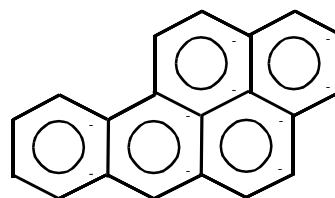


POLYCYCLIC ORGANIC MATTER

Polycyclic organic matter is a federal hazardous air pollutant and was identified as a toxic air contaminant in April 1993 under AB 2728.

CAS Registry Number: 50-32-8

Molecular Formula: $C_{20}H_{12}$



Benzo[a]pyrene

Polycyclic organic matter (POM) consists of over 100 compounds and is defined by the Federal Clean Air Act as organic compounds with more than one benzene ring that have a boiling point greater than or equal to 100 °C.

POM can be divided into the subgroups of polycyclic aromatic hydrocarbons (PAHs) and PAH-derivatives. PAHs are organic compounds which include only carbon and hydrogen with a fused ring structure containing at least two benzene (six-sided) rings. PAHs may also contain additional fused rings that are not six-sided. PAH-derivatives also have at least two benzene rings and may contain additional fused rings that are not six-sided rings. However, PAH-derivatives contain other elements in addition to carbon and hydrogen (CAPCOA, 1993).

In general, POM exists as a gas when its molecular weight is below 230 grams per mole, and is a particle above this molecular weight. This means that compounds with two rings (e.g., naphthalene) exist as a gas. Compounds with three to four rings (e.g., pyrene) exist either as a gas or particle depending on the temperature and pressure. Compounds with five rings (e.g., dibenzo[a,h]anthracene, benzo[a]pyrene) exist as particles in the atmosphere (Atkinson, 1995).

PAHs are primarily planar, nonpolar compounds that melt well above room temperature (U.S. EPA, 1987f). Generally, PAHs exist as colorless, white, or pale yellow-green solids that are attached to particulate matter. PAHs may also exist as solids in soil or sediment (ATSDR, 1993d). PAH-derivatives include nitro-PAHs, amino-PAHs, and oxygenated PAHs (phenols, quinones, and heterocyclic aromatic compounds containing sulfur and oxygen (Finlayson-Pitts and Pitts, Jr., 1986).

Benzo[a]pyrene is a PAH and is soluble in benzene, toluene, and xylene, but practically

insoluble in water (Merck, 1983). The following table lists the physical properties of benzo[a]pyrene.

Physical Properties of Benzo[a]pyrene

Synonyms: 3,4-benz[a]pyrene; benz[a]pyrene; BaP; BP

CAS Registry Number:	50-32-8
Molecular Formula:	C ₂₀ H ₁₂
Molecular Weight:	252.30
Boiling Point:	360 °C
Melting Point:	179 °C
Vapor Pressure:	1 mm Hg at 20 °C
Vapor Density:	8.7 (air = 1)
Density/Specific Gravity:	1.351
Log Octanol/Water Partition Coefficient:	6.04
Conversion Factor:	1 ppm = 10.3 mg/m ³

(HSDB, 1995; Merck, 1989; Sax, 1989; U.S. EPA, 1994a)

SOURCES AND EMISSIONS

A. Sources

POM is produced by the incomplete combustion of fossil fuels and vegetable matter. PAHs have been detected in motor vehicle exhaust, smoke from residential wood combustion, and fly ash from coal-fired electric generating plants (Finlayson-Pitts and Pitts, Jr., 1986). The primary stationary sources that have reported emissions of benzo[a]pyrene in California are petroleum refineries, industrial machinery manufacturers, and the wholesale trade in petroleum and petroleum products. The primary stationary sources that have reported emissions of PAHs in California are paper mills, manufacturers of miscellaneous wood products, and petroleum refining (ARB, 1997b).

B. Emissions

The total emissions of PAHs from stationary sources in California are estimated to be about 370,000 pounds per year, based on data reported under the Air Toxics “Hot Spots” Program (AB 2588). The table below lists the portion of these emissions of the individual isomers of PAHs. There are also approximately 2,600 pounds of unspecified polycyclic organic compounds and 250,000 pounds of unspecified PAHs in addition to those listed individually (ARB, 1997b).

Emissions for Individual PAH Isomers

Compound	Emissions (pounds/year)
Acenaphthene	6
Acenaphthylene	27
Anthracene	285
Benzo[a]pyrene	304
Benzo[a]anthracene	175
Benzo[b]fluoranthene	175
Benzo[k]fluoranthene	181
Benzo[g,h,i]perylene	10
Chrysene	275
Dibenz[a,h]anthracene	211
Dibenz[a,e]pyrene	3
Fluoranthene	
23	
Fluorene	32
Indeno[1,2,3-cd]pyrene	204
Naphthalene	360,000
Phenanthrene	63
Pyrene	42

(ARB, 1997b)

C. Natural Occurrence

POM can be formed from any naturally-occurring combustion, such as forest fires (U.S. EPA, 1994a). Benzo[a]pyrene occurs in crude oils, shale oils, and coal tars, and is emitted with gases and fly ash from active volcanoes (HSDB, 1995).

