 5-TeCP in soil at an operating sawmill in Finland where chlorophenols (predominantly 2,3,4,6-TeCP) were being used as a wood preservative. The highest concentrations of chlorophenols were found at depths of 5-40 centimeters. Soil concentrations of 157-338 mg 2,3,4,6-TeCP/kg dry soil were found at a sawmill in Finland 28 years after it had closed, indicating that this compound can persist for long periods (Haimi et al. 1992). Soil concentrations of 2,3,4,6-TeCP when the sawmill was in operation were not reported, and soil concentrations of other chlorophenols discussed in this profile were not measured.

A limited amount of data concerning chlorophenol sediment concentrations in areas of known surface water contamination is available. 2-CP and 4-CP were not detected in sediments, while the maximum concentrations of 2,4-DCP, 2,4,5-TCP, 2,4,6-TCP, 2,3,4,5-TeCP, 2,3,4,6-TeCP, and 2,3,5,6-TeCP were 10, 15, 3.7, 9.8, 4.9, and 2.8 pg/kg, respectively (Wegman and van de Broek 1983). In the same study, none of the isomers appeared in sediment samples collected from six locations in the vicinity of chemical and industrial waste water effluent discharge points. These findings may be misleading because of the poor sensitivity

(detection limit of 10 μg/kg) of the gas chromatography/electron capture detector (GC/ECD) analytical procedure. No 2-CP, 2,4-DCP, or 2,4,6-TCP was detected in sediment samples from northern Alberta, Canada, where water concentrations of these chlorophenols were low or not detectable (Morales et al. 1992). The limits of detection in sediments were 0.02 μg/g for 2-CP and 0.01 μg/g for 2,4-DCP and 2,4,6-TCP.

5.4.4 Other Environmental Media

The use of the chlorophenoxy herbicides may result in contamination with 2,4-DCP and 2,4,5-TCP. For example, Cook et al. (1983) analyzed the free and acid hydrolyzable residues of 2,4-DCP in millet resulting from treatment with 2,4-dichlorophenoxyacetic acid. The total residues of 2,4-DCP ranged from not detected (<0.02 ppm detection limit) to 0.031 ppm for postemergence and preharvest treatment. Only 15-19% of the 2,4-DCP residues were in the free unaltered form, while the remaining residues were conjugated to sugars and amino acids and converted to the free form by acid hydrolysis.

Few data were found on the levels of chlorophenols in U.S. foods. Most of the data or estimates are for concentrations in fish or shellfish. Based on the EPA (1980a) estimated bioaccumulation factor (BCF) of 150 in the edible portion of fish and assuming ambient water concentration of 30 ppb, tissue concentrations of 4.5 mg 2,4,6-TCP/kg bodyweight in fish were estimated by Scow et al. (1982). The authors stated that the 30 ppb value for water represents a maximum case exposure. 2-CP, 2,4-DCP, and 2,4,6-TCP were not detected in 22 composite samples of fish collected from harbors and tributaries of the Great Lakes (DeVault 1985). 4-CP, 2,4-DCP, and 2,4,6-TCP were not detected (detection limit 0.02 mg/kg) in fish from 13 Lake Michigan tributaries (Camanzo et al. 1987) or in fish from northern Alberta, Canada, (detection limit 0.01 μg/g) (Morales et al. 1992). Fish in the Fraser River estuary downstream from a lumber mill were found to contain chlorophenols including 2,4,5-TCP, 2,4,6-TCP, 2,3,5,6-TeCP, 2,3,4,6-TeCP, and 2,3,4,5-TeCP (Carey et al. 1988). Among the chlorophenols discussed in this profile, 2,3,4,6-TeCP was the most predominant compound, and the highest concentrations (49 ng/g) were found in sculpin, which had concentrations of about 400 times the concentration found in water in the estuary. Trichlorophenol (combined 2,4,5 and 2,4,6 isomers) concentrations of 29-629 ppb (wet weight) were measured in fish livers collected from the Pacific Ocean 6 km northwest of the discharge zone for the Los Angeles County waste water treatment plant by Gossett et al. (1983). Concentrations in edible tissues were not measured.

