

4. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

4.1 PRODUCTION

The commercial production of PAHs is not a significant source of these compounds in the environment. The primary source of many PAHs in air is the incomplete combustion of wood and fuel (Perwak et al. 1982). PAHs are a ubiquitous product of combustion from common sources such as motor vehicles and other gas-burning engines, wood-burning stoves and furnaces, cigarette smoke, industrial smoke or soot, and charcoal-broiled foods (IARC 1983). Natural sources include volcanoes, forest fires, crude oil, and shale oil (HSDB 1994).

Of the 17 PAHs included in this profile, only three are produced commercially in the United States in quantities greater than research level: acenaphthene, acenaphthylene, and anthracene. Acenaphthene is manufactured by passing ethylene and benzene or naphthalene through a red hot tube or by heating tetrahydroacenaphthene with sulfur to 180 °C. It can also be made from acenaphthenone or acenaphthenequinone by high-pressure hydrogenation in decalin with nickel at 180-240 °C (Windholz 1983). Another manufacturing process involves the isolation and recovery of acenaphthene from a concentrated tar-distillation fraction (Grayson 1978). Technical grades of acenaphthene are typically 98% pure (HSDB 1994). Acenaphthylene is produced by catalytic degradation of acenaphthene (Grayson 1978). Toxic Release Chemical Inventory (TRI) production data for acenaphthylene and acenaphthene are not available (TRI92 1994) and no other data on the production volumes for these compounds in the United States could be found.

Anthracene is produced commercially by recovery from the coal tar distillation fraction known as “anthracene oil” or “green oil.” Purification techniques, including heating and vacuum distillation, are required to remove the major contaminant, potassium carbazole (IARC 1985). Zone melting of solid anthracene and crystallization from benzene followed by sublimation are also effective purification techniques (Hampel and Hawley 1973). Technical grades of anthracene are typically 90-98% pure (HSDB 1994). Table 4-1 shows the number of facilities per state that manufacture or process anthracene, as well as a range of the maximum amounts of anthracene present at the facilities (TR192 1994). The following companies have been cited as current U.S. manufacturers of anthracene for sale/distribution: ABC Coke Division (Tarrant City, Alabama); Granite City Steel (Granite City, Illinois); Citizens Gas and Coke Utility (Indianapolis, Indiana); National Steel Corporation (Encore,

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Table 4-1. Facilities that Manufacture or Process Anthracene

State ^a	Number of facilities	Range of maximum amounts on site in thousands of pounds ^b	Activities and uses ^c
AL	7	1-1000	1, 4, 6, 8, 9
AR	1	1-10	3, 9
CA	1	10-100	1, 5
FL	2	1-100	8
IL	5	10-10000	1, 2, 4, 5, 6, 8, 10
IN	5	1-1000	1, 4, 5, 8
KY	2	1-100	1, 6, 11
LA	7	0-10000	1, 2, 5, 6, 9
MI	2	1-100	1, 4, 5, 6, 8
MN	1	1-10	1, 4
MO	1	1-10	13
MS	2	1-100	1, 6, 8
NJ	3	10-50000	1, 3, 4, 7, 8, 10
NY	2	1-1000	1, 5, 6, 8
OH	12	0-10000	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11
OK	1	10-100	2, 3, 9
PA	7	0-10000	1, 4, 5, 6, 7, 8, 10
SC	2	1-10	5, 8
TX	13	0-10000	1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 13
UT	2	10-50000	1, 3, 4, 7, 10
VI	1	10000-50000	1, 4, 7
WA	2	10-1000	1, 2, 6, 12
WV	3	10-10000	1, 5, 6, 9, 12

Source: TRI92 1994

^aPost office state abbreviations used^bData in TRI are maximum amounts on site at each facility.^cActivities/Uses

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|-------------------------------|----------------------------------|
| 1. Produce | 8. As a formulation component |
| 2. Import | 9. As a product component |
| 3. For on-site use/processing | 10. For repackaging |
| 4. For sale/distribution | 11. As a chemical processing aid |
| 5. As a byproduct | 12. As a manufacturing aid |
| 6. As an impurity | 13. Ancillary or other uses |
| 7. As a reactant | |

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Missouri); Koch Refining Company (Pine Bend, Montana); Amerada Hess Corporation (Port Reading, New Jersey); Reilly Industries, Incorporated (Cleveland, Ohio, and Lone Star, Texas); New Boston Coke Corporation (New Boston, Ohio); Bethlehem Steel Structural (Bethlehem, Pennsylvania); Geneva Steel (Vineyard, Utah); and Hess Oil Virgin Islands Corporation (St. Croix, Virgin Islands). It should be noted that another source (SRI 1994) lists no anthracene processing or manufacturing facilities. In 1982, more than 2,270 kg of anthracene were produced in the United States; more recent production data are not available (HSDB 1994).