AMBIENT CONCENTRATIONS

Several PAHs are routinely monitored by the statewide Air Resources Board (ARB) air toxics network. The table below gives the network's mean concentration, in nanograms per cubic meter (ng/m³), of various PAHs from January 1996 through December 1996 (ARB, 1997c).

PAH Compound	Mean Concentration (ng/m ³)
Benzo[a]pyrene	0.194
Benzo[b]fluoranthene	0.245
Benzo[g,h,i]perylene	0.619
Benzo[k]fluoranthene	0.100
Dibenz[a,h]anthracene	0.031
Indeno[1,2,3-cd]pyrene	0.327

When benzo[a]pyrene was formally identified as a toxic air contaminant, the ARB estimated a population-weighted annual ambient concentration of 0.53 ng/m³ based on 1988 to 1989 monitoring data (ARB, 1994e).

The United States Environmental Protection Agency (U. S. EPA) has also compiled ambient concentration data from several study areas throughout the United States during 1984-91. The overall mean concentration for POM was 8.4 ng/m³ (U.S. EPA, 1993a).

INDOOR SOURCES AND CONCENTRATIONS

According to two large field studies conducted in California, the major sources of indoor PAHs are tobacco smoking, woodburning in fireplaces and wood stoves, and infiltration of polluted outdoor air (ARB, 1992b; Sheldon et al., 1993).

The largest field study was conducted in northern California and measured 13 PAHs inside 280 homes during the winter. Concurrent outdoor samples were collected at each home for 24 hours. The homes were selected based upon the occupants' use of tobacco, fireplaces, wood stoves, and gas heat. The table below lists the average indoor concentrations for some PAHs

for each type of combustion source. Average indoor PAH levels ranged from about one-fourth

to 6 times the average of outdoor levels. When compared to concentrations inside homes with

no obvious combustion sources ("no source"), substantially higher concentrations of all 13 PAHs were measured inside homes where smoking occurred. In addition, woodburning in fireplaces and wood stoves appeared to cause slight to moderate increases in concentrations of benzo[a]anthracene, chrysene, benzo[fluoranthene], and benzo[a]pyrene indoors.

Investigators estimated that infiltration of polluted outdoor air was also a major contributor to concentrations of PAHs indoors, particularly outdoor air polluted by woodsmoke (Sheldon et al., 1993).

Average PAH Concentrations in Northern California Homes (ng/m³)

PAH Compound(s)	Smoking	Fireplace	Woodstove	Gas Heat	No Source
Benzo[a]pyrene	2.2	1.0	1.2	0.41	0.83
Benzo[e]pyrene	1.1	0.49	0.55	0.25	0.42
Indeno[ghi]perylene	2.8	1.7	1.9	0.92	1.4
Benzo[ghi]perylene	2.0	1.4	1.5	0.78	1.3
Pyrene	4.1	2.0	2.5	1.6	1.8
Chrysene	2.0	0.56	0.61	0.24	0.4
Fluoranthene	4.5	1.9	2.3	1.4	1.6
Benzo[a]anthracene	1.3	0.43	0.55	0.17	0.32
Benzo[fluoranthene]	3.7	1.6	2.0	0.81	1.5

(Sheldon et al., 1993)

Another field study measured 12 PAH compounds inside 125 southern California homes during a relatively warm fall season. At each home, two consecutive 12-hour samples were collected. Concurrent samples were also collected outside 65 of those homes. Average indoor PAH concentrations ranged from about one-half to two times the corresponding outdoor levels. The table below shows average concentrations (combined daytime/nighttime) for some PAHs. Levels of most PAHs were significantly higher in homes where smoking occurred than in nonsmokers' homes. As in the northern California study, investigators estimated that infiltration of polluted outdoor air was a major source of PAHs indoors (ARB, 1992b).

Average PAH Concentrations in Southern California Homes (ng/m³)

PAH Compound(s)	Indoor Average	Outdoor Average
Benzo[a]pyrene	0.70	0.30
Benzo[e]pyrene	0.39	0.28
Indeno[ghi]perylene	1.1	0.51
Benzo[ghi]perylene	2.4	1.0
Pyrene	2.8	2.2
Chrysene	0.30	0.39
Fluoranthene	2.2	2.5
Benzo[a]anthracene	0.16	0.18

(ARB, 1992b)

Concentrations of chrysene, benzo[b]fluoranthene, benzo[d]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[ghi]perylene, and indeno[1,2,3-cd]pyrene were measured in 17 public office buildings in Oregon and Washington. PAH levels were higher in smoking areas than in nonsmoking areas; investigators measured an average total PAH concentration of about 9.4 ng/m³ in the smoking areas, but only 2.4 ng/m³ in the nonsmoking areas (Turk et al., 1987).

