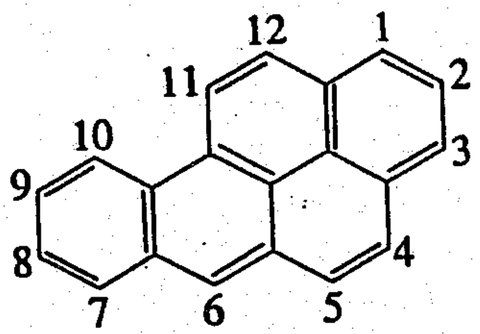
California Environmental Protection Agency

Air Resources Board

Benzo[a]pyrene

as a Toxic Air Contaminant



Part A
Exposure Assessment

July 1994

BENZO[a]PYRENE AS A TOXIC AIR CONTAMINANT

PART A

TECHNICAL SUPPORT DOCUMENT
PUBLIC EXPOSURE TO SOURCES AND EMISSIONS OF
BENZO[a]PYRENE IN CALIFORNIA

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July 1994

ACKNOWLEDGMENTS

The following people contributed to the preparation and review of this document: Michele Burkett, Faye Palmer, Doug Lawson, Steve Brisby, Peggy Jenkins, Michael Poore, and Chris Nguyen.

REPORT TO THE AIR RESOURCES BOARD ON BENZO[a]PYRENE

Part A - Public Exposure To Sources and Emissions of Benzo[a]pyrene in California

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I.

INTRODUCTION

This report summarizes the emissions, concentrations, exposure, and atmospheric persistence and fate of benzo[a]pyrene (BaP) in California. It also summarizes the health effects of BaP which includes an estimate of cancer potency. BaP is a component of a complex mixture of combustion-generated PAHs, several of which, according to the International Agency for Research on Cancer (IARC), are probable human carcinogens.

This report was developed in response to provisions of AB 1807 (Health and Safety Code sections 39650-39662), which became effective in January 1984. This legislation requires a two-phase process which separates risk assessment (identification) of toxic air contaminants (TACs) from risk management (control). During the identification phase, a report is developed which considers whether there are adverse health effects of a substance which may be, or, is emitted in California. After conducting a public hearing, the Board decides whether or not the substance should be identified as a TAC. If identified, the substance is listed by regulation as a TAC in the California Code of Regulations and enters the control phase.

With the adoption of the AB 2728 legislation (signed by the Governor in September 1992 and effective in January 1993), the procedure for identifying substances already classified as federal hazardous air pollutants (HAPs) as TACs was changed. Pursuant to the new legislation, the Board identified on April 8, 1993 all substances listed as federal HAPs as TACs. Benzo[a]pyrene is within the group of chemicals known as particulate polycyclic organic matter (POM) which is listed as a HAP and, therefore, BaP was identified as a TAC.

The cancer unit risk number for BaP, developed by the Office of Environmental Health Hazard Assessment (OEHHA), was evaluated by the Scientific Review Panel (SRP) on February 15, 1994 and on April 18, 1994, the SRP approved the BaP cancer potency number which will be used in the control phase of the AB 1807 process. It may also be used by the local districts for permitting decisions, and to assess the risk to public health in the AB 2588 "Hot Spots" program.

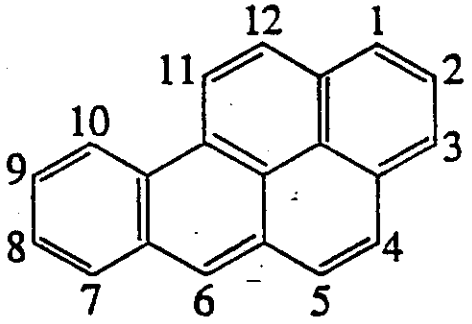
"Part A" of this report presents an assessment of the public's exposure to BaP concentrations in California's ambient air. Included in this assessment is a discussion of the data collection techniques (and the resulting data) used to quantify BaP in California's ambient atmosphere, an examination of major BaP source categories in California, "hot spot" sources and emissions of BaP, and the atmospheric fate of airborne BaP.

"Part B" of this report presents the Office of Environmental Health Hazard Assessment (OEHHA) staff assessment of the public health risk resulting from exposure to the average ambient concentrations of airborne BaP reported in Part A. Included in Part B is a discussion of the relevant health studies used in the health risk assessment, the identified mechanisms responsible for the anticipated adverse health effects resulting from BaP exposure, and the conclusions reached by the staff of the OEHHA.

A. BENZO[a]PYRENE AS A CHEMICAL COMPOUND

As shown in Figure I-1, BaP is a five ring polycyclic aromatic hydrocarbon (PAH) found in small (<1 micron) combustion-generated respirable particles from essentially all combustion sources. Such submicron size particles are in the "respirable" size range and thus can penetrate into the deepest recesses of the lungs and be deposited in alveoli. BaP may also be a component of some uncombusted petroleum-based fuels. It is a potent

FIGURE I-1
THE STRUCTURE OF BENZO[a]PYRENE



laboratory carcinogen and is listed by the U.S. Environmental Protection Agency (U.S. EPA) and the International Agency for Research on Cancer (IARC) as a "probable" human carcinogen. As mentioned above, BaP is part of a larger group of compounds (soots, tars and oils) designated by IARC as Group 1 "known human carcinogens". For information on structure and nomenclature of relevant PAHs see Finlayson-Pitts and Pitts (1986).

Investigation of BaP as a potential toxic air contaminant was prompted by concern that low-level public exposure to airborne BaP may result in adverse health effects, causing BaP to meet California's definition of a toxic air contaminant. As part of that evaluation, airborne BaP sampling and analysis began in November 1988, followed by the development of a database for BaP concentrations in California's ambient air. In addition to BaP, the ARB has collected monitoring data on five other PAHs. These are: benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), dibenz[a,h]anthracene (DBA), benzo[g,h,i]perylene (BgP), and indeno[1,2,3-c,d]pyrene (IDP).

B. MUTAGENICITY OF BaP AND OTHER PAHs

BaP is one compound of a complex mixture in ambient air which exhibits mutagenic activity in the Ames/Salmonella bioassay (Ames et al., 1975). BaP is a promutagen, i.e., it must first be metabolized by enzymes to a reactive intermediate before it can induce mutation. BaP is one of the more potent mutagenic PAHs that require metabolic activation (Dunkel et al., 1984).

Besides BaP, other PAHs are emitted or formed in the atmosphere which account for additional mutagenicity. Gas-phase reactions can convert volatile and semi-volatile PAHs to nitro-PAHs (e.g. nitroarenes) and nitro-PAH lactones (nitro-PACs) some of which are strong "direct-acting" mutagens (do not require addition of metabolizing enzymes in the Ames test). Laboratory studies have shown that a significant fraction of direct-acting mutagenicity is due to the presence of mono and dinitroarenes and nitro-PAH lactones (Atkinson and Arey, 1994; Pitts, 1987, 1993). Two of these studies found that the predominant nitroarenes were 2-nitrofluoranthene and 2-nitropyrene (Nielsen et al., 1984; Zielinska et al., 1989). Both proved to be strong direct-acting mutagens. Arey et al. (1988) found that nitroarenes contributed up to 10 percent of the total particle-bound mutagenicity of samples collected in the eastern part of the Los Angeles air basin. A recent study by Atkinson and Arey (1994) shows that 2- and 4-nitrodibenzopyranones were observed in both the gas and particle phases in ambient air samples collected in southern California. Approximately 20 percent of the total direct-acting mutagenicity can be attributed to their presence. In addition to 2- and 4-nitrodibenzopyranones, seven nitro-PAH lactones (tentatively identified as methylnitrodibenzopyranones and nitrophenanthropyranones) have been identified in the ambient air.

References to Chapter I

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II.

PHYSICAL PROPERTIES OF BENZO[a]PYRENE

BaP is a member of a group of compounds known as polycyclic aromatic hydrocarbons (PAHs). The PAHs are primarily planar, nonpolar compounds which are produced by incomplete combustion, promoted by oxygen starved combustion conditions and high temperatures, and melt at temperatures well above room temperature (U.S. EPA, 1987). These compounds consist of variously substituted fused aromatic rings; benzo[a]pyrene has five fused aromatic rings. Most of the PAHs have high-melting points, are virtually insoluble in water and have low vapor pressures (IARC, 1983). BaP is soluble in benzene, toluene, and xylene, but practically insoluble in water (Merck Index, 1983). BaP is generally present in the atmosphere in the particle-associated phase with the size of particulate matter three microns or less. Some of the physical and chemical properties of the particle-associated benzo[a]pyrene are shown in Table II-1.

TABLE II-1

PHYSICAL AND CHEMICAL PROPERTIES OF BaP

Property	Value
Chemical Formula	$C_{20}H_{12}$
Molecular Weight	252.32
Melting Point	179 - 179.3°C
Boiling Point	310 - 312°C
Vapor Pressure	5.5×10^{-9} Torr

References for Chapter II

IARC (International Agency for Research on Cancer). 1983. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Vol. 32. pp. 35-36.

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III.

PRODUCTION, USES, AND EMISSIONS OF BENZO[a]PYRENE

BaP comprises less than five percent of the total PAHs present in the atmosphere (Rondia, et al. 1983). In addition to BaP, other PAHs and PAH derivatives have been classified by IARC as "probable" human carcinogens (2A) and "possible" human carcinogens (2B). PAHs occur in the atmosphere primarily as adsorbed compounds on combustion-generated soot particles (U.S. EPA, 1987). Typical sources of BaP and related potentially carcinogenic PAHs are: exhaust from gasoline- and diesel-fueled vehicles, residential wood combustion, and stationary source fuel combustion.

PAHs are a subgroup of a larger class of substances known as POM. In addition to BaP, California facilities under the Air Toxics "Hot Spots" Information and Assessment Act (AB 2588) are required to report their emissions of 14 other PAHs including all five of the PAHs currently being sampled and analyzed from the ARB ambient air toxics network.

Every process involving combustion or strong heating of organic materials has the potential to result in BaP emissions (Rondia, et al. 1983). Most PAHs are formed during incomplete combustion of organic matter (Olsen, et al. 1969).

A. PRODUCTION

The staff is unaware of any commercial production of BaP in California.

B. USES

The staff is unaware of any direct uses of BaP in California. Limited amounts of BaP may be used for medical and other research purposes.

C. EMISSIONS

Although there are natural sources of BaP (e.g. volcanic activity), the anthropogenic sources are by far the most important to air pollution (Rondia, et al., 1983). Table III-1 lists the stationary point, stationary area, and mobile sources of BaP emissions. The major sources of BaP emissions in California are vegetative materials burning, mobile sources, rubber tire wear, residential combustion of wood, and combustion of coal. Vegetative materials and other waste burning is responsible for the majority of statewide BaP emissions from stationary sources. Appendix B contains background information about how the BaP emissions were estimated. Because BaP emissions vary according to the type of process, fuel, operation practices, and combustion conditions, most of the emission estimates are expressed as a range.

Emissions data are not available for several source groups that have processes that would be expected to result in BaP emissions. The statewide total for accountable BaP emission sources are estimated to range from 17,000 to 26,000 pounds per year (8.0 to 13.0 tons per year). BaP is also present in exhaust emissions from diesel and spark ignition engines. With the introduction of catalytic converters in the United States in 1974, mobile source emissions from light duty motor vehicles of BaP were reduced. As pre-1974 vehicles are taken out of service and low emission vehicles are introduced, BaP emissions will continue to be reduced. BaP is also a component of diesel exhaust which is being evaluated for identification under the AB 1807 process.

1. Stationary Area Sources

Stationary area sources individually emit small amounts of pollutants, but collectively can result in emission concentrations that significantly

TABLE III-1
ESTIMATED ATMOSPHERIC EMISSIONS OF BENZO[a]PYRENE IN CALIFORNIA[a]

	Pounds per year[b]	Inventory Year
Stationary Area Sources		
Vegetative Materials & Waste Burning[c]	11,000 - 13,000	1987
Fuel Combustion:		
Residential wood	110 - 1,400	1987
Natural gas	36	1987
Liquid material	4.8 - 9.6	1987
Residual oil	< 1 - 9	1987
Distillate oil	1 - 3[d]	1987
Diesel[e]	< 1	1987
Gaseous material	< 1	1987
LPG	not available	
Asphalt Paving Operations	< 0.01	1987
Asphalt Roofing Operations	< 0.01	1987
Stationary Point Sources		
Fuel Combustion:		
Coal	0.4 - 830	1986
Residual oil	16 - 610	1987
Natural gas	520	1987
Wood - Industrial	11 - 400[f]	1987
Distillate oil	7 - 19[c]	1987
Gasoline	< 1 - 3.3	1987
Diesel	< 1	1987
Coke	not available	
Incineration:		
Municipal waste	not available	
Sewage sludge	not available	
Hazardous waste	not available	
Medical waste	not available	
Other Industrial Processes:		
Oil refining	10 - 40	1988
Asphalt production plants	1 - 4	1987
Carbon black plants	< 0.1	1985
Charcoal production	not available	
Coking process	not available	
Creosote wood treatment	not available	
Roofing material mfg.	not available	
Iron and steel foundries	not available	
Secondary lead smelting	not available	
Mobile Sources		
On-Road Motor Vehicles	890 - 4,600	1987
Rubber Tire Wear	3,900	1987
Other Mobile Sources[g]	80 - 810	1987
Accountable Statewide Total	**17,000 to 26,000 (8.0 to 13.0 tons)**	

Notes to Table III-1:

[a] This table lists sources in order of emissions. It does not reflect the relative contribution of those sources to exposure. See Chapter IV, especially E.5 and E.6, for exposure information.

[b] Emissions have been rounded to, at most, two significant figures.

[c] This category includes range and forest management burning, wildfires, open burning, waste burning, and weed abatement. Emission factors for grass, leaves, and branches have been assumed to be applicable to all sources in this category.

[d] The upper limit of the applicable emission factors could be as high as 41 micrograms per kilogram for residual and distillate oil combustion (Rondia, et al., 1983 and U.S. EPA, 1987). Using this emission factor, the resulting upper estimate of emissions for distillate oil combustion would be ~400 pounds per year for stationary point sources and ~65 pounds per year for stationary area sources.

[e] This category includes a minor contribution from sources in the Outer Continental Shelf (OCS) area.

[f] The emission factor was reported to be non-detectable in some runs in some tests.

[g] Other mobile sources include: ships, trains, off-road vehicles, fork lifts and aircraft. Some categories include a minor contribution from sources in the OCS area.

impact a local or regional population. Stationary area sources are not included in the stationary point source inventory.

a. Vegetative Materials and Other Waste Burning

This category combines a number of diverse types of waste and debris burning (e.g., burning of vegetative materials, open burning for range and forest management, and wildfires). Based on the ARB's Emission Data System (ARB, 1990a), approximately 18.7 million tons of vegetative materials and waste (e.g., prunings and field crop debris), range and forest material, forests (due to wildfires), weeds, and other types of outdoor waste were burned in California during 1987.

The U.S. EPA published a range of BaP emission factors (0.3 to 0.35 milligrams per kilogram of waste) for grass, leaves, and branches (U.S. EPA, 1987). Due to a lack of emission factors for specific types of waste burning, the ARB staff assumed that the U.S. EPA's range of emission factors for grass, leaves, and branches is applicable to all types of vegetative materials and other waste burning. Using this information and the applicable conversion factors, the staff estimates that in 1987, 11,000 to 13,000 pounds of BaP were emitted into the ambient air as a result of the burning of vegetative materials and other waste.

b. Residential Wood Combustion

In 1987, approximately 1.1 million tons of wood were burned for residential heating purposes in California (ARB, 1990a). According to the U.S. EPA (1988), residential woodstoves have uncontrolled emissions ranging from 0.05 (dry wood) to 0.62 milligram of BaP per kilogram of wood burned. Based on this, the staff estimates that BaP emissions from residential wood combustion for heating purposes ranged from approximately 110 pounds to 1,360 pounds. No data are available regarding emissions from residential burning of wood for aesthetic purposes only.

c. Natural Gas Combustion

The ARB's Emission Data System indicates that during 1987, 838 billion cubic feet of natural gas had been combusted in the State (ARB, 1990a). BaP emission estimates were calculated using a natural gas density of 0.0433 pounds per cubic feet at 60 degrees Fahrenheit and 1 atmosphere, and an assumed emission factor of 1 microgram per kilogram of natural gas burned. The staff derived this BaP emission factor from the published natural gas POM emission factor of 25 micrograms per kilogram (U.S. EPA, 1987) assuming that the BaP emission factor is approximately four percent of the published POM emission factor. In 1987, stationary area sources of natural gas combustion generated approximately 36 pounds of BaP.

d. Liquid Material Combustion

Stationary area sources in the oil and gas production industry burned approximately 86 million gallons of unspecified liquid material in 1987 (ARB, 1990a). Assuming that the emission factor for diesel fuel combustion is applicable to this source category, BaP emissions were estimated to range from 4.8 to 9.6 pounds in 1987.

e. Residual Oil Combustion

In 1987, area sources burned approximately 27.5 million gallons of residual oil (ARB, 1990a). BaP emission estimates for residual oil combustion were based on published emission factors ranging from 1.1 micrograms of BaP per kilogram of residual oil to 2.2 pounds of BaP per trillion BTU-heat input (Rondia et al., 1983). Other parameters used in the BaP emission estimation equation were the heat content of residual oil (6.3 million BTU per barrel), the density of residual oil (approximately 7.88 pounds per gallon: U.S. EPA, 1985), and a conversion factor of 42 gallons per barrel. The estimated BaP emissions for 1987 ranged from less than one pound to nine pounds.

f. Distillate Oil Combustion

Area sources burned approximately 0.23 billion gallons of distillate oil in 1987 (ARB, 1990a). BaP emission factors for distillate oil combustion ranged from 0.66 to 1.96 micrograms per kilogram (Hangebrauck, 1964). Using this range of emission factors and an assumed distillate oil density of 7.05 pounds per gallon (U.S. EPA, 1985), the staff estimates that 1987 BaP emissions from this category ranged from one to three pounds.

g. Diesel Fuel Combustion

Stationary area sources of diesel fuel combustion include drilling and workover rigs used in oil and gas production (some of which are located in the OCS), and industrial sources of diesel fuel combustion.

Emission estimates for this category were based on a diesel fuel usage of 6.29 million gallons (or 4.8 million gallons if OCS sources are omitted: ARB, 1990a), and a range of emission factors for diesel vehicle internal combustion engines of 25.4 to 50.86 micrograms per gallon (U.S. EPA 1988). Diesel-fueled vehicle engine emission factors were used to estimate BaP emissions from diesel-fueled stationary internal combustion engines. Based on these assumptions, the staff estimates that BaP emissions from diesel oil combustion were less than one pound in 1987.

h. Gaseous Material Combustion

In 1987, stationary area sources in the oil and gas production industry burned approximately 7,200 million cubic feet of unspecified gaseous material (ARB, 1990a). Assuming that the emission factor for natural gas combustion is applicable to this source category, the 1987 BaP emissions were estimated to be less than one pound.

j. Liquid Petroleum Gas Combustion

In 1987, stationary area sources burned approximately 390 million gallons (ARB, 1990a) of liquid petroleum gas (LPG). No emission factor is available for LPG combustion and therefore, no BaP emission estimate has been made.

k. Asphalt Paving Operations

Asphalt (i.e., cutback asphalt, road oils, hot-mix asphalt and emulsified asphalt) usage totalled approximately 3.8 million tons in 1987 (ARB, 1990a). Using an arithmetic average BaP emission factor of 0.0133 microgram per cubic meter (U.S. EPA, 1987) and an asphalt density of 1,030 grams per liter, staff estimated that asphalt paving operations were responsible for less than 0.01 pound of BaP emissions in 1987.

l. Asphalt Roofing Operations

Approximately 2.24 million tons of asphalt were used for roofing operations during 1987 (ARB, 1990f). The average BaP emission factors for asphalt roofing operations range from 0.057 to 0.183 microgram per cubic meter (U.S. EPA, 1987). Using the usage data, range of emission factors, and an asphalt density of 1,030 grams per liter (U.S. EPA, 1985), the staff estimates that 1987 BaP emissions from this category were less than 0.01 pound.

2. Stationary Point Sources

Stationary point sources include facilities that have a specific location and have not been included in the mobile source inventory. Stationary point sources contributing to BaP emissions include stationary sources burning of hydrocarbon-based fuels or organic waste, and various industrial operations.

a. Coal Combustion

The primary source of coal combustion emissions in California is cement manufacturing. Published emission factors range from 0.117 microgram of BaP per kilogram of coal to 260 micrograms of BaP per kilogram of coal (U.S. EPA, 1987).

Based on the 1986 information from California's air pollution control districts and the coal usage data information obtained from the ARB's Emission Data System for criteria pollutant emissions (ARB, 1990b), the staff estimated that approximately 1.2 million tons of coal were burned in California by cement manufacturers during the 1986 inventory year. An additional 0.4 million tons of coal were burned in other operations, bringing the estimated coal combustion in the State to a total of 1.6 million tons.

Based on the information presented above, the staff estimates that BaP emissions from coal combustion ranged from 0.4 to 832 pounds in 1986.

b. Residual Oil Combustion

Published emission factors for this category range from 1.1 microgram per kilogram to 2.2 pounds of BaP per 10 trillion BTU-heat input (equivalent to approximately 41 micrograms per kilogram: Rondia et al., 1983; U.S. EPA, 1987). Stationary point sources in California burned approximately 1.85 billion gallons of residual oil (ARB, 1990b) with a heat content of 6.3 million BTUs per barrel (42 gallons per barrel), a density of approximately 7.88 pounds per gallon (U.S. EPA, 1985). Based on this information, the staff estimates that approximately 16 to 610 pounds of BaP were emitted in 1987 as a result of the combustion of residual oil in California.

c. Natural Gas Combustion

The staff derived a BaP emission factor (1 microgram per kilogram) for natural gas combustion by assuming that BaP is approximately four percent of the available POM emission factor. The POM emission factor is listed as 25 micrograms per kilogram of natural gas burned (U.S. EPA, 1987). Based on Emission Data System data, approximately 12.2 trillion cubic feet of natural gas were burned in California in 1987 (ARB, 1990b). Assuming that natural gas has a density of 0.0433 pounds per cubic feet at 60 degrees Fahrenheit and 1 atmosphere, 1987 BaP emissions from stationary natural gas combustion point sources were estimated to be 520 pounds per year.

d. Wood Combustion - Industrial

Approximately 5.6 million tons of wood were burned industrially in California during 1987 (ARB, 1990b). The controlled and uncontrolled emission factors for wood-fired boilers published by the U.S. EPA range from 0.001 to 0.024 milligram of BaP per kilogram of wood burned to 0.005 to 0.036 milligram of BaP per kilogram of wood burned, respectively (U.S. EPA, 1987). In a few reported test runs with controls, the emissions were reported as non-detectable.

Using the range of BaP emission factors for industrial wood combustion (0.001 to 0.036 milligram per kilogram), the staff estimates that BaP emissions from this source category ranged from 11 to 400 pounds in 1987.

e. Distillate Oil Combustion

Based on the data obtained from the ARB's Emission Data System (ARB, 1990b), the staff estimates that in 1987, approximately 1.4 billion gallons of distillate oil were burned by stationary point sources in California. Stationary point source BaP emission factors for distillate oil combustion ranged from 0.66 microgram per kilogram to 1.96 micrograms per kilogram (Hangebrauck, 1964). The density of distillate oil was assumed to be 7.05 pounds per gallon.

The ARB staff estimates that BaP emissions from stationary point sources of distillate oil combustion ranged from approximately 7 to 19 pounds in 1987.

f. Gasoline Combustion

Stationary point sources also use gasoline as industrial fuel. In 1987, these sources burned approximately 4.53 million gallons of gasoline (ARB, 1990b). Based on published emission factors ranging from 8 to 330 micrograms of BaP per gallon of gasoline burned in gasoline vehicle engines (U.S. EPA, 1987), the staff estimates that 1987 BaP emissions from gasoline combustion by stationary point sources ranged from less than 1 pound to 3.3 pounds.

g. Diesel Fuel Combustion

Based on the ARB's Emission Data System, approximately 3.24 million gallons of diesel fuel were burned by stationary point sources in California during 1987 (ARB, 1990b).

Using the applicable emission factors for mobile internal combustion engines (ranging from 25.4 to 50.86 micrograms per gallon), the staff estimates that 1987 BaP emissions from diesel-fueled stationary internal combustion engines were less than one pound.

h. Coke Combustion - Cement Manufacturing

The ARB staff estimates that approximately 460,625 tons of coke were burned during cement manufacturing operations in California (ARB, 1990b). Coke combustion could result in significant emissions of BaP.