The following compounds are not produced commercially in the United States: benz[a]anthracene, benzo[b]fluoranthene, benzo[e]pyrene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-c,d]pyrene, phenanthrene, and pyrene (HSDB 1994; IARC 1985).

4.2 IMPORT/EXPORT

The most recent data available on U.S. import and export volumes of individual PAHs are as follows: in 1986, 4,000 kg of acenaphthene were imported into the United States; in 1985, 5,730,000 kg of anthracene oil, 882,000 kg of anthracene ($\geq 30\%$ purity by weight), 1,040 kg of fluoranthene, and 57,400 kg of pyrene were imported into the United States; in 1984, 79,200 kg of chrysene, 9,440 kg of fluoranthene, 9.1 kg of fluorene, and 551 kg of phenanthrene were imported into the United States; in 1984, 502,000 kg of anthracene oil and pitch of tar coke were exported from the United States, increasing to 3,890,000 kg by 1987 (HSDB 1994; USDOC 1985). In 1985, the United States imported a total of almost 12 million gallons of creosote oil from the Netherlands, France, West Germany, and other countries and almost 185 million pounds of coal tar pitch, blast furnace tar, and oil-gas tar from Canada, Mexico, West Germany, Australia, and other countries (USDOC 1985). The only relevant information found on more recent import and export volumes is for the following group of compounds which contains two PAHs: acenaphthene, chrysene, cymene, and indene (NTDB 1994). Annual import volumes for this group of compounds were 2×10^6 , 3×10^6 , and 9×10^5 kg for the years 1991, 1992, and 1993, respectively. While these numbers set an upper limit on the import volume for any one of the compounds in this group, they do not provide any further information on import volumes of acenaphthene and chrysene.

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4.3 USE

There is no known use for acenaphthylene, benz[a]anthracene, benzo[b]fluoranthene, benzo[e]pyrene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, indeno[1,2,3-c,d]pyrene, or pyrene except as research chemicals (Hawley 1987; HSDB 1994).

Anthracene is used as an intermediate in dye production, in the manufacture of synthetic fibers, and as a diluent for wood preservatives. It is also used in smoke screens, as scintillation counter crystals, and in organic semiconductor research (Hawley 1987). Anthracene is used to synthesize the chemotherapeutic agent, Amsacrine (Wadler et al. 1986). Acenaphthene is used as a dye intermediate, in the manufacture of pharmaceuticals and plastics, and as an insecticide and fungicide (HSDB 1994; Windholz 1983).

Fluorene is used as a chemical intermediate in many chemical processes, in the formation of polyradicals for resins, and in the manufacture of dyestuffs (Hawley 1993; HSDB 1994).

Phenanthrene is used in the manufacture of dyestuffs and explosives and in biological research (Hawley 1987; HSDB 1994). Fluoranthene is used as a lining material to protect the interior of steel and ductile-iron drinking water pipes and storage tanks (NRC 1983).

4.4 DISPOSAL

PAHs serve as the basis for listing certain hazardous wastes under the Resource Conservation and Recovery Act (RCRA); they are listed as constituents for groundwater monitoring and are monitored in hazardous wastes as part of the RCRA land disposal restrictions (EPA 1989c). Specific regulations governing the generation, treatment, storage and disposal of hazardous wastes containing PAHs are listed in Chapter 7.

Approximately two-thirds of the PAHs in surface waters are particle-bound and can be removed by sedimentation, flocculation, and filtration processes. The remaining one-third of the dissolved PAHs usually require oxidation for partial removal/transformation (EPA 1980).