ATMOSPHERIC PERSISTENCE

Benzo[a]pyrene exists almost entirely in the particle phase in the atmosphere, and hence subject to wet and dry deposition. The average half-life and lifetime for particles in the troposphere is estimated to be about 3.5 to 10 days and 5 to 15 days, respectively. In addition, photolysis and reaction with ozone of particle-associated benzo[a]pyrene may occur, leading to

a shorter overall half-life and overall lifetime of benzo[a]pyrene than estimated from wet and dry deposition of the host particles alone (Balkanski et al., 1993; Atkinson, 1995).

Benzo[a]pyrene generally associates in the atmosphere with particulate matter three microns or less in size. Benzo[a]pyrene comprises no more than 5 percent of the total PAHs present in the atmosphere (Ronia, et al., 1983).

Besides benzo[a]pyrene, other PAHs are emitted or formed in the atmosphere. Volatile, 2- to 4-ring PAHs present in POM exist in the atmosphere at least partially in the gas phase. These gas-phase PAHs react with hydroxyl (OH) radicals, NO₃ radicals, and ozone in the atmosphere, with the OH radical reaction generally dominating as the PAH loss process (Atkinson and Arey, 1994). The estimated half-lives and lifetimes of the 2- and 4-ring volatile PAHs in the atmosphere due to reaction with the OH radical are in the range of 2 to 19 hours and 3 to 27 hours, respectively (Atkinson and Arey, 1994). The products of the OH radical reactions include hydroxyl-PAH, nitro-PAH (in low, less than 5 percent, yield), and ring-opened dicarbonyls.

Although generally of minor importance as a PAH atmospheric loss process, the nighttime NO₃ radical reactions lead to the formation of nitro-PAH in high yields for certain PAH (naphthalene, 1- and 2-methylnaphthalene and fluoranthene) and the NO₃ radical reactions can be an important atmospheric route to the formation of mutagenic nitro-PAH (Atkinson and Arey, 1994). The atmospheric photooxidations of phenanthrene and pyrene lead to the formation, in low yield, of nitro-PAH lactones (Atkinson, 1995).

AB 2588 RISK ASSESSMENT INFORMATION

The Office of Environmental Health Hazard Assessment reviews risk assessments submitted under the Air Toxics “Hot Spots” Program (AB 2588). Of the risk assessments reviewed as of April 1996, PAHs were a major contributor to the overall cancer risk in 43 of the approximately 550 risk assessments reporting a total cancer risk equal to or greater than 1 in 1 million, and contributed to the total cancer risk in 166 of these risk assessments. PAHs also were the major contributor to overall cancer risk in 8 of the approximately 130 risk assessments reporting a total cancer risk equal to or greater than 10 in 1 million, and contributed to the total cancer risk in 54 of these risk assessments (OEHHA, 1996a).

Indeno[1,2,3,-cd]pyrene and dibenz[a,h]anthracene each contributed to the total cancer risk in 2 of the approximately 550 risk assessments reporting a total cancer risk equal to or greater than 1 in 1 million. Indeno[1,2,3,-cd]pyrene also contributed to the total cancer risk in 1 of the approximately 130 risk assessments reporting a total cancer risk equal to or greater than 10 in 1 million (OEHHA, 1996a).

Benzo[a]anthracene, benzo[a]pyrene, and benzo[k]fluoranthene each contributed to the total cancer risk in 1 of the risk assessments reporting a total cancer risk equal to or greater than 1 in 1 million (OEHHA, 1996a).

HEALTH EFFECTS

Probable routes of human exposure to POM are inhalation, ingestion, and dermal contact.

Non-Cancer: No information is available on the acute effects of POM in humans. Enzyme alterations in the mucosa of the gastrointestinal tract and increased liver weights have been reported in animals exposed orally to several PAHs. Chronic exposure to benzo[a]pyrene in humans has resulted in dermatitis, photosensitization in sunlight, eye irritation and cataracts. Animal studies have reported effects on the blood and liver from oral exposure to benzo[a]pyrene and effects on the immune system from dermal exposure to benzo[a]pyrene (ATSDR, 1993d).

The U.S. EPA has not established a Reference Concentration (RfC) or an oral Reference Dose (RfD) for POM or for benzo[a]pyrene (U.S. EPA, 1994a).

