

## 6. POTENTIAL FOR HUMAN EXPOSURE

### 6.1 OVERVIEW

Creosote has been identified in at least 46 of the 1,613 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2002). However, the number of sites evaluated for creosote is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites, all 46 are located within the United States and none are located in the Commonwealth of Puerto Rico (not shown).

Coal tar creosote is a complex commercial mixture of some 300 organic constituents. The most common forms are derived from coal tar distillation, yielding coal tar creosote in temperature ranges between 210 and 280 EC. Coal tar and coal tar pitch share many of the polycyclic aromatic hydrocarbons (PAHs) components of coal tar creosote. For the coal tar derivatives, the composition of the mixture varies from batch to batch depending on the coking process used. Creosote consists primarily of PAHs and, therefore, the fate of many of the components of the mixture is similar to that of PAHs.

Coal tar creosote has been widely used as a wood-treatment pesticide since the turn of the century. As a result of this widespread and long-term use, workers in the wood-preserving industry have been exposed to coal tar creosote for many years. Human exposure to coal tar creosote can occur by inhalation or direct dermal contact. Studies have indicated that dermal exposure to creosote used in wood treatment or in coking oven processes contributed more significantly to the total body burden than respiratory exposures (Klingner and McCorkle 1994; Malkin et al. 1996; Van Rooij et al. 1993b). In other industries, such as rubber processing, occupational exposure to coal tar pitch volatiles may lead to excessive respiratory exposure to PAHs, including benzo[a]pyrene (Rogaczewska and Ligocka 1994). Individuals working in wood-preserving facilities are one of the largest exposed groups. Exposure may also occur during handling and installation of treated wood products in structures such as bridges, piers, retaining walls, cross ties, and fencing; as a result of burning treated scrap wood; and through contact with contaminated media at hazardous waste sites. The general public is unlikely to experience any significant exposure to liquid creosote through the direct use of wood preservative products because EPA canceled all nonwood uses of the material and restricted use of coal tar creosote products to certified applicators in January 1986 (EPA 1986b; R.U.P. 1994).

Figure 6-1. Frequency of NPL Sites with Creosote Contamination



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Children are exposed to creosote via the same routes that adults are, and small children are more likely than adults to be in close contact with yard dirt or playground dirt, lawns, and indoor (carpet) dust, all of which may be contaminated with creosote residues. Because of a tendency to put their unwashed hands and foreign objects into their mouths, and to chew on objects, children may be exposed to creosote through oral ingestion of the chemical. Dermal exposure may occur through contact with treated wood used for utility poles, bridges, fences, and railroad crossties. Children may be exposed by playing near pools of discarded creosote or by playing at abandoned hazardous waste sites.

Pharmaceutical creosote preparations are derived from the processing of such woody plants as beechwood (von Burg and Stout 1992). Wood creosote (beechwood creosote) is a yellow, transparent liquid with a characteristic smoky odor, obtained by fractional distillation of wood tar. It is composed primarily of phenol, phenols, cresols, guaiacols, xylenols, and small amounts of alkyl-2-hydroxy-2-cyclopenten-1-ones. It has been used as an expectorant, a “gastric sedative,” a gastrointestinal antiseptic, and particularly as an antidiarrheal agent (Ogata et al. 1993). Wood creosote and coal tar creosote are chemically distinct, and should not be confused with one another (see Chapter 4).

Coal tar creosote has been identified in at least 46 of the 1,613 current or former EPA National Priorities List (NPL) hazardous waste sites (HazDat 2002). However, the number of sites evaluated for creosote is not known. The frequency of these sites within the United States can be seen in Figure 6-1. Biotransformation by microbes is the primary process by which creosote constituents are degraded in soils, surface waters, and groundwater. The mixture is relatively stable and persistent in the environment; half-life data are not available. Wood creosote was not identified at any of the current or former NPL hazardous waste sites.

### 6.2 RELEASES TO THE ENVIRONMENT

There are no known natural sources of the creosote mixture (IARC 1973). However, several of the PAH constituents of the mixture are known to have natural sources; the reader is referred to the ATSDR *Toxicological Profile for Polycyclic Aromatic Hydrocarbons* (Agency for Toxic Substances and Disease Registry 1995) and the ATSDR *Toxicological Profile for Cresols* (Agency for Toxic Substances and Disease Registry 1992) for additional information on natural sources, releases, and levels of PAHs and cresols associated with creosote production, use, and disposal.

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Creosote has been identified in a variety of environmental media (surface water, ground water, soil, and sediment) collected at 46 of the 1,613 EPA NPL hazardous waste sites (HazDat 2002).

According to the U.S. Department of Agriculture (USDA), the major source of creosote released to the environment is waste water effluents from wood treatment facilities (USDA 1980). Companies that preserve wood with coal tar creosote may treat their aqueous wastes in on-site biological treatment plants or release the waste water into a municipal water treatment system (EPA 1975, 1978a). According to the Toxics Release Inventory (TRI), coal tar creosote manufacturing and processing facilities listed for 1999 (TRI99 2001) report that the major portion of creosote released to the environment is released to air and soil. Table 6-1 lists releases to the environment in 1999 from facilities that manufacture or process coal tar creosote. Only certain types of facilities are legally required to report; this is not an exhaustive list.

Coal tar creosote components may also be slowly released from the surface of treated wood products by oil exudation, leaching by rain water, or volatilization. Losses of creosote from impregnated wood are dependent on the kind of coal used to produce the coal tar, the kind of coke oven used to make the coal tar, and the conditions under which the wood is used (Leach and Weinert 1976).

Treatment of waste waters from wood-preserving processes that use creosote and/or pentachlorophenol produces bottom sediment sludge. EPA defines these as K001 sludges (EPA 1980); in the early 1990s, approximately 1,000 metric tons per year of K001 sludges were produced from active wood-preserving facilities (Davis et al. 1993). At that time, 55 wood-preserving facilities had been identified as NPL sites primarily because of contamination with K001 sludge (Davis et al. 1993).

Creosote-containing materials are also encountered at abandoned dump sites or abandoned facilities where creosote was produced or used in significant amounts. In addition to wood-preserving facilities, coal tar creosote was a by-product of the production of so-called town gas, an illuminating gas made from coal (Arvin and Flyvbjerg 1992; EPA 1987b; Flyvbjerg et al. 1993). Around the turn of the century, virtually every large community in the United States had such a manufactured gas facility (EPA 1987b). From 1816 to 1947, more than 11 billion gallons of coal tar were generated at manufactured gas plants in the United States (Lee et al. 1992). The total number of town-gas sites may have approached 11,000. Several hundred of the larger sites have been evaluated for the NPL. Coke-producing facilities also generate coal tar wastes, including cresol emissions to the atmosphere (Grosjean 1991).

**Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Coal Tar Creosote**

State <sup>b</sup>	Number of facilities	Reported amounts released in pounds per year <sup>a</sup>						
		Air <sup>c</sup>	Water	Underground injection	Land	Total on-site release <sup>d</sup>	Total off-site release <sup>e</sup>	Total on and off-site release
AL	7	234,952	1,914	No data	0	236,866	20,380	257,246
AR	3	31,068	1,209	No data	900	33,177	3,578	36,755
AZ	1	7,505	No data	No data	No data	7,505	No data	7,505
CA	4	4,215	10,564	No data	29,672	44,451	250	44,701
CO	2	8,593	280	No data	2,087	10,960	288,005	298,965
CT	1	500	No data	No data	No data	500	No data	500
FL	1	255	No data	No data	No data	255	No data	255
GA	2	2,300	8	No data	No data	2,308	No data	2,308
ID	1	5	No data	No data	30,000	30,005	No data	30,005
IL	4	26,968	2,901	No data	0	29,869	17,652	47,521
IN	3	7,055	400	No data	16,845	24,300	No data	24,300
KY	4	13,394	66	No data	0	13,460	4,742	18,202
LA	4	94,977	103	No data	0	95,080	No data	95,080
MI	1	10,529	No data	No data	No data	10,529	No data	10,529
MO	1	3,600	300	No data	No data	3,900	No data	3,900
MS	7	31,231	1,770	No data	0	33,001	79,961	112,962
NC	1	13	No data	No data	No data	13	No data	13
NE	1	5	No data	No data	0	5	No data	5
NJ	2	3,037	0	No data	0	3,037	0	3,037
NY	1	78	No data	No data	No data	78	No data	78
OH	3	61,945	1	No data	No data	61,946	1,531	63,477
OK	2	14	No data	No data	129,980	129,994	14,155	144,149
OR	5	17,370	5	No data	270,673	288,048	750	288,798
PA	5	27,416	66	No data	0	27,482	79,168	106,650
SC	2	14,450	53	No data	716,348	730,851	8	730,859

**Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Coal Tar Creosote  
(continued)**

State <sup>b</sup>	Number of facilities	Reported amounts released in pounds per year <sup>a</sup>						
		Air <sup>c</sup>	Water	Underground injection	Land	Total on-site release <sup>d</sup>	Total off-site release <sup>e</sup>	Total on and off-site release
SD	1	3,020	110	No data	No data	3,130	10,000	13,130
TN	1	500	No data	No data	No data	500	No data	500
TX	5	51,483	2,186	0	0	53,669	51,197	104,866
UT	3	9,195	No data	No data	12,478	21,673	250	21,923
VA	3	13,244	359	No data	0	13,603	12,782	26,385
WA	1	1,805	10	No data	No data	1,815	6,480	8,295
WI	3	15,336	No data	No data	0	15,336	18	15,354
WV	5	47,019	14	No data	0	47,033	26,031	73,064
Total	90	743,077	22,319	0	1,208,983	1,974,379	616,938	2,591,317

Source: TRI99 2001

<sup>a</sup>Data in TRI are maximum amounts released by each facility.

<sup>b</sup>Post office state abbreviations are used.

<sup>c</sup>The sum of fugitive and stack releases are included in releases to air by a given facility.

<sup>d</sup>The sum of all releases of the chemical to air, land, water, and underground injection wells.

<sup>e</sup>Total amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

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At older production facilities or places where wastes have been disposed off-site, the creosote materials are often mixed with other chemicals. For instance, pentachlorophenol (PCP) is commonly encountered at NPL sites involved with wood-preserving operations along with such metals as copper, chromium, and arsenic (Davis et al. 1993; Kuehl et al. 1990; Mueller et al. 1989, 1991). At many of these sites, PAHs from combustion sources other than coal tar may have been introduced. The wastes from old town-gas sites may contain benzene, toluene, ethylenebenzene, or xylenes, and sometimes cyanides (Arvin and Flyvbjerg 1992; EPA 1987b; Flyvbjerg et al. 1993).

No major sources of wood creosote releases to the environment have been reported.

**6.2.1 Air**

Atmospheric releases of creosote from wood-preserving plants are not well defined. Coal tar creosote constituents such as naphthalene, acenaphthalene, acenaphthene, phenanthrene, and fluorene have been detected in emissions at a pressure treatment facility that treated logs for use as utility poles and marine pilings (EPA 1986d). Releases may occur at several points in the treatment process, such as when cylinder doors are opened after a treatment cycle, or when creosote is transferred from the heater to the cylinder at the beginning of the impregnation process. Atmospheric releases vary from plant to plant, depending on the process design, and are considered to be significantly smaller than releases to surface water in aqueous effluents (Henningson 1983). It should be noted, however, that the more volatile PAHs may be less toxic (and especially less carcinogenic) than the less volatile PAHs.