In addition to environmental contamination of food, another potential source for chlorophenol contamination of food is migration from packaging materials. Shang-Zhi and Stanley (1983) reported levels of

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0.1-0.68 ppm 2,4,6-TCP and 0.14-0.55 ppm 2,3,4,6-TeCP in cardboard food containers. Analysis for other chlorophenols was not completed. Shang-Zhi and Stanley (1983) indicated that the source of chlorophenol contamination was polyvinyl acetate and starch adhesives used in carton manufacture.

5.5   GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Oral exposure to chlorophenol-contaminated food and water is the main route of exposure to the general population Water contaminated through chlorination is most likely to contain lower chlorinated phenols, while higher chlorinated phenols are more likely to be found in fish. Exposure to 2,4-DCP through contaminated food may result from the production of 2,4-DCP via degradation/metabolism of 2,4-dichlorophenoxy-based herbicides applied to food crops (Scow et al. 1982; WHO 1989). Although food monitoring data are lacking, exposure to 2,4-DCP through the ingestion of food is expected to be relatively minor. Estimates of total chlorophenol intake reviewed by WHO (1989) ranged from 2.2 μg/person/day assuming contaminated water and fish were the main sources of exposure, to about 10-40 μg/person/day assuming indoor rooms were treated with a chlorophenol preservative.

The identification of chlorophenols in urine and fat of persons not occupationally exposed to chlorophenols confirms general population exposure to these compounds. Analysis of urine from 197 children living near a herbicide manufacturing plant in Arkansas for 2,4-DCP, 2,4,5-TCP, and 2,4,6-TCP, identified these compounds in 27,54, and 11% of the samples, respectively (Hill et al. 1989). The 95th percentile concentrations (in ppb) were 7 for 2,4-DCP, 7 for 2,4,5-TCP, and 4 for 2,4,6-TCP. In the National Health and Nutrition Examination Survey (NHANES II), 2,4,5-TCP was detected (detection limit 5 ppb) in 3.4% of about 6,000 urine samples taken from a representative sample of nonoccupationally exposed persons from 64 communities in the United States during 1976-1980 (Kutz et al. 1992; Murphy et al. 1983). The maximum concentration detected was 56 ppb (Kutz et al. 1992). The investigators warn that because of the considerable variability among the recovery rates over time and between laboratories, the level for 2,4,5-TCP may be underestimated. The average fat concentrations of combined 2,3,4,6-TeCP and 2,3,5,6-TeCP and of 2,3,4,5-TeCP in autopsy specimens were 22 and 6 ng/g respectively in Kingston, Ontario, which is near the Great Lakes, relative to 7 ng/g for 2,3,4,6-TeCP, 2,3,5,6-TeCP, and 2,3,4,5-TeCP in tissue from persons living in Ottawa (Williams et al. 1984). 2,3,4,6-TeCP was detected in 29/46 adipose samples from persons in Finland not   occupationally exposed to chlorophenols, while 2,4,6-TCP was detected in only one adipose sample (Mussalo-Rauhamaa et al. 1989). The concentration of 2,3,4,6-TeCP in adipose tissue ranged from

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<0.00l (the detection limit) to 0.031 µg/g. 2,3,4,6,-TeCP was also found in 2/13 liver samples, while 2,4,6-TCP was not detected (0.001 µg/g detection limit) in any liver samples.

