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POLYCYCLIC AROMATIC HYDROCARBONS (PAH)
A Candidate Toxic Air Contaminant

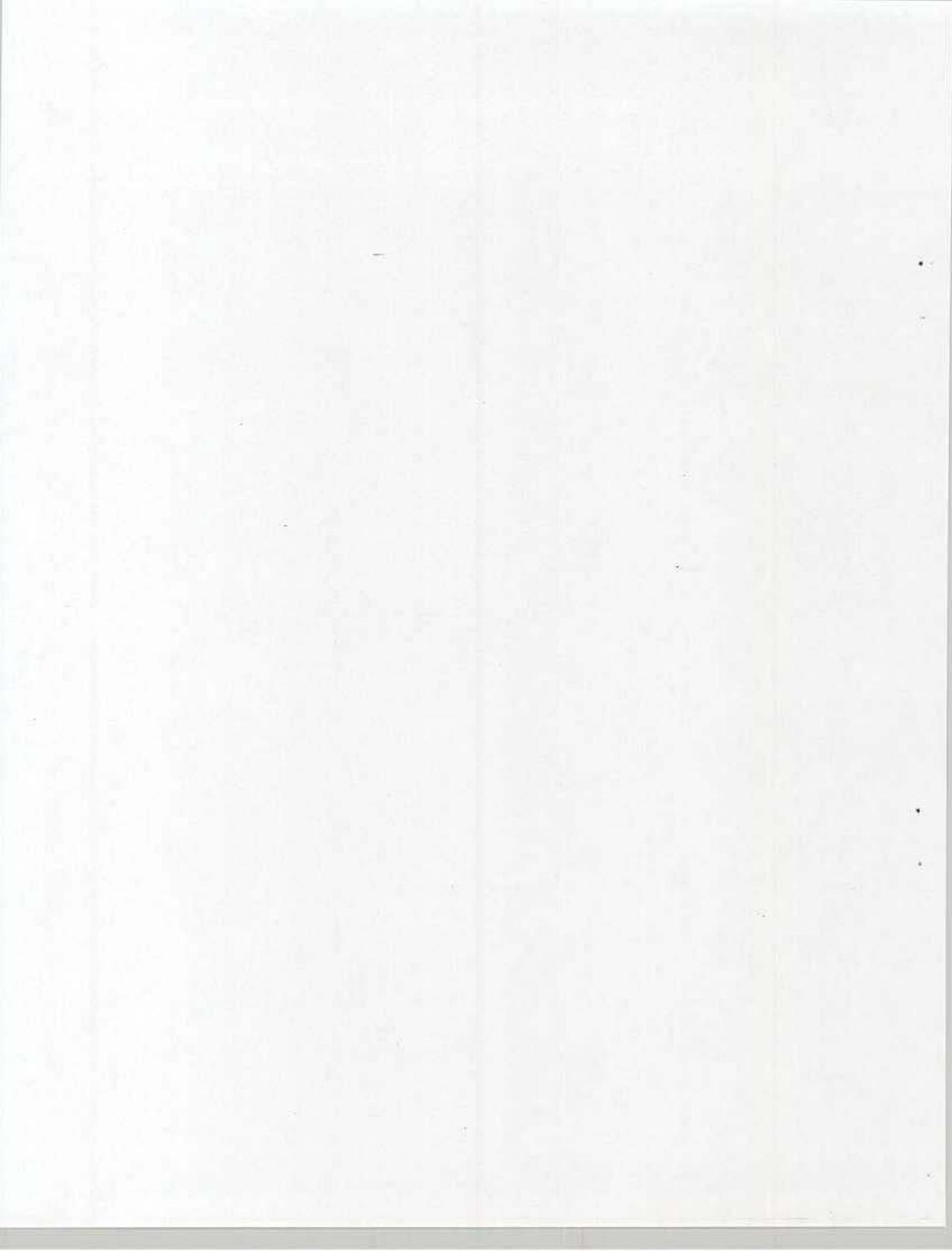
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Ralph Propper
Stationary Source Division
AIR RESOURCES BOARD
1102 Q Street
Sacramento, CA 95814

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POLYCYCLIC AROMATIC HYDROCARBONS (PAH):
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SUMMARY

Extracts of ambient particulates collected from Los Angeles photochemical smog in the early 1950's were found to be carcinogenic in experimental animals. Also in the early 1950's, benzo[a]pyrene (BaP), a PAH compound known to be a powerful carcinogen, was found in ambient particles collected in Great Britain. In 1977, such extracts were shown to be directly mutagenic (i.e., without microsomal activation, -S9) in the Ames bacterial assay. Since PAHs require such activation to express their mutagenicity (+S9), these results showed that ambient particles contain other compounds of concern, which may be derived from PAHs.