No emission factor for coke combustion is available, because emissions vary according to fuel type and process conditions. Therefore, no BaP emission estimate is available.

i. Municipal Waste Incineration

Published U.S. EPA emission factors for municipal waste combustion range from 0.008 to 0.13 gram of BaP per megagram of waste burned (U.S. EPA, 1988). No BaP emission estimate is available for municipal waste combustion because of the absence of a reliable estimate for the quantity of waste burned in California.

j. Sewage Sludge Incineration

Approximately 17,240 tons of sewage sludge were incinerated in California in 1987 (ARB 1988a). No BaP emission estimates for this source category were made because no emission factors are available.

k. Medical Waste Incineration

Approximately 20,050 tons of medical waste were incinerated in California during 1989 (ARB 1990b). No BaP emission estimates for this category were made because no emission factors are available.

l. Hazardous Waste Incineration

Approximately 180 tons of hazardous waste were incinerated in California (Eriksson, 1992). No BaP emissions estimates for this source category were made because no emission factors are available.

m. Oil Refining

Catalytic cracking processes are used in petroleum refineries to increase the production of gasoline from a given amount of crude oil. Three types of catalytic crackers have been used in the petroleum industry: fluid-bed catalytic cracking units, thermal catalytic cracking units, and hydroflow catalytic cracking units. The vast majority of catalytic cracking units are of the fluid-bed type (U.S. EPA, 1987).

In a recent publication (U.S. EPA, 1987), the U.S. EPA listed a controlled BaP emission factor of from non-detectable to 21.5 micrograms BaP per barrel of feed for fluid-bed catalytic cracking units used in petroleum refineries. California's 31 refineries in 1988 had an aggregated, rated charge capacity of approximately 2.3 million barrels of oil per calendar-day (<u>Oil and Gas Journal</u>, 1989). Data from the <u>Oil and Gas Journal</u> show that approximately 0.65 million barrels of fresh crude oil were processed by catalytic cracking units per stream-day. To convert barrels per stream-day to barrels per calendar-day, the staff multiplied barrels per stream-day by a conversion factor of 0.95 (<u>Oil and Gas Journal</u>, 1989). The available emission factor is specific only to catalytic cracking units; however, for lack of other emission factor data, the staff assumed that this factor can be extrapolated to estimate BaP emissions from such refinery processes as catalytic reforming and catalytic refining (which are potential sources of POM).

Assuming that all refining operations in California used fluid-bed catalytic cracking unit regenerators, and using the aggregate charge capacity data cited above, the staff estimates that refineries in California emitted approximately 40 pounds of BaP into the ambient air in 1988. If the calculation is based on 0.61 million barrels of oil per calendar-day (which is the volume processed by the catalytic cracking units only), the BaP emission estimate is approximately ten pounds per year. The staff concludes that BaP emission estimates from petroleum refining processes range from 10 pounds to 40 pounds per year.

n. Asphalt Production Plants

The BaP emission factors used for this source category range from 0.03 to 0.13 milligram of BaP per megagram of asphalt produced (U.S. EPA, 1987). The ARB's Emission Data System indicates that approximately 16.3 million tons of asphalt were processed in 1987 (ARB, 1990c). Based on this information, the staff estimates that 1987 BaP emissions from hot-mix asphalt plants ranged from 1 pound to 4.2 pounds.

o. Carbon Black Plants

In 1985, two facilities in California were responsible for the production of 54 million pounds of carbon black (U.S. EPA, 1987). Based on a POM emission factor of 0.0039 pound per ton (of which 0.09 percent is BaP: U.S. EPA, 1987), the staff estimates that in 1985, less than 0.1 pound of BaP was emitted into the ambient air from this activity.

p. Charcoal Production

Based on the ARB's 1987 Emission Data System (ARB, 1990d), approximately 121,770 tons of charcoal were produced in the State. Due to a lack of BaP emission factors for this source category, emission estimates can not be made.

q. Coking Operations

Coke ovens are sources of PAH emissions. The leaks from the oven doors have an estimated emission factor of 15 grams of PAH per ton of coal charged (Rondia, et al. 1983). The U.S. EPA uses an emission factor of 0.0005 gram of BaP per megagram of coal charged during coke quenching operations (U.S. EPA, 1988). No data are available regarding the extent of coking operations in California.

r. Creosote Wood Treatment

Data from the U.S. EPA indicate that there are facilities in California treating wood with creosote (U.S. EPA, 1987), although information regarding the exact number of facilities, the quantities of creosote used, and applicable BaP emission factors are not available. Consequently, a BaP emission estimate for this source category has not been made.

s. Roofing Material Manufacturing

Roofing material manufacturing may be a source of BaP emissions into the ambient air. Due to a lack of information regarding the quantity of roofing materials manufactured and applicable emission factors, no BaP emission estimates have been made.

t. Iron and Steel Foundries

Data from an ARB survey of Californian foundries (ARB, 1988b) indicate that 161,500 tons of iron and 198,200 tons of steel were processed in 1987. Data regarding air samples affecting workers indicate that BaP may be emitted from such facilities (U.S. EPA, 1987), however, any such emissions resulting from fuel combustion processes may have already been addressed under sources of fuel combustion. Since no emission factors are available for any other processes within these facilities, no BaP emission estimate for this source category has been made.

u. Secondary Lead Smelting

Data from an ARB survey of four operating secondary lead smelters in California (ARB, 1988b) indicate that there were 187,890 tons of metal processed while reclaiming metals from lead batteries, and an additional 12,545 tons of metal processed while reclaiming metals from other sources (e.g., lead oxide, dross, metal-containing dust, and sheathed cables).

The U.S. EPA reported source-tested POM concentrations in the stack gases following the final control device for secondary lead smelting operations (U.S. EPA, 1987). However, no emission factor for BaP has been reported or could be calculated from the data, therefore, no BaP emission estimate for this source category has been made.

3. Mobile Sources

Mobile sources include on-road motor vehicles and "other" mobile sources (e.g., off-road vehicles, boats, trains, aircrafts, and utility equipment combusting liquid fossil fuel), as well as tire wear by on-road vehicles. Mobile sources contribute more than 35 percent to the total BaP emissions. Within this category, light duty vehicles are responsible for 30 percent of BaP emissions while heavy duty diesel-powered vehicles contribute approximately 10 percent.

a. On-Road Motor Vehicles

On-road motor vehicle emission estimates are based on published emission factors (U.S. EPA, 1987 and Rondia, et al., 1983), vehicle-miles-traveled data, and fuel consumption data from the ARB's Emission Data System (ARB, 1990e). The staff estimates that in 1987, on-road motor vehicles in California emitted approximately 890 to 4,600 pounds of BaP into the ambient air.

b. Rubber Tire Wear

Degrading tires release BaP particles to the atmosphere. Calculations based on U.S. BaP emissions from rubber tire wear (11 tons per year) and the total U.S. mileage of approximately two trillion kilometers per year yield a BaP emission factor of five micrograms per kilometer (Rondia, et al. 1983).

Motor vehicles in California traveled an estimated 220 billion miles (352 billion kilometers) in 1987 (ARB, 1990e). Based on the BaP emission factor and the vehicle-miles-traveled in California, the staff estimates that rubber tire wear resulted in the emission of approximately 3,900 pounds of BaP into California's air in 1987.

c. "Other" Mobile Sources

Emissions from "other" mobile sources include sources such as trains, ships, aircraft, recreational vehicles, and utility and mobile equipment, including a small contribution from boats and ships located in the OCS area. The staff assumed that most emission factors applicable to light-duty passenger cars, light-duty trucks, medium-duty trucks and heavy-duty trucks were also applicable to "other" mobile sources burning similar fuels. The staff estimates that BaP emissions from this source category ranged from 80 to 810 pounds in 1987 (See Appendix B).

4. Trends

Most of the BaP emissions in California are from combustion including vegetative materials burning or combustion-related processes. The staff does not expect an increase in process rates from fuel or vegetative materials burning or from other industrial processes such as oil refining. Because BaP emissions are directly proportional to the amount of fuel burned or material processed, the staff expects BaP future emissions from fuel combustion or combustion-related processes to remain the same.

The BaP emissions from motor vehicles are directly proportional to the number of motor vehicles powered by petroleum-derived fuels. Before the introduction of catalytic converters, mobile sources were the major contributor of BaP emissions. This is consistent with the measured ambient concentrations of BaP in Los Angeles of 1.9 nanogram per cubic meter (ng/m^3) in 1969 (NAS, 1972) which is approximately twice current ambient level. Most light duty vehicles manufactured after 1974 and operated in the United States are equipped with catalytic converters. As the pre-1974 vehicles grow older, they are taken out of service. Therefore, the number of older vehicles are expected to decrease and the BaP emissions will also decrease. The introduction of the transitional low emission vehicles (TLEV), low emission vehicles (LEV) and clean fuels will lead to a significant reduction of ROG (reactive organic gases) and POM emissions. As a result BaP emissions are likely to be reduced as well.

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IV.

EXPOSURE TO BENZO[a]PYRENE

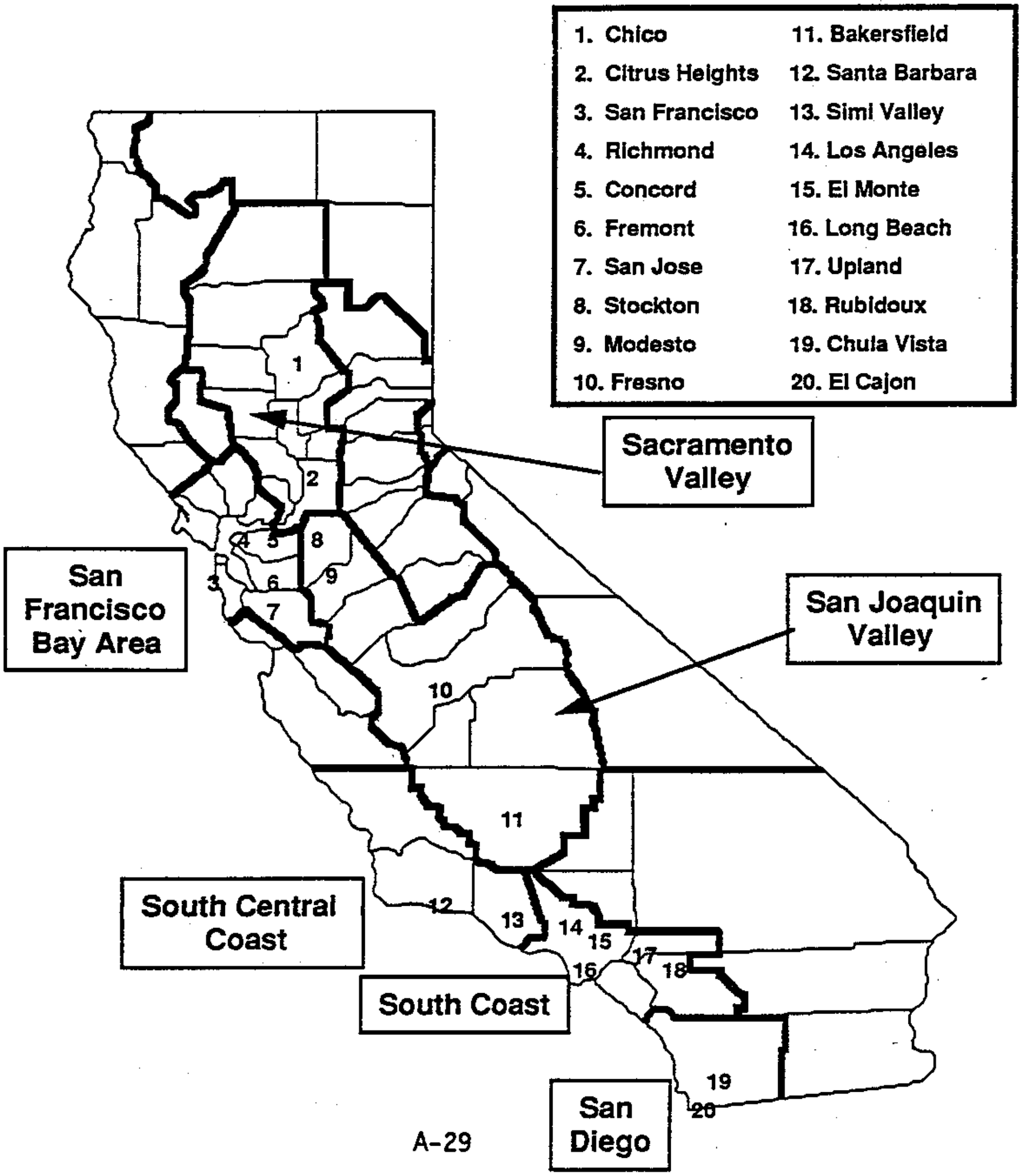
A. AMBIENT MONITORING IN CALIFORNIA

Data from the ARB ambient air toxics monitoring network were used to estimate statewide population-weighted exposure concentrations to BaP. The BaP sampling and analysis method employed by the ARB staff is based on collecting, once every six days, a 24-hour composite sample of atmospheric particulate matter with a diameter of less than 10 microns (PM_{10}) on quartz fiber filters. This is followed by extraction of the PAHs from the filters. BaP and other PAHs of concern are identified and quantified after injection of the extract into a high performance liquid chromatographic system. In addition to BaP, the ARB has collected monitoring data for five other PAHs. These data and the Standard Operating Procedure for the determination of selected PAHs in ambient air are found in Appendices A and B.

BaP from combustion sources is expected to exist in ambient air in a particle-associated phase. Studies have shown that BaP is associated with particulate matter less than three microns in size. Current ARB sampling methods collect all particulate matter of 10 micron in size, or less. Vapor phase BaP has never been detected in ambient air by researchers on the field. There is no evidence that once the BaP is associated with particulate matter and collected on a filter, that it vaporizes and is lost during sampling. The available evidence indicates that there are no losses between the time of sampling and analysis if properly stored. The detailed discussion of the atmospheric lifetime and fate of BaP can be found in Chapter V.

Some areas of the state may experience significantly greater concentrations "hot spots" of BaP than those detected at the ARB ambient air monitoring network. PM_{10} and Coefficient of Haze data were used to identify in areas of California with the greatest potential for "hot spots" exposure to BaP.

FIGURE IV-1
CALIFORNIA'S TOXIC MONITORING NETWORK
November 1988 through October 1989



B. AMBIENT CONCENTRATIONS OF BAP

Twelve months of BaP data (November 1988 through October 1989) from the ARB toxic ambient monitoring network were used to estimate the statewide ambient exposure concentrations to this substance. The toxic monitoring network is made up of 20 monitoring sites statewide, with nine of the sites located in Southern California (south of Bakersfield), and the other 11 located in the northern portion of the state. The location of each monitoring network site is depicted in Figure IV-1.

For this time period the data from the Chico, Fremont, Richmond, Upland, El Monte, and Santa Barbara sites were not used in the analysis because there are insufficient data from these sites to adequately characterize an annual exposure. For this analysis toxics monitoring network data were available only for 14 of the 20 sites. A summary of the available data is presented in Table IV-1.

Although we recognize that 365 samples may not be necessary to characterize a representative mean statewide annual concentration, we do not know the minimum number of samples nor the minimum number of sites required to satisfactorily quantify the error in the mean annual exposure estimates. Therefore, all analyses and estimates for exposure presented here are subject to an unknown level of uncertainty and should be used with appropriate caution.

The monitoring values for each site are summarized in Table IV-2. For each site, the minimum, maximum, median, and mean annual concentration, as well as the standard deviation, are reported. Basin summary results are also included.

Of the 332 observations reported, 130 were below the limit of detection (LOD) of 0.05 nanograms per cubic meter. The LOD represents the lowest concentration at which a measurement can be made with statistical confidence.

TABLE IV-1

SUMMARY OF THE AVAILABLE BENZO[a]PYRENE DATA
November 1988-October 1989

	N	D	J	F	M	A	M	J	J	A	S	O	# of Samples
SOUTHERN CALIFORNIA SITES													
South Coast Air Basin													
Long Beach	o	o	o	o	o	o	o	o	o	o	o	o	24
Los Angeles	o	o	o	o	o	o	o	o	o	o	o	o	24
Rubidoux	o	o	o	o	o	o	o	o	o	o	o	o	24
South Central Coast Air Basin													
Simi Valley	o	o	o	o	o	o	o	o	o	o	o	o	24
San Diego Air Basin													
Chula Vista	o	o	o	o	o	o	o	o	o	o	o	o	24
El Cajon	o	o	o	o	o	o	o	o	o	o	o	o	23
NORTHERN CALIFORNIA SITES													
San Francisco Bay Area Air Basin													
Concord	o	o	o	o	o	o	o	o	o	o	o	o	24
San Francisco		o	o	o	o	o	o	o	o	o	o	o	22
San Jose	o	o	o	o	o	o	o	o	o	o	o	o	23
San Joaquin Valley Air Basin													
Bakersfield	o	o	o	o	o	o	o	o	o	o	o	o	24
Fresno	o	o	o	o	o	o	o	o	o	o	o	o	25
Modesto	o	o	o	o	o	o	o	o	o	o	o	o	24
Stockton	o	o	o	o	o	o	o	o	o	o	o	o	23
Sacramento Valley Air Basin													
Citrus Heights	o	o	o	o	o	o	o	o	o	o	o	o	24

An "o" indicates that at least one sample was collected during the month.

To estimate values below the LOD, staff used the Gleit method (Gleit, 1985) described in Appendix C.

Mean annual BaP concentrations were calculated as the mean of available monthly means. This approach provides equal weighting for each month even when the number of samples per month varies. Mean annual concentrations ranged from a minimum of 0.11 nanogram per cubic meter at Chula Vista to a maximum of 1.48 nanograms per cubic meter at Fresno. Basin averages ranged from a minimum of 0.36 nanogram per cubic meter in San Diego to a maximum of 1.13 nanograms per cubic meter in the San Joaquin Valley. Because the Sacramento Valley and South Central Coast air basins have only one site each, they cannot be used in this comparison.

Figure IV-2 compares the mean annual concentrations of BaP for the 14 monitoring sites used in the analysis. The San Joaquin and Sacramento Valley sites appear to have slightly higher concentrations of BaP than those in the other air basins. Figure IV-3 presents statewide monthly mean concentrations to illustrate that BaP, like particulate matter, has elevated concentrations during the winter months.

C. POPULATION WEIGHTED EXPOSURE ESTIMATES

Mean population outdoor ambient exposure estimates were calculated using the November 1988 through October 1989 toxic monitoring network BaP data. Population-weighted exposures for the South Coast Air Basin and San Francisco Bay Area Air Basin were estimated by interpolating mean annual exposure estimates from each BaP monitoring site to census tract centroids. For the remaining basins, the mean annual exposure estimate was calculated as the average of site means within a basin. It was then assumed that all people within those counties with a monitoring site were exposed to this estimated basin-wide mean concentration. Data from the Citrus Heights site were used to estimate BaP exposure concentrations for Sacramento County residents only. Since Simi Valley was the only site in the South Central Coast Air Basin for which data was available, exposure concentrations were estimated

TABLE IV-2

SUMMARY OF AMBIENT BENZO[a]PYRENE DATA
November 1988-September 1989

	(nanograms per cubic meter)				
	Minimum Conc.	Maximum Conc.	Median Conc.	Mean* Conc.	Std.** Dev.
South Coast Air Basin					
Long Beach	<LOD	3.28	0.11	0.53	0.64
Los Angeles	<LOD	1.22	0.26	0.41	0.37
Rubidoux	<LOD	1.38	0.07	0.19	0.25
Basin Summary	**<LOD**	**3.28**	**0.12**	**0.38**	**0.45**
South Central Coast Air Basin					
Simi Valley	**<LOD**	**1.07**	**0.12**	**0.18**	**0.22**
San Diego Air Basin					
Chula Vista	<LOD	0.61	<LOD	0.11	0.14
El Cajon	<LOD	5.50	0.06	0.61	1.07
Basin Summary	**<LOD**	**5.50**	**<LOD**	**0.36**	**0.76**
San Francisco Bay Area Air Basin					
Concord	<LOD	2.60	0.06	0.48	0.75
San Francisco	<LOD	1.08	<LOD	0.26	0.31
San Jose	<LOD	4.20	0.13	0.75	1.10
Basin Summary	**<LOD**	**4.20**	**0.10**	**0.50**	**0.79**
San Joaquin Valley Air Basin					
Bakersfield	<LOD	6.70	0.11	0.81	1.40
Fresno	<LOD	14.00	0.14	1.48	2.46
Modesto	<LOD	9.70	0.07	1.19	1.83
Stockton	<LOD	6.50	<LOD	1.04	1.91
Basin Summary	**<LOD**	**14.00**	**0.10**	**1.13**	**1.79**
Sacramento Valley Air Basin					
Citrus Heights	**<LOD**	**10.00**	**0.10**	**1.39**	**2.00**
Basins Mean Concentration* **				**0.66**	

* Means of individual basins are the mean of the basin's site means.

** Basin standard deviations are pooled values of the standard deviations across sites within a basin.

*** The Basins mean concentration is the average of the six basin means.

FIGURE IV-2
MEAN ANNUAL BENZO[a]PYRENE SITE CONCENTRATIONS
(November 1988-October 1989)

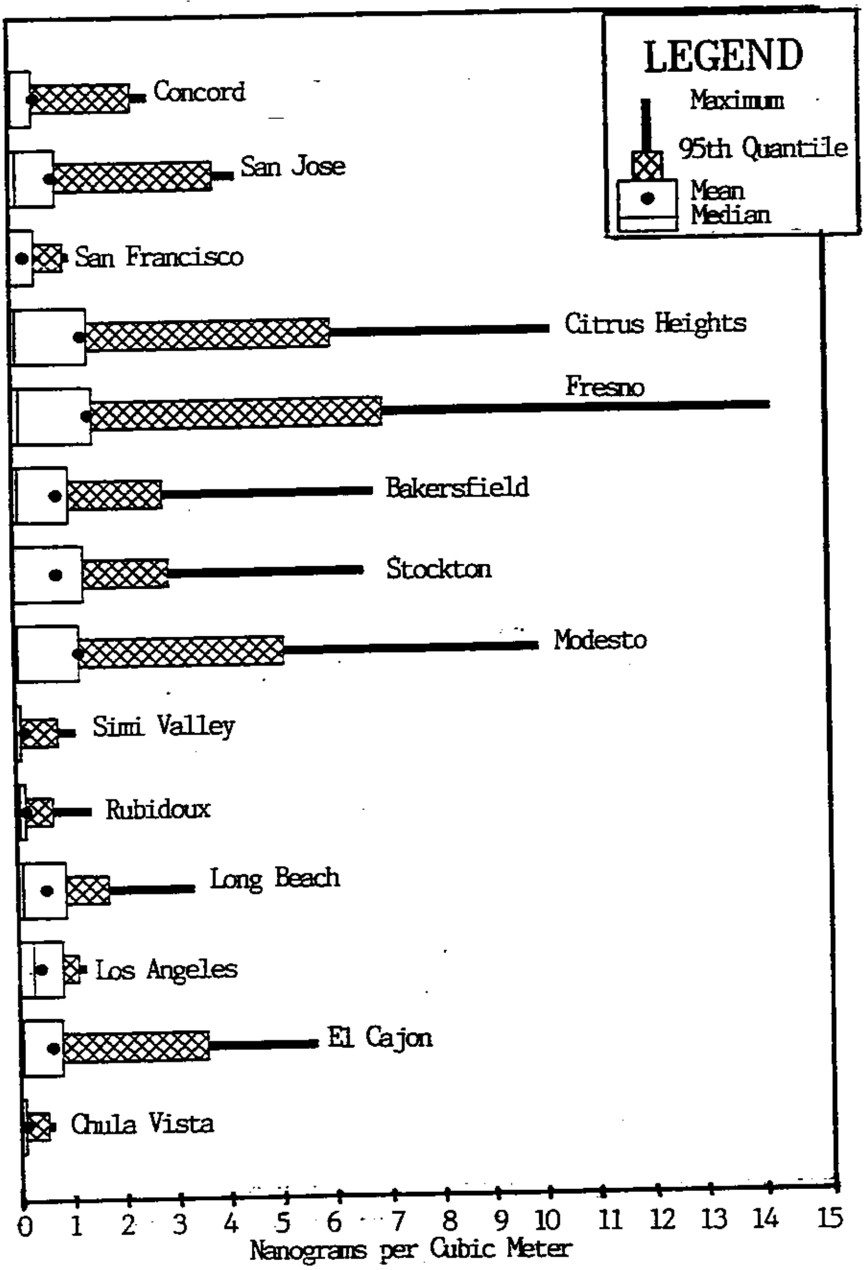
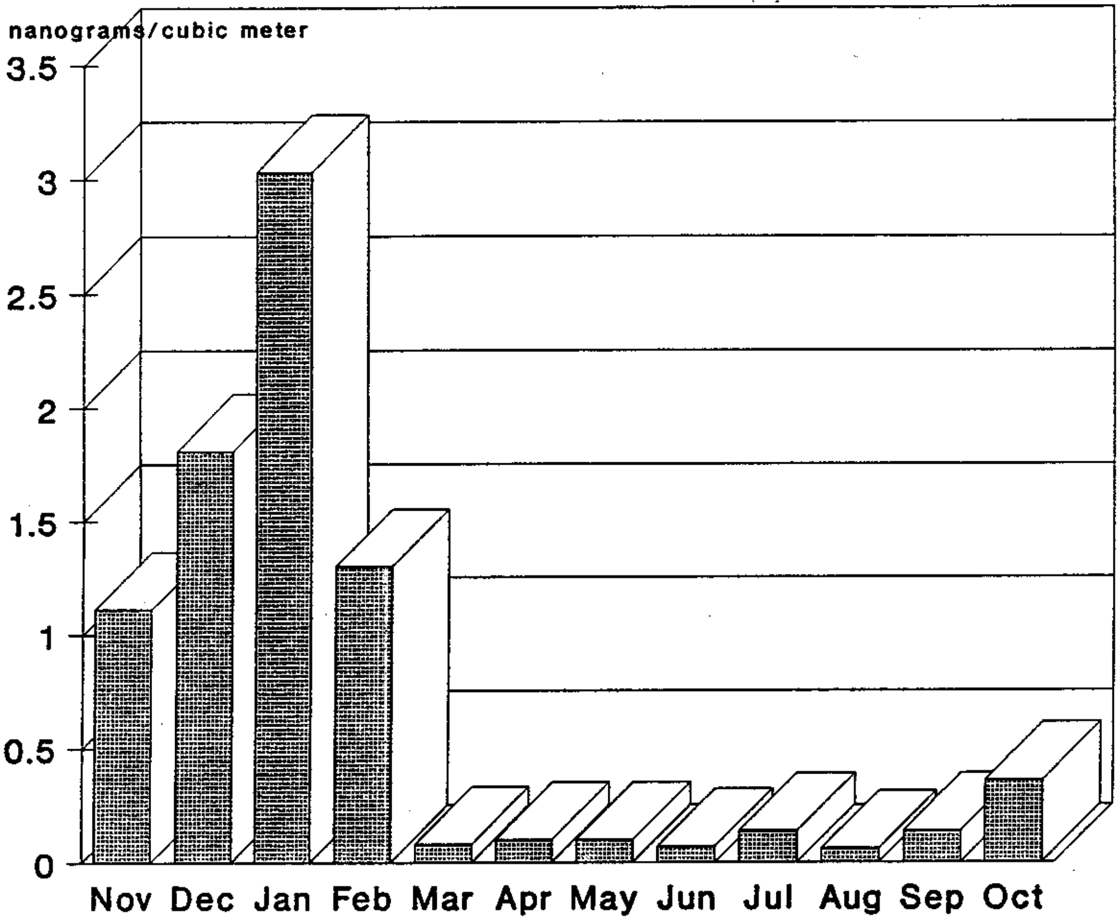


FIGURE IV-3
STATEWIDE MONTHLY MEAN BENZO[A]PYRENE CONCENTRATIONS
(November 1988-October 1989)



only for Ventura County residents. Population data used in the exposure analysis represent 1980 census data updated to 1985.