No information is available on adverse reproductive or developmental effects of POM in humans (U.S. EPA, 1994a). Oral exposure to benzo[a]pyrene in animals has been reported to result in adverse reproductive effects, including reduced incidence of pregnancy and decreased fertility, and developmental effects such as reduced viability of litters and reduced mean pup weight, and decreased fertility in offspring (U.S. EPA, 1994a; ATSDR, 1993d). Benzo[a]pyrene has been demonstrated to cause transplacental carcinogenesis in animals (ATSDR, 1993d).

Cancer: Results from epidemiologic studies have indicated an increase in lung cancer occurs in humans exposed to coke oven emissions, roofing tar emissions, and cigarette smoke. Each of these mixtures contains a number of PAHs. Respiratory tract tumors have been reported in animals exposed via inhalation to benzo[a]pyrene and forestomach tumors, leukemia, esophageal and laryngeal tumors from oral exposure (U.S. EPA, 1994a).

The U.S. EPA has classified benzo[a]pyrene in Group B2: Probable human carcinogen, and has calculated an oral unit risk estimate of 2.1×10^4 (microgram per liter)⁻¹. This means that if an individual were to ingest water containing benzo[a]pyrene at 0.005 micrograms per liter over an entire lifetime, that person would theoretically have no more than a 1-in-1-million increased chance of developing cancer (U.S. EPA, 1994a). The International Agency for Research on Cancer (IARC) has classified benzo[a]pyrene in Group 2A: Probable human carcinogen based on sufficient evidence in animals and limited evidence in humans (IARC, 1987a).

The State of California has determined under Proposition 65 that several POM compounds (including benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, chrysene, indeno[1,2,3-cd]pyrene, 3,7-dinitrofluoranthene, and 3,9-dinitrofluoranthene) are carcinogens (CCR, 1997). The inhalation potency factor that has been used as a basis for regulatory action in California is 1.1×10^3 (microgram per cubic meter)⁻¹ for benzo[a]pyrene (OEHHA, 1994). In other words, the most potential excess cancer risk for a person exposed over a lifetime to 1 microgram per cubic meter of benzo[a]pyrene is 1,100 in one million. The oral potency factor that has been used as a basis

for regulatory action in California is 12 (milligram per kilogram per day)¹ for benzo[a]pyrene (OEHHA, 1994).

There are also a number of PAHs now listed that do not have specific cancer potency factors, but can be assessed using a relative potency scheme with benzo[a]pyrene as a reference compound. These compounds and the suggested potency equivalency factor (PEF) are listed below. The PEF may be used for both inhalation and oral exposure pathways, although data used for their development were prioritized so inhalation exposure was given higher priority than other routes of exposure. This weighting scheme for PAHs was developed by the Air Toxicology and Epidemiology Section of the Office of Environmental Health Hazard

Assessment in the document entitled Benzo[a]pyrene as a Toxic Air Contaminant (ARB, 1994e). When a specific potency value is developed for a chemical, it should be used in place of the PEF.

Potency Equivalency Factors (PEF)

<u>PAH or Derivative</u>	<u>CAS Number</u>	<u>Suggested PEF</u>
benzo[a]pyrene	50-32-8	1.0 (index compound)
benzo[a]anthracene	56-55-3	0.1
benzo[b]fluoranthene	205-99-2	0.1
benzo[j]fluoranthene	205-82-3	0.1
benzo[k]fluoranthene	207-08-9	0.1
dibenz[a,j]acridine	224-42-0	0.1
dibenz[a,h]acridine	226-36-8	0.1
7H-dibenzo[c,g]carbazole	194-59-2	1.0
dibenzo[a,e]pyrene	192-65-4	1.0
dibenzo[a,h]pyrene	189-64-0	10
dibenzo[a,i]pyrene	189-55-9	10
dibenzo[a,l]pyrene	191-30-0	10
indeno[1,2,3-cd]pyrene	193-39-5	0.1
5-methylchrysene	3697-24-3	1.0
1-nitropyrene	5522-43-0	0.1
4-nitropyrene	57835-92-4	0.1
1,6-dinitropyrene	42397-64-8	10
1,8-dinitropyrene	42397-65-9	1.0
6-nitrocrysene	7496-02-8	10
2-nitrofluorene	607-57-8	0.01
chrysene	218-01-9	0.01
dibenz[a,h]anthracene*	53-70-3	0.4
7,12-dimethylbenzanthracene*	57-97-6	21.8

3-methylcholanthrene*	56-49-5	1.9
5-nitroacenaphthene*	602-87-9	0.01

The nitro PAHs are those listed as IARC class 2B. Although chrysene is an IARC class 3 carcinogen, the U.S. EPA classifies it as Group B2 (ARB, 1994e).

* An inhalation unit risk factor has been developed for this PAH for purposes of implementing Proposition 65. PEF determined by dividing the inhalation unit risk factor for the PAH by the inhalation unit risk factor for benzo[a]pyrene.