Polycyclic aromatic hydrocarbons (PAHs) are a complex class of compounds with a characteristic structure of fused aromatic rings. The simplest member of the PAH family is naphthalene. This two-ring compound is found in the vapor phase PAHs consisting of five or more rings tend to be solids adsorbed onto particulate matter; while those consisting of two to four rings tend to be distributed between the vapor and solid phases.

PAHs are ubiquitous. Many of them are bacterial mutagens; some are highly carcinogenic. Furthermore, some of their nitro-derivatives found on both primary respirable particles (e.g., diesel soot) and ambient particles are powerful bacterial mutagens, and some are animal carcinogens. PAHs are emitted as products of incomplete combustion and pyrolytic processes. PAHs which are particle-associated can persist in the atmosphere for several days to several weeks depending on particle size and atmospheric conditions. For these PAHs, the main mechanism of removal from the atmosphere is wet or dry deposition. PAHs present in the gas phase generally persist for shorter periods, due to atmospheric reactions. For example, during daylight hours, all PAHs react with hydroxyl radicals and nitrogen dioxide to form nitro-PAHs. Reaction with dinitrogen pentoxide at nighttime is usually slower, but can be important for the formation of such nitro-PAHs.

Most of the measured larger PAH compounds reside on respirable particles. BaP has been used as a surrogate PAH. However, BaP levels may not be a good indicator of total PAH in the ambient air because of its atmospheric reactivity, especially in smoggy environments. BaP levels have been declining over the years, but could rise due to increased wood burning, refuse combustion, and diesel fuel use. Winter levels tend to be higher than summer levels.

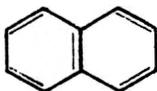
CHEMISTRY AND ANALYTICAL METHODS

A. CHEMISTRY

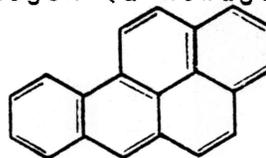
PAHs are formed during the incomplete combustion of organic matter (e.g., gasoline combustion and wood-burning stoves). The mechanism of formation of PAH is assumed to involve the production of free radicals of hydrocarbons in the chemically reducing zone of a flame burning with a supply of oxygen insufficient for complete combustion. These radicals combine to form PAHs which, upon cooling, may volatilize or condense onto particulate matter.

PAHs have a structure based on fused benzene rings, and occasionally a cyclopenta-fused ring. Following are structural formulas for (a) naphthalene, the simplest PAH compound, and (b) benzo[a]pyrene, a potent human carcinogen (a hexagon indicates an aromatic benzene ring):

(a)



(b)



PAHs have very low solubility in water, although oxidized derivatives may have appreciable solubility. All PAHs absorb ultraviolet visible light quite strongly, which can assist in their identification and quantification. For a review, see Finlayson-Pitts and Pitts, 1986.

B. SAMPLING AND ANALYSIS

A widespread sampling method has been hi-vol sampling on glass fiber filters. The organic fraction is separated from the rest of the collected particulate matter by extraction into an organic solvent. Many uncertainties result from such sampling, however. The material so extracted can include much non-PAH material, and subsequent definitive analysis is difficult and has often not been done. Particulate sampling will exclude the significant volatile PAH components, which can be blown off filters during sample collection. Reactions sometimes occur on the filters, creating artifacts.

More recent sampling methods include the use of a variety of polymeric adsorbents to collect the volatile constituents as well as the particle-associated PAHs (and minimize artifact formations), followed by rapid sample analysis. Still, no definitive ambient concentrations for overall PAH in California have yet been reported. Some data should be available in early 1988 as the result of work contracted by the ARB, being conducted by the University of California's Statewide Air Pollution Research Center (SAPRC).

Instrumental techniques for the characterization, identification, and measurement of PAH in extracts of environmentally relevant samples include various chromatographic and spectrometric techniques, such as MS, GC-MS, GC, HPLC, MS-MS.

PAH EMISSION SOURCES

Emissions of PAHs can be divided into two general categories: stationary combustion sources and mobile sources. In most of the state's urban areas, most of the emissions are probably from mobile sources. Table 1 presents emissions estimated by ARB's Emissions Inventory Branch in 1987 for California. All estimates are for 1984 emissions, except for wood (1981), wild fires (1983), agricultural burning and related (1983), and about 60% of the coal, oil, and gas category (1983).