The results of the exposure concentrations analysis for the study period are summarized in Table IV-3, which include the upper and lower variability bounds estimates (Efron, 1982). The larger the difference between the mean annual exposure concentration estimate and the upper and lower bounds, the greater the uncertainty in the estimate.

The statewide population-weighted BaP exposure estimate produced from the toxic monitoring network data is 0.53 nanogram per cubic meter. The South Central Coast Air Basin had the lowest BaP mean annual estimated exposure at 0.18 nanogram per cubic meter. Sacramento County had the highest mean annual BaP exposure estimate at 1.39 nanograms per cubic meter. The estimated population of the study area was nearly 20 million, which represents a large majority of the urban population, and approximately 64 percent of the state's total population.

Figure IV-4 shows the number of people in the study area estimated to be exposed to various mean annual BaP concentrations. All of the study population (nearly 20 million people) are exposed to at least 0.1 nanogram per cubic meter of BaP, while approximately 77 percent of the study population (around 15.4 million people) is estimated to be exposed to less than the statewide population-weighted annual average concentration of 0.53 nanogram per cubic meter of BaP. Approximately 19 percent of the study population (around 3.7 million people) are exposed to BaP concentrations at or above the statewide population-weighted annual average, while approximately 14 percent of the study population (around 2.8 million people) are estimated to be exposed to 1.1 nanograms per cubic meter (more than twice the population-weighted average concentration of 0.53 nanogram per cubic meter).

TABLE IV-3
POPULATION-WEIGHTED MEAN ANNUAL EXPOSURE ESTIMATES

(nanograms per cubic meter)

	Lower Bound	Exposure Estimate	Upper Bound	Represented Population
South Coast Air Basin				
Long Beach	0.21	0.57	0.95	
Los Angeles	0.24	0.41	0.65	
Rubidoux	0.06	0.19	0.32	
Population-weighted Exposure:		**0.43**		**10,092,133**
South Central Coast Air Basin				
Simi Valley	0.06	0.18	0.30	
Exposure (for Ventura County):		**0.18**		**600,200**
San Diego Air Basin				
Chula Vista	0.04	0.11	0.19	
El Cajon	0.12	0.61	1.18	
Exposure:		**0.36**		**2,131,600**
San Francisco Bay Area Air Basin				
Concord	0.19	0.48	1.00	
San Francisco	0.12	0.26	0.46	
San Jose	0.23	0.75	1.48	
Population-weighted Exposure:		**0.34**		**4,394,374**
San Joaquin Valley Air Basin				
Bakersfield	0.20	0.81	1.62	
Fresno	0.42	1.48	2.99	
Modesto	0.36	1.19	2.37	
Stockton	0.14	1.04	2.02	
Exposure:		**1.13**		**1,778,400**
Sacramento Valley Air Basin				
Citrus Heights	0.43	1.39	2.61	
Exposure (for Sacramento County):		**1.39**		**893,800**
Statewide Population-weighted Exposure (Lower Bound of Exposure):		**0.53**		**19,890,507**

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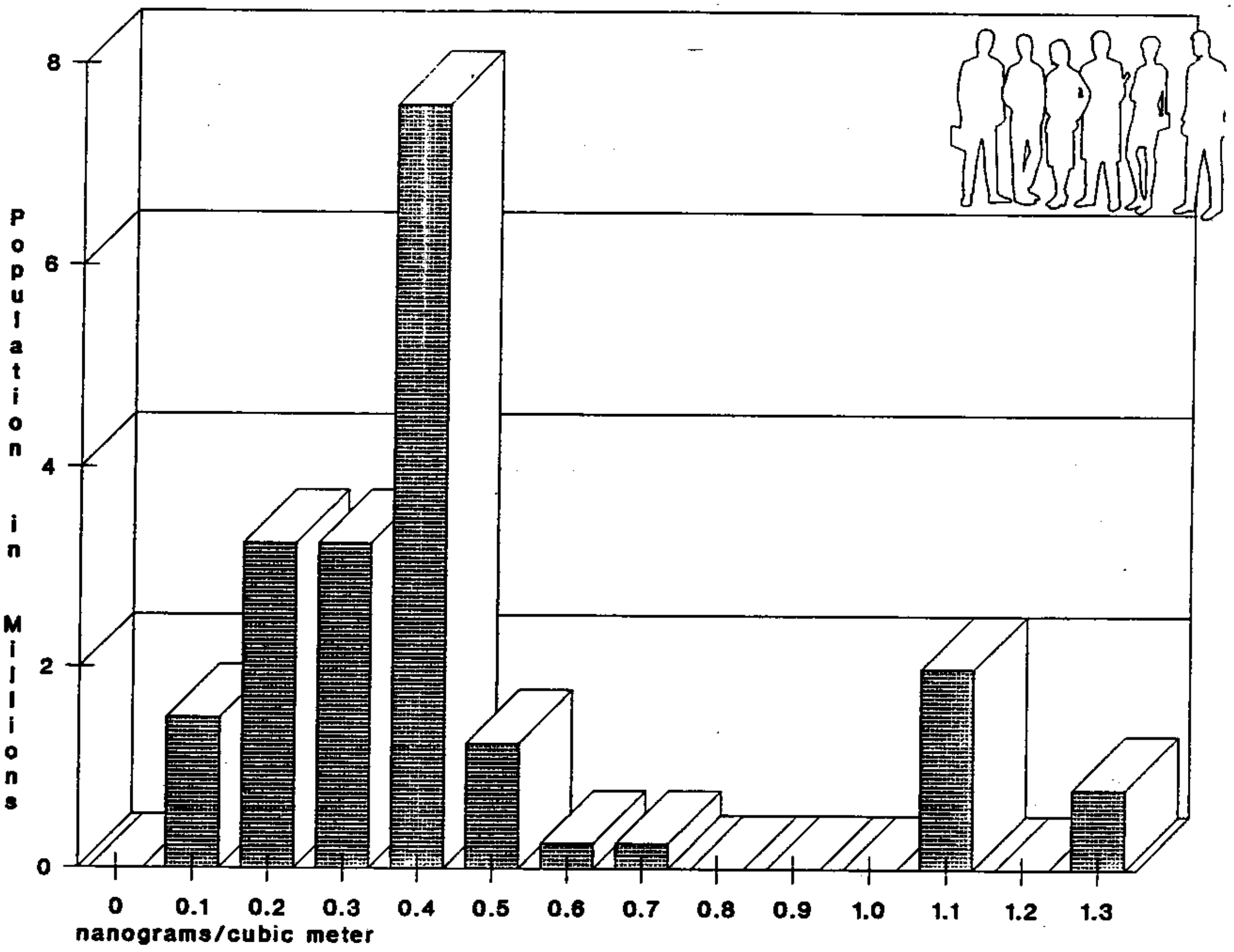
* See page A-29 section C, for the method of calculation.

FIGURE IV-4
ESTIMATES OF THE POPULATION EXPOSED TO VARIOUS MEAN ANNUAL CONCENTRATIONS
(Based on November 1988-October 1989 Data)



D. EXPOSURE CONCENTRATION OF BaP NEAR EMISSION SOURCES

High localized concentrations "hot spots" of BaP and associated, potentially carcinogenic PAHs may result in significantly greater health impacts for a local population than the health impacts associated with statewide ambient concentrations. Staff analyzed size-selected particulate matter (PM_{10}) and Coefficient of Haze data to identify areas with the greatest potential for BaP "hot spot" exposure concentration. Two mountain communities, Quincy and Mammoth Lakes, were identified as having a high potential for elevated BaP concentrations.

The ARB collected samples and measured concentrations of BaP from the PM_{10} monitoring network at Quincy and Mammoth Lakes. The data represented by Figures IV-5 (Quincy) and IV-6 (Mammoth Lakes) show that the two mountain communities experienced higher concentrations of BaP during November 1988 through February 1989, as compared to the levels measured during the same period at the ARB toxics monitoring network stations. The highest value from the statewide air toxics monitoring network was 14.0 nanograms per cubic meter, measured at the Fresno station. The mean BaP concentration during the study period was 9.4 nanograms per cubic meter for Quincy, and 4.8 nanograms per cubic meter in Mammoth Lakes. The maximum concentration in both Quincy and Mammoth Lakes was 19 nanograms per cubic meter. The minimum concentrations ranged from 1.7 nanograms per cubic meter in Quincy and 0.4 nanogram per cubic meter in Mammoth Lakes.

ARB-funded studies have measured ambient BaP and associated PAH concentrations at several locations (Flessel et al., 1984; Winer et al., 1987; Atkinson et al., 1988). The resulting BaP data from sampling sites in Richmond, Martinez, Concord, Pittsburg, Claremont, Torrance, Glendora, Yuba City, Mammoth Lakes, Oildale, Reseda, Pt. Arguello and San Nicolas Island, California, are given in Tables 1 through 3 in Appendix D. Where available, the BaP concentration data are also given. The majority of the measurements (not including the background sites of Pt. Arguello and San

Nicolas Island) were made during pollution episode conditions when BaP concentrations were expected to be at their highest. The BaP concentrations ranged from sub-quantifiable levels at the background sites of Pt. Arguello and San Nicolas Island (the limit of detection is estimated to have been approximately <10 picograms per cubic meter) to a high at Mammoth Lakes during the woodburning season of approximately 12 nanograms per cubic meter. Both the results obtained from the ARB monitoring network and the study of Atkinson et al., (1988) showed the elevated BaP levels during the woodburning season.

FIGURE IV-5
QUINCY BENZO[a]PYRENE PM10-DERIVED "HOT SPOT" DATA

(Based on November 1988-February 1989 Data)

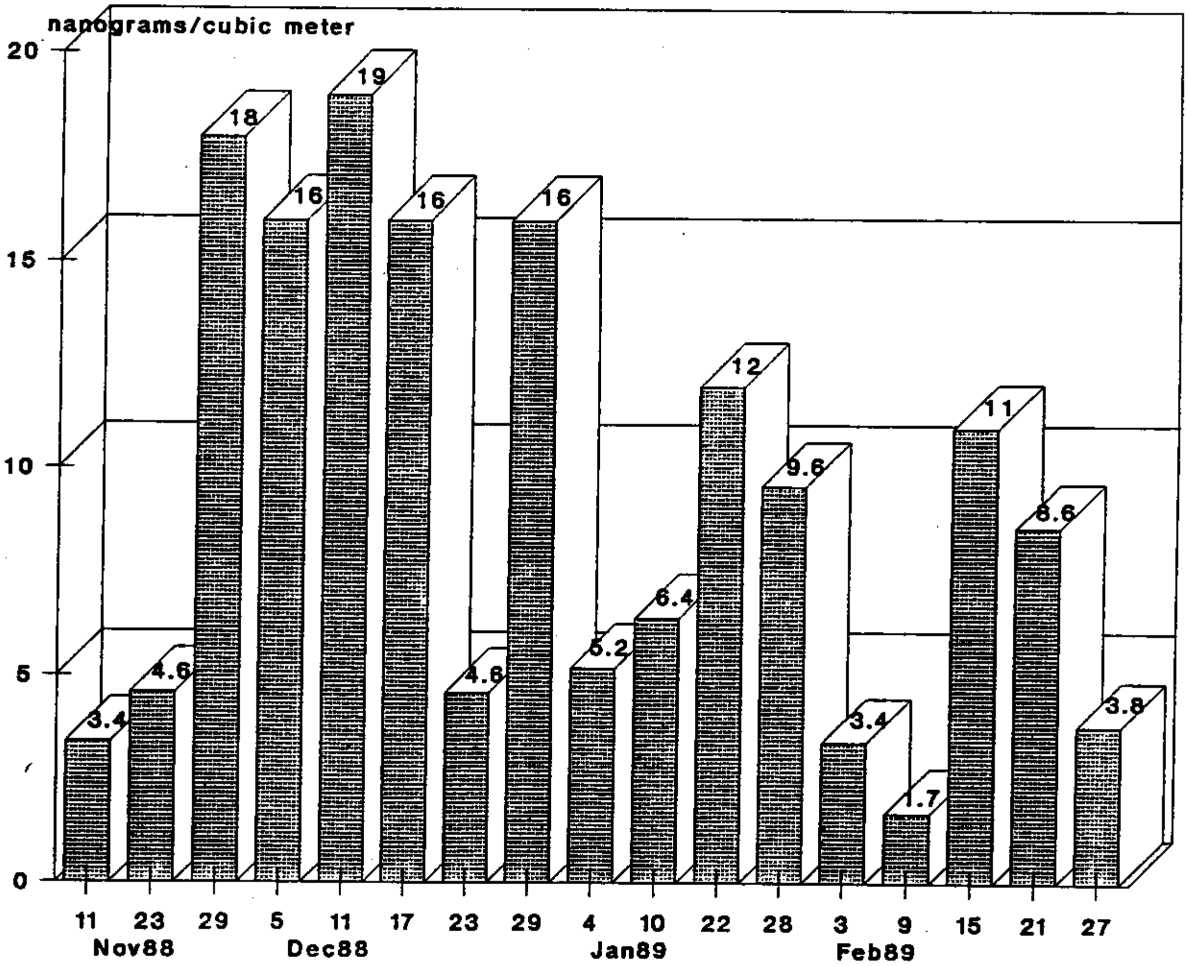
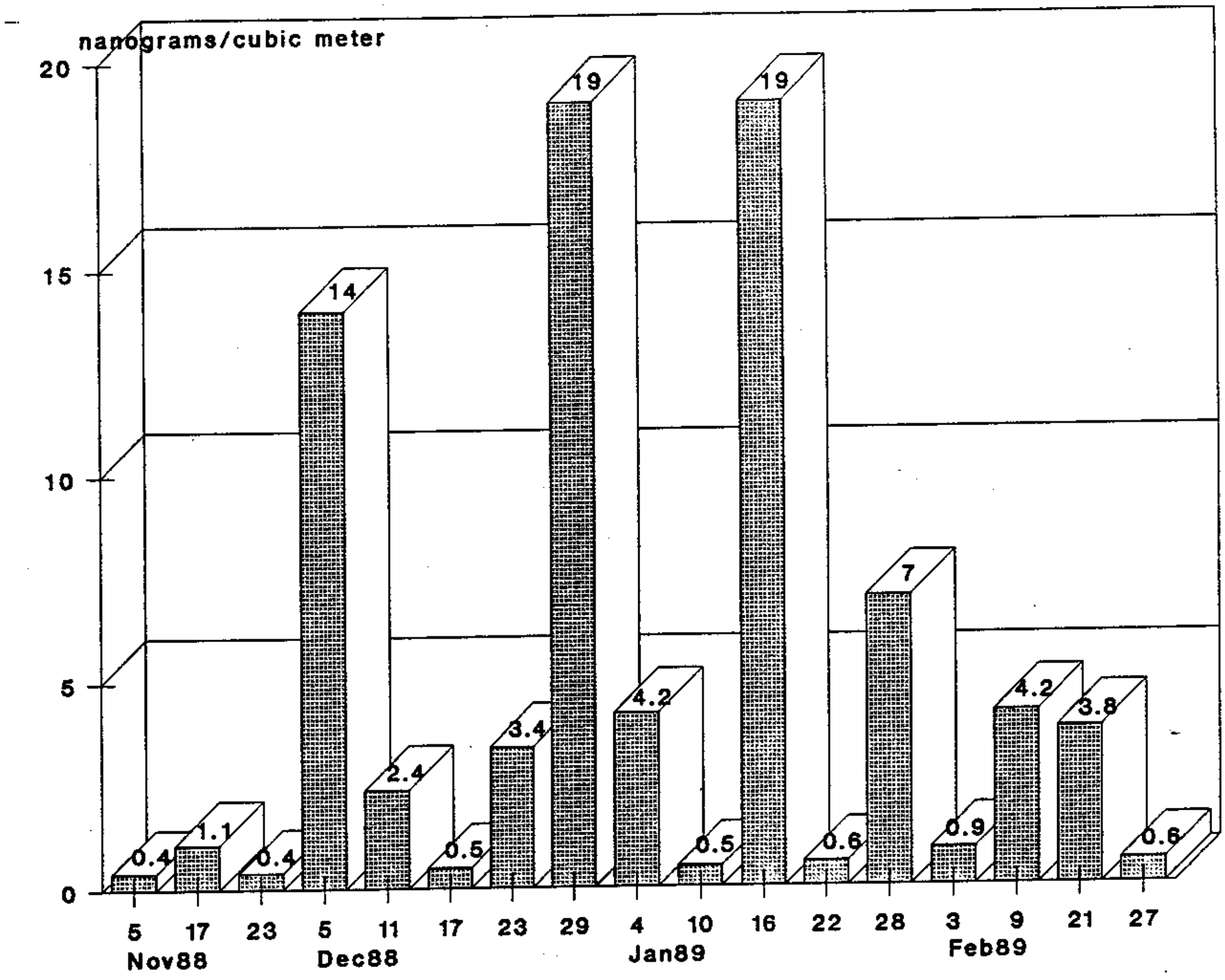


FIGURE IV-6
MAMMOTH LAKES PM10-DERIVED BENZO[a]PYRENE "HOT SPOT" DATA

(November 1988--February 1989)



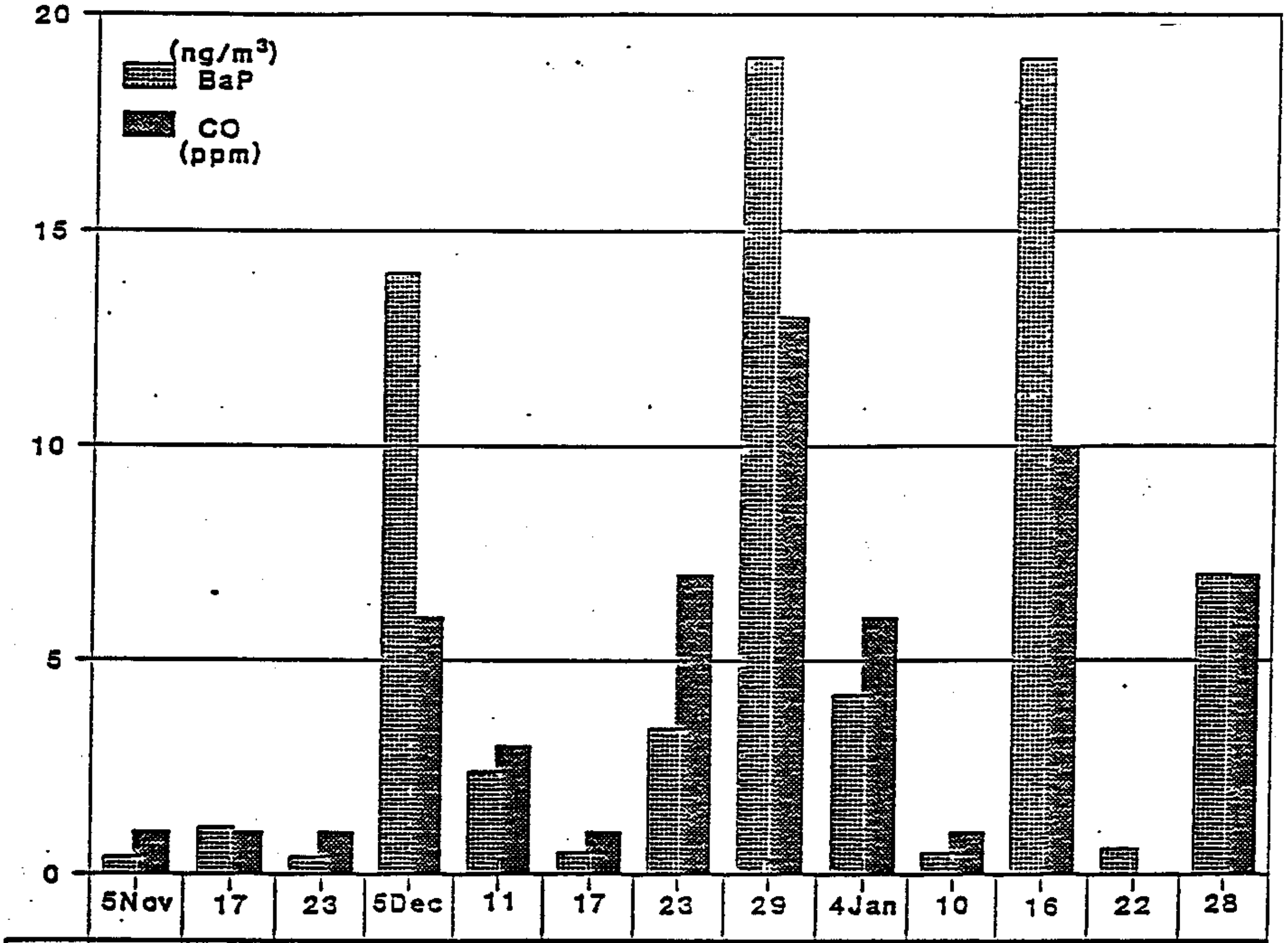
The atmospheric concentrations of BaP can be affected by the chemical properties of BaP, the chemical nature of the atmosphere into which it is emitted, the area geography, meteorological conditions, and the characteristics of BaP emission sources.

Intensive woodburning for residential heating during the winter months is a major source of BaP emissions. It is reasonable to assume that an increase in wintertime BaP concentrations would be associated, to some extent, with the increase in residential wood combustion that accompanies cold weather. Sheldon et al. (1993) reported a wintertime average geometric mean of 1.03 nanograms per cubic meter in Placerville, California, where over 50 percent of study households used woodburning as a source of heat. This level is about twice the statewide population average of 0.53 nanogram per cubic meter. In nearby Roseville, where very few respondents used wood as a heat source, average ambient BaP concentrations were 0.54 nanogram per cubic meter. BaP emissions are also associated with winter tourist activities (motor vehicle use, electricity generation, and ski resort operation).

Meteorological conditions (mixing height, wind, available sunlight) can cause fluctuations in BaP concentrations in the atmosphere even though emissions from BaP sources do not increase. The influence of meteorological conditions on BaP concentrations in Mammoth Lakes was explored by using information about the relationship between carbon monoxide and particulate matter concentrations. The same meteorological conditions (mixing height, wind) that encourage particulate matter accumulation in the atmosphere also encourage the accumulation of carbon monoxide.