Occupational exposure to chlorophenol isomers may occur during chemical production and during subsequent use as intermediates in the synthesis of higher chlorinated phenols, phenolic resins, dyes, and drugs (Exon et al. 1984; Krijgsheld and Van der Gen 1986). Exposures result from inhalation and/or dermal contact and are most likely associated with process, storage, or fugitive emissions at chemical manufacturing plants. NOES (1990) estimates that 2,796 workers, principally clinical laboratory technicians at hospitals, are potentially exposed to 4-CP. Chemists comprise the majority of the 975 workers potentially exposed to 2-CP and the 852 workers potentially exposed to 2,4,6-TCP, while janitors; engineers; and furnace, kiln, and oven operators are among the 895 workers potentially exposed to 2,4,5-TCP (NOES 1990). No estimates of the number of workers exposed to the other chlorophenols discussed in this profile were available.

Occupational exposure to chlorophenols may also occur during the incineration of wastes containing chlorinated chemicals (Angerer et al. 1992a, 1993) and through indirect exposure following worker inhalation and subsequent metabolism of chlorobenzene (Kusters and Lauwerys 1990; Yoshida et al. 1986). In a study of 53 municipal waste incinerator workers' urine, concentrations of 2,4-CP and 2,4,5-TCP were small but significantly (p,0.05; nonparametric U-test of Wilcoxon, Mann, and Whitney) greater than the urinary concentrations of these chlorophenols in 248 persons with no known occupational exposure to organic chemicals (Angerer et al. 1992a, 1993). However, 4-CP and combined 2,3,4,6-TeCP and 2,3,5,6-TeCP urine concentrations were small but significantly higher in the control group, which included 88 people from urban communities, than in the incinerator workers. The investigators suggested that the higher 4-CP urine concentrations in the urban population were a result of atmospheric exposure to chlorobenzene, but they did not have an explanation for the higher tetrachlorophenol concentrations (Angerer et al. 1992a). Median and 95 percentile concentrations (µg/g creatinine) of chlorophenols in the urine from the two populations are shown below.

	Waste Incineration (n=53)		Controls (n=248)	
	Median	95%	Median	95%
4-CP	1.2	3.8	1.7	6.6
2,4-DCP/2,5-DCP	10.5	86.6	3.9	46.4
2,4,5-TCP	1.2	3.2	0.8	4.0
2,4,6-TCP	0.9	2.3	0.6	3.7
2,3,4,6-TeCP/2,3,5,6-TeCP	0.3	1.5	1.2	25.6

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An industrial hygiene investigation of workers exposed to chlorophenols at a sawmill indicated that dermal exposure was the most important route (Lindroos et al. 1987). The workers were exposed to a wood preservative that contained 80% 2,3,4,6-TeCP, 10-20% 2,4,6-TCP, and 5% pentachlorophenol. Median urinary concentrations of total chlorophenols were 7.8 μmol/L in workers with the skin as the main route of exposure, 1.4 μmol/L in workers with combined inhalation and skin exposure, and 0.9 μmol/L in workers with inhalation as the principal route of exposure.

As with the general population, occupational exposure to chlorophenols can also occur following accidents that result in the release of these chemicals to the environment, such as the previously discussed train derailment. On the day of the accident, 2-CP air concentrations of 0.02-0.7 mg/m^3 (0.004-0.19 ppm) were detected in the immediate vicinity (Scow et al. 1982). Eighteen days after the spill, air concentrations were reduced to <2 μg/m3 (<0.5 ppb). Urine levels in the clean-up workers were 1.98 mg/L approximately 2 months following the spill; however, the pathways, duration, and time of exposure were not recorded, so that the exposure levels cannot be estimated (Scow et al. 1982).

Potential exposure to chlorophenols tends to be limited because of the pronounced odor and taste imparted by the presence of these substances. For example, the odor of 2,4-DCP can be detected in water at 0.35 μg/L (Hoak 1957), and 2,4-DCP can be tasted in water at 8 pg/L (Burttschell et al. 1959). Odor thresholds as low as 0.3-9 15 μg/L in water have also been reported for chlorophenols (Hoak 1957). Although chlorophenols have low odor thresholds in water, 2-CP, 4-CP, 2,4-DCP, and 2,4,6-TCP have been noted to affect the flavor of fish at concentrations of about 2 to 43 times lower than the odor thresholds for these compounds in water (Persson 1984). Data for the other chlorophenols discussed in this profile were not available.