Table I
ESTIMATED PAH SOURCE CATEGORIES AND EMISSIONS IN CALIFORNIA

<u>Sources</u>	<u>Emissions (tons)</u>
Stationary Combustion	
Wood	89
Wild Fires	19
Agricul. Burning and Related	118
Coal, Oil, and Gas	3.6
Mobile Sources	<u>55</u>
Total:	285 tons

As the table shows, residential wood burning and agricultural burning are the two largest sources of PAH emissions. Wood burning is an increasing source of emissions. Other stationary combustion sources include commercial and industrial boilers, and incineration of municipal solid waste and hazardous waste. PAHs are also emitted from industrial processes, including iron and steel production, catalytic cracking of petroleum, production of asphalt-based paving and roofing products, and production of carbon black and charcoal (EPA, 1983 A). Mobile sources contribute PAHs from exhaust emissions and tire wear. PAH concentrations in diesel exhaust are significantly higher than in gasoline-engine exhaust, especially when the latter involves light-duty engines equipped with catalytic converters.

Nitro-PAHs in the ambient air (such as 1-nitropyrene and 9-nitroanthracene) are due to direct emissions and also result from atmospheric transformation of the parent PAHs (Finlayson-Pitts and Pitts, 1986). The most abundant particle-associated nitro-PAH in California air has been shown to be 2-nitrofluoranthene (Arey et al., 1987). Current evidence suggests that it is produced by a gas-phase reaction of fluoranthene with nitrogen dioxide, initiated by hydroxyl radical attack (Pitts et al., 1985).

Indoor air exposures to PAHs result from tobacco smoke, wood-burning stoves, and other indoor activities. Exposure also results from eating some foods (NRC, 1983).