Mammoth Lakes data on BaP and carbon monoxide concentrations were examined by ARB staff to determine whether a statistical correlation exists between meteorological conditions and the fluctuations in BaP concentrations depicted in Figure IV-6. Both pollutants are generated during combustion processes. Figure IV-7 depicts the data, which was determined to have

FIGURE IV-7
MAMMOTH LAKES BENZO[A]PYRENE VS. CARBON MONOXIDE CORRELATION
(November 5, 1988--January 28, 1989)



	5Nov	17	23	5Dec	11	17	23	29	4Jan	10	16	22	28
BaP	0.4	1.1	0.4	14	2.4	0.5	3.4	19	4.2	0.5	19	0.6	7
CO	1	1	1	6	3	1	7	13	6	1	10	0	7

a correlation coefficient (r) of 89 percent. This indicates that meteorological conditions probably contributed to the variation in BaP values for this period. Warm weather Coefficient of Haze and PM_{10} data suggest that high BaP concentrations would be limited to the winter time in these communities.

E. ANNUAL AVERAGE CONCENTRATIONS OF SELECTED PAHs AND PAHs WHICH MUST BE REPORTED UNDER AB 2588

In addition to benzo[a]pyrene, the ARB 19 station air toxics monitoring network collects ambient monitoring data for five other PAHs. These are: benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), dibenz[a,h]anthracene (DBA), benzo[g,h,i]perylene (BgP), and indeno[1,2,3-c,d]pyrene (IDP). The most recent data on these five PAHs that have been thoroughly reviewed under ARB's rigorous quality assurance program are from 1990. The number of samples collected in 1990 ranged from 152 for DBA, BgP, and IDP to 447 for BbF and BkF. Mean concentrations and standard errors were calculated from the reported concentrations in 1990. Mean concentrations ranged from a minimum of 0.25 nanograms per cubic meter for BkF to a maximum of 1.37 nanograms per cubic meter for BgP.

AB 2588 requires facilities to report emissions of the following PAHs: anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, dibenzo[a,e]pyrene, dibenzo[a,h]pyrene, dibenzo[a,i]pyrene, dibenzo[a,l]pyrene, indeno[1,2,3-c,d]pyrene, and naphthalene.

Calculated means and standard errors for measured ambient concentrations in 1990 are in the table on page A-45.

TABLE IV-4

POLYCYCLIC AROMATIC HYDROCARBONS ANNUAL AVERAGE CONCENTRATIONS in ng/cubic.meter

1990

PAH	No. Samples	Mean Conc.	S. Error
Benzo[b]fluoranthene (BbF)	447	0.63	0.07
Benzo[k]fluoranthene (BkF)	447	0.25	0.03
Dibenz[a,h]anthracene (DBA)	152	0.26	0.05
Benzo[g,h,i]perylene (BgP)	152	1.37	0.15
Indeno[1,2,3-c,d]pyrene (IDP)	152	1.14	0.19
Benzo[a]pyrene (BaP)*	332	0.66	-

* Average of the means of six air basins (see Table IV-2, page A-32).

F. INDOOR EXPOSURE CONCENTRATIONS

Section 39660.5(d) of the Health and Safety Code mandates that "the state board shall identify the relative contribution to total exposure to the contaminant from indoor concentrations, taking into account both ambient and indoor air environments." Following is a summary of Appendix E which discusses levels of BaP in indoor air, food, and drinking water.

Indoor air exposure to BaP plays an important part in determining an individual's total exposure to BaP. Jenkins et al. (1992) reported that the average adult Californian spends nearly 62 percent of the time inside their home (approximately seven percent spend at least 95 percent of their time at home), where exposure to BaP and other pollutants may occur at levels well above the typical ambient air exposure concentrations the individual may experience. Additionally, many Californians work in indoor environments that may be contaminated with airborne BaP from a variety of sources. An individual's activities, such as smoking, welding and cooking, often lead to elevated personal and indoor air levels of BaP, with outdoor penetration also providing a major portion of indoor BaP (Butler et. al., 1993), however, the major indoor sources of airborne BaP appear to be tobacco smoking and residential wood combustion.

Two large-scale investigations of PAHs, including BaP, in indoor air have been conducted recently in California. In the southern California PTEAM (Particle Total Exposure Assessment Methodology) study, researchers measured BaP inside more than one hundred homes (Sheldon et al., 1992). This study, conducted during the fall of 1990, measured BaP in both smokers' and nonsmokers' homes; other combustion sources of BaP were not typically present inside the study homes. In the second study, investigators measured BaP inside 280 homes in two northern California towns, Placerville and Roseville, during the winter. This study examined the effect of woodstoves, fireplaces, gas heating, and smoking on indoor BaP and PAH concentrations; researchers also measured BaP concentrations inside houses with no obvious combustion sources. These two studies provide a basis for evaluating indoor exposures of California residents to BaP and other PAHs.

1. Tobacco Smoke

Tobacco smoking is a major contributor of BaP pollution indoors, and produces a complex mixture of toxic and irritating compounds. Two components of tobacco smoke pollute indoor air: exhaled mainstream smoke (the aerosol inhaled by the smoker), and sidestream smoke (the aerosol emitted from the burning end of a cigarette between puffs). The combination of exhaled mainstream smoke and sidestream smoke is called environmental tobacco smoke. Sidestream smoke contributes the greater amount of BaP to indoor air. Investigators report sidestream to mainstream smoke ratios for BaP ranging from 2.1:1 to 9.4:1 per cigarette (Eatough, D.J. et al., 1990; DHHS, 1986; First, 1984). These ratios correspond to sidestream emissions ranging from 20 to 140 nanograms BaP per cigarette (Ibid).

From two studies of California homes, Sheldon et al. (1993) and Sheldon et al. (1992) reported average indoor BaP concentrations ranging from 0.43 to 2.2 nanograms per cubic meter in smokers' homes. Cigarette smoking was the most significant indoor source in both studies. For the average Californian, spending about 15 hours per day at home, the estimated inhaled dose is about 6 to 27 nanograms of BaP per day. For homebound residents, exposure results in estimated inhaled doses of about 9 to 44 nanograms of BaP daily. The low end of the exposure estimate represents low levels of smoking and the use of natural ventilation (open windows and doors). The high end of this exposure estimate represents high levels of smoking and a closed-up residence.

Turk et al. (1987) estimated comparable BaP concentrations during workdays in office buildings with smoking; investigators reported an average of 1.07 nanograms per cubic meter. Extrapolating from their data, the estimated inhaled dose of BaP in public buildings where smoking occurs is about seven nanograms daily, based on an eight hour period spent in the office.

2. Fireplaces and Woodstoves

Indoor wood combustion can be a significant source of BaP. According to California data developed by Sheldon et al. (1993) and Traynor et al. (1987), average indoor BaP concentrations of 0.34 to 1.2 nanograms per cubic meter can result from woodstove use. The typical Californian, spending about 15 hours at home, would inhale an estimated 4 to 15 nanograms of BaP per day. People spending 24 hours indoors would potentially inhale about 7 to 24 nanograms of BaP daily from this source. However, the indoor concentrations and inhaled doses from wood combustion will vary greatly due to seasonal differences in woodstove use, and other factors.

Woodburning in fireplaces can also contribute substantially to BaP concentrations indoors. Sheldon et al. (1993) measured an average indoor concentration of 1.0 nanogram per cubic meter for 46 homes using fireplaces. For a typical Californian, spending about 15 hours per day inside the home, a daily inhaled dose of about 12 nanograms is estimated. For homebound residents, the estimated inhaled daily dose is 20 nanograms.

Elevated BaP concentrations can result from improper operation of woodstoves and fireplaces. Sheldon et al. (1993) reported that operation of a woodstove with its doors open resulted in high BaP levels indoors; authors did not report specific values. Traynor et al. (1987) reported a BaP concentration of 3.5 nanograms per cubic meter resulting from a test of a woodstove operating with its doors open. This was a significant elevation over BaP concentrations of 0.34 to 0.94 nanograms per cubic meter from airtight stoves operated with closed doors.

Much higher than average BaP concentrations can also result indoors from the use of leaky woodstoves or fireplaces. Traynor et al. (1987) reported extremely high levels when operating a leaky Franklin-type stove, measuring estimated real-time averages of 13 and 44 nanograms per cubic meter over two burn periods. The newer, more efficient airtight woodstoves appear to emit less indoors then the older, leakier woodstove models. Elevated BaP concentrations resulting from leaky woodstove tests were not used for developing exposure estimates because the tests represent worst case scenarios that are believed to be rare occurrences in California.

3. Other Indoor Sources

It is unclear whether the use of natural gas appliances contributes to BaP concentrations indoors. In a study of about 50 homes using gas heat, Sheldon et al. (1993) did not find an increase in BaP concentrations when compared to homes with no obvious combustion sources. However, two small studies by Chuang et al. (1986, 1988) suggest that the use of gas ranges may elevate BaP indoors to a small degree. Additional research is needed to evaluate possible contributions of gas appliances and their use.

Other possible indoor sources of BaP include kerosene heaters, burning of food, incense burning, and some hobbies that involve the use of combustion devices. Kerosene heaters can produce high levels of BaP but are used infrequently in California. Other indoor sources are probably minor contributors.

4. Infiltration of Outdoor Air

A major source of indoor BaP pollution is the infiltration of polluted outdoor air. In a study of two northern California communities, Sheldon et al. (1993) concluded that outdoor air polluted by woodsmoke contributed significantly to indoor air concentrations of BaP. In a southern California PAH study where there were few strong indoor sources of BaP, investigators found indoor concentrations to be highly correlated with levels measured outdoors (Sheldon et al., 1992). This finding suggests that infiltration of polluted outdoor air was a significant source of indoor BaP for that study. Waldman et al. (1989) and Kaarakka et al. (1986) reported similar results in studies conducted in New Jersey and Wisconsin.

5. Indoor Air Contribution to Total Exposure

The major indoor sources of BaP inhalation exposure are environmental tobacco smoke and woodburning in fireplaces and stoves. Gas stoves and furnaces, cooking, and the inadvertent burning of food may also contribute to BaP levels indoors. A presentation of estimated daily doses of BaP from indoor air inhalation is found in Table IV-4. Californian adults spend, on average, about 62 percent of the day inside the home (about 15 hours per day) and about six percent of the day outdoors (1.2 hours per day; Jenkins et al., 1992). The estimated inhaled dose from outdoor exposure would be 0.53 ng/m^3 (population-weighted exposure) x 20 m^3 (average amount of air inhaled per day) x 0.06 (percentage of time per day spent outdoors) = 0.64 nanogram per day. Therefore, comparing this dose with the estimates in Table IV-4, the inhaled dose of BaP received in homes with indoor combustion sources can range from about five times up to several orders of magnitude higher than the dose received outdoors. However, the inhaled dose of BaP received indoors would typically be expected to be at the low end of this range.

6. Indoor Concentrations Compared to Outdoor Concentrations

Indoor BaP levels vary widely due to differences in the presence and strength of indoor sources. Relative indoor and outdoor levels are also highly variable. In and around individual residences or buildings, indoor/outdoor ratios can vary from less than one to as high as 94 (Sheldon et al., 1993; Sheldon et al., 1992; Turk et al., 1987). Typically, indoor/outdoor ratios appear to be at the lower end of this range. Highest indoor/outdoor ratios tend to result from tobacco smoking, or such events as the operation of a leaky woodstove or backdrafting from a poorly maintained woodburning appliance (Sheldon et al., 1993; Sheldon et al., 1992; Traynor et al., 1987; Neulicht and Core, 1982).

TABLE IV-5
ESTIMATED INHALED DOSES OF BENZO[a]PYRENE FROM INDOOR AIR

Based on Percent of Time Exposed (in nanograms per day)

	8 hours (33%)	15 hours (62%)	24 hours (100%)
Smoking	7[d]	6 - 27[a,b]	9 - 44[a,b]
No source*	3[d]	3 - 10[a,b]	4 - 17[a,b]
Woodstoves	--	4 - 15[a,c]	7 - 24[a,c]
Fireplaces*	--	12[a]	20[a]

* The inhaled doses for these scenarios apply only when woodstoves or fireplaces are used. For most areas of California, this would occur only in fall or winter.

References

a. Sheldon et al. (1992)
b. Sheldon et al. (1992)
c. Traynor et al. (1987)
d. Turk et al. (1987)

Calculations:

Assumption: Assume 20 cubic meter of air is breathed per 24-hour period.
Example: If the average indoor BaP concentration is 1.13 ng/m^3, the 24-hour inhaled dose estimate is 22.6 ng (20 m^3 x 1.13 ng/m^3).

Tobacco smoking typically raises indoor levels above those outdoors. In smokers' homes, an average indoor/outdoor ratio of 5.8 and a median ratio of about 1.9 were reported in a recent California study (Sheldon et al., 1993). Turk et al. (1987) reported an average indoor/outdoor ratio of 7.6 for smoking areas of public buildings in the Northwest; indoor BaP concentrations were higher than outdoor concentrations for 12 of 15 buildings tested.

Woodburning can also elevate indoor BaP over outdoor levels. Sheldon et al. (1993) calculated mean indoor/outdoor ratios of 1.2 and 2.6 for homes using fireplaces and woodstoves, respectively. However, median ratios were less than one, due in part to the elevation of outdoor levels from woodburning emissions to the outdoors. High chimney emissions of woodsmoke to the outdoors can lower indoor/outdoor ratios, even when the woodburning appliance is emitting some BaP indoors (Sheldon et al., 1993; Traynor et al., 1987).

In most cases, indoor concentrations of BaP appear to be lower than those outdoors. In southern California, researchers reported a mean indoor/outdoor ratio of 0.87 and a median ratio of 0.64 (Sheldon et al., 1992). In the northern California study, mean indoor/outdoor ratios for homes using gas heat or having no significant indoor combustion sources ranged from 0.61 to 0.67.

7. Cancer Risk from Indoor Exposure

People in California are often exposed to levels of BaP above the statewide population-weighted average for outdoor air (0.53 ng/m^3). In indoor environments, environmental tobacco smoke (ETS) and other combustion sources such as woodburning can raise people's exposure to BaP.

Using OEHHA's best estimate of risk, and average indoor concentrations in California homes where smoking occurred (Sheldon et al., 1993; Sheldon et al., 1992), exposure to BaP in smoking environments is estimated to result in 0.5 to 2.4 potential cancer cases per million people exposed for most of their day. People at risk from such exposures include residents of smokers' homes who stay indoors all day, and those exposed at both work and home. On a given day, about seven percent of adult Californians spend at least 95 percent of their time at home (Wiley et al., 1991). The higher risk number is estimated from wintertime concentration data in smokers' homes (2.2 ng/m^3 average indoor BaP) and represents exposure in relatively closed-up homes. The lower risk number is estimated from summertime concentration data in smokers' homes (0.47 ng/m^3 average indoor BaP) and represents summertime exposure in homes with some opening of doors and windows. The calculations are as follows:

$$\text{(a)}\quad 2.2 \times 10^{-3}\mu g/m^3 \;\; X \;\; \frac{1.1 \times 10^{-3}\text{ cancers}}{(\mu g/m^3)\text{ (person)}} \;\; X \;\; 10^6\text{people} = 2.4 \text{ cancers per million}$$

$$\text{(b)}\quad 0.47 \times 10^{-3}\mu g/m^3 \;\; X \;\; \frac{1.1 \times 10^{-3}\text{ cancers}}{(\mu g/m^3)\text{ (person)}} \;\; X \;\; 10^6\text{people} = 0.5 \text{ cancers per million}$$

In homes with no obvious combustion sources, researchers (Ibid) documented exposures that were comparable to or lower than the statewide ambient average.

G. EXPOSURE THROUGH OTHER ROUTES

1. Multipathway Exposure

Exposure assessment involves determining concentrations of the various pollutants in media by which humans are exposed. Air emissions contaminate not only the air, but deposit onto water, soil, and vegetation, thereby entering the food chain. These media represent the additional possible pathways of exposure to ambient BaP concentrations. In order to estimate long-term exposures resulting from ambient concentrations, the risk assessment must address both inhalation and noninhalation pathways of exposure. Exposure through noninhalation pathways results when pollutants are deposited on soil, crops, and surface waters and people come into contact with those media through ingestion or dermal exposure. BaP and other PAHs can accumulate in road and house dust and be a significant source of exposure through ingestion, especially for toddlers. Roberts et al., (1993) in a study of eight homes in Columbus, Ohio reported a range of BaP concentrations of 1.5 to 41 ppm with an average of 9.6 ppm.

Both primary (direct) and secondary (indirect) pathways may contribute to the total exposure to a pollutant. The paths of exposure are routes by which the person is exposed through direct inhalation, ingestion of dirt and contaminated food products, water ingestion, or dermal absorption (from contaminated dirt deposited on the skin). Secondary pathways of exposure are those which result from assimilation of the pollutant into a food source. The potential primary and secondary noninhalation pathways of concern are:

Primary

- Dermal Exposure
- Water Ingestion
- Crop Ingestion (Direct Deposition)
- Soil Ingestion

Secondary

- Mother's Milk
- Fish Ingestion
- Crop Ingestion (Root Uptake)
- Poultry Meat and Eggs
- Meat from: Cattle, Goats, Pigs, Sheep
- Dairy Products

The potential risk from BaP could be significantly higher at some monitoring locations if additional pathways are considered. The consideration of the pathways such as soil ingestion, dermal absorption, and mother milk is appropriate for all locations. However, some communities may be exposed through other pathways. For these communities, the additional pathways (ingestion of home grown produce, chicken and eggs raised on a farm, or fish ingestion) could be the main exposure route for BaP. An oral potency value is available for BaP and noninhalation potency can be estimated. Site-specific information for each of the 14 monitoring locations was not readily available. Therefore, the carcinogenic risks presented in this report are based on the inhalation pathway only.

2. Food Ingestion

BaP is found in many different foods, in concentrations that vary depending on the source and type of the food and the manner in which it was prepared. Most raw foods grown in uncontaminated environments contain little or no BaP, however, vegetable and fruit crops can become contaminated with BaP from atmospheric deposition, polluted soil, or polluted water. The Total Human Environmental Exposure Study (THEES) demonstrated that personal activities, lifestyle, and diet can strongly influence individual exposures. In particular, the single largest contribution appears to be the ingestion of BaP-containing foods (Buttler et al., 1993).

Raw seafood may contain BaP derived from polluted water or sediments. Levels in edible marine species, especially filter feeders (e.g., clams and oysters) are likely to reflect the extent of PAH contamination of the water.

Raw meats do not usually contain BaP; however, meats and other foods can become contaminated depending on how they are cooked or prepared. For example, smoked meat, fish, and cheese, and meats cooked at high temperatures or close to a flame (especially meat with a high fat content) can have BaP levels up to 50 micrograms per kilogram.

BaP has been detected in grains, cereal products, vegetable oils, margarine, coffee, tea, and whiskey (Santodonato et al., 1981; NRC, 1983). Table IV-6 provides a sample of some of the levels of BaP measured in various foods.

TABLE IV-6
LEVELS OF BENZO[a]PYRENE IN VARIOUS FOODS
(in microgram per kilogram wet weight)

Cooked meats, sausage	0.17-0.63
Cooked bacon	1.6-4.2
Charcoal-broiled meats	2.6-11.2 (50.4 recorded)
Heavily smoked ham	Up to 23 (107 recorded, Iceland)
Cooked fish	0.9
Smoked fish	0.3-60
Cereal grains	0.2-4.1
Flour and bread	0.1-4.1
Bakers' dry yeast	1.8-40.4 (less if grown on mineral oils)
Soybean	3.1
Refined vegetable oils, fats	0.4-36
Margarine, mayonnaise	0.2-6.8
Salad	2.8-12.8
Tomatoes	0.2
Spinach	7.4
Kale	12.6-48.1 (only 10% removed after washing)
Apples	0.1-0.5
Fruits (not apples)	2-8
Dried prunes	0.2-1.5
Roasted coffee and solubles	0.1-4
Malt coffee	Up to 15
Tea	3.7-21.3
Whiskey	0.04 micrograms per liter
Beer	not detected
Milk	not detected

Source: National Research Council (1983)

Estimating the amount of BaP that a person might ingest in their food is a problem because of the large variation in the levels of BaP in foods. Among other factors, the manner of cooking has a major effect on BaP levels; substantial person-to-person variation might thus be expected.

Santodonato et al. (1981) estimated that a person ingests between 160 to 1,600 nanograms BaP per day through the food they eat. This wide-ranging estimate was derived by multiplying an estimate of typical levels of BaP in food (0.1 to 1.0 parts per billion) by the average total daily food consumption of all types of food (1,600 grams per day). Likewise, Harris et al. (1982) estimated that the typical ingestion of BaP through food was approximately 50 nanograms of BaP per day, and also stated that consumption of large amounts of charcoal-broiled food could result in ingestion of as much as 6,000 nanograms BaP per day. The values were calculated by multiplying estimates of the average consumption of different types of food by levels of BaP measured in those food types. Lioy et al. (1988) estimated the amount of BaP ingested through food from their measurements of BaP levels in composite (weekly).samples obtained from family meals. Their estimates ranged from 10 to 4,005 nanograms BaP per week. For an estimate of daily

TABLE IV-7

ESTIMATED DOSES OF BENZO[a]PYRENE THROUGH INGESTION (nanograms/day)

	Low est.	Average	High est.	References
Food	160	---	1600	a
	---	50	6000	b
	1.4	---	572	c
Water (2 liters/day)	---	1.1		a

References:
a. Santodonato et al. (1981)
b. Harris et al. (1982)
c. Lioy et al. (1988)

ingestion, those values divided by seven are approximately 1.4 to 572 nanograms BaP per day (.001 to 0.57 micrograms BaP per day).

The three estimates presented above compare reasonably well, considering that different approaches were used in deriving them. Combined, the estimates predict that an individual may ingest from approximately 1 to 6,000 nanograms of BaP per day in their food. It should be emphasized that this wide range reflects the large variability of BaP levels in food and, consequently, the uncertainty in predicting the amount of BaP a person may ingest. Table IV-6 presents information on the estimated doses of BaP through ingestion of food and water.

3. Water Ingestion

Drinking water contributes much less BaP, in most cases, to total exposure than does food ingestion (National Research Council, 1983). Raw surface waters may become contaminated with BaP and other PAHs from local sources such as municipal sewage, coke oven effluents, or road run-off (Basu and Saxena, 1978; NRC, 1983; Santodonato et al., 1981). However, routine treatment of surface water to obtain drinking water appears to reduce BaP (and other PAH) concentrations considerably (Ibid). In contrast, raw groundwater generally contains lower amounts of BaP and other PAHs than surface water (Santodonato et al., 1981).

Limited data exist on BaP concentrations in California drinking water. A Department of Health Services (DHS) drinking water survey indicates that Californians' exposure to BaP through drinking from groundwater sources may be negligible (A. Milea, 1990; DHS, 1986). The DHS monitored a number of organic compounds in wells between January 1984 and December 1985, but did not find evidence of BaP contamination. The monitored wells were used by large public water systems having over 200 connections and were located near heavy industrial areas - sites which were considered to have the greatest potential for well contamination. All measurements of BaP were below the detection limit of 10 micrograms per liter (Ibid, 1986). However, the limit of detection in this study is high; some researchers have recommended that raw waters contain no more than 1.0 microgram per liter total PAH (Basu and Saxena, 1978). DHS has not monitored BaP in California surface waters (A. Milea, 1992).

Santodonato et al. (1981) estimated that a person ingests approximately 1.1 nanograms BaP per day through drinking water, derived by multiplying their estimate of the average concentration of BaP in U.S. drinking water (0.55 nanograms per liter) by the average daily consumption of water (two liters per day). The highest BaP concentration calculated by the authors was 2.1 nanograms BaP per liter. However, as previously discussed, BaP concentrations in California's groundwater appear to be low; a Californian's exposure to BaP from ingesting drinking water from this source may be negligible. Data on BaP in surface water are currently unavailable for California.

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V.

ATMOSPHERIC PERSISTENCE AND FATE OF BaP

It is estimated that the atmospheric lifetime of BaP (excluding BaP that is bound within a particle or is stabilized by adsorption) is a few hours in sunny, polluted atmospheres. For BaP within a particle and unavailable for reaction, or BaP stabilized due to adsorption, the expected atmospheric lifetime is approximately 10 days or less due to dry deposition of the particles. The atmospheric lifetime of BaP, which may be responsible for much of the measured mutagenicity from the atmosphere (ARB #A732-154), will depend on the nature (e.g., chemical reactivity) of the atmosphere into which the BaP is emitted and the form (i.e., hot vapor-phase BaP, "pure" BaP particle, within a particle, or adsorbed to a particle) of the emitted BaP.

The following text is a discussion of the pertinent issues and information relevant to the atmospheric persistence and fate of BaP.

A. PERSISTENCE

The atmospheric fate of chemical compounds emitted into the troposphere are governed by a number of chemical and physical removal processes. Laboratory studies carried out over the past 20 years indicate that the important gas-phase chemical reaction pathways which must be considered include:

- o Photolysis during daylight hours
- o Reaction with the hydroxyl (OH) radical during daylight hours

- Reaction with the hydroperoxyl (HO_2) radical, mainly during afternoon/evening hours
- Reaction with the nitrate (NO_3) radical during nighttime hours
- Reaction with nitrogen dioxide (NO_2)
- Reaction with ozone (O_3), and
- Reaction with gaseous nitric acid (HNO_3).