5.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans and briefly considers potential pre-conception exposure to germ cells. Differences from adults in susceptibility to hazardous substances are discussed in 2.6 Children's Susceptibility.

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, and breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or

formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor; they put things in their mouths; they may ingest inappropriate things such as dirt or paint chips; they spend more time outdoors. Children also are closer to the ground, and they do not have the judgement of adults in avoiding hazards (NRC 1993).

In a study that analyzed urine samples from 197 children living near a herbicide manufacturing plant in Arkansas for 2,4-DCP, 2,4,5-TCP, and 2,4,6-TCP, these compounds were identified in 27,54, and 11% of the samples, respectively (Hill et al. 1989). The 95th percentile concentrations (in ppb) were 7 for 2,4-DCP, 7 for 2,4,5-TCP, and 4 for 2,4,6-TCP. No measurements have been made of chlorophenols or their metabolite levels in aminiotic fluid, meconium, cord blood, or neonatal blood that indicate prenatal exposure; nor have measurements been made of chlorophenols or metabolite levels in breast milk. However, because of their relative rapid metabolism and excretion in the urine, chlorophenols are not expected to accumulate in maternal tissues.

There are no known unique exposure pathways for children to chlorophenols. However, 4-CP has been used at home as disinfectant, and 2,4-DCP has been used for mothproofing and as a miticide (WHO 1989), while the higher chlorophenols have been used as germicides, algicides, and fungicides. Thus, children may be exposed via accidental ingestion. Because children like to play outdoors and put fingers in their mouths, they may also be exposed via incidental ingestion and dermal contact of contaminated soil. The most likely way that children can be exposed is via drinking water that has beetrdisinfected with chlorine. Exposure to 2,4-DCP through contaminated food may result from the production of 2,4-DCP via degradation of the herbicide 2,4-dichlorophenoxyacetic acid applied to food crops or via ingestion of fish contaminated with TeCP. However, dietary exposure is expected to be minor as chlorophenols generally do not accumulate in animal tissues.

No studies have been found that examine the exposure of children from parents' work clothes, skin, hair, tools, or other objects removed from the workplace. Chlorophenols have been used as biocides. 2,4,6-TCP and the tetrachlorophenols have also been used as wood preservatives. No known information is available at this time concerning exposure from application of wood preservatives, herbicides, and other consumer products and this exposure is unlikely to be significant.

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5.7   POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In comparison to members of the general population, workers in certain occupational groups have much greater potential for exposure to high concentrations of chlorophenols (Scow et al. 1982). While quantitative data are not available, workers involved in the production of either chlorophenols or chemicals synthesized from chlorophenols are potentially the most heavily exposed (WHO 1989). Exposure may occur through both inhalation and dermal absorption. Workers in plants that use chlorobenzene are also likely to be heavily exposed to monochlorophenols via the metabolism of inhaled chlorobenzene to monochlorophenols (Kusters and Lauwerys 1990; Ogata et al. 1991; Yoshida et al. 1986). However, most of the inhaled chlorobenzene was metabolized to 4-chlorocatechol rather than chlorophenols, as the average exposed worker excreted three times more 4-chlorocatechol than chlorophenols in the urine (Kustus and Lauwerys 1990; Yoshida et al. 1986) Thus, exposure via metabolism of chlorobenzene is not an important route of exposure.

Workers at sawmills where the higher chlorinated phenols are used as wood preservatives have the highest potential for being exposed to tetrachlorophenols (WHO 1989). The observation of higher urinary concentrations of mixed tetrachlorophenols during hot humid weather when use of protective clothing was minimal (geometric means 196.7 ppm hot humid weather; 98.5 ppm cooler weather) suggests that dermal exposure is an important route of tetrachlorophenol exposure in these workers (Kleinman et al. 1986). The higher volatility of tetrachlorophenols in warmer weather may have also contributed to the higher urinary concentrations of mixed tetrachlorophenols found when the weather was hot. Higher general population exposure may occur through dermal or oral contact with contaminated soils and/or groundwater in the vicinity of disposal or accident sites and through dermal or oral contact with surface waters into which chlorinated effluents have been discharged (Scow et al. 1982). In addition, inhalation and metabolism of chlorobenzene found in urban air can result in higher exposure to monochlorophenols (Angerer et al. 1992b, 1993).