On a hot, sunny day evaporation of creosote from the surface of treated wood may release coal tar creosote constituents to the atmosphere. Only the volatile creosote components such as acenaphthene and naphthalene will volatilize; the heavier fractions will remain on the wood (USDA 1980). Volatilization may also be greater during warmer months when ambient temperatures are higher. Gevao and Jones (1998) observed greater volatilization of acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene from creosote-treated wood at 30 EC than at 4 EC.

In a terrestrial microcosm study, release of  $^{14}\text{C}$ -labeled creosote components to the atmosphere from treated wood accounted for 1.0% of total acenaphthene and 1.4% of phenanthrene, whereas 93.5 and 95% of these components, respectively, were retained in the wood (Gile et al. 1982).

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Other potential sources of atmospheric releases include incineration of scrap wood treated with the mixture and re-entrainment of dust and soils contaminated with components of the mixture in the vicinity of hazardous waste sites. Creosote was not detected in any air samples of the 46 current or former NPL sites where creosote was identified in some environmental medium (HazDat 2002).

According to TRI99 (TRI99 2001), an estimated total of 743,077 pounds of coal tar creosote, amounting to 37.6% of the total environmental release, was discharged to air from manufacturing and processing facilities in the United States in 1999. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

No sources of wood creosote releases to the atmosphere have been reported.

### 6.2.2 Water

The major source of creosote released into surface waters and ground water is waste water effluents from wood-preserving facilities (USDA 1980). In previous years, waste water generated from wood treatment facilities was often discharged to unlined evaporation/settling lagoons where a sludge was formed. Water-soluble creosote components then percolated through the soil to reach the groundwater table. Waste waters may include process water generated from steam conditioning of the wood; preservative formulation recovery and regeneration water; water used to wash excess preservative from the surface of the wood; condensate from drying kilns used to dry preserved or surface-protected wood; water that accumulates in door and retort sumps; and rain falling on or in the immediate vicinity of the treating cylinder and work tank area. Groundwater contamination from creosote waste waters and sludge stored in unlined surface water impoundments at a wood treatment facility has been reported in Pensacola, Florida (USGS 1988a; Elder and Dresler 1988; Goerlitz et al. 1985). Similar contamination problems have been reported in Conroe, Texas (Borden 1986), and St. Louis Park, Minnesota (Hickock et al. 1982).

Given the very viscous nature of coal tar creosote or creosote-containing wastes, significant migration into groundwater supplies is seldom encountered unless the soils are extremely porous. For instance, a very sandy substrate at the American Creosote Works NPL site at Pensacola, Florida, allowed a significant plume of wood-preserving wastes to enter the ground water (Goerlitz et al. 1985). In most instances, the main concern over creosote materials entering well water is that minute quantities (ng/L) of coal tar components produce extremely objectionable tastes and odors (Arvin and Flyvbjerg 1992).



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In addition to discharges or migration into ground water from disposal sites, coal tar creosote has often been introduced to receiving waters as the result of spills while transporting coal tar materials on barges or during loading and unloading accidents around docks or navigation facilities. Well documented examples include a spill near Slidell, Louisiana, on the Bayou Bonfouca (DeLeon et al. 1988). During the years 1986–1991, 1,400 incidents of chemical and petroleum spills into the Newark Bay were documented; among these were spills of 53,000 gallons of liquid asphalt and 75 gallons of creosote (Gunster et al. 1993).

Water-soluble creosote constituents (e.g., phenols) may be released to surface water or ground water by leaching from the surface of creosote-contaminated soils at hazardous waste sites or from treated wood products, such as marine pilings, coming into contact with water. For example, some studies have shown that creosote is lost to a greater extent from marine timber than from timber placed in fresh water as a result of wood cell contraction caused by the high concentration of salts in sea water (Henningsson 1983). Creosote has been detected in groundwater samples collected at 27 of the 46 NPL sites and in surface water samples collected at 8 of the 46 sites where creosote has been identified in some medium (HazDat 2002).

According to TRI99 (2001), an estimated total of 22,319 pounds of coal tar creosote, amounting to 1.1% of the total environmental release, was discharged to water from manufacturing and processing facilities in the United States in 1999. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

No sources of wood creosote releases to water have been reported.

### 6.2.3 Soil

Coal tar creosote may be released to soils at wood treatment facilities as a result of bleeding of the product from treated timber in stockyard and storage areas. Rain water may also wash the soluble components directly from the surface of treated timber and into the soil (Henningsson 1983). Localized, but severe, contamination of soils is often encountered on the grounds of older (often abandoned) wood-preserving or town-gas facilities (Davis et al. 1993; EPA 1987b).

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There is also a potential for release of creosote to soil from hazardous waste sites. Creosote has been detected in soil samples collected at 30 of the 46 NPL sites and in sediment samples collected at 6 of the 46 NPL sites where creosote has been identified in some medium (HazDat 2002).

According to TRI99 (2001), an estimated total of 1,208,983 pounds of creosote, amounting to 61.2% of the total environmental release, was discharged to land from manufacturing and processing facilities in the United States in 1999. The TRI data (Table 6-1) should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

No sources of wood creosote releases to soil have been reported.

### 6.3 ENVIRONMENTAL FATE

As with other chemical mixtures, the fate and transport processes affecting creosote can be extremely complex. Creosote components may partition to the air, water, soil, or biota depending on their physical and chemical properties. Compounds initially released to the atmosphere may undergo atmospheric deposition and reach surface water directly or through runoff carrying soil-bound compounds (Stangroom et al. 1998). For coal tar creosote materials encountered in old production facilities or waste disposal sites, materials contained in the top several feet of soil will have become "weathered," with virtually all the phenolic and heterocyclic fractions having volatilized, oxidized, or biodegraded (von Burg and Stout 1992). The lighter fractions of the PAH materials will also have degraded. The remaining weathered creosote will show limited ability to move off-site. Johnston et al. (1993) studied the PAH composition of coal-tar-containing samples collected at a number of coal gasworks sites in Australia. Most of these sites were abandoned nearly a century ago. The samples were taken from areas where the coal tar components would have undergone environmental modification to varying degrees since deposition. They concluded that aqueous partitioning and volatilization are probably the main processes that control environmental modification of coal tar at gasworks sites.

Newly produced creosote, or materials from a spill or a more recent disposal site, may pose more serious toxicity concerns. A complicating factor in interpreting the available literature is that creosote alone may not be the only source of toxicity. Especially at NPL or other waste disposal sites, such chemicals as pentachlorophenol (PCP) or heavy metals may be involved. Without an extensive battery of chemical analyses, perhaps combined with bioassay tests, making even semi-quantitative judgements on toxicity issues can be problematic. Much of the remedial work conducted under the Superfund program has

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simply aimed to reduce the volume of wastes at NPL sites with creosote contamination. A large percentage reduction by total weight does not always translate into a corresponding reduction in toxicity (Brooks et al. 1998; Hyötyäinen and Oikari 1999b; Mueller et al. 1991).

### 6.3.1 Transport and Partitioning

Coal tar creosote constituents released to surface waters will differentially partition to the water column or to sediments depending on their water solubility and sorptive properties. For example, PAHs, the major constituents of creosote, generally tend to sorb strongly to soil and sediment particulates, and often have low aqueous solubilities and mobility (Hickock et al. 1982). Many components in the PAH fraction, particularly the higher molecular weight (HMW) PAHs, will remain in a virtually stationary tar-like mass at the place where they were deposited. Nitrogenous bases present in creosote waste water (e.g., aniline, toluidines, and xylydines) are relatively soluble, mobile, and persistent in ground water (Pereira et al. 1983). However, behavior at a given site is also dependent on site-specific characteristics. For example, PAHs, phenol, and heterocyclic components of creosote wood treatment process wastes were found to migrate en masse in ground water through a contaminated sand and gravel aquifer in Pensacola, Florida; sorption of these different classes of organic constituents in the low organic carbon (<0.1%) aquifer materials was not important (USGS 1986). In an investigation of coal-tar contaminated surface sediments, PAHs were observed to have moved 400 meters in ground water from buried subsurface coal tar; persistence of the PAHs, naphthalene in particular, was partially attributed to anoxic conditions (Madsen et al. 1993, 1996). Additionally, sediment-bound creosote components may be released over time. In a laboratory study of creosote-contaminated sediment and natural lake water, Hyötyäinen and Oikari (1999b) found that creosote-derived 4- to 6-ring PAHs released from the sediment during incubation were toxic to water fleas (*Daphnia magna*) and to the photoluminescent bacteria *Vibrio fischeri*.

In an investigation of the partitioning of PAHs from coal tar wastes at manufactured gas plant sites into ground water, partitioning of the various fractions of the complex mixture was observed to be inversely related to solubility, with the more soluble compounds partitioning to water more readily (Lee et al. 1992). Although coal tar is a complex mixture of compounds with varying physical and chemical properties, data analyzed with regard to a partitioning model indicated that ideal behavior was observed for the individual compounds and that the model was useful in estimating concentrations in ground water.

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In an investigation of the extent of creosote contamination at four wood-preservative plants with process water surface impoundments, unspecified creosote components were found to have moved 20–60 feet vertically from the impoundments to the water table and up to 500 feet horizontally from the sources (Ball 1987).

In a 50-day microcosm study of the aquifer materials of the Libby, Montana, Superfund site, 59% of radiolabeled phenanthrene was bound to the soil, while only 2.2% was volatilized (Mohammed et al. 1998).

In a terrestrial microcosm study, 2.7% of radiolabeled phenanthrene and 4.3% of radiolabeled acenaphthene were found in soil samples taken in a 10-cm zone around creosote-treated posts, whereas concentrations of the compounds that remained in the posts were 95 and 93.5% of the amounts applied, respectively, after 2.5 months (Gile et al. 1982).

In an investigation of the release of creosote from treated wood into fresh water and sea water, naphthalene, phenanthrene, acenaphthene, dibenzofuran, fluorene, and 2-methylnaphthalene were found to be the major components that migrated into water (Ingram et al. 1982). The rate of migration was found to increase significantly with increasing temperature within the range of 20–40 EC; slower migration occurred from aged than from freshly treated pilings. In a microcosm study of the leaching of PAHs from creosote-impregnated pilings into aquatic environments, the aqueous concentration of PAHs increased with the number of pilings used (Bestari et al. 1998). These authors calculated a rate loss of creosote from the wood pilings into the water of approximately  $50 \mu\text{g}/\text{cm}^2/\text{day}$  ( $273 \text{ mg}/\text{piling}/\text{day}$ ). Creosote was observed to be removed from the water rapidly after 7 days, and was close to background concentrations ( $0.8\text{--}6.7 \mu\text{g}/\text{L}$ ) by 84 days; losses were attributed to photolysis and microbial degradation, while sorption to sediment was not significant.