For the great majority of organic compounds present in the gas phase, the most important of the loss processes remain photolysis and reaction with OH and NO_3 radicals, and with O_3.

For a limited number of gaseous organic compounds, one or more of the other reactive chemical species in the troposphere may react with organic compounds at significant rates. For example, HO_2 radicals react with formaldehyde and, more slowly, with acetaldehyde and glyoxal; NO_2 reacts with dialkenes; and gaseous HNO_3 reacts with basic compounds such as the amines.

For chemical compounds present in the adsorbed phase, photolysis and reaction with O_3, NO_2, HNO_3, dinitrogen pentoxide (N_2O_5), nitrous acid (HONO), sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) may contribute to the degradation. For certain of these reactions involving adsorbed organics, synergistic interactions may be of importance.

The physical removal processes can be defined in a simplistic manner as accretion (or coagulation) of particles, and dry and wet deposition of gases and particles. Removal of gases and particles at ground surfaces (including snow and other moist surfaces) is referred to as dry deposition, while removal of these species by precipitation is referred to as wet deposition. There is a general lack of experimental data concerning these processes for most organic compounds (Bidleman, 1988).

The atmospheric lifetime τ of a chemical is defined as the time to decay to a concentration of 1/e (= 0.368) of that initially present. Also,

$$\frac{1}{\tau} = \frac{1}{\tau_{chemical}} + \frac{1}{\tau_{physical}} \quad (1)$$

where $\tau_{chemical}$ and $\tau_{physical}$ are the lifetimes of the chemical with respect to only chemical reaction and only physical loss processes, respectively. These chemical and physical lifetimes are composites of those for the individual loss processes. For example:

$$\frac{1}{\tau_{chemical}} = \frac{1}{\tau_{photolysis}} + \frac{1}{\tau_{OH}} + \frac{1}{\tau_{NO_3}} + \frac{1}{\tau_{O_3}} \quad . \quad . \quad . \quad (2)$$

where $\tau_{photolysis}$, τ_{OH}, τ_{NO_3} and τ_{O_3} are the lifetimes with respect to photolysis, reactions with the OH radical, reactions with the NO_3 radical,and reaction with O_3, respectively. In turn, these reactive loss processes are determined by the rate constants, k_x, for reaction and the ambient atmospheric concentrations, [X], of the reactive intermediates.

For example:

$$\frac{1}{\tau_{OH}} = k_{OH}[OH]$$

For photolysis, the photolysis rate depends on the absorption cross section (σ), the photolysis quantum yield (ϕ), and the radiation intensity (J), all of which are wavelength dependent:

$$\frac{1}{\tau_{photolysis}} = k_{photolysis} = \int_{\sim 290\ nm}^{\sim 800\ nm} \sigma_\lambda \phi_\lambda J_\lambda d\lambda$$

B. FATE

BaP is a member of the chemical class known as polycyclic (or polynuclear) aromatic hydrocarbons (PAHs), which are formed during combustion at high temperatures (Bockhorn et al., 1982; Prado et al., 1985; Toqan et al., 1985; Kittelson et al., 1985; Finlayson-Pitts and Pitts, 1986) and are emitted from essentially all combustion sources. Atmospheric chemistry and fate were reviewed through 1985 by Finlayson-Pitts and Pitts (1986). In addition to being present in combustion emissions (e.g., cigarette smoke), BaP is also found as a component of fossil fuels (IARC, 1983).

BaP from combustion sources can be emitted in either the vapor or particle-associated (adsorbed) phase. BaP has a vapor pressure at 298 Kelvin (room temperature) of 5.6×10^{-9} torr (Yamasaki et al., 1984), and because of this low vapor pressure (which would lead to a maximum mixing ratio in the gas phase of 0.008 parts-per-billion), is expected to exist in ambient air as particle-associated BaP.

No evidence for "blow-off" of BaP from filters onto downstream solid adsorbent traps has been seen (Arey et al., 1987; Coutant et al., 1988), nor has vapor phase BaP been observed in ambient air (Coutant et al., 1988).

The processes to be considered are:

- o Physical loss processes for the particles on which, or in which, BaP resides.
- o Adsorbed-phase reactions of BaP on the particles.

1. Physical Loss Processes

The particles with which BaP is associated will undergo wet and dry deposition. The average atmospheric lifetimes for particles due to dry deposition as a function of particle diameter (presented by Graedel and Weschler, 1981), are given in Table V-1:

TABLE V-1
AVERAGE ATMOSPHERIC LIFETIMES FOR PARTICLES DUE TO DRY DEPOSITION

Diameter (μm)	Lifetimes (days)
0.002	0.01
0.02	1
0.2	10
2	10
20	1
200	0.01

The particles with which BaP is associated generally exhibit a particle size range of <3μm (Pierce and Katz, 1975) and hence the atmospheric lifetime of these particles due to dry deposition is expected to be on the order of 10 days.

In the case of wet deposition, a Washout Ratio (W), defined as

$$W=C_{rain}/C_{air}$$

relates the particle concentration in the rain (C_{rain}) to that in the ambient air (C_{air}). The deposition rate (F) is given by

$F=W \times J \times C_{air}$ where J is the precipitation rate.

For particles of 0.1-10 μm diameter and for particle-associated organics such as the polychlorinated biphenyls (PCBs) and the C_{20}-C_{23} n-alkanes, the washout ratio W is $10^{5\pm1}$ (Eisenreich et al., 1981; Ligocki et al., 1985). With a washout ratio of this magnitude, essentially complete scavenging of the particles and their associated organics occurs during a rain event (Leuenberger et al., 1985). Rain-out is an episodic event in California, which will lead to generally shorter BaP lifetimes in the winter months than during the summertime.

Considering only its physical atmospheric removal processes, the lifetime of BaP due to particle dry deposition is expected to be around 10 days, with an additional efficient (albeit episodic) removal process involving the rain-out of particles. However, according to Roberts et al. (1993) BaP can accumulate and persist much longer in soils than in the air. BaP can be tracked into the house and persisted in carpets where it is protected from degradation by sunlight, moisture, bacteria etc.

2. Chemical Loss Processes

In addition to the physical removal of the particles with which the BaP is associated, BaP can also be transformed by a number of chemical processes in the adsorbed phase. These include photolysis and reaction with O_3, SO_2, NO_2 and/or HNO_3, and N_2O_5. Chemical loss processes were reviewed by Finlayson-Pitts and Pitts (1986). A large number of experimental investigations of these potential reaction pathways have been carried out (see, for example, Pitts et al., 1978, 1980, 1985, 1986; Katz et al., 1979; Jager and Hanus, 1980; Korfmacher et al., 1980; Peters and Seifert, 1980; Butler and Crossley, 1981; Blau and Güsten, 1981; Grosjean et al., 1983; Brorström et al., 1983; Van Vaeck and Van Cauwenberghe, 1984; Behymer and Hites, 1985, 1988; Brorström-Lunden and Lindskog, 1985; Kamens et al., 1985, 1986, 1988; Lindskog et al., 1985; Yokley et al., 1985, 1986; Güsten, 1986; Valerio et al., 1987; Arey et al., 1988; Coutant et al., 1988; Nielsen, 1988). Interpretation of the experimental laboratory studies data is difficult due to the diverse substrates used, and in many cases, the conflicting data obtained.

Some differences may be attributed to the availability of the BaP for reaction (i.e., whether it was present as an adsorbed surface layer or included in the particles, or whether the particles were "freshly" emitted or were "aged" particles).

Reaction with O_3. The test results concerning the stability of BaP adsorbed onto surfaces in the presence of O_3 are often conflicting. Katz and coworkers (Katz et al., 1979) and Peters and Seifert (1980) observed that BaP reacted in the presence of ambient levels of O_3, and Pitts et al., (1980) identified the BaP-4,5-epoxide, a strong direct-acting mutagen in the Ames assay, as a product of the reaction of O_3 with BaP deposited onto glass fiber filters. These studies indicated a BaP lifetime with respect to reaction with O_3 (at ambient concentrations, i.e., levels reached in polluted atmospheres) on the order of an hour. In contrast, Grosjean et al. (1983) observed no loss of BaP, either deposited onto blank filters or on filters coated with ambient particles, fly ash or diesel particles, when exposed to 100 ppb of ozone for three hours. Brorström et al. (1983) observed no definite evidence for losses of BaP (or other PAH) under high volume sampling conditions with the addition of 200 ppb of O_3. However, it should be noted that in this latter study, no BaP was added to the ambient particles.

In contrast, the relativity recent studies of Van Vaeck and Van Cauwenberghe (1984), Lindskog et al. (1985) and Pitts et al., (1986) all showed that BaP exhibited significant losses (typically 50 percent) when exposed to 50-1500 ppb of O_3 for time scales of 0.5-6 hours. Van Vaeck and Van Cauwenberghe (1984) observed that the percentage conversion of BaP in diesel exhaust particles exposed to 1.5 ppm of O_3 under high-volume sampling conditions increased slightly with the exposure time--from 62 percent at 0.5 hour to 87 percent at 4 hours. Lindskog et al., (1985) observed conversions of BaP (on soot generated in a smoke generator) at 6 hour exposure times [45 percent relative humidity (RH)] increasing from 3 percent at 0.1 ppm O_3 to 80 percent at 1.0 ppm O_3. Pitts et al. (1986) observed an approximately 50 percent conversion of BaP independent of the O_3 concentration (0.05-0.29 ppm O_3 at 1 percent RH) and the humidity (1-50 percent RH at

0.20 ppm O_3) for a three hour exposure time. The BaP was either adsorbed on filters or present in particles collected close to a freeway, and the exposures were both passive (in a chamber) and in a flow system. Another recent study found degradation of BaP on ambient particles enriched with BaP and exposed to 0.18 ppm O_3, but no degradation on ambient particles sampled with an O_3 enriched (0.18 ppm) vapor stream (Coutant et al., 1988).

These data are generally consistent with the fact that BaP reacts with O_3, providing that the BaP is available for reaction. This is suggested by the often initially rapid BaP degradation followed by significantly slower BaP losses (Pitts et al., 1986; Coutant et al., 1988). Those experiments in which BaP was coated or deposited onto surfaces should then exhibit reactive losses of BaP, as generally observed (Katz et al., 1979; Peters and Seifert, 1980; Pitts et al., 1980, 1986). Fresh diesel particles (Van Vaeck and Van Cauwenberghe, 1984) and ambient particles collected near a freeway (Pitts et al., 1986) also showed BaP losses upon exposure to O_3. In contrast, BaP included in particles (as may be expected to be the case for aged particulate matter or particles to which condensation of secondary aerosol has occurred--expected to be the case in urban atmospheres), will not be available for reaction with gaseous ozone. Under these conditions, BaP will be observed to be nonreactive (Brorström et al., 1983; Coutant et al., 1988).

Reaction with Oxides of Nitrogen. A number of studies have been carried out to investigate the reaction of BaP when BaP-associated particles are exposed to oxides and oxyacids of nitrogen (Pitts et al., 1978, 1985; Jager and Hanus, 1980; Butler and Crossley, 1981; Grosjean et al., 1983; Brorström et al., 1983; Ramdahl et al., 1984; Yokley et al., 1985; Lindskog et al., 1985; Brorström-Lunden and Lindskog, 1985; Kamens et al., 1986; Arey et al., 1988). Although all of these studies observed losses of BaP and, generally, formation of nitro-BaP upon exposure of BaP-containing particles to NO_2 and/or HNO_3, the data reported are conflicting as to whether NO_2 or HNO_3 is the reactive species. In recent studies in which HNO_3 was removed from the NO_2 exposure gas, no reaction of adsorbed BaP with NO_2 was observed (Grosjean et al., 1983; Yokley et al., 1985). In contrast, Lindskog et al., (1985) did not detect any reaction of BaP on soot with HONO or HNO_3, but did observe reaction with NO_2 and NO_3 + HNO_3 mixtures. In this latter study, the buffering effect of the soot may have played a role, and oxy- rather than nitro-PAH derivatives were generally observed as products.

It seems likely that HNO_3 is a nitrating agent for adsorbed BaP, and that NO_2 without HNO_3 will not react. Whether the HNO_3 acts as a catalyst for reaction by NO_2 or is the sole nitrating agent has not been resolved. These BaP reactions are substrate dependent (Jager and Hanus, 1980; Ramdahl et al., 1984; Yokley et al., 1985) and, as noted above for the O_3 reactions, presumably require that the BaP be accessible for reaction.

In those studies in which several PAH were examined, the formation of the nitro derivatives followed the reactivity ranking of the PAH toward electrophilic nitration (Nielsen, 1984). According to Nielsen's ranking, BaP and anthracene are in the same reactivity grouping and more reactive than benz[a]anthracene and pyrene, which in turn are more reactive than benzo[e]pyrene and chrysene with, finally, flouranthene, phenanthrene and naphthalene being the least reactive of the PAH commonly found in ambient air. The presence of nitro-BaP in combustion emissions (Gibson, 1982, 1983; Paputa-Peck et al., 1983) is consistent with the high reactivity of BaP toward electrophilic nitration, and its presence in ambient air (Gibson, 1982; Wise et al., 1985) may be due to these combustion emissions.

In ambient air, NO_2 and HNO_3 will both be present. Recently, Arey et al., (1988) studied the disappearance of BaP-d_{12}, adsorbed onto ambient particles, and the formation of nitro-BaP-d_{11} under high-volume sampling conditions during a wintertime high-NO_x (maximum NO_x concentrations approximately 1 ppm) pollution episode in the Los Angeles air basin. BaP-d_{12} losses of approximately 40 percent were observed during the daylight sampling period on one of the two days, and 6-nitro-BaP-d_{11} was observed as a product in approximately 0.01 percent yield during the 12-hour sampling periods. Thus, the formation of 6-nitro-BaP under ambient conditions is likely to be unimportant, especially if most of the ambient particle-adsorbed BaP is unavailable for reaction.

Photolysis. Numerous studies have been carried out to investigate the photolysis and photo-oxidation of BaP on various surfaces (Korfmacher et al., 1980; Blau and Güsten, 1981; Behymer and Hites, 1985, 1988; Kamens et al., 1985, 1986; Yokley et al., 1986; Valerio et al., 1987). All studies employing a range of substrates have concluded that photolysis rates are highly substrate dependent (Korfmacher et al., 1980; Behymer and Hites, 1985, 1988; Yokley et al., 1986), with the darker substrates leading to lower photolysis rates, presumably due to stabilization of the BaP incorporated in the particles (Behymer and Hites, 1985, 1988; Yokley et al., 1986).

Kamens et al. (1988) observed that the BaP photolysis rate (on freshly generated wood and gasoline combustion soot) depended on the temperature and ambient water concentration, with a BaP lifetime at 293 Kelvin and approximately 50 percent relative humidity at midday of approximately one hour. In contrast, for dark fly ashes, half-lives on the order of several days were observed (Behymer and Hites, 1988). Once again it can be concluded that BaP is reactive, and thus may be expected to photolyze in ambient atmospheres, but the extent to which this occurs will depend on the exact nature of the BaP adsorbed state.

Ambient Air Data. Further information concerning the atmospheric reactions and lifetimes of BaP arises from ambient air data. Arey et al. (1988) have shown that under wintertime high-NO_x conditions in southern California (with mid-day temperatures attaining 95°F) losses of BaP-d_{12} during 12-hour sampling periods were <40 percent, and nitration of BaP-d_{12} was of negligible importance. Losses of particle-incorporated BaP would, presumably, have been lower. From an analysis of ambient air and combustion emissions data, Schuetzle and Frazier (1986) found that the benzo[e]pyrene (BeP) to BaP ratio in ambient air of approximately 1.8:1 was very similar to the ratio observed in emission sources. Since BaP is much more reactive than BeP toward electrophilic reaction (Nielsen, 1984), reaction with O_3 (Van Vaeck and Van

Cauwenberghe, 1984) and photolysis (Behymer and Hites, 1988), this observation suggests that once the BaP and BeP are adsorbed on particles they do not undergo significant degradation in the atmosphere.

Nielsen (1988) investigated the dependence of the BaP to BeP ratio on the wind direction (and hence, the vicinity of the source) in Denmark. Higher BeP concentrations were associated with local sources, and the BaP to BeP ratio was found to correlate with the BeP concentration, suggesting that BaP was being degraded in the atmosphere. The author concluded that the BaP decay was relatively fast (Nielsen, 1988).

Atkinson et al. (1988) measured PAH and PAH-derivatives at seven sites throughout California. Consistent with the work of Nielsen (1988), the sites with the highest BaP to BeP ratios, Mammoth Lakes (BaP to BeP = 1.5:1) and Concord (BaP to BeP = 1.3:1), also had the highest BeP concentrations. Furthermore, the BaP to BeP ratio was lowest at Glendora (BaP to BeP = 0.35:1), a site where significant atmospheric reaction had occurred as evidenced by the formation of 2-nitropyrene from pyrene (Atkinson et al., 1988). (For a more complete discussion of the PAH transformations in the atmospheres sampled, see Section X of Atkinson et al., 1988). The apparent inconsistency in the data of Schuetzle and Frazier (1986) and those of Nielsen (1988) and Atkinson et al., (1988) probably reflects differences due to comparisons of averaged values from generally aged emissions (Schuetzle and Frazier, 1986) versus BaP concentrations resulting from a single emission source (such as wood smoke at Mammoth Lakes) and/or fresh emissions (Nielsen, 1988; Atkinson et al., 1988).

Although it is difficult to estimate a lifetime for BaP from these laboratory and ambient air data, it must be concluded that, due to chemical reaction and/or photolysis, the lifetime of whatever fraction of the BaP is available for reaction is on the order of a few hours in polluted urban atmospheres during summertime. This lifetime will depend on the nature (chemical reactivity) of the atmosphere into which the BaP is emitted. For

BaP within the particles and unavailable for reaction, or BaP stabilized due to adsorption, the expected particle lifetimes leads to an atmospheric lifetime for BaP of <10 days due to dry deposition of the particles.

Besides BaP, other PAHs are emitted or formed in the atmosphere which account for additional mutagenicity. A recent study completed by Atkinson et al. (1994), shows that the reactions with OH and NO_3 radicals often lead to the formation of mutagenic nitro-PAHs (nitroarenes) and other nitropolycyclic aromatic compounds including nitro-PAH lactones and nitrodibenzopyranones. These atmospheric reactions have a significant effect on ambient mutagenic activity. Approximately 20 percent of the total direct-acting mutagenicity can be attributed to the presence of 2- and 4-nitrodibenzopyranones in the ambient air. In addition to 2- and 4-nitrodibenzopyranones, seven nitro-PAH lactones (tentatively identified as methylnitrodibenzopyranones and nitrophenanthropyranones) have been identified in the ambient air. Recent evidence indicates that it is likely that the presence of nitro-PAH lactones formed in the atmosphere contribute significantly to the mutagenicity of ambient air.

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Appendix A

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF SELECTED POLYAROMATIC HYDROCARBONS (PAH) IN AMBIENT AIR

CALIFORNIA AIR RESOURCES BOARD
MONITORING AND LABORATORY DIVISION

S.O.P. No. MLD 028

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF SELECTED POLYAROMATIC HYDROCARBONS (PAH) IN AMBIENT AIR

1.0 Scope

This is a high performance liquid chromatographic (HPLC) standard operating procedure for the determination of benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), dibenz[a,h] anthracene (DA), benzo[ghi]perylene (BP), and indeno[1,2,3-cd]pyrene (IP) in the ambient air utilizing a portion of PM10 filters.

2.0 Summary of Method

2.1 Ambient air is drawn through 8" x 10" PM10 quartz fiber filters at 1.1 M^3/min. for a 24-hour period. Ref the ARB Q/A Manual.

2.2 The PAH's are extracted from a 2" X 5" strip of each filter using 10 % acetonitrile in dichloromethane solvent with sonication. The extract is injected into the HLPC system and identified and quantified by reference to injected external standards with the use of fluorescence detection.

3.0 Interferences/Limitations

3.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing mis-interpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by running method blanks.

3.2 Interferences co-extracted from the samples will vary considerably from source to source. Individual samples may require a cleanup procedure to achieve the desired sensitivity.

3.3 The chromatographic conditions described have been optimized for the analysis of the six PAHS.

4.0 Apparatus

4.1 A gradient HPLC system consisting of a mobile phase reservoir, high pressure pumps, an injection valve or automatic sampler, a C-18 reverse phase column, a fluorescence detector and a data system.

4.2 Sampling system: Atmospheric suspended particulate matter is collected on an 8 X 10 inch quartz fiber filter, over a 24 hour period, with a size selective inlet high volume air sampler.

4.3 Culture tubes (50mL) with teflon lined screw-type caps.

4.4 Ultrasonic bath apparatus, 400 watt output.

4.5 Macro Kuderna-Danish Concentrators such as Supelco #6-4685.

4.6 Amber screw cap vials (4ml), with teflon lined septum caps, such as Sun Brokers # 1560.

4.7 Gelman Acroprep syringeless 0.45 um PTFE membrane sample filler units.

4.8 Filtration and degassing system for mobile phase solvents such as Waters Part #851234.

4.9 Various volumetric pipets, flasks and graduated cylinders.

4.10 Hotplate.

5.0 Reagents

5.1 All six PAHs at 98+% purity.

5.2 10 % Acetonitrile in Dichloromethane, UV Grade. Mix 400 cc of UV Grade Acetonitrile with 3600 cc of UV Grade Dichloromethane.

5.3 Acetonitrile and water mobile phase solvents, HPLC grade, such as Burdick & Jackson product # 016 and EM Science # WX004 respectively.

5.4 Control solutions are prepared in acetonitrile. A stock solution of 100 ug/mL is prepared by dissolving 10 mg of each PAH in 100 mL of acetonitrile.

5.5 NBS SRM 1647b PAH Reference Solution, is used to calibrate the method. Calibration standards spanning the range of interest are prepared from the stock reference solution.

6.0 Sample Analysis

6.1 Sample Extraction

6.1.1 Cut a 2" x 5" filter paper strip into 1/2 square inch squares and place in a 50 mL screw cap culture tube.

6.1.2 Add 20 mL of 10% ACN/DCM to the culture tube and cap tightly.

6.1.3. Sonicate the culture tube for 30 minutes. Let set for 1 hour, then sonicate for another 30 minutes. Transfer the extract to a 40 ml K-D receiver. Rinse extraction flask with an additional 20 ml dichloromethane and evaporate to <2 mL using the K-D concentrator.

6.1.4 Dilute the concentrated extract to 4.0 ml. Rinse K-D receiver sides with sample. Transfer the sample to an amber screw-capped vial by filtering through a 0.45 micron Acuprep filter attached to a 10 ml syringe.

6.1.5 Rinse all glassware thoroughly with acetone and dichloromethane and let drain. Store the extracts in a refrigerator until analysis.

6.1.6 Each batch of 20 extractions must contain a blank filter sample and a "spiked" filter sample (spiked with SRM 1647a). These quality control samples must be taken through the same extraction process as used for the samples.

6.2 HPLC Analysis

6.2.1 Operating parameters are as follows:

Column:	Vydax 201TP54 (0.46 X 25 cm)
Temperature:	25C
Mobile phase:	50/50 H20/ACN to 100 ACN 25 min.
Detector:	Water's Fluorescence 470
Flowrate/Run Time:	2 mL/min; 30 min.
Retention Time:	21 - 24 min.
Inject Vol.:	10 - 30 uL.

6.2.2 Equilibrate the column for 30 minutes before the first analysis. Analyze a blank to check for method interferences.

6.2.3 Initially, calibrate the instrument using four standard concentrations each analyzed in triplicate. The results are used to prepare a calibration curve. Linear response is indicated when an r of at least 0.98 for a linear least squares fit of the data is obtained.

6.2.4 Check the calibration of the instrument for each analytical run by analyzing a calibration and a control standard. The concentration obtained must fall within the UWL and LWL of the control sample value (± 2 S.D.). Plot all control analyses on the method control chart. The day to day response for the calibration standards should be within 10%.

6.2.5 Prepare a multi-method routine to control the automatic sampler. Analyze a control and run a sample duplicate every ten analyses. If PAH's are not detected under the stated analytical conditions, a larger aliquot is injected.

7.0 Calculations:

$$\text{ng/M}^3 = \frac{(\text{ng/ml})(\text{ml of extract})\,(1000) * 10}{(\text{minutes sampled})\,(\text{SLPM air flow})}$$

8.0 Method Sensitivity and Precision

Calibribration Concentration Levels (ng/mL)

	1	2	3	4	5
BbF	4.16	8.32	16.6	33.3	66.6
BkF	4.70	9.40	18.8	37.6	72.5
BaP	4.92	9.84	19.7	39.4	78.7
DA	3.64	7.28	14.6	29.1	58.2
BP	3.76	7.52	15.0	30.1	60.2
IP	4.37	8.74	17.5	35.0	69.9

Percent RSD, Correlation Coefficients, & Calculated LODs

BbF	0.9	1.3	0.3	0.6	0.2	.9999	0.01
BkF	0.4	0.6	0.1	0.1	0.1	.9999	0.01
BaP	1.0	0.8	0.1	0.1	0.2	.9999	0.01
DA	0.8	1.2	0.1	0.3	0.2	.9996	0.03
BP	0.8	0.9	0.6	0.5	0.2	.9993	0.02
IP	8.1	3.7	1.2	1.2	0.2	.9999	0.05

LOD (ng/M^3) = "X" intercept + 3 S.D. of #1 (lowest) Std.