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Acenaphthene, acenaphthylene, benz[a]anthracene; benzo[a]pyrene, benzo[b]fluoranthene, chrysene, dibenz[a,h]anthracene, indeno[1,2,3-c,d]pyrene, and fluoranthene are all good candidates for rotary kiln incineration at temperatures ranging from 820 to 1,600 °C and residence times of seconds for liquids and gases, and hours for solids (EPA 1981a; HSDB 1994). Benz[a]anthracene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, indeno[1,2,3-c,d]pyrene, and fluoranthene all are good candidates for fluidized-bed incineration at a temperature of 450-980 °C and residence times of seconds for liquids and gases and longer for solids (EPA 1981a; HSDB 1994). Benz[a]anthracene also is a good candidate for liquid injection incineration at a temperature range of 650-1,600 °C and a residence time of 0.1 to 2 seconds (EPA 1981a; HSDB 1994). Liquids containing pyrene should be atomized in an incinerator. Combustion is improved by mixing with a more flammable solvent. Solids should be combined with paper or other flammable material prior to incineration (UN 1985). Benz[a]anthracene, chrysene, dibenz[a,h]anthracene, benzo[k]fluoranthene, benzo[j]fluoranthene, benzo[b]fluoranthene, and benzo[a]pyrene laboratory wastes can be oxidized using agents such as concentrated sulfuric acid, potassium dichromate, or potassium permanganate (IARC 1985). Water contaminated with benzo[g,h,i]perylene can be decontaminated by carbon adsorption (EPA 1981c). Anthracene in waste chemical streams may be subjected to ultimate disposal by controlled incineration (HSDB 1994; EPA 1981a).

Bioremediation is emerging as a practical alternative to traditional disposal techniques (Cemiglia 1993; Thomas and Lester 1993; Wilson and Jones 1993). It has only recently been considered as a viable treatment method for contaminated soils but is now being used or is under consideration by the EPA for clean-up in over 135 Super-fund and underground storage tank sites (Carraway and Doyle 1991; Sims 1990; EPA 1989d). *In situ* treatment involves addition of nutrients, an oxygen source, and, sometimes, specifically adapted microorganisms that enhance degradation. Current *in situ* treatments have been used with some success for removal of two- and three-ring PAHs but generally are considered ineffective for removal of most PAHs from soil (Wilson and Jones 1993).

On-site methods such as landfarming also have been used successfully to degrade PAHs with three or fewer aromatic rings. The waste material is applied to the soil as a slurry and the area is fertilized, irrigated, limed, and tilled. The major disadvantage of landfarming is that contaminants can move from the treatment area. To enhance treatment and minimize movement of contaminants, prepared beds have been used. For this type of remediation, the contaminated soil is removed to a specially

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prepared area lined with a low permeability material and the bed is managed to optimize degradation (Wilson and Jones 1993).

A third type of bioremediation involves the use of a bioreactor in a dedicated treatment area. The contaminated soil is excavated, slurried with water, and treated in the reactor. The horizontal drum and airlift-type reactors are usually operated in the batch mode but may also be operated in a continuous mode. Because there is considerable control over the operating conditions, treatment often is quick and effective. Contaminated groundwater and effluent also may be treated in either fixed-film or stirred-tank bioreactors. However, bioreactors are still in the developmental stages and further research is required to optimize their efficiency and cost effectiveness (Wilson and Jones 1993). A pilot-scale evaluation of the bioreactor method was carried out in a joint Superfund Innovative Technology Evaluation (SITE) project and a project to collect information for the Best Demonstrated Available Technologies (BDAT) database (Lewis 1993). Five 64-L bioslurry reactors were charged with a 30% (wt/vol) ratio of creosote-contaminated soil from a Superfund site, inoculated with PAH degraders, and inorganic nutrients were added. Total PAH -degradation averaged $93.4 \pm 3.2\%$ over all reactors during the 12-week study, with 97.4% degradation of the 2- and 3-ring PAHs and 90% degradation of the 4- to 6-ring PAHs.

Huesemann et al. (1993) carried out a 16-week laboratory study to assess the biotreatability of PAHs in refinery American Petroleum Institute (API) oil separator sludge. Two biotic treatments were evaluated: (1) a nutrient-amended, inoculated, aerated slurry reactor, and (2) an oxygen-sparged reactor. A sterile, nitrogen-sparged reactor was used as a control. Naphthalene, anthracene, phenanthrene, and benzo[a]pyrene were completely biodegraded in 4 weeks in both biotic reactors. Chrysene biodegraded in 4 weeks in the aerated reactor and in 16 weeks in the oxygen-sparged reactor. No significant changes in pyrene concentration were observed in the oxygen-sparged reactor and only a 30% degradation was observed in the aerated reactor. The authors concluded that aerobic biotreatment was successful in removing most BDAT PAHs from refinery API oil separator sludge.