In an investigation of the volatilization of PAHs from creosote-treated wood, desorption of acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene was directly related to concentration and was greater at 30 EC than at 4 EC (Gevao and Jones 1998). The authors reported desorption half-lives of 0.7–31 years at 4 EC and 0.3–1 year at 30 EC for fluoranthene and acenaphthene, respectively. It is also possible to have volatilization from surface soil to the atmosphere. Coal tar constituents have Henry's law constant ranging from 0.11 to  $8.65 \times 10^{-8} \text{ atm m}^3/\text{mole}$  and vapor pressures of  $1.2 \times 10^{-8}$  to 95 mmHg (Swann et al. 1983), indicating that some newly leached compounds may rapidly volatilize from both moist and dry soil before binding to soil can occur.

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Limited uptake of some creosote constituents has been detected in plants exposed to creosote-treated wood in nearby soil. Only 0.04% of applied acenaphthene and 0.1% of phenanthrene partitioned to plant tissue in one study (Gile et al. 1982). While systemic uptake may be minimal, such coal tar creosote components as PAHs can adsorb to plant roots or surfaces. This seems a common way that vegetables or other produce for human consumption can pick up trace amounts of creosote materials (Agency for Toxic Substances and Disease Registry 1995).

Animals such as voles, crickets, snails, pill bugs, and worms have exhibited the capacity to assimilate radiolabeled creosote components in terrestrial microcosm studies. Creosote components were found to accumulate to the greatest extent in the vole, with bioconcentration factors (BCFs) of 12–31. The  $^{14}\text{C}$  mass balance content of the animals was 1.2% of applied acenaphthene and 0.8% of applied phenanthrene versus 4.3 and 2.7%, respectively, in soils (Gile et al. 1982). In addition, mussels taken from creosote-treated pilings have been found to contain significantly more benzo[a]pyrene, a creosote constituent, than those growing elsewhere (Dunn and Stich 1976). Accumulation of creosote-derived PAHs has been reported in benthic organisms in Pensacola Bay (Elder and Dresler 1988; Rostad and Pereira 1987). Fluoranthene, pyrene, benzo[a]pyrene, anthracene, chrysene, and phenanthrene were detected in higher concentrations in tissues of snails (*Thais haemastoma*) and oysters (*Crassostrea virginica*) taken from offshore sites near an onshore wood-treatment plant compared with those from control sites. Experimental and estimated  $\log K_{ow}$  values for many of the main constituents of coal tar are 1.22–5.22 (HSDB 2000; Meylan and Howard 1995). Based on these values, BCFs of 5–5,500 have been estimated and are consistent with reported experimental BCFs of 2–9,200 for fish and aquatic organisms, indicating that bioaccumulation may be important in the fate of some components of coal tar (Kobayashi et al. 1979; Linder et al. 1985).

## 6.3.2 Transformation and Degradation

### 6.3.2.1 Air

Little information was found in the available literature concerning the transformation of wood or coal tar creosote components in the atmosphere. Some volatile coal tar constituents may undergo oxidation by vapor phase reaction with photochemically produced hydroxyl radicals, with calculated half-lives of 2 hours to 10 days based on experimental and estimated rate constants of  $1.12\text{--}103 \times 10^{12}$  cm/molecules-second at 25 EC and using an average atmospheric hydroxyl radical concentration of  $5 \times 10^5$  molecules/cm<sup>3</sup> (Atkinson 1989; Meylan and Howard 1993). Rates may be slowed since some components will exist as

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particulate matter in the atmosphere (Eisenreich et al. 1981). Additionally, some components of coal tar may undergo nighttime reactions with nitrate radicals (Atkinson et al. 1987). Based on an experimental rate constant of  $3.8 \times 10^{-12}$  cm/molecules-second for phenol, and an atmospheric nitrate radical concentration of  $2 \times 10^8$  molecules/cm<sup>3</sup>, a half-life of 15 minutes can be calculated for the compound (Atkinson 1989).

Among the more volatile constituents of creosote are the cresols in its phenolic fraction. These materials comprise only about 1% of the creosote by weight, but it is the cresol components that give creosote its distinctive odor and its resin-like properties. The more generally recognized source categories related to coal tar production or products containing creosote include coal tar distillation facilities or coke ovens, but another source may come from chemical transformation in the air around urban centers (Grosjean 1991).

The air of many urban areas shows appreciable levels of volatile organic compounds (VOCs) such as toluene. A major source is often nonstationary sources such as automobiles since toluene is an octane booster in nonleaded gasolines. Toluene can react with hydroxyl radicals to form the same types of cresols found in the phenols portion of creosote. Although other reaction pathways can lead to the rapid degradation of these cresols, appreciable transient build-ups of cresol vapors are possible. Degradation products include a variety of nitrocresols, aliphatic carbonyls, and ketoacids. These degradation products can become part of other atmospheric reactions in the air of typical urban areas. These transient cresol concentrations could amount to 10–13% of the toluene levels. This cresol source is worth further study in urban areas showing exceptionally high levels of VOCs in the ambient air (Grosjean 1991).

### 6.3.2.2 Water

Coal tar constituents present in surface waters may be degraded by direct and indirect photolysis. Estimated aqueous photolysis half-lives of 8.4, 71, and 21 hours have been reported for phenanthrene, naphthalene and fluoranthene, respectively (Zepp and Schlotzhauer 1979). Other coal tar constituents which may undergo aqueous photolysis are acenaphthalene, anthracene, benzene, quinoline, phenol, cresol, and carbazide. In a microcosm study, PAHs leached from creosote-impregnated wood pilings were degraded in aquatic environments by photolysis and microbial degradation, while sorption to sediment was not significant (Bestari et al. 1998). Photolysis in water is not expected to be a major route of the environmental fate of creosote constituents, particularly for the less soluble compounds.

## 6. POTENTIAL FOR HUMAN EXPOSURE

Coal tar creosote components are degraded in aquatic environments mainly by microfaunal metabolism (Borthwick and Patrick 1982; Ingram et al. 1982). Microorganisms may act on the creosote-treated wood itself or on creosote components that have leached from the treated wood. Quinoline, the major tar base in creosote, has been reported to be degraded in surface water and ground water by bacteria of the genus *Pseudomonas* (Bennett et al. 1985). Biotransformation of the phenolic components of creosote apparently also occurs under anaerobic conditions in contaminated ground water (Ehrlich et al. 1983; Goerlitz et al. 1985). Adaptation of soil microorganisms to PAH contaminants in ground water originating from creosote treatment plant wastes has also been reported (Wilson et al. 1985).

Work on NPL sites has helped identify numerous bacteria and fungi that can biodegrade creosote materials. In addition to *Pseudomonas*, bacteria in the genus *Alcaligenes* can degrade phenolic compounds under aerobic conditions (Mueller et al. 1989). So long as the ground water is not completely anoxic, numerous soil microorganisms can degrade creosote materials. Work at NPL sites suggests that up to 90% of the creosote degradation is associated with biologically mediated processes. Although this can lead to an appreciable reduction in the quantity of the creosote materials, it is the phenolic and lower molecular weight (LMW) PAHs that are degraded while the HMW PAHs that have been shown to resist biological attack may persist. In a study of biodegradation of creosote-contaminated ground water from the American Creosote Superfund Site, Mueller et al. (1991) observed a toxic and teratogenic response of inland silverside (*Merida beryllina*) embryos to the biotreated water at both 10 and 100% concentrations. They attributed the response to the cumulative effects of carcinogenic HMW PAHs that remained after 14 days of incubation. The higher levels of biodegradation observed for the LMW PAHs was attributed to their greater aqueous solubility and consequent greater bioavailability.

Much less is known about biodegradation processes under more anoxic conditions, which would be typical of ground water and vadose zone waters. Work on town-gas sites in Europe has demonstrated that where nitrate levels are high, or where nitrate is supplied to ground water, various facultative bacteria can degrade coal tar components using the nitrate or nitrite as an electron acceptor (Flyvbjerg et al. 1993). In general, however, biodegradation under anoxic conditions appears to proceed very slowly. Even when supplied with ample quantities of such electron acceptors as nitrates, half-lives in excess of 20 days were observed in laboratory microcosms for the anoxic biodegradation of dimethylphenol components in creosote, and cresol components showed little indication of significant disappearance unless the experiments were continued in excess of 90 days (Arvin and Flyvbjerg 1992).

## 6. POTENTIAL FOR HUMAN EXPOSURE

Creosote components have been detected in surface water samples taken near a wood-treatment facility that ceased operation 30 years earlier (Black 1982). The creosote, which appeared to have permeated the sandy surface soils down to an impervious clay layer, was entering the river via seepages and springs. Weathering processes produced only minor constitutive changes in the creosote with relative losses of the lower molecular weight components. These changes probably reflected the greater volatility and solubilities of the 2–3 carbon ring PAHs.

**6.3.2.3 Sediment and Soil**

Coal tar creosote components are slowly released from treated wood products by oil exudation, rainwater leaching, and by volatilization of the lighter fractions (Henningsson 1983). USDA (1980) reported that the major components of creosote were not detected in soil samples taken to a depth of 6 inches within 2–24 inches from treated poles, presumably as a result of biotransformation of mobilized components by soil microorganisms. Creosote components released to soils in waste water effluents have been found to be biotransformed by soil microbes under aerobic conditions (Middleton 1984). Bacteria of the genus *Pseudomonas* isolated from a creosote-contaminated waste site have been reported to degrade creosote-derived quinoline (Bennett et al. 1985). Acclimation to creosote phenolic constituents by soil microorganisms has also been demonstrated (Smith et al. 1985).

Where the coal tar creosote is in well-oxygenated conditions, lignin degrading fungi like the white rot fungus *Phanerochaete sordida* can remove much of the PAH fraction (Davis et al. 1993). This fungus can also biodegrade PCP, which has often become mixed with the wastes found at creosote production or disposal sites.

Many of the same bacteria and fungi capable of biodegrading creosote components in aqueous systems can be found in soils. Especially where the creosote is close to the surface and under aerobic conditions, the vast majority of the phenolics can be consumed in less than a year (von Burg and Stout 1992). The majority of the lighter fractions of the PAH components (from 53 to 75% by weight) can be biodegraded within 2 months (there was no significant depletion of heavier fractions with 5-ring or higher PAHs) (Davis et al. 1993).

While biodegradation of PAHs in soil may be enhanced using bioremediation procedures, not all techniques are equally effective at reducing toxicity. In a study of PAH-contaminated soil from the Reilly Tar Superfund Site in St. Louis Park, Minnesota, although total EPA priority pollutant PAH



## 6. POTENTIAL FOR HUMAN EXPOSURE

concentrations were decreased 48–74% following treatment with one of four bioremediation technologies, following two of the four techniques, toxic (mutagenic) compounds were still present (Brooks et al. 1998). None of the four techniques tested was successful at removing the 5- and 6-ring HMW PAHs.

However, persistence of the PAHs, naphthalene in particular, has been observed in seep sediments where groundwater contaminated from buried subsurface coal tar emerged at the base of a hill; persistence of the LMW PAH naphthalene was attributed mainly to anoxic conditions (Madsen et al. 1993, 1996).