NOTE: All LODs were rounded off to 0.05 ng/M^3

Appendix B

BENZO[a]PYRENE EMISSIONS ESTIMATES FOR VARIOUS TYPES OF SOURCES

I. Benzo[a]pyrene Emission Estimates for Stationary Point Sources

As indicated in the main text, BaP is a product of incomplete combustion for which the emissions are highly variable with process type and operating conditions. The available emission factors exhibit wide variability (even among test results), therefore the emission estimates are generally expressed as ranges of emissions.

Equation (1) below can be used to estimate BaP emissions from stationary sources such as residual oil combustion, distillate oil combustion and coal combustion sources.

$$\text{BaP Emissions} = \text{Process Rate} \times \text{EmFac} \times \text{ConFac} \qquad (1)$$

Where:

EmFac = Emission Factor

ConFac = Conversion Factors, if needed

For emissions from refineries, Equation (2) can be used. There are an estimated 10 to 40 pounds per year of BaP emitted to the atmosphere statewide from fluid catalytic cracking (FCC) refinery processes. As of 1979, FCC units constituted about 94 percent of total cracking feed capacity (US EPA, 1987). The staff assumed that the FCC emission factor was applicable to all cracking operations. The staff estimated BaP emissions statewide from refinery processes as follows:

$$\text{BaP Emissions} = \text{Charge Capacity X EmFac X ConFac} \qquad (2)$$

Where:

Charge Capacity = 2.3×10^6 barrels per calendar-day

EmFac = Emission Factor

= 21.5 ug BaP/barrel feed (controlled)

ConFac = Conversion Factor

Substituting the values of charge capacity (EmFac and ConFac), the equation becomes:

$$\text{BaP Emissions} = \frac{2.3 \times 10^6\,\text{bbl}}{\text{day}} \times \frac{21.5\ \text{ug BaP}}{\text{bbl}} \times \frac{365\ \text{days}}{\text{year}} \times \frac{1\ \text{lb}}{453.6\ \text{gm}} \times \frac{10^{-6}\,\text{gm}}{1\ \text{ug}}$$

$$= 40\ \text{lbs per year}$$

Emissions from stationary point sources are summarized in Table 1.

Table 1: Stationary Point Sources

SOURCE	PROCESS RATE	REF.	EMISSION FACTORS	REF.	EMISSIONS (lbs/yr)
Combustion:					
Coal	1.6 x 10^6 tons	a, b	0.117 - 260 ug/kg	c	0.4 - 832
Coke	0.5 x 10^6 tons	a, b	not available		not available
Residual oil	1.85 x 10^9 gallons	a	1.1 ug/kg to 2.2 lbs/10^{12} Btu (~41ug/kg)	d c	16 - 611
Distillate oil	1.4 x 10^9 gallons	a	0.66 - 1.96 ug/kg (or as high as 41 ug/kg)[f]	e c, d	7 - 19 (up to 400[f])
Diesel	3.24 x 10^6 gallons	a	25.4 - 50.88 ug/gal	g	0.18 - 0.36
Gasoline	4.53 x 10^6 gallons	a	8.0 - 330 ug/gal	c	0.08 - 3.3
Natural gas	12.2 x 10^{12} ft^3	a	1 ug/kg[h]	h	520
Industrial wood	5.6 x 10^6 tons	a	0.001 - 0.036 mg/kg[i]	c, i	11 - 400
Incineration:					
Municipal waste	not available		0.008 - 0.13 g/10^6 gm	g	not available
Sewage sludge	17.24 x 10^3 tons	j	not available		not available
Biomedical waste	20.05 x 10^3 tons	k	not available		not available
Other:					
Refineries (FCC)	0.61 - 2.3 x 10^6 bbl/day	l	ND - 21.5 ug/bbl	c	10 - 40
Asphalt plants	1.63 X 10^7 tons	m	0.03 - 0.13 mg/10^6 gm	c	1 - 4.2
Carbon black	54 x 10^6 lbs	c	3.5 x10^{-6} lb/ton	c	0.09

(continued on next page)

Table 1 Notes

[a] ARB, 1990a.

[b] ARB/APCD Survey, 1986.

[c] US EPA, 1987 (EPA-450/4-84-007p).

[d] Rondia et al, 1983.

[e] Hangebrauck, 1964 (JAPCA, pp. 267-278: July, 1964).

[f] Based on publications that do not differentiate between fuel types, the upper limit of the applicable BaP emissions factors could be as high as 41 micrograms per kilogram, not only for residual oil (as indicated in one of the publications) but also for distillate oil combustion.

[g] US EPA, 1988 (EPA-450/4-88-006a).

[h] This emission factor is derived by assuming that BaP is approximately 4 percent of the published POM emission factor reported in US EPA, 1987 (EPA-450/4-84-007p).

[i] This emission factor value was reported to be non-detectable in some runs in some tests of devices with control equipment (EPA-450/4-84-007p).

[j] ARB, 1988a: Survey conducted by the Stationary Source Division.

[k] ARB, 1990e.

[l] Oil & Gas Journal: March, 1989.

[m] ARB, 1990c.

II. Benzo[a]pyrene Emission Estimates From Stationary Area Sources

BaP emissions from stationary area sources are emissions from those stationary sources not otherwise included in the stationary point source inventory. Stationary area sources include sources associated with fuel combustion such as from boilers or stationary internal combustion engines used in oil and gas extraction and agricultural production, and also include agricultural burning and other processes. BaP emission estimates were made using published emission factors where available and are summarized in Table 2.

III. Benzo[a]pyrene Emission Estimates from Mobile Sources

A. On-Road Motor Vehicles

On-road vehicle emissions of BaP are based on emission factors that were available in the literature in various references and in various units, either in terms of vehicle miles traveled or in terms of fuel used. Emissions were calculated with all available emission factors and the full range of resultant emissions reported. Estimates were made for light-duty passenger vehicles, light and medium duty trucks, heavy duty trucks that run on diesel and gasoline fuels, urban buses, and on-road motorcycles.

The applicable BaP emission estimation equations are as follows:

$$\text{BaP Emissions} = \text{VMT} \times \text{EmFac} \times \text{ConFac} \qquad (3)$$

OR

$$\text{BaP Emissions} = \text{Fuel used} \times \text{EmFac} \times \text{ConFac} \qquad (4)$$

Where:

EmFac = Emission Factor

ConFac = Conversion Factors, if needed

Estimated emissions from on-road motor vehicles are summarized in Table 3.

B. Other Mobile Sources

Estimates were made for other mobile sources in a similar manner to those for on-road vehicles (assuming the emission factor for the appropriate fuel burned by each source type) and are summarized in Table 4.

C. Rubber Tire Wear

BaP is emitted from motor vehicle tire wear as a result of friction between the road surface and tires. BaP emissions from on-road vehicle tire wear are estimated and summarized in Table 5. There is insufficient information to estimate BaP emissions from tire wear for other mobile sources, such as trail bikes, tractors, or recreational vehicles.

Table 2: Stationary Area Sources

SOURCE	PROCESS RATE[a]	EMISSION FACTORS	REF.	EMISSIONS (lbs/year)
Residential wood	1.1×10^6 tons	0.05 - 0.62 mg/kg	b	110 - 1,360
Residual oil	2.75×10^7 gal	1.1 ug/kg to 2.2 lb/10^{12} Btu (~41 ug/kg)	c d	0.23 - 8.96
Distillate oil	2.27×10^8 gal	0.66 - 1.96 ug/kg (or as high as 41 ug/kg)[f]	e c, d	1 - 3.1 (up to 65[f])
Diesel[g]				
-Including OCS	6.29×10^6 gal	25.4 - 50.86 ug/gal	b	0.35 - 0.70
-Without OCS	4.80×10^6 gal	25.4 - 50.86 ug/gal		(0.27 - 0.53)
Liquid material	8.6×10^7 gal	25.4 - 50.86 ug/gal[h]	b	4.8 - 9.6
Natural gas	8.38×10^{11} ft^3	1 ug/kg[i]	i	36
Gaseous material	7.2×10^9 ft^3	1 ug/kg[j]	j	0.3
LPG	3.9×10^8 gal	not available		not available
Agricultural & other waste burning	1.87×10^7 ton	0.3 - 0.35 mg/kg	d	11,200 - 13,100
Asphalt paving	3.8×10^6 tons	0.0133 ug/m^3	d	<.01
Asphalt roofing	2.2×10^6 tons	0.057 - 0.183 ug/m^3	d	<.01

(Continued on next page)

Table 2 Notes

[a] ARB, 1990f.

[b] US EPA, 1988 (EPA-450/4-88-006a).

[c] Rondia et al, 1983.

[d] US EPA, 1987 (EPA-450/4-84-007p).

[e] Hangebrauck, 1964. (JAPCA, pp. 267-278: July, 1964).

[f] Based on publications that do not differentiate between fuel types, the upper limit of the applicable BaP emission factors could be as high as approximately 41 microgram per kilogram not only for residual oil combustion (as indicated in one of the publications) but also for distillate oil combustion.

[g] This category includes a contribution (of approximately 24 percent) from diesel burned in Outer Continental Shelf (OCS) activities.

[h] Assumes the emission factor for diesel combustion is applicable to liquid material combustion.

[i] This emission factor is derived by assuming that BaP is approximately 4 percent of published POM emission factor reported in US EPA 1987 (EPA-450/4-84-007p).

[j] Assumes the emission factor for natural gas combustion is applicable to gaseous material combustion.

Table 3: On-Road Motor Vehicles

TYPE OF VEHICLE	VMT[a] (10^5 mile/day)	FUEL USED[b] (10^3 gal/day)	EMISSION FACTORS[c]	REF.	RANGE OF EMISSIONS (lbs/year)	RESULTANT EMISSIONS (lbs/year)
Light Duty Passenger						
Non-Catalytic		4,122.05	8.0 - 330 ug/gallons	d	27 - 1,095	27 - 1,095
	515.34		2.72 - 25 ug/mile	d	113 -1,037	
Catalytic		16,832.61	0.98 - 50 ug/gallons	d,e	13.3 - 677	13 - 677
	3,490		0.07 ug/mile	d	19.7	
Diesel	144		0.2 - 31.7 ug/mile	e	2.32 - 367.3	2 - 367
Light Duty Truck						
Non-Catalytic		1,219.74	8.0 - 330 ug/gallon	d	7.0 - 324	7 - 324
	137.62		2.72 - 25 ug/mile	d	30.12 - 277	
Catalytic		5,472.78	0.98 - 50 ug/gallons	d,e	4.32 - 220	4 - 220
	890.9		0.07 ug/mile	d	5.02	
Diesel	36.64		0.2 - 31.7 ug/mile	e	0.59 - 94	0.6 - 94
Medium Duty Truck						
Non-Catalytic		556.09	8.0 - 330 ug/gallon	d	4.0 - 148	4 - 148
	55.3		2.72 - 25 ug/mile	d	12.1 - 111.3	
Catalytic		2416.89	0.98 - 50 ug/gallon	d,e	1.9 - 97	1.5 - 97
	258.9		0.07 ug/mile	d	1.5	

(Continued on next page)

Table 3 (continued)

TYPE OF VEHICLE	VMT[a] (10^5 mile/day)	FUEL USED[b] (10^3 gal/day)	EMISSION FACTORS[c]	REF.	RANGES OF EMISSIONS (lbs/year)	RESULTANT EMISSIONS (lbs/year)
Heavy Duty Truck						
Non-Catalytic		3,122.02	273 ug/gallon	d	686	686
Catalytic		143.93	273 ug/gallon	d	32	32
Diesel		4,364.42	25.4 - 50.86 ug/gallon	f	89.2 - 179	89 - 180
Urban Buses		137.90	25.4 - 50.86 ug/gallon[g]	f	2.8 - 5.6	3 - 6
On-Road Motorcycles		84.09	273 ug/gal to 3.6 mg/kg	d e	18.5 682	19 - 680
Total[h]						888 - 4,606

[a] VMT: Vehicle miles traveled per day. Data retrieved from ARB's Emission Data System (ARB, 1990b).

[b] Fuel Used (in thousand gallons per day): Data retrieved from ARB's Emission Data System (ARB, 1990b).

[c] Emission Factors in different units from various references.

[d] US EPA, 1987. Locating and Estimating Air Emissions from Sources of Polycyclic Organic Matter (POM). US EPA, Research Triangle Park, NC. EPA-450/4-84-007p (September).

[e] Rondia, et al., 1983.

[f] US EPA, 1988. Data from EPA-450/2-88-006a, a compilation by the U.S. Environmental Protection Agency.

[g] Assumes the emission factor for heavy duty diesel trucks is applicable to urban buses.

[h] The total may not be the same as the sum of the emissions due to rounding.

Table 4: Other Mobile Sources

Source	Usage Data[a] (10^3 gallons)	Emission Factors	REF.	Emissions (lbs/year)
Diesel-Powered Engines[b]				
-Including OCS	1,133,898	25.4 - 50.86 ug/gallon[c]	d	63 - 127
-Without OCS	1,111,563	25.4 - 50.86 ug/gallon		62 - 125)
Gasoline-Powered Engines[e]	239,845	8 - 330 ug/gallon[f]	d	4 - 174
Two-Stroke Engines[g] (Gasoline)	15,824	273 ug/gallon to 3.6 mg/kg	h i	10 - 342
LD Fork Lifts (LPG)	50,643	not available		not available (insignificant)
Steamships (Residual Oil)				
-Including OCS	521,221	1.1 - 41 ug/kg[j]	j	4.6 - 171
-Without OCS	508,423	1.1 - 41 ug/kg		4.4 - 167
Aircraft (Jet fuel)	2.5×10^6 LTOs			not available
Total[k]				
-Including OCS				82 - 814
-Without OCS				80 - 808

(continued on next page)

Table 4 Notes

[a] ARB, 1990f.

[b] This category includes trains, heavy-duty (HD) farm and non-farm equipment, light-duty (LD) fork lifts, commercial boats, recreational vehicles, and refrigeration units. The category includes a contribution from boats and ships operating in the Outer Continental Shelf (OCS) area.

[c] These emission factors are default values from on-road motor vehicles burning the corresponding fuel.

[d] US EPA, 1988. Toxic Air Pollutant Emission Factor - A Compilation for Selected Air Toxic Compounds and Sources. US EPA, Research Triangle Park, NC. EPA-450/2-88-006a.

[e] This category includes agricultural aircraft, commercial boats, HD farm and non-farm equipment, LD fork lifts, recreational vehicles, pleasure boats, 4-wheel drive off-road vehicles, and refrigeration units.

[f] These emission factors are default values from on-road motor vehicles burning the corresponding fuel.

[g] This category includes trail bike motorcycles, snowmobiles, and residential utility equipment.

[h] US EPA, 1987. Locating And Estimating Air Emissions from Sources of Polycyclic Organic Matter (POM). US EPA, Research Triangle Park, NC. EPA-450/4-84-007p (September).

[i] Rondia, et al., 1983.

[j] No emission factor is available for steamships; therefore, we have assumed that the emission factor for stationary point sources burning residual oil is applicable to this category. This category includes a contribution from steamships operating in the Outer Continental Shelf (OCS) area.

[k] Total may not be the same as the sum of individual categories due to rounding.

LD: Light Duty

LPG: liquid petroleum gas

LTOs: number of landings and take-offs.

Table 5: Vehicular Rubber Tire Wear

Source	Process Rate[a]	Emission Factor	REF.	Emissions (lbs/year)
Rubber Tire Wear	3.5×10^{11} km	5 ug/km	b	3,900

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[a] ARB, 1990b.

[b] Rondla, et al., 1983.

Appendix C

THE GLEIT AND BOOTSTRAP STATISTICAL METHODS

Gleit's Method

Gleit's method accounts for the concentrations below the LOD* by setting them equal to the "below-LOD mean" μ_{BLOD}, the mean of the portion of the normal distribution below the LOD. Setting the unknown concentrations to their average value seems intuitively reasonable, and the simulations reported in Gleit's paper show that his method is more accurate than other commonly used approximations.

The below-LOD mean of a normal distribution of a variable with a limit of detection L is given (in terms of L and the mean μ and the standard deviation σ of the distribution) by equation 1:

$$\mu_{BLOD} = \mu - \sigma^{*}[f((L-\mu)/\sigma)/F((L-\mu)/\sigma)] \qquad (1)$$

In equation (1), f and F are, respectively, the probability density function and cumulative distribution function of the standard normal distribution. The below-LOD means are computed from equation (2) in terms of parameters of the associated normal distribution: the LOD L, the mean concentration from Table IV-2, and the estimated standard deviation.

$$\exp(\mu+0.5^{*}\ \sigma^{2})^{*}F((L-\mu-\sigma^{2})/\sigma)/F(L-\mu/\sigma) \qquad (2)$$

We now describe how Gleit's method estimates the mean and variance of the assumed normal distribution. The mean and variance cannot be estimated by merely substituting into standard formulas if below-LOD concentrations are to be set to the below-LOD mean. On the one hand, the mean and variance must be known in order to calculate the below-LOD mean from (1); on the other hand, the below-LOD mean must be known if it is to be used in the calculation of the mean and variance. Statistical theory, by asserting that a "best-fitting" mean and variance for the distribution exist, provides a way out of this dilemma. Gleit uses a simple iterative procedure to compute these best-fitting parameters. Since his procedure can be simply described in words, a written description is given, supplemented where necessary by equations written in a notation more convenient than Gleit's.

Starting with initial guesses $\mu(0)$ and $\sigma^2(0.)$ for the mean and variance, the procedure repeatedly generates new estimates of the mean and variance by the two-step computation described below until successive estimates of the mean and variance converge sufficiently (The K-th pair of estimates are denoted by $\mu(K)$ and $\sigma^2(K)$.). The two steps are:

(a) The K+1-st below-LOD mean $\mu_{BLOD}(K+1)$ is computed by substituting $\mu(K)$ and $\sigma(K)$ (the square root of $\sigma^2(K)$) into equation (1).

(b) The K+1-st estimate of the mean, $\mu(K+1)$, is computed in the usual way with $\mu_{BLOD}(K+1)$ substituted for the sample values below the LOD. The K+1-st estimate of the variance, $\sigma^2(K+1)$, is also computed in the usual way, with an analogous substitution for sample values below the LOD: the squared deviations from the mean of concentrations below the LOD are set equal to the average squared deviation from the mean of the below-LOD portion of the distribution.

Let the N sample items be X(1),....,X(N), and let p be the number of sample items below the LOD. $\mu(K+1)$ is computed by:

$$\mu(K+1) =(1/N)\ \Sigma\ Y(J),\ \text{where } Y(J)=X(J) \text{ if } X(J)\ R\ L$$
$$\text{and } Y(J)= \mu_{BLOD}(K+1) \text{ otherwise}$$

$\sigma^2(K+1)$ is computed by:

$$\sigma^2(K+1)=(1/N)\ \Sigma\ D^2(J),\ \text{where } D^2(J)=(X(J) - \mu(K+1))^2$$
$$\text{if } X(J)\ M\ L, \text{ and } \overset{2}{D}\ (J)= \overset{2}{\sigma}_{BLOD}\ (K+1) \text{ otherwise.}$$

The quantity${}^2\sigma_{BLOD}(K+1)$, the average squared deviation of the below-LOD portion of the distribution, is computed from the following equation:

$${}^2\sigma_{BLOD}(K+1)= \sigma^2(K)^*[1-Z(K)^*(f(Z(K))/F(Z(K))\ )],$$
$$\text{where } Z(K)=(\ (L-\mu(K))/\sigma(K)\ ).$$

Gleit's method nearly always converges in a few steps unless there are only a few distinct values above the detection limit, in which case it may converge very slowly. Gleit's method and closely related methods appear to be the best available estimators of the mean when the sample includes values below the LOD, as is demonstrated by the simulations reported in Gleit's paper.

Kruskal-Wallis Test

The Kruskal-Wallis Test is a rank statistic defined by the equation:

$$T = 12/(N(N+1)) \quad (R_i - 1/2n_i(N+1))^2/n_i$$

Where N is the total number of data to be ranked, n_i is the number of data in any one group to be ranked and R_i is the sum of the ranks in a group.

The exact distribution of T is found under the assumption that all observations were obtained from the same or identical population. The method is that of randomization which was used also in finding the distribution of the Mann-Witney Test. Under the above assumptions, each arrangement of the ranks 1 to N into groups is equally likely and occur with equal probability which is the reciprocal of the number of ways the N ranks may be divided into groups being tested. The value of T is computed for each arrangement. The probabilities associated with equal values of T are then added to give the probability distribution of T.

Shapiro-Wilk Test

The Shapiro-Wilk test is an analysis of variance test for normality. The test statistic is obtained by dividing the square of an appropriate linear combination of the sample order statistics by the symmetric estimate of variance. This ratio is both scale and origin invariant, and hence, the statistic is appropriate for a test of the composite hypothesis of normality.

Bootstrap Confidence Intervals

The Bootstrap Methodology is a way of generating confidence bounds for the sample mean from the empirical distribution using minimal assumptions.

The primary assumption made in the Bootstrap is that the sample is representative of the underlying distribution. The fundamental theory behind the Bootstrap is beyond the scope of this memo, so the interested reader may pursue the topic by investigating the following references:

B. Efron, The Two Sample Problem with Censored Data, PROCEEDINGS OF THE FIFTH BERKELEY SYMPOSIUM ON MATHEMATICAL STATISTICS AND PROBABILITY (1967), no. 4, pp. 831-853.

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Appendix D

TABLES OF BENZO[a]PYRENE DATA

Table 1
Ambient BaP Concentrations for Locations in Contra Costa County, CA
(from Flessel et al., 1984)

Location Site and Dates[a]			BaP (nanograms/cubic meter)
Richmond	8/6/81	Day	0.1
	8/6-7/81	Night	0.1
	8/7/81	Day	0.1
Martinez	8/6/81	Day	0.1
	8/6-7/81	Night	0.1
	8/7/81	Day	0.1
Concord	8/6/81	Day	0.1
	8/6-7/81	Night	0.1
	8/7/81	Day	0.1
Pittsburg	8/6/81	Day	0.1
	8/6-7/81	Night	0.1
	8/7/81	Day	0.1
Richmond	10/20-21/81	Night	0.1
	10/21/81	Day	0.2
	10/21-22/81	Night	0.1
Martinez	10/20-21/81	Night	0.8
	10/21/81	Day	0.4
	10/21-22/81	Night	0.1
Concord	10/20-21/81	Night	1.1
	10/21/81	Day	0.4
	10/21-22/81	Night	1.5
Pittsburg	10/20-21/81	Night	0.2
	10/21/81	Day	0.2
	10/21-22/81	Night	0.2
Richmond	1/13-14/82	Night	2.0
	1/14/82	Day	0.8
	1/14-15/82	Night	2.6
Martinez	1/13-14/82	Night	0.4
	1/14/82	Day	0.2
	1/14-15/82	Night	1.5
Concord	1/13-14/82	Night	2.6
	1/14/82	Day	0.6
	1/14-15/82	Night	2.6
Pittsburg	1/13-14/82	Night	1.3
	1/14/82	Day	0.5
	1/14-15/82	Night	1.1

Table 2
Ambient Benzo[a]pyrene and Benzo[e]pyrene Concentrations for Claremont and Torrance, CA (from Winer et al., 1987)

Location sites and dates[a]			(nanograms/cubic meter) BaP	 BeP
Claremont	9/14/85	0600-1200 hr	0.09	0.28
Claremont	9/14/85	1200-1800 hr	0.04	0.13
Claremont	9/14/85	1800-2400 hr	0.14	0.36
Claremont	9/15/85	0000-0600 hr	0.03	0.13
Torrance	2/24-25/86	Night	1.6	2.1
Torrance	2/25/86	Day	0.6	2.1

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[a] See Winer et al. (1987) for full details of pollution episodes sampled.