5.8   ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of the chlorophenols are available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research

designed to determine the health effects (and techniques for developing methods to determine such health effects) of the chlorophenols.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

5.8.1   Identification of Data Needs

Physical and Chemical Properties. The physical and chemical properties of chlorophenols have been well studied, and reliable values for key parameters for most chlorophenols are available for use in environmental fate and transport models (see Table 3-2). Therefore, further studies of the physical and chemical properties of chlorophenols are not essential at the present time.

Production, Import/Export, Use, Release, and Disposal. According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1996, became available in May of 1998. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

Chlorophenols have a variety of different uses (HSDB 1998). 2,4-DCP is used as an intermediate in the production of herbicides and the manufacture of compounds used in mothproofing, antiseptics, and seed disinfectants. It is also used to produce miticides and wood preservatives. 4-CP is used as an intermediate in the production of acaricides, rodenticides, and dyes; it is used most commonly as a local antiseptic for dental procedures. 2-CP is used in the production of higher chlorinated phenols, dyestuffs, preservatives, and as a disinfectant/bacteriocide/germicide. It is also used for extracting sulfur and nitrogen compounds from coal. 2,4,5-TCP is used as a fungicide/bactericide; an intermediate in the manufacture of herbicides, hide and leather processing; and in swimming pool and sick-room related surfaces. 2,3,4,6-TeCP is used as a fungicide, pesticide, a slimicide for paper mills, and a preservative. 2,3,4,5-TeCP and 2,3,5,6-TeCP are used primarily as fungicides (HSDB 1998). Chlorophenols are potentially hazardous chemicals and are subject to a variety of regulations (see Chapter 7).

Data regarding the production methods for the chlorophenols are available; however, data regarding current production and import/export of the chlorophenols are extremely limited (HSDB 1994; Krijgsheld and van de Gen 1986; TR192 1994). No TRI data are currently available (domestic production or environmental release) for the monochlorophenols, 2,4-DCP, or the tetrachlorophenols. General disposal information for chlorophenols is adequately described in the literature. At low concentrations in aqueous media, microbial degradation followed by adsorption on activated charcoal is the common disposal method (WHO 1989).

Environmental Fate. The behavior of chlorophenols in solid and aqueous media depends on numerous physicochemical variables. These chemicals are partitioned to and transported in the air, soil, and water. The pH of soil and water is a major factor controlling their partitioning among the media, their mobility, and their ultimate fate in the environment. These processes are well characterized.

Atmospheric chlorophenols, primarily associated with production processes, are apparently removed by free radical oxidation, photolysis, and both wet and dry deposition (Bunce and Nakai 1989; Scow et al. 1982). More specific data regarding atmospheric dispersion and photochemical reaction rates are needed for occupational settings. Volatilization of the higher chlorinated phenols from water and soil is expected to be a slow process, but there were no experimental data located in the available literature. Experimental data are available pertaining to many of the transformations of chlorophenols in the environment including biodegradation in water, soil, and sediment and photodegradation in water. Confirmation of the estimated slow rate of volatilization in addition to data regarding the overall half-lives for chlorophenols in air are needed to estimate potential inhalation exposure near hazardous waste sites that contain chlorophenols. Data regarding the overall half-life in water and soil are needed to estimate potential oral and dermal exposure to chlorophenols.

Bioavailability from Environmental Media. The observation of systemic effects following inhalation, oral, and dermal exposure indicates that the chlorophenols are readily absorbed (see Chapter 2 for more details). Systematic studies of the bioavailability of the chlorophenols from different media have not been completed. Because the compounds are relatively lipophilic and become adsorbed to soil and sediments, a study of the bioavailability of these compounds from soil relative to water following oral exposure are needed.