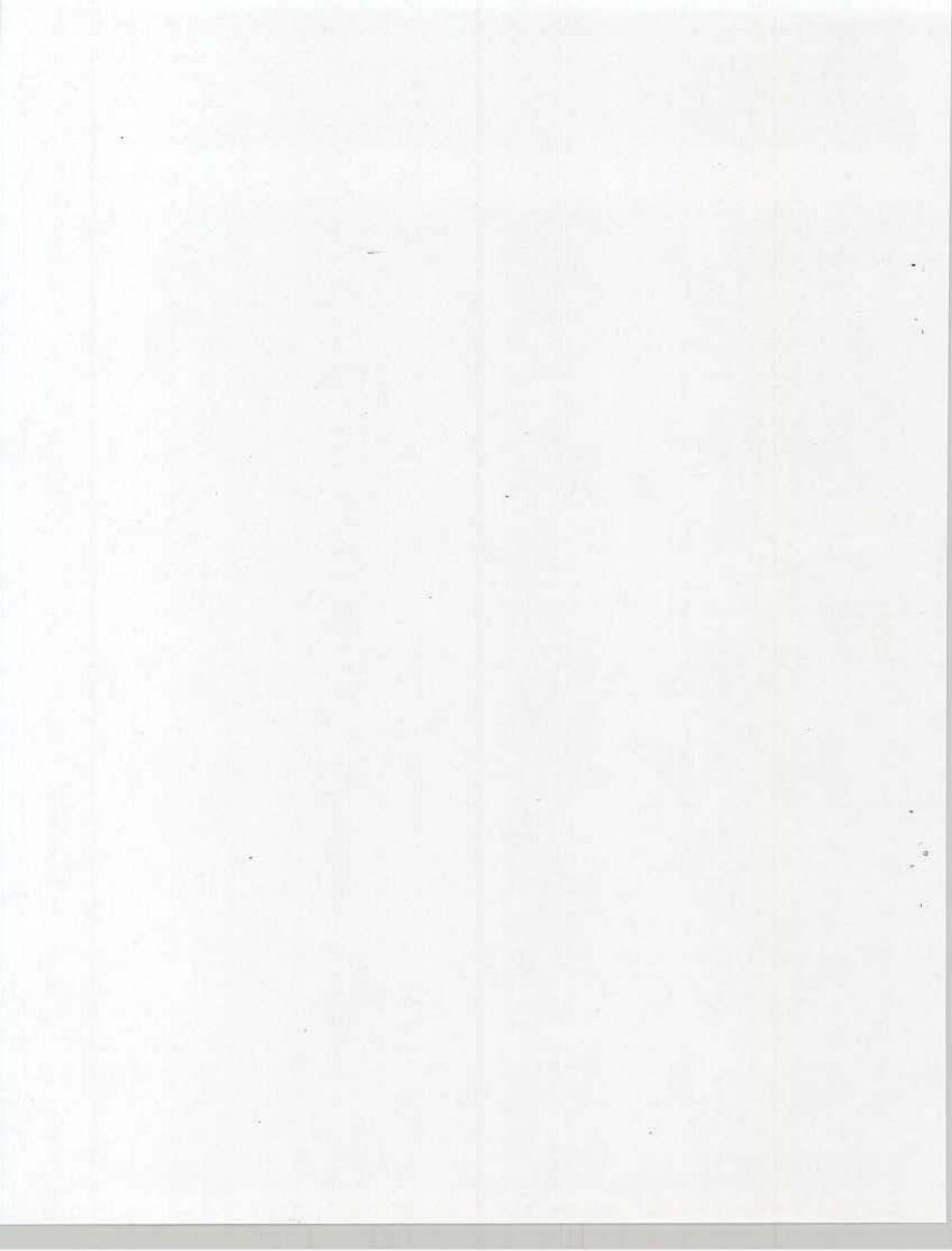
AMBIENT CONCENTRATIONS OF PAH

Roughly ten percent of benzene-soluble organic materials extracted from collected particulate matter may consist of PAHs. Therefore, particulate PAH concentrations in Contra Costa County may range up to approximately 100 ng/m³, and volatile PAH concentrations may be an order of magnitude higher (Flessel et al, 1987). Concentrations measured in California by various researchers are difficult to compare because not all measure the same types of PAHs, and because volatile PAHs have only recently been measured. Furthermore, mixtures and concentrations vary by location, season and time of day.

In a recent literature review of indoor concentrations, McCann et al. (1986) reported a range of mean or median values for BaP of 0.0007 to 0.0135 ug/m³.

Nitro-PAHs often have very high bacterial mutagenicity (both direct-acting [-S9], and with microsomal activation [+S9]). Particulate nitro-PAH levels are typically present at levels of a few percent of the parent PAH. Nitro-PAHs can also result from atmospheric conversion of parent PAHs, as noted above. In Torrance (Arey et al., 1987), daytime levels of 2-nitrofluoranthene were half as high (at 0.3 ng/m³) as BaP levels.

Mutagenicity data for ambient air can also be provided. Flessel et al. (1985) found a seasonally averaged concentration in Contra Costa County of about 20 revertants/m³ (rev/m³) (+S9), and about half that value without S9. Concentrations during peak commute periods near LA freeways (Finlayson-Pitts & Pitts, 1985) ranged up to about 120 rev/m³ (-S9) (hourly average). In Torrance, Arey et al. (1987) found 120 rev/m³ (-S9), with a few percent of that due to nitro-PAH. Much of the rest may be due to more complex PAH such as hydroxy-nitro-PAHs, or to other as-yet unknown PAH derivatives. Results from a current ARB monitoring contract (Atkinson et al., 1987) show up to 140 rev/m³ (+S9) and 130 rev/m³ (-S9) at Martinez (near Industry), and up to 84 rev/m³ (+S9) and 15 rev/m³ (-S9) at Mammoth Lakes (wood smoke impact) in February, 1987.



V. HEALTH EFFECTS SUMMARY

The health effect of most concern in considering PAHs is cancer due to chronic exposures. IARC (March 1987 working group) considers three complex materials or processes (coal tars, coal-tar pitches, and coke production) to be in Group 1, known human carcinogens. These materials or processes involve PAHs. In Group 2A, probable human carcinogens, IARC includes benz[a]anthracene, benzo[a]pyrene, and dibenz[a,h]anthracene. In Group 2B, possible human carcinogens, IARC includes at least three benzofluoranthenes (b, j and k), four dibenzopyrenes (a,e; a,h; a,i; a,l) and 5-nitroacenaphthene. Several nitro-PAHs have been found to be more potent mutagens than the parent PAHs and of concern as carcinogens (Rosenkranz and Mermelstein, 1985; Wislocki et al., 1986). Animal carcinogenicity data is also available for some nitro-PAHs, such as nitropyrenes. Of 37 PAHs detected in air, EPA rated 16 as carcinogenic and ten of those as strongly carcinogenic (EPA, 1979).

Various health data also exist for diesel exhaust inhalation, as well as for animal skin painting with other PAH-containing extracts from other combustion sources. Inhalation of diesel exhaust has been shown to be carcinogenic (Rosenkranz and Mermelstein, 1985).

EPA's Carcinogen Assessment Group has developed a unit risk value for benzo[a]pyrene (BaP) of 3.4×10^{-3} per $\mu\text{g}/\text{m}^3$. Using this unit risk value and the value of $0.46 \text{ ng}/\text{m}^3$ annual average of BaP from Table 2, an individual risk value for BaP alone of 1.6×10^{-6} can be calculated. Although considerable literature on BaP exists, it may not be the best indicator of the biologic effects of total PAHs (NRC, 1983). One of the challenges of the health effects assessment will be devising an appropriate weighting system for the various PAHs or their source categories.

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