For sediments, much of the literature involves biologically oriented tests to identify hotspots with pronounced degrees of toxicity to aquatic and marine species. For instance, bioassays using benthic amphipods and highly creosote-contaminated sediments from Eagle Harbor in Washington's Puget Sound showed several toxic hotspots with acute toxicity to the infaunal marine amphipod *Rhepoxynius abronius* (Swartz et al. 1989). The authors suggest similar causal factors may underlie the common pattern of hepatic lesions and neoplasms observed in English sole from Eagle Harbor. As with bioremediation, natural attenuation of creosote-contaminated sediment may continue to present risks to aquatic organisms as sediment-bound creosote constituents may be released over time. In a laboratory study using contaminated sediment and natural lake water, Hyötyäinen and Oikari (1999b) found that creosote-derived 4- to 6-ring PAHs released from the sediment during incubation were toxic to water fleas (*D. magna*) and to the photoluminescent bacteria *V. fischeri*.

Work at coal tar creosote-contaminated sites on the Elizabeth River in Virginia, indicates a strong positive correlation between exposure to the creosote-contaminated sediments and the incidence of hepatic neoplasms on a resident forage fish, the mummichog (*Fundulus heteroclitus*) (Vogelbein et al. 1990). Similar cancer epizootics in fishes are found at other major harbor sites (e.g., the lower Hudson River, Boston Harbor, and Los Angeles harbor) showing creosote or PAH-laden sediments. Such findings have been proposed (Vogelbein et al. 1990) as indicators of serious toxic concerns in coastal and estuarine environments that may have human health implications if bioaccumulation can be documented.

#### 6.3.2.4 Other Media

Very little information was found in the available literature on the transformation or degradation of coal tar creosote or wood creosote in animals or plants. Eisler (1987) found that many aquatic organisms are able to rapidly metabolize and eliminate PAHs, the major constituents of the commercial mixture.

## 6. POTENTIAL FOR HUMAN EXPOSURE

Transport and transformation of creosote in the environment may affect the coal tar creosote constituents in treated wood. The USDA reported that the relative levels of 18 major creosote residues in treated marine pilings did not change following 9.5 years of service; of the originally applied creosote, 93% was retained on the wood (HSDB 2000). Both creosote and total PAHs decreased during the in-service period.

**6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT**

Reliable evaluation of the potential for human exposure to creosote depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. In reviewing data on creosote levels monitored in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable.

**6.4.1 Air**

No information was found in the available literature regarding ambient atmospheric concentrations of wood or coal tar creosote-derived components (i.e., PAHs) in the United States (HSDB 2000). Workplace air concentration data are discussed in Section 6.5. Data on ambient atmospheric concentrations of PAHs derived from other sources can be found in the ATSDR *Toxicological Profile for Polycyclic Aromatic Hydrocarbons* (Agency for Toxic Substances and Disease Registry 1995).

**6.4.2 Water**

No information was found in the available literature regarding ambient water concentrations of wood or coal tar creosote-derived components (i.e., PAHs) in the United States (HSDB 2000). However, in a microcosm study, Bestari et al. (1998) reported that measured background concentrations of 16 monitored creosote-derived PAHs in the microcosm water ranged from nondetectable to 1.5 µg/L which was comparable to background estimates for a variety of natural water sources.

Results from 2 years of groundwater sampling at an abandoned wood treatment facility in Conroe, Texas, where coal tar creosote had been used for about 20 years, showed that monitoring wells were contaminated with levels of up to 3,490 µg/L naphthalene, 1,263 µg/L methylnaphthalene, 425 µg/L dibenzofuran, and 302 µg/L fluorene. The contaminants had apparently migrated through the clay and

## 6. POTENTIAL FOR HUMAN EXPOSURE

sand soils on the site from three waste pits. A plume of groundwater contamination by organics at trace levels was found to extend up to 300 feet from the waste pit locations (Bedient et al. 1984).

At the Koppers Company, Inc. NPL site in Texarkana, Texas, where a creosote wood treatment facility existed for 51 years prior to being converted to a residential area and an industrial site (sand and gravel company), creosote-derived naphthalene, acenaphthene, fluorene, pyrene, and phenanthrene were measured in ground water at levels ranging from nondetectable to  $10^5$  ppb (Agency for Toxic Substances and Disease Registry 1994). Surface water at the site had no detectable levels of the acid or base/neutral compounds that were monitored.

### 6.4.3 Sediment and Soil

PAH contamination of soil has been found at the site of a wood-preservation facility that operated in Slidell, Louisiana, from 1892 to 1970, when a fire destroyed the plant facilities. It is believed that environmental releases of creosote occurred throughout the plant's operating history and as the result of the 1970 fire, when creosote was released from storage tanks and flowed over the ground and into adjacent water bodies. Waste creosote and debris have accumulated in eight areas at the site. The deposits are up to 2 feet thick and have contaminated underlying soils (based on visual inspection) to as much as 1 foot below the surface. PAH concentrations show a rapid decrease with increasing depth, ranging from 15,680 mg/kg (ppm) at the surface to 1 mg/kg (ppm) within 9 feet. PAH concentrations as high as 2,488 mg/kg also have been measured in the soils matrix of the shallow aquifer (Acharya and Ives 1994).

Several PAH constituents of creosote were detected in soil samples taken at an abandoned wood treatment facility in Conroe, Texas, at depths of up to 25 feet. Maximum concentrations of the compounds were detected in samples collected at the 0.7–1.8-foot depth. Maximum concentration levels were 3.7 mg/kg for naphthalene, 3.4 mg/kg for methylnaphthalene, 3.8 mg/kg for dibenzofuran, 4.2 mg/kg for fluorene, and 2.2 mg/kg for anthracene. An investigation of vertical variations in contaminant concentrations in the soil zone above the water table revealed that, in general, >90% of the organics were removed within the first 5 feet at the location studied. Organics can be degraded by microbes, adsorbed onto soil, or altered by interactions with soil humus (Bedient et al. 1984).

At the Koppers Company, Inc. NPL site in Texarkana, Texas, where a creosote wood treatment facility existed for 51 years prior to being converted to a residential area and an industrial site (sand and gravel

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company), creosote-derived pyrene, fluoranthene, phenanthrene, and anthracene (base/neutral compounds) were measured in surface and subsurface soils at levels ranging from nondetectable to 1,000 ppm (Agency for Toxic Substances and Disease Registry 1994).

In sediment samples from a creek adjacent to the Koppers Company, Inc. NPL site, creosote-derived base/neutral compounds were detected at concentrations up to 100 ppm; one creosote-derived base/neutral compound was detected in downstream sediment at a maximum of 1 ppm (Agency for Toxic Substances and Disease Registry 1994). Creosote-derived base/neutral compounds were also detected in the sediment of the drainage ditch at the site, at levels ranging from 1–100 ppm.

Coal tar creosote-derived phenanthrene, 1,2-benzanthracene, and benzo[a]pyrene have been detected in river sediments at concentrations of up to 231, 62, and 16 mg/kg (wet basis), respectively, directly downstream from the site of a former wood treatment facility. At 4,000 meters from the source, these levels decreased to 0.35, 1.02, and 0.40 mg/kg (wet basis), respectively (Black 1982). Creosote-derived PAHs were also detected in the sediments of Pensacola Bay and a drainage stream in the vicinity of a former wood treatment facility near Pensacola, Florida. PAH concentrations ranged from 200 µg/g for naphthalene to 140 mg/kg for anthracene in stream sediments; concentrations in Pensacola Bay ranged from 75 µg/kg for benzanthracene to 190 µg/kg for fluoranthene (Elder and Dresler 1988).

PAH concentrations have been determined in sediment cores collected from the Arthur Kill, Hackensack River, and Passaic River in northern New Jersey. These rivers are in industrialized areas near former creosote wood-preserving facilities that operated through the 1960s and 1970s. Temporal distributions were determined in each core based on the activities of the radionuclides <sup>210</sup>Pb and <sup>137</sup>Cs. Sediments at depths corresponding to the years 1978 and 1964 contained total PAHs at concentrations of 1.71 mg/kg (ppm) for 1978, and not detected to 35.7 mg/kg for 1964 (Huntley et al. 1993). In a study of Eagle Harbor, an estuarine bay of the Puget Sound in which sediments were contaminated with creosote from a wood treatment facility, total PAHs were detected at concentrations as high as 6,461 mg/kg (Swartz et al. 1989).

In the vertical profile of sediments in a seep area at the base of a hill where PAHs emerged after being transported approximately 400 meters in ground water from a buried subsurface coal tar source, naphthalene was detected at 2–45 ppm (Madsen et al. 1996).

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**6.4.4 Other Environmental Media**

Since wood and coal tar creosotes are complex mixtures, techniques for relating apparent bioaccumulation or biomagnification in food chains to human health concerns are not well defined. Fish or shellfish directly exposed to coal tar creosote wastes will be tainted by offensive odors and tastes. Extracts of shellfish taken from the wharf of the biological station in St. Andrews and from Passamaquoddy Bay (both in New Brunswick, Canada) indicated contamination with creosote oil (Zitko 1975). Concentrations of creosote oil found were as follows:

<u>Shellfish</u>	<u>Location</u>	<u>Concentration, µg/g lipid</u>
mussel	Biological Station	1,046
periwinkle	Biological Station	3,254
	Passamaquoddy Bay	459
whelk	Biological Station	354
	Passamaquoddy Bay	202
clam	Passamaquoddy Bay	459

The biological station's wharf had been periodically repaired using lumber treated with coal tar creosote; no other sources of coal tar creosote in the vicinity of the Passamaquoddy Bay sampling site were known. The author suggested that the differences in creosote oil concentration in periwinkles and whelks collected in the same localities may indicate that PAHs are not bioaccumulated. However, in an estuarine environment near a Pensacola, Florida, creosote-contaminated wood-preservation facility site, a native mollusc (*T. haemstoma*) and a nonnative mollusc (*C. virginica*) both exhibited bioaccumulation of fluorene, pyrene, and phenanthrene at up to 10 times greater than observed in controls (Elder and Dresler 1988).

Additionally, a study at a creosote spill near Lake Pontchartrain in Louisiana, provided some indications that biomagnification through food chains leading to humans can take place. This study documented the bioaccumulation of creosote-derived PAH fractions in the marsh clam *Rungia cuneata* (DeLeon et al. 1988). With total PAH levels in the ambient water #25 ppb, caged clams introduced to an area near a major creosote spill showed tissue concentrations of benzopyrenes up to 600 ppb after 4 weeks of exposure. This clam is a major food item for crustaceans such as the blue crab that are part of commercial fisheries in the Lake Pontchartrain area.

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Creosote-treated wood such as marine pilings may be left in the environment for many years. The USDA reported that residual creosote in marine pilings after 25, 40, and 59 years of service ranged from 280 to 380 kg/m<sup>3</sup> (HSDB 2000).

**6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE**

Potential sources of non-occupational human exposure to creosote include contact with creosote-treated wood products (e.g., railroad ties used for landscaping), incineration of creosote-treated scrap lumber, and contact with contaminated environmental media at hazardous waste sites (e.g., ingestion of contaminated ground water). At the Koppers Company, Inc. NPL site in Texarkana, Texas, where a creosote wood treatment facility existed for 51 years prior to being converted to a residential area and an industrial site (sand and gravel company), a study by the Texas Department of Health found an increased incidence of skin rashes in residents who had dermal contact with soil at the site (Agency for Toxic Substances and Disease Registry 1994).