Table 3
Ambient Benzo[a]pyrene and Benzo[e]pyrene Concentrations for Locations Throughout California (from Atkinson et al., 1988)

Location sites and dates[a]			(nanograms/cubic meter) BaP	 BeP
Glendora 8/13/86	Sample #1	Day	0.26	0.62
Glendora 8/13-14/86	Sample #2	Night	0.62	1.54
Glendora 8/15-16, 16, 17, 18, 18-19/86	Sample #3	Day	0.18	0.41
Glendora 8/15-16, 16-17, 17-18, 18-19/86	Sample #4	Night	0.18	0.65
Glendora 8/20/86	Sample #5	Day	0.23	0.83
Glendora 8/20-21/86	Sample #6	Night	0.32	0.95
Yuba City 10/16-17,18-19,20-21,23-24/86	Sample #1	Day	0.31	0.35
Concord 12/8,9/86; 1/19/87	Sample #1	Day	1.77	1.91

(continued on next page)

Table 3 (continued)

Location sites and dates[a]	(nanograms/cubic meter) BaP	 BeP
Concord Sample #2 Day 1/18,21,22/87	3.23	2.77
Concord Sample #3 Night 12/6-7,7-8,8-9/86	6.15	4.22
Concord Sample #4 Night 1/17-18,18-19,21-22/87	8.15	5.76
Concord Sample #5 Night 12/10-11/86; 1/14-15/87	1.93	1.52
Mammoth Lakes Sample #1 Day 2/14,16,17,21,22,26,28/87	3.56	2.57
Mammoth Lakes Sample #2 Night 2/16-17,17-18,20-21,27-28;2/28-3/1/87	12.49	8.00
Mammoth Lakes Sample #3 Night 2/14-15,15-16,21-22,22-23,25-26/87	3.14	2.05
Oildale Sample #1 Night 3/30,31/87; 4/1,2,7,8,9,10/87	0.42	0.44
Oildale Sample #2 Night 3/29-30/87; 4/9-10,10-11/87	0.17	0.25
Oildale Sample #3 Night 3/31-4/1/87; 4/1-2,7-8,8-9/87	0.88	0.98
Reseda Sample #1 Day 5/28,29,30,31/87; 6/1,2,14,15/87	0.47	0.71
Reseda Sample #2 Night 5/27-28,28-29,29-30,30-31,5/31-6/1; 6/1-2,2-3,13-14,14-15/87	0.13	0.28
Pt. Arguello Sample #1 Day 7/4,5,6,7,8,9,10,11,12/87	c	0.005
Pt. Arguello Sample #2 Night 7/4-5,5-6,6-7,7-8,8-9,9-10,10-11,11-12/87	c	0.008
San Nicolas Island Composite 6/19,24,25; 7/13,14,15; 8/27,28,29; 9/2,3/87; 6/19-20,24-25,25-26/87; 7/13-14,14-15,15-16/87; 8/27-28,28-29,29-30/87; 9/3-4/87	c	0.005

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[a] See Atkinson et al. (1988) for full details of composite-ing.
[b] Average of replicate GC/MS injections.
[c] Amount present too low to quantify.

REFERENCES TO APPENDIX E.

Atkinson, R., J. Arey, A. M. Winer, B. Zielinska, T. M. Dinoff, W. P. Harger, and P. A. McElroy, 1988. A Survey of Ambient Concentrations of Selected Polycyclic Aromatic Hydrocarbons (PAH) at Various Locations in California. Final Report, California Air Resources Board Contract No. A5-185-32, May.

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Winer, A. M., R. Atkinson, J. Arey, H. W. Biermann, W. P. Harger, E. C. Tuazon, and B. Zielinska, 1987. The Role of Nitrogenous Pollutants in the Formation of Atmospheric Mutagens and Acid Deposition. Final Report, California Air Resources Board Contract No. A4-081-32, March.

Appendix E

BENZO[a]PYRENE EXPOSURE FROM INDOOR AIR, FOOD, AND DRINKING WATER

APPENDIX E

BENZO[a]PYRENE EXPOSURE FROM INDOOR AIR, FOOD, AND DRINKING WATER

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March 1994

I. INDOOR SOURCES OF BENZO[a]PYRENE

The major sources of BaP to indoor air in California are tobacco smoking, woodburning, and infiltration of polluted outdoor air. Incomplete, oxygen-starved combustion conditions favor BaP production (NAS, 1972; EPA, 1987). Research indicates that BaP forms most readily from combustion of the more complex organic molecules, such as those found in tobacco or wood (EPA, 1987; NAS, 1972; Peters and DeAngelis, 1981).

A. ENVIRONMENTAL TOBACCO SMOKE

Tobacco smoking is a major contributor of BaP pollution indoors, and produces a complex mixture of toxic and irritating compounds known as environmental tobacco smoke. The main sources of environmental tobacco smoke are sidestream smoke and exhaled mainstream smoke. Sidestream smoke largely consists of the aerosol emitted from the burning end of a cigarette between puffs. Mainstream smoke is the aerosol inhaled by the smoker. Sidestream smoke contributes the greater amount of BaP to indoor air. Investigators report sidestream to mainstream smoke ratios for BaP ranging from 2.1/1 to 9.4/1 per cigarette (Eatough, D.J. et al. (1990); DHHS, 1986; First, 1984). These ratios correspond to sidestream emissions ranging from 20 to 140 nanograms BaP per cigarette (Ibid).

Researchers report BaP levels in mainstream smoke ranging from 20 to 40 nanograms per cigarette (Appel et al., 1990; DHHS, 1986). Appel et al. (1990) reported from 96 to 292 nanograms BaP in the mainstream smoke of five brands of cigars. Exhaled mainstream smoke contains some portion of these reported levels, depending on the amount of BaP retained by the respiratory tract. Cigarette filters appear to reduce the amount of BaP in mainstream smoke, but can substantially increase the amount of this pollutant in sidestream smoke (DHHS, 1989; NRC, 1976).

There are few adequate environmental chamber studies which examine BaP as a constituent of environmental tobacco smoke. In a recent study, Vu-Duc and Huynh (1989) measured an initial BaP concentration of 58.4 nanograms per cubic meter (ng/m^3) in sidestream smoke produced by ten commercial filter cigarettes. The authors reported a BaP half-life of 2.0 hours under the conditions of the study.

B. WOODBURNING

Indoor BaP concentrations from wood smoke are determined by a number of factors, including woodstove or fireplace design, manner of installation and maintenance of woodstoves, and the activities of starting, stoking and feeding wood fires.

Airtight woodstoves emit considerably less BaP indoors than many of the older, more leaky models. This was demonstrated in work by Traynor et al. (1987), who estimated the indoor source strengths from three airtight models and one non-airtight model of woodstoves. The airtight stoves emitted an average of 50 nanograms BaP per hour. The leaky, Franklin-type stove emitted at a much greater rate, from about 2000 to 7000 nanograms per hour. When operated like a fireplace (with its doors open), one airtight stove emitted 760 nanograms per hour.

Improper installation of seals between woodstoves and flues can lead to higher BaP levels indoors (Core et al., 1982). Similarly, the build-up of creosote and/or ash inside a woodstove or its venting system can lead to greater BaP pollution indoors (Ibid.).

The activities of starting, stoking and reloading woodstoves can temporarily elevate indoor BaP levels. Traynor and co-authors (1987) reported that these activities caused at least one short-term increase in pollutant levels from airtight stoves. This was also demonstrated in a more dramatic fashion in tests of a leaky Franklin-type stove.

In 1988, the Environmental Protection Agency (EPA) promulgated standards of performance for residential wood heaters (woodstoves and fireplace inserts). Phase II of this regulation requires that wood heaters be certified to meet particulate matter emission standards of 4.1 grams/hour for catalytic heaters and 7.5 grams/hour for non-catalytic heaters. The California Air Resources Board has adopted a similar suggested control measure which provides guidelines for local air pollution control districts (CARB, 1989). The suggested control measure includes an accelerated schedule, so that residential wood heaters sold on or after January 1, 1991 shall meet EPA's Phase II standards. The EPA did not estimate reductions of pollutants other than particulate matter; however, they believe that the new standards will reduce polycyclic aromatic hydrocarbons (PAHs). Lower BaP emissions indoors and reduced infiltration from outdoor air may result from the new regulation.

Recent standards set by the California Energy Commission (CEC) require closeable metal or glass doors for fireplaces in new residential buildings (CEC, 1988). These standards also require installation of combustion air intakes which draw from outside air, and installation of tight-fitting flue dampers with readily accessible controls. These standards may effect the infiltration of pollutants generated by fireplace use.

C. GAS APPLIANCE USE

Under laboratory conditions, soot and carbon black are produced by burning natural gas (EPA, 1987). Since PAHs, including BaP, are constituents of soot, BaP may be formed from natural gas combustion in the laboratory. However, data are unclear as to whether natural gas combustion produces BaP under the conditions present in the home. In addition, food burned around gas burners during cooking activities may also produce BaP. In a study of combustion sources in northern California homes, Sheldon et al. (1993) did not find an elevation of BaP concentrations in homes using gas heat when compared to homes with no obvious combustion sources. However, two studies by Chuang et al. (1986, 1988) suggest that the presence and use of gas appliances can elevate BaP levels indoors. Homes with gas ranges had measurably higher BaP levels than homes with electric ranges. The study by Sheldon et al. (1993) monitored BaP in about 50 gas heating homes; the studies by Chuang et al. (1986, 1988) were range-finding studies in a smaller number of homes. These studies are further discussed in Section II.

D. MISCELLANEOUS SOURCES

A number of sources can produce BaP in indoor air. These include kerosene stoves, cooking and grilling, certain hobbies, and burning candles or incense. Although the advertising of unvented kerosene stoves for residential use is prohibited in California, a small percentage of residents in the State use this heat source. Sheldon et al. (1993) reported that indoor kerosene stove use elevated indoor air levels of BaP significantly in a small number of homes; the actual concentrations were not reported. Waldman et al. (1989) and others have documented BaP in indoor air from kerosene stove use in other states.

Sheldon et al. (1992, 1993) were not able to identify BaP in indoor air from such sources as incense, candles or cooking and grilling in their two California studies. However, BaP emissions from these sources have been measured or noted by others.

Some hobbies can elevate exposures to BaP in indoor air. Buttler et al. (1993) reported extremely high personal exposures of 793 and 2028 nanograms per day for a man welding for two days in his basement. Waldman et al. (1989) reported elevated concentrations of BaP in a home where a resident used a heat stripper to remove paint, but the authors did not report the resulting level.

E. INFILTRATION AS A SOURCE OF INDOOR BENZO[a]PYRENE

A major source of indoor BaP pollution is the infiltration of polluted outdoor air. In a recent study of 280 homes in two northern California communities, Sheldon et al. (1993) concluded that outdoor air polluted by woodsmoke contributed significantly to indoor air concentrations of BaP. Indoor/outdoor concentration ratios for study homes were generally less than one, suggestive of a significant outdoor BaP source. Researchers estimated that from 40 to 100 percent of indoor concentrations were derived from outdoor air; this was true for homes in the no source, gas heat, fireplace, and woodstove categories. Researchers estimated that about half of the BaP in outdoor air was transported indoors.

In the absence of major indoor sources, researchers in Riverside, California also found polluted outdoor air to be a major source of indoor concentrations of BaP. Sheldon et al. (1992) reported that indoor BaP concentrations were highly correlated with levels measured outdoors. This finding suggests that infiltration of polluted outdoor air was a significant source of pollution for that study. For median values, investigators estimated that about 66 percent of the BaP in outdoor air was transported indoors. In this study, there were few indoor sources of BaP; also, homes with cigarette smokers were underrepresented.

In Waldman et al. (1989) the researchers concluded that space heating was the major source of ambient BaP and that it subsequently filtered indoors. In this case, the fuel for space heating was kerosene and fuel oil; the appliances were vented outdoors in a manner similar to woodstoves. Kaarakka et al. (1986) also found that smoke from burning of garden refuse appeared to be the source of BaP levels inside one test home. This Wisconsin-based study is further discussed in Section II.B.1.

II. INDOOR AIR EXPOSURE TO BENZO[a]PYRENE

This section reviews studies on BaP concentrations in indoor air. Measured BaP concentrations differ significantly among buildings, among locations inside a building, and by season. These variations result from many factors, including differences in building design, the number and types of indoor sources present, and people's activities that result in either indoor or outdoor BaP emissions.

Two large-scale investigations of PAHs, including BaP, in indoor air, have been conducted recently in California. In the PTEAM (Particle Total Exposure

Assessment Methodology) study, researchers measured BaP inside more than one hundred homes in the southern California community of Riverside (Sheldon et al., 1992). This study, conducted during the summer/fall of 1990, measured BaP in both smokers and nonsmokers homes; other combustion sources of BaP were not typically present inside the study homes. Data in the Riverside study were weighted to represent the population of homes in that city (61,520 households). In the second study, investigators measured BaP and other PAHs inside 280 homes in two Northern Californian communities, Placerville and Roseville, during the winter of 1992. This study, later referred to as the northern California PAH study, examined the effect of woodstoves, fireplaces, gas heating, and cigarette smoking on indoor PAH concentrations. Researchers also measured BaP concentrations inside houses with no obvious combustion sources of BaP; these homes are referred to as "no source" homes. Because homes were selected and placed into categories based on the presence and use of major indoor PAH sources, the data were not weighted to the communities' population. These two studies provide a substantial basis for evaluating exposures of California residents to BaP and other PAHs from indoor air.

In the studies reviewed here, researchers collected BaP samples on glass fiber or Teflon filters, and analyzed them using either gas chromatography/mass spectroscopy (GC/MS) or high pressure liquid chromatography (HPLC) with fluorescence detectors. The lack of standardization in methodology for BaP may account for some of the variation in results among studies.

A. INDOOR BENZO[a]PYRENE FROM ENVIRONMENTAL TOBACCO SMOKE (ETS)

The presence of environmental tobacco smoke generally raises BaP concentrations indoors, often above outdoor levels. The U.S.-based studies reported here examine cigarette smoking but do not include other types of tobacco products.

1. Benzo[a]pyrene Levels in Homes from ETS

Tobacco smoking raised indoor BaP concentrations by a substantial margin in the northern California PAH study (Sheldon, 1993). Smoking raised BaP levels for all statistics reported (geometric mean, arithmetic mean, 25th, 50th and 75th percentiles). Investigators reported a highly significant difference between geometric means for 63 smokers' homes and 39 "no source" homes. Researchers reported an average BaP concentration of 2.2 ng/m^3 in smokers' homes, compared to a level of 0.83 ng/m^3 in "no source" homes. Tobacco smoking was the only combustion source in the study which consistently raised indoor BaP levels above outdoor levels of this pollutant.

Cigarette smoking also raised BaP concentrations in indoor air in the Riverside PTEAM study (Sheldon et al., 1992). In 21 smokers' homes, the average nighttime BaP concentration was 0.43 ng/m^3, but was only 0.25 ng/m^3 in 85 nonsmokers' homes. During the day, the average BaP concentration was 0.51 ng/m^3 in 17 smokers' homes, but was only 0.20 ng/m^3 in 85 nonsmokers' homes. Analyses indicate that these differences in average BaP concentrations in smoking and non-smoking homes are statistically significant.

In Wisconsin, Kanarek et al. (1985) compared BaP levels in both smokers' and nonsmokers' homes. Investigators reported elevated levels of BaP in smokers' homes both before (Phase 1) and after (Phase 2) weatherization and insulation modifications were made. Researchers monitored 12 to 18 smokers' homes and 20 to 30 nonsmokers' homes for 24-hour periods during the winters of 1982-83 and 1983-84. In smokers' homes, authors reported average BaP levels of 1.15 and 1.51 ng/m^3 for Phases 1 and 2 (see Table 2). Most of the measurements (about 65 percent) were above the minimum detection limit for both phases. Residents smoked an average of nine cigarettes per day. In non-smokers' homes, researchers reported lower levels, averaging 0.66 and 0.87 ng/m^3 before and after weatherization. The post-weatherization average became significantly lower (0.37 ng/m^3) when a high outlier was discounted. Researchers judged the source for this outlier to be smoke from a leaky fireplace.

In two smaller studies conducted in Columbus, Ohio, Chuang et al. (1986, 1988) reported similar increases in BaP indoors from tobacco smoking. During the winters of 1984 and 1986/87, researchers conducted a pilot and a follow-up range-finding study. Of the two, the effect of tobacco smoking was clearer in the range-finding study. In that study, researchers monitored living room and kitchen areas for two eight-hour periods during waking hours; in the pilot study, researchers took an additional overnight sample in each master bedroom. To compare indoor with outdoor levels in both studies, researchers placed an air monitor outside each of eight homes.

In the range-finding study, Chuang et al. (1988) reported highly significant increases in BaP concentrations as a result of cigarette smoking. The 16-hour average BaP level was 1.13 ng/m^3, as calculated from reported data, with a reported range of 0.32 to 3.3 ng/m^3 (see Table 1). Values from nonsmokers' homes were lower, with a calculated 16-hour average of 0.42 ng/m^3 and a reported range of 0.25 to 0.83 ng/m^3. Investigators estimated an average increase of 0.08 ng/m^3 BaP per each additional cigarette smoked (Chuang, J. et al., 1991). Tobacco smoking elevated indoor BaP levels above outdoor levels for each of the homes sampled.

TABLE 1

BENZO[a]PYRENE CONCENTRATIONS IN SMOKERS' AND NONSMOKERS' HOMES DURING A 16-HOUR PERIOD

		BaP Concentrations (ng/m^3)		# of Cigarettes
	Home #	Living Room	Kitchen	Living Rm./Kitchen
Smokers	2	1.20	0.62	16/10
	3-1*	0.34	0.56	9/ 6
	4	1.40	0.60	15/ 7
	5	3.30	1.60	20/11
	6	1.40	0.32	12/ 9
Average		1.53	0.74	12
Overall Average:		**1.13**		
Nonsmokers	1	0.28	0.25	0/0
	7	0.31	0.28	0/0
	8-1*	0.83	0.31	0/0
	8-2*	0.67	0.49	0/0
Average		0.52	0.33	0
Overall Average:		**0.42**		

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* These homes were sampled on two different days.
Reference: Chuang et al. (1988)

In the pilot study, Chuang et al. (1986) reported substantial increases in indoor BaP levels from tobacco smoking. Eight-hour averages ranged from 1.37 to 2.64 ng/m^3 per sampled room in smokers' homes. In nonsmokers' homes, per room averages were lower, from 0.59 to 0.66 ng/m^3. Unlike the range-finding study, outdoor levels were often higher than indoor levels, and ranged from 1.24 to 3.17 ng/m^3.

Alfeim and Ramdahl (1984) reported that tobacco smoking increased total PAHs in a Norwegian home. The authors presented a profile of the PAH constituents from an 8-hour period of heavy smoking (18 cigarettes, five cigarillos and one cigar) and from a 19-hour period when the open fireplace was in use. About 6 ng/m^3 BaP was produced from tobacco smoking; about twice that was produced during woodburning in the fireplace.

TABLE 2
AVERAGE BENZO[a]PYRENE CONCENTRATIONS IN SMOKING AND NONSMOKING AREAS OF U.S. HOMES AND PUBLIC BUILDINGS

	# of Hrs.	# of	Average BaP Concentration (ng/m^3)		
Location	Sampled	Buildings	Smokers	Nonsmokers	Ref.
N. Calif.-homes	24	53/39	2.2	0.83-0.41*	a
So.Calif.- homes					
Day	12	17/85	0.51	0.20	b
Night	12	21/85	0.43	0.25	b
Ohio-homes	16	5	1.13	0.42	c
Wisconsin-homes					
Phase 1	24	12/30	1.15	0.66	d
Phase 2	24	12/30	1.51	0.87	
Pacific NW					
Buildings	10-12**	15/16	1.07	0.39	e

* Values represent two categories of nonsmokers homes in same study.

** Estimated number of hours; text indicates that buildings were monitored during working hours.

References:

a. Sheldon et al. (1993)
b. Sheldon et al. (1992)
c. Chuang et al. (1988)
d. Kanarek (1985)
e. Turk et al. (1987)

2. Benzo[a]pyrene Levels in Public Buildings from ETS

The most comprehensive study on BaP levels in public buildings was conducted in the Pacific Northwest by Turk et al. (1987) from January 1984 to April 1985. Researchers reported higher BaP concentrations in areas of public buildings where smoking was allowed. Investigators monitored smoking and nonsmoking areas of 16 buildings. Most of the buildings were either schools or government buildings. The researchers noted that cigarette smoking was more restricted than would be expected in private commercial buildings. The buildings ranged from 0.5 to 90 years in age. In smoking-permitted areas, researchers measured an average concentration of 1.07 ng/m^3, ranging from 0.12 to 3.60 ng/m^3 (see Table 2). Corresponding BaP values in nonsmoking areas in the same study were lower; investigators measured an average level of 0.39 ng/m^3 ranging from 0.09 to 1.35 ng/m^3. Indoor concentrations from smoking areas were consistently higher than concentrations measured outside each building. The margin of increase was often high; the mean indoor-to-outdoor ratio was 7.6/1.

Elliot and Rowe (1975) reported high levels of BaP during public gatherings in an air conditioned arena. Researchers monitored this arena 17 times with crowds that varied from about 9,000 to 14,000 people. Although 'No Smoking' signs were posted, the restriction was not enforced. Authors reported an average BaP concentration of 12.5 ng/m^3 with a range of 7.1 to 21.7 ng/m^3. This represents a two-fold increase in the BaP level as the population increased by less than half. The indoor concentrations were 10 to 18 times the reported background concentration of 0.69 ng/m^3.

B. INDOOR BENZO[a]PYRENE FROM WOODBURNING

Indoor woodburning can raise levels of BaP in the home, often above measured outdoor levels. While the contribution from burning wood in the newer models of airtight stoves appears to be relatively small, other types of woodburning devices can pollute indoor air significantly. Substantial increases in BaP concentrations indoors have been measured as a result of burning wood in fireplaces, poor maintenance or installation of woodstoves, use of some of the older woodstove models, and certain woodstove operating practices.

1. Woodstoves

Woodstove use raised indoor BaP concentrations above those in homes without obvious combustion sources in the northern California PAH study (Sheldon et al., 1993). BaP concentrations in homes using woodstoves were significantly higher at the 0.10 level from concentrations in "no source" homes when comparing geometric means (statistical analysis performed on geometric means only). In the 56 homes where woodstoves alone were used for heating, an average BaP concentration of 1.2 ng/m^3 was reported, and was higher than the level of 0.83 ng/m^3 reported in the 39 "no source" homes. Investigators also reported that in homes where stoves were operated like a fireplace, with their doors open, BaP and other PAHs tended to be very high (specific values were not reported.) Relatively high BaP concentrations inside "no source" homes, resulting from infiltration of woodsmoke pollution in outdoor air, may minimize differences between the woodburning homes and the "no source" homes.

Traynor et al. (1987) tested three airtight stove models and one non-airtight model (a leaky, Franklin-type stove with visible gaps in its construction) in a California home. The investigators monitored pollutants from 6 to 20 hours for airtight stove tests and for shorter periods for tests of the non-airtight stove. Each stove was operated for a minimum of five hours. In addition to three monitors placed inside the home, researchers also measured BaP from a location outside the home.

Investigators reported relatively low indoor BaP concentrations resulting from the operation of three airtight stove models, ranging from 0.34 to 0.94 ng/m^3 for six tests (see Table 3). This range is similar to that reported in nonsmokers' homes where woodburning was minimal (see Table 2). Benzo(a)pyrene concentrations during tests of airtight stoves averaged 6 times greater than levels measured in the home when woodstoves were not in use; the average background measurement was 0.10 ng/m^3. When investigators operated an airtight stove like a fireplace (with its doors open), BaP concentrations rose to an indoor concentrations of 3.5 ng/m^3. The investigators measured dramatically higher BaP concentrations indoors when operating the Franklin-type (leaky) stove, with estimated real-time averages of 13 and 44 ng/m^3 for each burn period. The BaP level soared to a real-time average of 370 ng/m^3 in a third "worst-case" test, during which investigators observed a large amount of smoke indoors.

Operation of the non-airtight stove elevated indoor BaP levels by a substantial margin over outdoor levels; this was true to a lesser extent for the "fireplace" stove test. Conversely, during airtight stove tests, outdoor BaP levels were higher than indoor levels in most cases.

In the Pacific Northwest, Core et al. (1982) measured low levels of BaP indoors while operating woodstoves. The investigators monitored indoor air in five homes during burn and nonburn periods. Stoves were in use for an average of six hours per day for the two to five days that homes were monitored. This study was conducted during May of 1980, and is therefore not representative of the colder winter months when greater woodstove use is expected. Researchers measured BaP levels ranging from below the limit of detection (0.05 ng/m^3) to about 0.3 ng/m^3 from 24-hour air samples (see Table 3). A significantly higher concentration, 26.3 ng/m^3, was measured in a fifth home where researchers observed smoke leakage during fuel loading (Core et al., 1982; Neulicht and Core, 1982). This fugitive emission was caused by partial blockage of the flue by wood ash and creosote. Creosote build-up on the glass door surface indicated a long-term pattern of smoke leakage for this appliance. When this woodstove was not in use, BaP was not measurable indoors. Investigators did not measure BaP outdoors; however, other measurements indicated that air infiltration rates were relatively low in the higher concentration home.