Food Chain Bioaccumulation. Chlorophenols bioconcentrate in aquatic (fish) organisms to a limited extent, with the greatest bioaccumulation (up to 400) observed for the tetrachlorophenols (Carey et al. 1988). The extent of bioconcentration is limited by relatively rapid metabolism and excretion (Veith et al. 1980). Additional data on the bioaccumulation of chlorophenols within both aquatic and terrestrial organisms are needed.

Exposure Levels in Environmental Media. Reliable monitoring data for the levels of chlorophenols in contaminated media at hazardous waste sites are needed so that the information obtained on levels of chlorophenols in the environment can be used in combination with the known body burden of chlorophenols to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites. Few data are available concerning the levels of chlorophenols in ambient air or near known sources of atmospheric pollution. Limited monitoring data on chlorophenol levels in surface water are available. Additional monitoring for current data for better characterization of the ambient chlorophenol concentrations in air, surface water, groundwater, soils, and sediment are needed. These data are particularly needed in the vicinity of industrial and municipal chlorinated wastewater discharge points and hazardous waste sites, where individuals may be exposed by oral and/or dermal contact, such that estimates of human intake can be made.

Exposure Levels in Humans. This information is necessary for assessing the need to conduct health studies on these populations. Limited data regarding chlorophenol levels in urine in humans and adipose tissue are currently available. Toxicokinetic data on occupationally and environmentally exposed humans are needed to determine whether there are biomarkers of exposure. Because chlorophenols are metabolites of other chemicals, measurement of these compounds in biological samples (e.g., blood, urine) can provide an estimate of internal dose but may not provide information about the dose of chlorophenols to which individuals were exposed.

This information is necessary for assessing the need to conduct health studies on these populations.

Exposures of Children No exposure and body burden studies have been conducted on children; therefore, it is not known whether children are different from adults in their weight-adjusted intake of chlorophenols, or if unique exposure pathways for children exist. There is also no monitoring of chlorophenol levels in food (crops, fish), nor in environmental media, following application of herbicides and wood preservatives. Children whose parents work in manufacturing facilities that produce or use

5. POTENTIAL FOR HUMAN EXPOSURE

chlorophenols may also potentially be exposed to chlorophenols via parents' work clothes, skin, hair, tools, or other objects removed from the workplace; however, no studies exist on this means of exposure. A take home exposure study may be warranted if such occupational exposure settings are identified. Measurement of chlorophenols and their metabolites in breast milk will also help to determine whether children may be exposed via milk ingestion.

There are no known specific means to decrease exposure, but since children may be more susceptible to chlorophenols, it may be helpful to evaluate methods to do so.

Exposure Registries. No exposure registries for chlorophenols were located. These substances are not currently compounds for which a subregistry has been established in the National Exposure Registry. These substances will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to these substances.

The development of an exposure registry would provide valuable data on exposure levels and frequency. In addition to providing information on exposure levels and duration, a registry would be useful in identifying sources of exposure such as hazardous waste sites and manufacturing and use facilities. Knowledge about exposure levels and sources would be valuable in developing strategies to control unnecessary sources and these exposures. The ability to correlate sources and exposure levels with health effects would be useful in identifying disease conditions that may result from exposure to the chlorophenols.

5.8.2 On-going Studies

As part of the Third National Health and Nutrition Evaluation Survey (NHANES III), the Environmental Health Laboratory Sciences Division of the National Center for Environmental Health, Centers for Disease Control, will be analyzing human urine samples for 2,4-DCP, 2,4,5TCP, 2,4,6-TCP, and other phenolic compounds. These data will give an indication of the frequency of occurrence and background levels of these compounds in the general population. The measurement of these compounds is being used as a marker of pesticide exposure, rather than just an indication of chlorophenol exposure.