Risk of exposure to creosote constituents through contact with contaminated ground water will vary with the individual chemicals involved as well as with the mix of chemicals present at any one time and the environmental conditions. Physical and chemical properties of the compounds, including solubility and molecular weight, will affect distance which a contaminant plume may travel from the source, as well as its susceptibility to biodegradation or sorption (King and Barker 1999). The environment in which contamination occurs is also of importance since natural attenuation of chemical compounds may be dependent on whether oxidizing or reducing conditions are present. In an investigation of natural attenuation of contaminant plumes from an emplaced coal tar creosote source, King et al. (1999) observed greater and more rapid decreases in plume mass for some compounds, such as phenol, *m*-xylene, and carbazole, while the dibenzofuran plume mass and extent remained relatively constant, and the plume mass and travel distance from the source for naphthalene and 1-methylnaphthalene increased throughout the 4-year study. Therefore, potential for exposure to creosote constituents present in ground water will differ from location to location and over time.

Direct exposure of homeowners to wood treatment products containing creosote should be limited, since EPA has restricted the sale and use of such products to certified applicators. Industrial sources have noted that there have been no reports or instances of health effects allegations in the last 20 years (ending in 1996), except for rare reports of skin irritation resulting from public contact with creosote-treated wood.

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Another potential source of nonoccupational exposure is the therapeutic use of coal tar shampoos for anti-dandruff therapy, coal tar ointments for treatment of eczematous dermatitis, and mineral coal tar for the treatment of psoriasis. Adsorption of PAHs may occur through the skin, lungs, and gastrointestinal tract (Strickland et al. 1996). van Schooten et al. (1994) measured the urinary excretion of a specific PAH metabolite, 1-hydroxypyrene, to assess the internal dose of PAH after acute dermal application of coal tar shampoo. The shampoo selected for the experiment had a PAH concentration of 2,840 mg/kg, including pyrene (285 mg/kg) and benzopyrene (56 mg/kg). In other brands, the concentrations were at least 100 times lower. A single use of the coal tar shampoo resulted in increased 1-hydroxypyrene excretion in all participants. The mean increase of totally excreted 1-hydroxypyrene on day 1 was 10 times the pre-experiment background values. On day 2, the mean increase was 5 times. Interindividual variation was considerable, with a variation in the first day increase of between 3 and 20 times. The 1-hydroxypyrene values observed in coke oven workers are similar to the values obtained on day 1 after a single treatment with coal tar shampoo (0.4–8.3  $\mu\text{mol/mol}$  creatinine) (van Schooten et al. 1994). However, exposure levels determined using the 1-hydroxypyrene biomarker may be affected by the time of measurement following exposure (Viau and Vyskocil 1995). Viau and Vyskocil observed maximum excretions of 1-hydroxypyrene in urine a few hours after exposure to pyrene in a coal tar-based shampoo or following dermal contact with either creosote or pyrene.

Occupational exposure to PAHs and other constituents of creosote may occur in several industries where workers are exposed to coal tar creosote, coal tar, coal tar pitch volatiles, or products containing creosote. Such occupations include jobs in the wood preserving industry, railroad work (installation and removal of crossties), treated lumber installation work involving structures such as fences or bridges, electric utility work involving treated poles, coke oven work, jobs in the rubber industry or tire plants, road paving work, roofing work, chimney cleaning, aluminum smelting work, iron foundry work, steel plant work, and site remediation work involving creosote-contaminated environmental media.

Individuals working in the wood-preserving industry comprise the largest portion of the population potentially exposed to coal tar creosote. Workers employed at creosote pressure-treatment facilities may be exposed by direct dermal contact or by inhalation of volatilized components. Potential exposure to coal tar creosote in these plants is minimized by the use of closed systems for receiving, transferring, mixing, storing, and applying the mixture to wood products. Similarly, dermal exposure from the handling of freshly treated wood is minimized by the use of highly mechanized processes. Exposure via inhalation, however, is more likely to occur. For example, worker exposure may be significant during opening of treatment cylinder doors and cylinder cleaning operations (EPA 1981b). Inhalation and

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dermal exposure are also more likely in plants using nonpressure treatment methods such as thermal and dip treatments in open tanks. An estimated 100 workers were involved in commercial thermal and dip treatment operations in the late 1970s. Some of these workers experienced consistently high inhalation exposures (USDA 1980). Other historical nonpressure treatment exposures included an estimated 50,000 individuals (e.g., homeowners, farmers, landscapers) who applied creosote in noncommercial brush, dip, spray, and soak treatments (EPA 1981a). Dermal contact and inhalation may have resulted in exposure to high concentrations of creosote components for these individuals, but the exposures were usually of intermittent frequency (USDA 1980). However, designation of creosote products as restricted use pesticides by EPA in 1986 has probably decreased the number of individuals potentially exposed in these nonpressure wood treatment applications (EPA 1986b).

In 1996, there were 25,000 workers employed in 75–100 domestic wood treatment plants using coal tar creosote. As a result of the use of engineering controls and personal protective equipment (e.g., respiratory protection and impervious gloves) required in the 1986 settlement of the EPA Special Review process,<sup>1</sup> airborne exposures to creosote components in the workplace are generally below the OSHA permissible exposure limit (PEL) of 0.2 mg benzene soluble particulates per m<sup>3</sup> air (Rivers 1990).

However, prior to the consistent use of these controls by industry, workers were potentially exposed to higher airborne concentrations of creosote constituents. For example, the concentrations of creosote (i.e., coal tar pitch volatiles) components in 3- to 8-hour personal air samples, taken over a 2-day period at a railroad tie treatment facility in Somerville, Texas, were found to range from 0.003 to 1.211 mg/m<sup>3</sup> (NIOSH 1980b). Another industrial hygiene survey of worker exposure to creosote at a wood-treatment facility in Tacoma, Washington, showed coal tar pitch volatiles in personal air samples ranging from <0.0004 to 0.112 mg/m<sup>3</sup> (NIOSH 1981b). The higher concentrations were found at the end of the treatment process when the cylinder was opened. NIOSH investigated creosote exposure among dock builders in Brooklyn, New York, in 1980. Employees were reported to have substantial direct skin contact with creosote. Breathing zone concentrations of the cyclohexane extractable fraction of the coal tar pitch volatiles ranged from 0 to 0.059 mg/m<sup>3</sup> of air (NIOSH 1981a). Comprehensive studies of worker

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A Special Review of a currently registered pesticide may be initiated by EPA when validated data indicate that certain types of toxicity (e.g., carcinogenicity, developmental toxicity, acute effects) exist for humans or for non-target plant or animal species. A formal process exists for notifying registrants and other interested parties, requesting further data regarding the pesticide in question, analyzing and reporting risks and benefits, and requesting public review. The final regulatory decision may be implemented over a period of time or it may be imposed immediately as an emergency action based solely on the EPA's finding of immediate danger to human health or the environment.



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exposure to creosote in wood treatment plants have been conducted by Koppers Company, alone and in conjunction with NIOSH (Markel et al. 1977; SRI 1993). Data from these studies indicated that, on the average, employee exposure to particulate polycyclic organic materials (PPOM) was within the permissible level of  $0.2 \text{ mg/m}^3$  recommended by NIOSH for coal tar pitch volatiles. The only components that could be reliably measured in the vapor-phase fractions collected were naphthalene, methylnaphthalene, and acenaphthene. The concentrations of these chemicals ranged from 0.54 to  $2.0 \text{ mg/m}^3$ . Fluorene and phenanthrene-anthracene were detected in trace quantities, but were not quantifiable. Benzene-soluble particulates (PPOM) ranged from 0.02 to  $0.10 \text{ mg/m}^3$ . The World Health Organization reported that air concentrations of creosote-derived PAHs were  $0.05\text{--}650 \text{ }\mu\text{g/m}^3$  at a wood treatment plant where railway sleepers were treated with creosote; the main creosote constituents detected were naphthalene, fluorene, and phenanthrene (HSDB 2000). At a second plant, where a coal tar solution was used to treat railway sleepers and telephone poles, PAHs were detected in the air at  $0.004\text{--}11 \text{ mg/m}^3$  (HSDB 2000).

A gravimetric analytical method has been used in most of these workplace monitoring studies. This method involves the collection of airborne particulates on glass fiber filters and subsequent extraction by solvents, such as benzene or cyclohexane. The extracted fraction of the particulate matter is determined by weighing. As a result of two significant shortcomings of this method, the inability to identify constituents of the airborne particulates and to sample vapor phase components, EPA (1981a) concluded that definitive information was not available on the identity of airborne components of creosote in workplace atmospheres. EPA (1981a) also stated that quantitative estimates of dermal exposures were not available for treatment plant workers. Quantitative inhalation or dermal exposure data for workers applying creosote in nonpressure treatment scenarios and for downstream workers who install, handle, or contact treated wood products were also unavailable. An industrial hygiene survey of wood treatment facilities conducted in Finland revealed that vapor phase components were an important source of worker exposure. Vapors were collected on XAD-2 resin (recovery 82–102%) and analyzed by gas chromatography (GC). PAHs were collected on glass fiber filters and analyzed with high-pressure liquid chromatography (HPLC) using a fluorescence detector. Most of the airborne contaminants in worker breathing zones were in the vapor phase, with naphthalene the main component, averaging 52% of the total concentration; the proportion of particulate PAHs to total concentration of vapors was  $<0.5\text{--}3.7\%$ . The major components in the vapors have acute toxicity potential but are not as tumorigenic or mutagenic as the less volatile PAHs (Heikkilä et al. 1987). A recent study by Becker et al. (1999) demonstrated the feasibility of quantifying thiaarenes (sulfur-containing polycyclic aromatic hydrocarbons). Using GC

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with atomic emission detection, these authors measured thiaarene concentrations of 0.4–19.0  $\mu\text{g}/\text{m}^3$  in the personal air space of workers at an aluminum reduction plant who were exposed to coal tar pitch volatiles.

Exposure to coal tar creosote may also occur during installation of treated poles, during inspection and maintenance operations, and through casual contact (USDA 1980). One of the major end point uses of creosote is treatment of railroad cross ties. Since cross ties are installed mechanically by railroad companies, workers generally have minimal dermal exposure in this process. Exposure via inhalation, however, is considered to be moderate and consistent during this type of installation procedure. In other situations, cross ties may be installed manually, in which case, there is consistent moderate to high exposure via skin contact as well as by inhalation. The amount of exposure via skin contact ranges from low to high depending on whether workers wear protective clothing. Skin contact is considered minimal for railroad personnel who inspect ties in use, as well as for the general public who may have casual contact with creosote-treated cross ties. In instances where crossties are used for landscaping purposes, contractors involved in the sale and installation of freshly treated ties experience consistent moderate inhalation exposure and minimal to occasionally high dermal exposure.

Installation of treated lumber and timbers in structures such as bridges, piers, retaining walls, fences, and barns involves a significant amount of manual contact. Likewise, the installation of switch ties, cross planks, crossarms, block flooring, and fence posts is usually done manually. In these situations, human exposure via inhalation is considered moderate while exposure via skin contact may vary from minimal to high depending on the type of protective equipment used (USDA 1980).

Exposure of individuals installing treated fence posts, lumber, and timbers via inhalation of creosote volatiles (e.g., acenaphthene and naphthalene) can also occur when freshly treated materials are handled under calm, hot, sunny conditions (USDA 1980). Exposure may be even greater during warmer months when ambient temperatures are higher. Acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene were observed to undergo more volatilization from creosote-treated wood at 30 EC than at 4 EC (Gevao and Jones 1998).

The risk of direct dermal contact is particularly high for workers installing treated poles. Activities such as attaching fittings often preclude the use of protective gloves, and as a result of creosote bleeding from the treated poles, the potential for dermal contact of workers performing maintenance operations persists for years after installation (Henningsson 1983).

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Individuals employed in industries that manufacture and process creosote or products containing creosote may be exposed to the highest concentrations of this compound. The National Occupational Exposure Survey (NOES), conducted by NIOSH from 1981 to 1983, estimated that 241 workers employed at 3 facilities were potentially exposed to creosote in the United States (NOES 1990). The NOES database does not contain information on the frequency, concentration, or duration of exposure; the survey provides only estimates of workers potentially exposed to chemicals in the workplace.

Rubber processing workers at a tire plant in Poland who were occupationally exposed to coal tar pitch volatiles were found to have been exposed to excessive ( $>0.2 \text{ mg/m}^3$ ) levels of PAHs, including benzo[a]pyrene (Rogaczewska and Ligocka 1994). Measurements of benzo[a]pyrene were generally in the range of  $<4\text{--}142 \text{ ng/m}^3$ , but were as high as  $3,470\text{--}6,060 \text{ ng/m}^3$  for workers who weighed the raw materials.

In an investigation of the effect of decreased dermal exposure to creosote on the internal dose of PAHs in workers at a creosote wood impregnation plant, the use of Tyvek coveralls worn beneath outer work-clothes decreased the internal dose of pyrene (Van Rooij et al. 1993b). Workers not wearing the overalls had total pyrene skin contamination of  $47\text{--}1,510 \text{ }\mu\text{g/day}$  and had urinary levels of 1-hydroxypyrene of  $6.6 \text{ }\mu\text{g}$ . For dermally protected workers, dermal pyrene contamination was approximately 35% less than that of the unprotected workers and urinary levels of 1-hydroxypyrene were  $3.2 \text{ }\mu\text{g}$ . The low level of efficacy was attributed to uncovered skin areas (face, wrists, ankles). Volatile pyrene in the breathing-zone air was measured at  $0.3\text{--}3.0 \text{ }\mu\text{g/m}^3$ . The authors determined that for creosote workers, the level of dermal exposure to PAHs is the main determinant of the internal exposure dose; 15 times more pyrene was absorbed through dermal uptake than through respiratory uptake. Data from earlier studies indicate that the daily skin contamination with pyrene was higher for creosote workers (median of  $350 \text{ }\mu\text{g}$ ) compared with that measured for coke oven workers ( $70 \text{ }\mu\text{g}$ ) and road pavers ( $117 \text{ }\mu\text{g}$ ); for aluminum workers, a pyrene level of  $395 \text{ }\mu\text{g}$  was measured (Van Rooij et al. 1993b).

Previously, the only information on biological indicators of exposure to coal tar found in the available literature involved a study of 1-hydroxypyrene in the urine of a creosote wood-treatment plant worker (Jongeneelen et al. 1985). The pyrene metabolite, 1-hydroxypyrene, is now more commonly used as a biological indicator to assess total PAH exposure in several industries as well as for nonoccupational uses of coal-tar based products (Malkin et al. 1996; Strickland et al. 1996). Elovaara et al. (1995) studied inhalation and dermal exposure to naphthalene and 10 large PAHs in creosote impregnation plant workers. Air concentrations of the compounds were measured and compared with measurements of

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urinary 1-hydroxypyrene. Urinary concentrations, due to high dermal exposures were high (16–120  $\mu\text{mol/mol}$  creatine) even in the morning, were lower in postshift measurements (19–85  $\mu\text{mol/mol}$  creatine) and then were highest in the evening (27–122  $\mu\text{mol/mol}$  creatine), indicating that time of sampling is important. The authors concluded that the biomarker was useful in determining exposure to 3- to 6-ring PAHs, but not to naphthalene volatiles.

Jongeneelen (1992) related urinary concentrations of 1-hydroxypyrene for coke oven workers exposed to fumes containing PAHs to measured levels of coal tar pitch volatiles in order to equate the biological indicator data with lung cancer relative risk levels determined using epidemiological data obtained from U.S. and European coke plants. A urinary concentration of 2.3  $\mu\text{mol/mol}$  creatine was equated with the threshold limit value (TLV) (ACGIH) of 0.2  $\text{mg/m}^3$  for coal tar pitch volatiles, and consequently with the relative risk for lung cancer of approximately 1.3 for a group of exposed workers. Although an empirical relationship between the biomarker 1-hydroxypyrene and relative cancer risk in an exposed group may be determined, because creosote constituents vary from source to source, and because the carcinogenic PAH fraction and the routes of exposure will also vary, the health risks related to exposure to coal tar creosote versus coal tar pitch volatiles versus coal tar will differ between exposed groups such as creosote and coke oven workers (Viau et al. 1995). Viau et al. (1995) did conclude, however, that PAHs from background environmental contamination and from smoking could be excluded from consideration of urinary excretion of 1-hydroxypyrene within a certain group of workers.

Coal-handling workers at a coke oven who were exposed to coal-tar sludge (67% coal tar) through dermal contact had increased urinary 1-hydroxypyrene concentrations following work shifts (Malkin et al. 1996). Urinary concentrations of the biomarker increased from a preshift mean of 1.00  $\mu\text{mol/mol}$  creatine to a postshift level of 1.7  $\mu\text{mol/mol}$  creatine. The increases were attributed to dermal exposure, as exposure to volatile pyrene was determined to be minimal.

A review paper of studies using the concentration in urine of 1-hydroxypyrene as a biomarker of PAH exposure included levels reported in various studies (Strickland et al. 1996). The respective pre- and postshift urinary excretion levels of 1-hydroxypyrene for coke oven workers were 0.89 and 2.47  $\mu\text{mol/mol}$  creatine; for asphalt pavers, respective levels were 1.35 and 1.76  $\mu\text{mol/mol}$  creatine.

Other biomarkers used to determine exposure to the creosote include urinary concentrations of 1-naphthol, 2-naphthol, and 1-pyrenol. Naphthalene is the main volatile present in creosote vapors. For workers exposed to creosote volatiles during tar distillation, Bieniek (1997) measured volatile

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concentrations of 0.77 mg/m<sup>3</sup> for naphthalene, 0.016 mg/m<sup>3</sup> for 1-naphthol, and 0.012 mg/m<sup>3</sup> for 2-naphthol; corresponding urinary concentrations of 693.1 and 264.4 μmol/mol creatine were measured for 1- and 2-naphthol, respectively.

For workers exposed to creosote by chiseling coal tar pitch layer or by handling creosote-impregnated wood, exposure to total PAHs and 4- to 6-ring PAHs was 50 times higher for the worker exposed to the coal tar pitch layer while exposure to volatile naphthalene was >6 times higher for the wood handlers (Heikkilä et al. 1995). Total PAHs and 4- to 6-ring PAHs were measured at 440 and 290 μg/m<sup>3</sup>, respectively, in the work area of the chiseler. Urinary concentrations of 1-pyrenol were 2–4 times higher for the chiseler compared with the wood handlers. Volatile naphthalene was measured at 1,000 μg/m<sup>3</sup> in the work area of the wood handlers and 160 μg/m<sup>3</sup> in the work area of the chiseler. Urinary concentrations of 1-naphthol were 15–20 times higher for the wood handlers as compared with the chiseler.

Workers in a creosote railroad tie impregnation plant exposed to 1.5 mg/m<sup>3</sup> naphthalene, 5.9 μg/m<sup>3</sup> particulate PAH, and 1.4 μg/m<sup>3</sup> 4- to 6-ring PAHs were measured for the urinary biomarker 1-naphthol (Heikkilä et al. 1997). Postshift urinary concentrations were a mean of 20.5 μmol/L; urinary concentrations in occupationally nonexposed male smokers were below the detection limit of 0.07 μmol/L. The authors concluded that 1-naphthol was a good biomarker for determining exposure to volatile naphthalene from creosote, but was not a good indicator of inhalation or dermal exposure to PAHs from creosote.

Polycyclic aromatic hydrocarbons are capable of forming adducts with DNA in cells. Exposure to PAHs from creosote were measured in the personal work areas of coke oven workers in the Czech Republic (Lewtas et al. 1997). Measured levels of DNA adducts in white blood cells of a nonoccupationally exposed population were well correlated with the low to moderate environmental exposures. The DNA adducts of the coke oven workers who were exposed to carcinogenic PAHs at levels of <math>5\text{--}200,000\text{ ng/m}^3</math> (<math>0.005\text{--}200\text{ }\mu\text{g/m}^3</math>) did not correlate well with the exposure levels. These authors concluded that various mechanisms were responsible for the lower DNA-binding potency at the higher exposure levels, precluding the use of a linear model for dose-response extrapolation in risk assessment.

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**6.6 EXPOSURES OF CHILDREN**

This section focuses on exposures from conception to maturity at 18 years in humans. Differences from adults in susceptibility to hazardous substances are discussed in 3.7 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, 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, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults to avoid hazards (NRC 1993).

Children are exposed to creosote via the same routes that adults are, including inhalation of contaminated air, ingestion of ground water used as a source of drinking water, and dermal contact with contaminated soil or products treated with coal tar creosote. Additionally, small children are more likely than adults to be in close contact with yard dirt or playground dirt, lawns, and indoor (carpet) dust. Creosote residues bound to soil or dust particles in carpets or on bare floors may present an exposure route for infants and toddlers through dermal contact and oral ingestion. Children are known to participate in frequent hand-to-mouth activity and to have a tendency to put foreign objects into their mouths. As a result of this behavior, children may ingest creosote present in soil and dust or through direct transfer of the chemical from their skin to their mouths. Children are lower to the ground than adults and something which may exist at arm or hand level for an adult may be at mouth level for a child. Because of behavior such as putting their mouths on objects or chewing on objects, children may be exposed to coal tar creosote through oral ingestion of the chemical through chewing on treated wood, such as fences, bridge, or pier railings. Adsorption of PAHs may occur through the skin, lungs, and gastrointestinal tract. However, exposure to certain levels of creosote constituents does not mean that the compounds will be bioavailable at those levels. No U.S. data were found on exposure or body burden measurements made on children.

Coal tar creosote is widely used for the preservation and water-proofing of wood which is used for utility poles, railroad ties, log homes, fence posts, barns, bridges, piers, and marine pilings. Creosote is also used in roofing and road paving; is used and/or produced in coke oven operations, and in the aluminum, iron, and steel industries; and is used therapeutically in coal-tar based shampoos, as a treatment for

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psoriasis and eczema, and as a treatment for intestinal ailments. Prior to its designation as a Restricted Use Pesticide in 1986, it was available for home and farm use.

Children are likely to play in or near areas where adults would be less likely to venture, such as areas with no trespassing signs, in creeks, on the ground, in the dirt, in ditches near where utility poles are present, and on or near railroad tracks. Additionally, children are likely to collect and bring home found pieces of wood for use in building clubhouses or treehouses. Because coal tar creosote is used to preserve utility poles and railroad ties, playing near utility (telephone or electrical) poles and near or on railroad tracks may pose a risk of exposure to children. Children are subject to inhalation exposure, which may be of increased risk during warmer months when volatilization of PAHs may be higher. Gevao and Jones (1998) observed greater volatilization of acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene from creosote-treated wood at 30 EC than at 4 EC. However, if the creosote constituents have leached downward from the treated wood and are present in the soil surrounding the utility poles or railroad tracks, volatilization from the soil surface is not as likely, as the majority of the coal tar creosote would be bound to the soil particles. In that case, and in the case of direct contact with treated poles or railroad ties, children are more likely to be exposed dermally and through oral ingestion which may occur when they put unwashed hands in their mouths. No U.S. data were found documenting significant exposure to children through such means as ingested soil or dust particles.

Children may be exposed to coal tar creosote when playing near abandoned hazardous waste sites or if their parents are occupationally exposed to creosote-contaminated soil through involvement with site remediation or clean-up procedures and bring soil-bound contamination into the home on work clothes or footwear, despite preventative procedures which may be in place at the work site. Creosote constituents have been measured in the surface soil at levels as high as 15,680 ppm (PAHs) at the site of an old wood preservation facility in Slidell, Louisiana, that was destroyed by fire (Acharya and Ives 1994). At an abandoned wood treatment facility in Conroe, Texas, PAH constituents of creosote have been detected in the 0.7- to 1.8-foot soil depth at maximum concentrations of 3.7 ppm for naphthalene, 3.4 ppm for methylnaphthalene, 3.8 ppm for dibenzofuran, 4.2 ppm for fluorene, and 2.2 ppm for anthracene (Bendient et al. 1984). At the Koppers Company, Inc. NPL site in Texarkana, Texas, where a creosote wood treatment facility existed for 51 years prior to being converted to a residential area and an industrial site (sand and gravel company), creosote-derived pyrene, fluoranthene, phenanthrene, and anthracene (base/neutral compounds) were measured in surface and subsurface soils at levels ranging from nondetectable to 1,000 ppm (Agency for Toxic Substances and Disease Registry 1994).

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Although biodegradation of creosote in soil, on treated wood, in waste water effluent, and in aquatic environments has been observed, the process may only serve to reduce the total amount of creosote present. While the phenolic and LMW PAHs are degraded, the HMW PAHs that have been shown to resist biological attack may persist. Thus, it is possible that children exposed to the creosote constituents remaining in soil or other media following some biodegradation may be exposed to the more toxic components of creosote. However, the presence of creosote components in soil does not mean that the soil-bound compounds will be bioavailable if ingested. In a study of PAHs and their metabolites in the blood, feces, and urine of rats, the authors observed that rats that were orally exposed to contaminated soils showed significantly higher excretion of unchanged 1-OH-pyrene and benzo[a]pyrene in feces, and significantly lower excretion of 1-OH pyrene in both feces and urine, than did rats that were dosed with the pure compounds, indicating that the ingested soil-bound compounds were less available in the body for metabolism (van Schooten et al. 1997). Similar results were observed in a study of mice that ingested soil-bound coal tar (Koganti et al. 1998). In that study, the bioavailability of PAHs from soil-bound coal tar was estimated to be 9–75% less (based on 1-OH-pyrene excreted in urine) than that observed in mice dosed with an organic extract of the soil; estimates of PAH bioavailability based on chemical-DNA adduct formation ranged from nondetectable to 76%. Other authors have observed differences in bioavailability of soil-bound creosote constituents between types of soil. Goon et al. (1991) observed higher oral bioavailability of soil-bound benzo[a]pyrene with sand soil versus clay soil. The clay fraction of soil is more chemically and physically reactive than the sand fraction, allowing for greater adsorption. In the same study, the authors also observed, however, that the oral bioavailability of the compounds in soil remained at a similar level for the first 30 days following contamination, but decreased by 6 months following the initial contamination.

Children may be exposed to creosote constituents brought into the home by parents or other household members who are occupationally exposed. Creosote residues may be present on clothing items and shoes of workers employed in industries where creosote-derived products are used or produced, and utility company workers who are in contact with treated wood. Exposure to children may occur through dermal contact with contaminated items. Because children are likely to be in close contact with carpet or floors, transfer of contaminated dirt from work shoes to carpeting provides a means of exposure. Respiratory exposure from contact with occupationally exposed workers is not likely to be significant.

A potential source of exposure in infants is the presence of creosote constituents in breast milk. The hydrocarbons found in coal tar creosote are lipophilic substances and, as such, may potentially be found in breast milk, although this has not been assessed. No data were found in the available literature on the



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presence of creosote constituents in breast milk. It has been determined that creosote-derived PAHs may cross the placenta (Agency for Toxic Substances and Disease Registry 1993a). For more information on the health effects of PAHs, the reader is referred to the ATSDR *Toxicological Profile for Polycyclic Aromatic Hydrocarbons* (Agency for Toxic Substances and Disease Registry 1995).

Data were not available in the literature on the weight-adjusted intake of creosote by children. In one documented case, creosote fumes caused methemoglobinemia in an infant, leading to temporary hypoxia and cyanosis (Dean et al. 1992).

Data were not available in the literature on the dietary exposure of creosote to children. Based on the bioaccumulation of creosote constituents in fish and other aquatic organisms, and the potential for uptake or contamination in plant food sources, dietary exposure is theoretically possible, but is unlikely to be significant. An exception to this may be in residential areas such as that built on the old Koppers Company, Inc. site. Homegrown produce grown in contaminated soils may provide a significant source of exposure to children. The drinking of chaparral tea may result in oral exposure to wood creosote. Case reports of people who have drunk chaparral tea indicate kidney damage as a likely outcome (Gordon et al. 1995).

## 6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Individuals living in the vicinity of hazardous waste sites and abandoned wood-treatment plants contaminated with coal tar creosote may experience higher levels of exposure than the rest of the general population. These environmental exposures generally are at a lower dose but of longer duration than the occupational exposures.

Individuals who apply coal tar creosote directly to wood, including farmers, carpenters, and homeowners who come in contact with creosote-treated wood products, are believed to be exposed to the highest levels of creosote components via inhalation and dermal contact. It has been estimated that historically about 4,000 workers may have been routinely exposed and up to 50,000 people may have been intermittently exposed to coal tar creosote through its application as a preservative to wood products (USDA 1980). The size of this population may have decreased since EPA restricted the use of creosote to certified applicators.

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Other individuals who are potentially exposed to coal tar creosote, coal tar, coal tar pitch volatiles, or products containing creosote include coke oven workers, rubber industry or tire plant workers, road paving workers, roofers, chimney cleaners, aluminum smelting workers, iron foundry workers, steel plant workers, and site remediation workers who are involved with creosote-contaminated soils or water.

Whether from bioaccumulation or from direct exposure, fish and shellfish may accumulate creosote constituents at concentrations high enough to prompt public health officials to issue consumption advisories. As of September 1994, creosote was involved in the two fish consumption advisories listed below (EPA 1995):

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State	Waterbody	Geographic Extent
Louisiana	Bayou Bonfouca	7 miles
Oregon	Willamette River	1,000 foot radius from McCormack and Baxter wood treatment site

## 6.8 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 creosote is available. Where adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (NTP), is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of creosote.

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.

### 6.8.1 Identification of Data Needs

**Physical and Chemical Properties.** Limited physical property data, such as boiling point and density (see Table 4-2), are available for the coal tar creosote mixture. Additional physical and chemical property data, such as water solubility, vapor pressure,  $K_{oc}$ , and Henry's law constant values would be useful in order to predict the partitioning and transformation of coal tar creosote components in air, water, and soil. These values are currently not available because their determination is complicated by the fact that creosote is a mixture of variable composition. However, data on vapor pressure, water solubility, etc., are available for individual components of creosote, and these can be used to estimate the behavior of creosote.

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**Production, Import/Export, Use, Release, and Disposal.** Manufacturing methods are well described in the literature. Production figures are limited because of the confidential nature of this business information. Uses of creosote, both coal tar and beechwood, are well described. Since the use of coal tar creosote as a wood preservative has been restricted, the potential of the population to be exposed is greatly diminished. The major releases of creosote resulting from treatment processes at wood-preserving plants are known, but the levels are not well quantified. Current production, release, and disposal information would assist in identifying the levels of creosote present in the environment and, thus, populations potentially exposed as a result of these processes. Creosote sludge from production processes can be treated and disposed on-site with proper groundwater monitoring. Creosote can no longer be disposed in hazardous waste landfills unless treated to EPA specified standards. Creosote-treated wood used in industrial applications can be burned in an industrial incinerator or boiler; however, treated wood used in domestic or farm applications should be buried rather than incinerated.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit substance release and off-site transfer information to the EPA. The TRI, which contains this information for 1999, became available in 2001. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

**Environmental Fate.** The limited information available regarding transport and partitioning of creosote components among environmental compartments indicates mobility of water soluble PAHs, phenol, and heterocyclic constituents of the mixture in water; sorption of PAH components in soils; and bioconcentration of creosote-derived PAHs by terrestrial and aquatic organisms. In an examination of the partitioning of coal tar-derived PAHs into ground water and the usefulness of a computer model to simulate such, Lee et al. (1992) found that theoretically “ideal” behavior was observed for the individual compounds and that the model was useful in estimating concentrations in ground water. This finding indicates that, although coal tar is a complex mixture of compounds with varying physical and chemical properties, the fate of the individual compounds may be modeled as if they were present as single contaminants. Additional studies on the behavior of the transport of the individual components of creosote when present as a mixture may be necessary. Biotransformation appears to be the most important degradation process in soils and aquatic environments. Additional data on the transport of volatile creosote components in the atmosphere and the partitioning of creosote released to surface waters and soils would be useful. Quantitative data on the rates of biotransformation in soils, surface water, and ground water under aerobic and anaerobic conditions would also be useful. Data on the degradation rates or relative persistence of the HMW PAHs would be particularly useful since these components of

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creosote are among the more toxic fraction, and are less soluble and less readily degraded than the LMW PAHs. The importance of other transformation processes, such as photolysis, photooxidation, and hydrolysis, in relation to biotransformation and rates of transport between media, should also be defined. These data would be useful to help define potential pathways of human exposure and to estimate ambient concentrations of creosote components in environmental media.

**Bioavailability from Environmental Media.** Very limited information was found in the available literature regarding the uptake of creosote components by living organisms from contaminated water and soil at hazardous waste sites. Studies have been done with persistent constituents (e.g., PAHs) which show that plant uptake from soils is limited (Agency for Toxic Substances and Disease Registry 1995; Gile et al. 1982), whereas bioconcentration in aquatic organisms from contaminated surface waters has been demonstrated. Data from human and animal studies indicate that creosote components are absorbed following ingestion or inhalation, or after dermal contact with the mixture. Additional data on the bioavailability of creosote components following ingestion or inhalation of creosote-contaminated soils would be helpful. Of particular importance are data on the bioavailability of the HMW PAHs that may persist in soil and are resistant to many bioremediation techniques.

**Food Chain Bioaccumulation.** Very limited information was found in the available literature regarding the biomagnification of creosote-derived compounds among food chain trophic levels. Many aquatic organisms are able to rapidly metabolize and eliminate PAHs, the major constituents of the commercial mixture (Eisler 1987). However, the marsh clam *Rungia cuneata*, which is a major food item for crustaceans such as the blue crab that are part of commercial fisheries, showed tissue concentrations of benzopyrenes up to 600 ppb after 4 weeks of exposure to creosote after a major spill; total PAH levels in the ambient water were #25 ppb (DeLeon et al. 1988). Additional studies are needed to determine whether this bioaccumulation indeed moves up the trophic chain to pose human exposure concerns. Also, vegetables and other produce grown in or around deposits of creosote wastes may uptake or be contaminated by creosote constituents through adsorption to roots or surfaces. Since these materials will be hard to remove through washing or other food preparation processes, consumption of these may provide a route for exposure. Additional data are needed on the ability of agricultural plants to uptake creosote constituents.

EPA (1993) has issued Fish Sampling and Analysis Guidance that provides an overview of the issues involved in considering fish consumption advisories for PAHs. Since PAHs may be derived from

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creosote or other sources such as the combustion of petroleum products, state-issued advisories for PAHs should also be examined to see if creosote-derived sources are at issue.

**Exposure Levels in Environmental Media.** Limited information is available regarding ambient concentrations of creosote-derived PAHs in soils (Davis et al. 1993; EPA 1987b; HazDat 2002) and no data are available regarding atmospheric concentrations of creosote components. Very limited information is available on concentrations of component compounds in surface waters (DeLeon et al. 1988) and sediments (Madsen et al. 1993, 1996), including those receiving wood treatment plant effluents. Data are still lacking for contaminated media in the vicinity of hazardous waste sites. These data would be useful to estimate the exposure of populations coming into contact with components of the mixture through inhalation of contaminated air, consumption of contaminated surface water or ground water, or direct dermal contact with environmental media.

Reliable monitoring data for the levels of creosote in contaminated media at hazardous waste sites are needed so that the information obtained on levels of creosote in the environment can be used in combination with the known body burden of creosote to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

**Exposure Levels in Humans.** A population exists that is potentially exposed to creosote through contact with contaminated media at hazardous waste sites and with treated wood products. A second potentially exposed workforce population exists at wood treatment facilities and in other industries in which creosote-derived products are produced or used. Currently, no information exists that demonstrates tissue levels of any components of the mixture in these populations. Although exposure is now estimated in occupationally exposed workers using urinary concentrations of biomarkers, such as 1-hydroxypyrene, actual exposure levels are harder to determine. Estimates of human exposure to creosote constituents, or body burdens of creosote components, are complicated by the lack of information on exposure to creosote constituents and levels of creosote-derived components in the environment. Collecting information on tissue levels of creosote components in humans would be necessary to examine the relationship between levels of creosote-derived compounds in the environment, human tissue levels, and subsequent development of health effects. This information is necessary for assessing the need to conduct health studies on these populations.

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**Exposures of Children.** Data on the exposure levels and body burden measurements of creosote constituents in children are needed to determine the risks associated with exposure. Because small children are likely to engage in hand-to-mouth activity (with unwashed hands) and to be in close contact with dirt, lawns, and indoor (carpet) dust, and because creosote residues bound to soil or dust particles in carpets or on bare floors, may present an exposure route for infants and toddlers through dermal contact and oral ingestion, bioavailability from soil data are necessary. Bioavailability data are also necessary to determine the amount of contaminant that children may be exposed to through dermal contact with treated wood, such as may occur when children play on railroad tracks. Data on the bioavailability of creosote constituents from treated wood are also necessary because through behaviors such as putting their mouths on objects or chewing on objects, children may be exposed to creosote through oral ingestion of the chemical through chewing on treated wood, such as fences, bridge, or pier railings.

Data are also necessary on whether children are different from adults in their weight-adjusted intake of creosote compounds. Creosote compounds may be present in dietary sources such as fish or food grown in or near contaminated soils. While data on the oral bioavailability of some soil-bound components of creosote are available, it is necessary to determine the exposure contribution of such sources to children and to determine the contribution to body burden in children.

Data are necessary on the number of children (<18 years of age) who may be occupationally exposed to creosote and on the levels of exposure they may experience. It is possible that some workers in industries such as tire plants or those involved in roofing or road paving may be exposed to creosote in their daily tasks. Information on this is may be important in assessing whether occupational exposure in children is similar to the levels observed for all occupationally exposed workers.

Child health data needs relating to susceptibility are discussed in 3.12.2 Identification of Data Needs: Children's Susceptibility.

**Exposure Registries.** No exposure registries for creosote were located. This substance is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The substance 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 this substance.

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**6.8.2 Ongoing Studies**

A search of federally funded research in progress (FEDRIP 2000) revealed several studies that are discussed in this section. Creosote is currently subject to a Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) registration standard and data call-in by EPA. In addition, the Creosote Council II is planning to conduct a research program that includes testing for worker exposure and protection.

Remedial investigation/feasibility studies being conducted at the 46 NPL sites where creosote has been found and at the numerous creosote-contaminated Resource Conservation and Recovery Act (RCRA) corrective action sites should provide data on concentrations of the mixture in contaminated media in the vicinity of hazardous waste sites. For example, creosote constituents have been found in surface water impoundments and soil samples taken near wood treatment facility sites in Colorado, Louisiana, Texas, and Montana.

The Cornell University Superfund Basic Research and Educational Pilot Program was (1992) established with the aim to conduct research on the bioavailability and impact of hazardous substances in health and ecological risk, specifically as related to exposure, neurological, and immunological effects; and the remediation of sites containing polychlorinated biphenyls (PCBs), PAHs, and heavy metals. Relevant areas of study include biodegradation of non-aqueous phase liquids (NAPLs), kinetic controls on environmental fate in soil and aquifers, sequestration in soil and its effects on bioavailability, and microscale parameters modeling macroscale fate in soil. A current study led by Dr. Madsen concerns the determination of factors leading to the persistence of creosote-derived PAHs (naphthalene and phenanthrene) in fresh water sediments at a field site.

The USDA is sponsoring a study by researchers led by Dr. Lee at Purdue University on the interaction of organic chemicals, including coal tar, with soils. Researchers are investigating and modeling the abiotic processes controlling the mobility and bioavailability of organic compounds in soil. They will be determining the adsorption of and release rates of PAHs from a coal tar/soil waste matrix.

The U.S. Geological Survey is investigating the fate and transport of immiscible contaminants, including coal tar and creosote wastes, in subsurface ground water. Models will be developed to simulate and predict the migration of slightly soluble, highly volatile immiscible contaminants in the field. These models will eventually aid in the design of control and abatement techniques.



## 6. POTENTIAL FOR HUMAN EXPOSURE

Researchers at Brown University (Dr. Suuberg principal investigator) are conducting a study funded by OSTI to determine the vapor pressures and heats of vaporization of heavy, primary coal tars. The researchers are attempting to provide needed physical property data by means of direct measurements of the vapor pressures of coal tar fractions. They are also attempting to determine vapor pressures using well-established techniques and modifications of those techniques.

Data from field and laboratory studies of creosote-contaminated ground water are being analyzed by the U.S. Geological Survey to determine the transformation pathways of selected organic compounds, assess the relative importance of physical, chemical, biochemical, and microbial processes in the transformation of these compounds under ambient conditions, and study relevant biotransformation processes occurring in the subsurface ground water.

The National Science Foundation is sponsoring a study led by Dr. Richard Bartha of Rutgers University on the multisubstrate biodegradation kinetics of PAHs from creosote, coal tar, and diesel fuel. The relative biodegradabilities and substrate interactions of PAHs in sole and multi-substrate systems will be determined and related to dissolution kinetics processes governing bioavailability. An integrated mathematical model of the behavior of PAHs in NAPL-contaminated soils will be developed and validated.

The National Science Foundation is sponsoring a study by Princeton University (Dr. Catherine Peters, principal investigator) regarding the chemical, physical, and microbiological processes governing the behavior of mixtures of PAHs in NAPL-contaminated soils.

Dr. Luthy and co-workers at Carnegie-Mellon University, in a study sponsored by Department of Energy, are investigating the physicochemical and biochemical solubilization and mineralization of coal tar-derived PAHs. The study will address the rate-controlling processes for microbial degradation of the PAHs in both the environment and in waste water treatment processes; the kinetics of solute solubilization and rates of mineralization will be determined. The possible synergistic interactions between PAH-degrading bacteria and biosurfactant/emulsifier-producing bacteria will also be investigated. The results of the research should be applicable to both remediation of coal-tar contaminated soils in the environment and treatment systems for coal conversion process effluents.

EPA is sponsoring a study led by Dr. Mahaffey of the Ecova Corporation to develop an *in situ* process that will enhance the rate and efficiency of the biodegradation of hydrophobic organic chemicals at

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military installations and Superfund sites. Research activities will focus on the identification of chemical or biological emulsifiers (surfactants) that will enhance the bioavailability of petrogenic waste (including creosote and coal tars), and thus enhance their biodegradation.

Researchers at Tienzyme, Inc. (B.W. Bogan, principal investigator) in State College, Pennsylvania, are investigating the use of surfactant- or surfactant/lipid-based formulations to enhance the removal of HMW PAHs from creosote- and tar-contaminated soils by bioremediation involving white-rot fungi.

The USDA is sponsoring several studies on creosote. Dr. Chow, Dr. Retner, and co-workers at the University of Illinois are investigating the effects of accelerated aging on the rate of biodegradation of creosote-treated red oak ties by common oak decay fungi. The effects of natural weathering on the rate of biodegradation of creosote-treated ties selected from tracks located in the Midwest will be examined. Computer models will compare the rates of biodegradation results of naturally weathered ties and ties exposed to accelerated aging processes.

Researchers at Mississippi State University (Dr. Borazjini, principal investigator) are investigating the *in situ* bioremediation of creosote and PCP contaminated water in an attempt to develop a rapid biological technique for the cleanup of ground water using oxygen, surfactants, cofactors, and micronutrients. Surfactants will be evaluated for their abilities to enhance the bioremediation of wood-preserving process waste water containing high concentrations of PCP, PAHs, oil, and grease.

Dr. Choong and other researchers at Louisiana State University are investigating the recycling of utility poles for use in engineered wood products. Creosote in the poles will be removed using organic extractants and steam, and the poles will be evaluated to determine their residual decay resistance and to determine the effect of residual creosote on the physical, mechanical, and gluing properties of the used utility poles. The study will include the reduction of the poles into smaller sized, defect-free wood materials for the production of engineered woods, as well as the determination of the effect of joint designs on the strength properties of the wood laminated composites made from the pieces of the poles.