In a 1985-86 study of twenty Wisconsin homes, researchers measured low levels of BaP during operation of airtight stove models. Daisey et al. (1989) reported 48-hour BaP concentrations ranging from 0.07 to 1.34 ng/m^3 inside seven homes during periods when woodstoves were operated. When woodstoves were not in use, BaP levels were lower, and ranged from below the limit of detection (0.009 ng/m^3) to 0.17 ng/m^3. Other potential sources of BaP, such as tobacco smokers or kerosene space heaters, were excluded from the study. The highest 48-hour concentration of BaP, 1.34 ng/m^3, was measured inside a house during a period when the woodstove door was left open for an extended period of time. The authors stated that the measured concentrations may underestimate actual concentrations since the relatively high air sampling rate used may have lowered the indoor pollutant concentrations. As part of the same study, Kaarakka et al. (1986) reported a BaP concentration of 0.38 ng/m^3 resulting from a damped down, smoldering fire. The authors also reported a BaP level of 0.12 ng/m^3 resulting from outdoor brush and leaf burning with subsequent infiltration indoors. These pollutant levels were measured during the supposed nonwood-burning periods of the study, and discarded from study averages and ranges as outliers.

Sexton and co-workers (1986) found somewhat higher BaP levels in a study of six woodburning homes in Waterbury, Vermont. Investigators conducted the study during the winter of 1982, and only used homes of nonsmokers. Researchers monitored each home for one to four days. The authors reported an average concentration of 0.8 ng/m^3 for the six homes studied, with a range of 0.1 to 3.4 ng/m^3. Large standard deviations for in-home 24-hour averages and the over-all average for the six homes indicated significant intra-home and inter-home variability.

In a well-insulated test home in Chattanooga, Tennessee, investigators were unable to detect BaP in the majority of tests of three non-airtight woodstove models (TVA/CPSC, 1985). BaP was above the relatively high limit of detection (2 ng/m^3) in only three of 28 tests. The two highest concentrations (8.2 and 9.8 ng/m^3) were associated with closed damper conditions, an operating mode commonly used to prolong a fire at night. Unlike most other studies, PAHs were collected on an XAD-2 resin trap. A 195-micron frit disk and glass wool were used in the trap but were not analyzed for BaP, which may account, in part, for the high number of samples in which BaP was not detected.

In a Boston, Massachusetts area home, Moschandreas et al. (1981) reported increases in BaP concentrations in indoor air from the use of a basement woodstove. Researchers monitored kitchens, living rooms and master bedrooms of two residences. An adjacent outdoor site was monitored at each home. Occupants burned wood in the basement stove on 9 of 11 monitoring days. As a result, reported BaP concentrations indoors were nearly five times the matched outdoor concentrations (specific values were not presented).

TABLE 3

BENZO[a]PYRENE CONCENTRATIONS IN WOODBURNING HOMES IN THE U.S.

	Location	Sampling Time(hr)	No. of Homes	BaP Concentration (ng/m^3) Average	(Range)	Ref.
Woodstoves						
	No. Calif.	24	56	1.2		a
	Truckee					
	airtight	6-19	1	----	0.34- 0.94	b
	leaky	*		13-44[2]		
	Pacific NW	24				
	--low		4	----	ND - 0.3	c
	--high		1	26.3[1]	----	
	Wisconsin	48	7	----	0.07- 1.34	d
	Vermont	24	6	0.8[3]	0.1 - 3.4	e
Fireplaces						
	No. Calif.	24	46	1.0	----	a
	Truckee[z]	19.6	1	3.5[1]	----	b
	New Jersey	24	1	3.5[4]	1.7 - 5.7	g
	Boston	24	1	11.4[1]	----	f

* Sampling time not provided.

ND: Not Detected

z Woodstove operated like a fireplace (i.e. - with its doors open)

1. Single home, single test average.
2. Average concentration over entire burn period using real-time particulate concentration data.
3. Arithmetic average of 24-hour measurements from six homes.
4. Arithmetic average of four 24-hour tests in a single home.

References:

a. Sheldon et al. (1993)
b. Traynor et al. (1987)
c. Core et al. (1982)
d. Kaarakka et al. (1986); Daisey et al. (1989)
e. Sexton et al. (1986)
f. Moschandreas et al. (1981)
g. Dong and Bozzelli (1989)

2. Fireplaces

Fireplace use also raised indoor BaP concentrations above levels in homes without obvious combustion sources in the northern California PAH study (Sheldon et al., 1993). The geometric means of BaP concentrations inside 46 homes using fireplaces was significantly different from the mean in 39 "no source" homes at the 0.01 level; statistical analysis was performed on geometric means only. Investigators reported an average BaP concentration of 1.0 ng/m^3 in homes using fireplaces; the corresponding level in "no source" homes was 0.83 ng/m^3. Relatively high BaP levels in "no source" homes, due to infiltration of woodsmoke from outdoors, may minimize the differences between BaP levels inside homes using fireplaces and the "no source" homes.

In an unoccupied New Jersey home, Dong and Bozzelli (1989) measured significantly higher concentrations of BaP in indoor air during fireplace use. The authors reported an average level of 3.5 ng/m^3 with a range of 1.69 to 5.70 ng/m^3 for four separate tests of woodburning in an open-wall fireplace. This average level is consistent with the concentration reported by Traynor et al. (1987) that resulted from a woodstove operated as a fireplace, with its doors open. In a fifth experiment, the indoor BaP concentration rose to 14.4 ng/m^3 when researchers used the fireplace with the damper closed. Researchers burned wood for 1.5 to 2.5 hours during each 24-hour sampling period. When the fireplace was not in use, researchers measured a background level of 0.16 ng/m^3.

In a single woodburning episode in the fireplace of a Boston area home, Moschandreas et al. (1981) measured a BaP concentration of 11.4 ng/m^3. Over twelve days when the fireplace was not in use, the average concentration was 0.6 ng/m^3. The activities of light smokers may have contributed to pollutant levels in this residence.

In a weatherized Wisconsin home, Kanarek et al. (1985) measured a BaP level of about 17 ng/m^3 arising from emissions from a leaky free-standing fireplace. Emissions arising from both fireplace and woodstove use contributed to air levels of about 3 to 5 ng/m^3 inside several nonsmoking homes.

Alfheim and Ramdahl (1984) measured BaP and total PAH concentrations inside a Norwegian house located in an isolated, forested area. During 6 to 19 hour sampling periods, investigators burned wood inside an airtight woodstove and/or an open fireplace. The authors reported indoor BaP concentrations of 13 and 18 ng/m^3 on two separate days as a result of the fireplace burning. These BaP levels corresponded to total PAH concentra$ons of 150 and 206 ng/m^3. Relatively lower PAH concentrations resulted from use of woodstoves alone. The authors did not report indoor BaP values resulting from solo woodstove use. Burning wood in a fireplace resulted in about a two-fold increase in BaP concentrations when compared with heavy tobacco smoking in the experimental home.

C. GAS APPLIANCE USE

Sheldon et al. (1993) did not find an increase in BaP concentrations in 53 homes using natural gas heat when compared to 39 homes with no obvious combustion sources (referred to as "no source" homes). Investigators reported an arithmetic mean concentration of 0.41 ng/m^3 in gas heating homes but a mean concentration of 0.83 ng/m^3 in "no source" homes. BaP levels were relatively high in "no source" homes; outdoor air polluted by woodsmoke appeared to infiltrate these homes. Also, some homes with certain indoor sources of BaP, such as kerosene stoves, may have been placed into this category.

Data from the two studies by Chuang et al. (1986, 1988) suggest that gas furnace and stove use may contribute to higher BaP levels. In a pilot and a follow-up range-finding study, the researchers monitored air levels inside two to four nonsmokers' homes with gas appliances. Investigators also sampled indoor air from one to two all-electric homes used as controls. In the pilot study, eight-hour room averages from "gas appliance" homes were 1.36, 1.65 and 1.07 ng/m^3 in kitchen, living room and bedroom areas, respectively. Similar averages from electric homes were lower, and ranged from below the limit of detection (concentration not presented) to 0.14 ng/m^3. However, woodsmoke from fireplaces may have contributed to the higher levels in some homes. Infiltration of polluted outdoor air may also have affected indoor levels; outdoor levels from co-located samplers were high, and ranged from 1.24 to 3.17 ng/m^3.

D. INDOOR CONCENTRATIONS COMPARED TO OUTDOOR CONCENTRATIONS

Indoor BaP levels vary widely due to differences in the presence and strength of indoor sources and other factors. Relative indoor and outdoor levels are also highly variable. Indoor/outdoor ratios can vary from less than one to as high as 94 (Sheldon et al., 1993; Sheldon et al., 1992; Turk et al., 1987). Typically, indoor/outdoor ratios appear to be at the lower end of this range. High indoor/outdoor ratios for homes or buildings tend to result from specific types of activities. These include: tobacco smoking, the operation of a leaky woodstove, backdrafting from a poorly maintained woodburning appliance, or use of some unvented combustion appliances such as kerosene heaters (Sheldon et al., 1993; Sheldon et al, 1992; Traynor et al., 1987; Neulicht and Core, 1982).

The presence of environmental tobacco smoke typically raises indoor BaP concentrations above outdoor concentrations. Sheldon et al. (1993) reported an average indoor-to-outdoor ratios of 5.8 for smoking homes. Smoking was the only combustion category where BaP levels were consistently higher indoors than outdoors; in over half of the 53 homes monitored, indoor levels were greater than levels outdoors. The indoor/outdoor ratio for the "no source" category of homes was 0.61.

Turk et al. (1987) reported similar trends. In public buildings where smoking occurred, investigators reported indoor/outdoor BaP ratios varying from 0.3 to 61.2 for individual buildings; the average indoor-to-outdoor ratio was 7.6. The geometric mean indoor/outdoor ratio was 2.16. Indoor BaP concentrations were higher than outdoor concentrations in 12 of 15 buildings tested. In contrast, for nonsmoking areas of public buildings, BaP levels were higher than outdoor levels in only 4 of 16 tests (15 buildings were monitored). In nonsmoking areas, BaP concentration ratios ranged from 0.3 to 14.0 for individual tests; the mean indoor/outdoor ratio was 0.85 when the highest value (14.0) was excluded. The geometric mean indoor/outdoor ratio was 0.86. This study was conducted in the Pacific Northwest.

Smoking also elevated indoor/outdoor ratios in the Riverside PTEAM study (Sheldon et al., 1992). For smokers' homes, the indoor/outdoor ratio was about 1 at nighttime, but was 3.0 during the day. However, smokers' homes were somewhat underrepresented in this study, and other indoor sources of BaP were minimal; consequently indoor/outdoor ratios were less than one for most of the

125 homes monitored. During the day, indoor-to-outdoor BaP concentration ratios averaged less than one for about half of the study homes. At nighttime, indoor-to-outdoor ratios were greater than one for only about 25 percent of the study homes.

In homes that used fireplaces and woodstoves, Sheldon et al. (1993) reported average indoor-to-outdoor ratios of 1.2 and 2.6 respectively. Woodsmoke pollution in outdoor air in the immediate vicinity of the woodburning homes tended to lower indoor/outdoor BaP ratios for these categories. The 75th percentile indoor-to-outdoor ratios were 1.1 and 1.2 for these categories, indicating that indoor BaP concentrations were greater than outdoor concentrations for about 25 percent of the study homes.

E. CANCER RISK FROM INDOOR EXPOSURE

People in California are often exposed to levels of BaP above the statewide population-weighted average for outdoor air (0.53 ng/m^3). In indoor environments, environmental tobacco smoke (ETS) and other combustion sources such as woodburning can raise people's exposure to BaP substantially.

Using OEHHA's best estimate of risk, and average indoor concentrations in California homes where smoking occurred (Sheldon et al., 1993; Sheldon et al., 1992), exposure to BaP in smoking environments is estimated to result in 0.5 to 2.4 potential cancer cases per million people exposed for most of their day. The calculations are as follows:

(a) $$2.2 \times 10^{-3}\ \mathrm{ug/m^3}\ \mathrm{X}\ \frac{1.1 \times 10^{-3}\ \mathrm{cancers}}{(\mathrm{ug/m^3})\ (\mathrm{person})}\ \mathrm{X}\ 10^{6}\ \mathrm{people} = 2.4\ \mathrm{cancers\ per\ million}$$

(b) $$0.47 \times 10^{-3}\ \mathrm{ug/m^3}\ \mathrm{X}\ \frac{1.1 \times 10^{-3}\ \mathrm{cancers}}{(\mathrm{ug/m^3})\ (\mathrm{person})}\ \mathrm{X}\ 10^{6}\ \mathrm{people} = 0.5\ \mathrm{cancers\ per\ million}$$

People at risk from such exposures include residents of smokers' homes who stay indoors all day, and those exposed at both work and home. On a given day, about 7 percent of adult Californians spend at least 95 percent of their time at home (Wiley et al., 1991). The higher risk number above is estimated from wintertime concentration data in smoker's homes (2.2 ng/m^3 average indoor BaP) and represents exposure in relatively closed-up homes. The lower risk number is estimated from summertime concentration data in smokers' homes (0.47 ng/m^3 average indoor BaP) and represents summertime exposure in homes with some opening of doors and windows.

In homes with no obvious combustion sources, researchers (Ibid.) documented exposures that were comparable to or lower than the statewide ambient average.

III. OTHER ROUTES OF EXPOSURE TO BENZO[a]PYRENE

A. FOOD INGESTION

BaP is commonly found in many different kinds of food, at levels that are quite variable depending on the source and type of the food and the manner in which it was prepared. Most raw foods grown in uncontaminated environments contain little or no BaP; however, vegetable and fruit crops can become contaminated with BaP through atmospheric deposition and from polluted soil or water. Raw seafood may also contain BaP derived from polluted water or sediments. Levels in edible marine species, especially filter feeders (e.g., clams and oysters) are likely to reflect the extent of PAH contamination of the water. On the other hand, most fish can metabolize PAHs; thus, raw fish would be expected to contain little BaP. Raw meats do not usually contain BaP; however, meats and (other foods can become quite contaminated depending on the way in which they are cooked or prepared. For example, foods (meat, fish, and cheese) which have been smoked, meats cooked at high temperatures, and meats cooked close to a flame (especially meats with a high fat content) all tend to have high BaP levels (50 ug/kg and more in some cases). BaP has also been detected in grains, cereal products, vegetable oils, margarine, coffee, tea, and whiskey (Santodonato et al., 1981; National Research Council, 1983). Table 4 provides a sample of some of the levels of BaP measured in various foods. Although those data come from international sources and may not all apply to food consumed in California, they provide a general picture of the extent of BaP contamination of many kinds of food and illustrate the great variability seen in BaP levels.

A recent study conducted in Phillipsburg, New Jersey (Lioy et al., 1988), measured BaP levels in food samples obtained from ten families. Every day for two weeks, each family set aside a portion of each meal eaten at home. The investigators subsequently compiled the portions such that they analyzed two one-week samples for each family. They found that the amount of BaP per gram of wet weight of food ranged from 0.004 to 1.2 ng/g (ppb). This measured range is consistent with the estimate made by Santodonato et al. (1981) of a typical range of BaP concentrations in food of from 0.1 to 1.0 ppb.

B. WATER INGESTION

BaP and other PAHs can enter the water supply from local sources, such as oil spills, industrial and municipal effluents, and road run-off. Airborne, combustion-produced PAHs may also make a major contribution to the aquatic environment (Santodonato et al., 1981). In general, BaP levels in surface water tend to be higher than in ground water. However, routine treatment of surface water to obtain drinking water has been shown to reduce BaP (and other PAH) concentrations considerably (Basu and Saxena, 1978; National Research Council, 1983).

Santodonato et al. (1981) noted that drinking water samples (most from surface water sources) obtained from 15 sites in the eastern United States showed BaP concentrations ranging from 0.2 to 2.1 nanograms per liter. BaP was not detected in two of the samples. The authors used those data to estimate an average concentration in U.S. drinking water of 0.55 nanograms per liter. There is insufficient data at this time to estimate BaP levels in California drinking water. Approximately 40 percent of the California population uses groundwater to supply domestic needs. The California Department of Health Services monitored a number of organic compounds in wells between January, 1984 and December, 1985, but did not find evidence of BaP contamination (A. Milea, 1990; DHS, 1986).

TABLE 4
LEVELS OF BENZO[a]PYRENE IN VARIOUS FOODS (ug/kg wet weight)

Cooked meats, sausage	0.17-0.63
Cooked bacon	1.6-4.2
Charcoal-broiled meats	2.6-11.2 (50.4 recorded)
Heavily smoked ham	Up to 23 (107 recorded, Iceland)
Cooked fish	0.9
Smoked fish	0.3-60
Cereal grains	0.2-4.1
Flour and bread	0.1-4.1
Bakers' dry yeast (yeasts grown on mineral oils are lower)	1.8-40.4
Soybean	3.1
Refined vegetable oils, fats	0.4-36
Margarine, mayonnaise	0.2-6.8
Salad	2.8-12.8
Tomatoes	0.2
Spinach	7.4
Kale (only 10% removed by washing)	12.6-48.1
Apples	0.1-0.5
Fruits (not apples)	2-8
Dried prunes	0.2-1.5
Roasted coffee and solubles	0.1-4
Malt coffee	Up to 15
Tea	3.7-21.3
Whiskey	0.04 ug/L
Beer	ND
Milk	ND

ND = not detected.

Source: National Research Council (1983)

However, since the detection limit of 10 micrograms per liter is high, significant levels of BaP may have been present, but undetected. The wells that were monitored for BaP were used by large public water systems (over 200 connections) and were located near heavy industrial areas (sites which were considered to have the greatest potential for well contamination). There are no data on BaP in California's surface waters (A. Milea, 1990).

IV. ESTIMATES OF PRESENTED DAILY DOSE FROM INDOOR AIR INHALATION AND WATER / FOOD INGESTION

Exposure to BaP in the indoor environment can be substantial. Estimates of daily presented doses from exposure to BaP in indoor air and from ingestion of contaminated food and water are discussed below and summarized in Tables 5 and 6. The term "presented dose" is used alternately with "inhaled" or "ingested dose." These terms do not necessarily indicate the biological dose, since they do not take into account the actual fraction absorbed by the body.

Inhaled dose estimates for both the home-bound and the average California resident are presented. About seven percent of California's residents spend at least 95 percent of their time at home, and are represented by 24-hour (100 percent) estimates. The average adult Californian spends about 62 percent of his or her time inside the home on a given day (Jenkins et al., 1992) and is represented by estimates based on 15-hour exposures. Because of the large variation in BaP levels in indoor air, food and water, the ranges of potential daily doses are fairly large.

Primarily data from California studies are used to develop estimates of inhaled doses for residents of this state. The two major studies of PAHs inside homes in California, the Riverside PTEAM study and the northern California PAH study, present data from two different kinds of exposure scenarios (Sheldon et al., 1992). In the Riverside study, investigators studied randomly selected homes during a time when few combustion sources were used. Additionally, residents used natural ventilation (open windows and doors) a majority of the time. Consequently, indoor BaP and PAH concentrations from this study tend to be low. In the northern California

PAH study, conducted in Placerville and Roseville, investigators measured used. Measurements were taken in the wintertime, when residents were more likely to keep doors and windows closed. As a result, BaP and other PAHs tend to be higher in this study.

Estimates of total exposure have a similar distribution; a low end and a high end estimate are presented for each category (see Table 5). These estimates are presented as a range. Inhaled doses of BaP from a variety of "medium" exposure scenarios are most likely to fall within this range. An example of a "medium" exposure scenario might include residents who use their fireplaces or woodstoves for fewer hours per day than in the northern California study, and use them only occasionally.

A. INDOOR AIR INHALATION

1. Environmental Tobacco Smoke

Tobacco smoking substantially increases the inhalation exposure of residents to BaP. Extrapolating from data obtained in the Riverside PTEAM study and from the northern California PAH study, the inhaled dose in smokers' homes is estimated to be about 9 to 44 nanograms per day for home-bound residents (see Table 5). These 24-hour estimates are derived by multiplying BaP concentrations obtained in the two studies (0.47 ng/m^3 and 2.2 ng/m^3) by the average volume of air inhaled daily by humans (20 cubic meters). The 0.47 ng/m^3 value was obtained by averaging the nighttime and daytime values for smokers' homes from the Riverside study (see Table 2). For the average Californian, who spends 62 percent (about 15 hours) of the day at home, the inhaled dose in a smoker's home is about 6 to 27 nanograms per day. The upper end of these dose estimates reflects heavy tobacco smoking or smoking in a closed-up residence; the lower end represents light smoking or the use of natural ventilation.

Turk et al. (1987) estimated exposure levels in office buildings with smoking during work days. Extrapolating from their data, the inhaled daily dose of BaP in public buildings where smoking occurs is about 21 nanograms when a full 24-hour exposure occurs. However, since most workers spend only about 8 hours per day in the office, a more realistic estimate of the inhaled dose in public buildings where smoking occurs is about 7 nanograms daily.

2. Woodburning

Indoor use of woodstoves can contribute significantly to an individual's total exposure to BaP. Based on California data developed by Sheldon et al. (1993) and Traynor et al. (1987) (see Table 3), inhaled 24-hour doses of 7 to 24 nanograms can result. These estimates assume continuous exposure, which is not likely for the typical Californian. For the average person, spending only 62 percent of their time inside the home, the estimated dose is from 4 to 15 nanograms per day. The upper end of these dose estimates reflects a scenario of heavy use of woodstoves; re-infiltration of woodsmoke from community air is also a contributor in this scenario. The lower end of these dose estimates reflects scenarios such as the use of airtight woodstoves or woodstoves used for only brief periods of time.

Burning wood in fireplaces can also increase human exposures significantly. A typical resident using their fireplace is exposed to an estimated average of 12 nanograms per day, assuming they spend 62 percent of their time indoors. For the resident spending 24 hours a day at home, the estimated inhaled dose would be 20 nanograms per day. Only one dose estimate is presented here, and is based on data from the northern California PAH study (see Table 3).

Data presented by Traynor et al. (1987) on BaP concentrations resulting from use of a leaky, Franklin-style woodstove were not used to develop total exposure estimates. These data represent a worst-case scenario that is likely to reflect a very rare event, if such a scenario could occur at all.

3. Use of Gas Appliances

Data on the effect of cooking and gas stove use are inadequate to develop daily dose estimates. It is unclear if these sources contribute to indoor BaP levels Estimates of inhaled 24-hour doses based on BaP concentrations in homes with no smoking and no or minimal woodburning range from about 4 to 17 nanograms daily. Inhaled 15-hour doses for the average resident range from about 3 to 10 nanograms daily. Gas appliance use and miscellaneous combustion sources such as incense or candle use, or kerosene stove use, may contribute to a portion of the exposures in these homes.

Table 5

ESTIMATED INHALED DOSES OF BENZO[A]PYRENE FROM INDOOR AIR

Average Inhaled Dose (nanograms per day)
Based on Percent of Time Exposed

	8 hours (33%)	15 hours (62%)	24 hours (100%)
Smoking	7[d]	6 - 27[a,b]	9 - 44[a,b]
No source*	3[d]	3 - 10[a,b]	4 - 17[a,b]
Woodstoves	--	4 - 15[a,c]	7 - 24[a,c]
Fireplaces*	--	12[a]	20[a]

*The inhaled doses for these scenarios apply only when woodstoves or fireplaces are used. For most areas of California, this would occur only in fall or winter.

References

a. Sheldon et al. (1992)
b. Sheldon et al. (1992)
c. Traynor et al. (1987)
d. Turk et al. (1987)

Calculations:
Assumption: Assume 20 m^3 of air is breathed per 24-hour period.
Example : If the average indoor BaP concentration is 1.13 ng/m^3, the 24-hour inhaled dose estimate is 22.6 ng (20 m^3 X 1.13 ng/m^3).

B. FOOD INGESTION

Estimating the amount of BaP that a person might ingest in their food is problematic because of the large variation seen in the levels of BaP in foods. Among other factors, the manner of cooking has a major effect on BaP levels; substantial person-to-person variation might thus be expected. Santodonato et al. (1981) estimated that a person ingests between 160 to 1600 nanograms of BaP per day through food (see Table 6). The authors derived this crude estimate by multiplying an estimate of typical levels of BaP in food (0.1 to 1.0 ppb) by the average total daily food consumption by man of all types of food (1600 grams per day). Likewise, Harris et al. (1982) estimated that the typical ingestion of BaP through food was approximately 50 nanograms per day and also stated that consumption of large amounts of charcoal-broiled food could result in ingestion of as much as 6000 nanograms per day. The values were calculated by multiplying estimates of the average consumption of different types of food by levels of BaP measured in those food types. Lioy et al. (1988) estimated the amount of BaP ingested through food from their measurements of BaP levels in composite (weekly) samples obtained from family meals. Their estimates ranged from 10 to 4005 nanograms per week. To obtain an estimate of daily ingestion, those values divided by seven are approximately 1.4 to 572 nanograms per day (.001 to 0.57 micrograms per day).

The three estimates presented above compare reasonably well, considering that different approaches were used in deriving them. Combined, the estimates predict that a person may ingest from about one to 6000 nanograms per day of BaP in their food. Again, it should be emphasized that this large range reflects the large variability of the BaP levels in food and, consequently, the uncertainty in predicting the amount of BaP a person may ingest.

C. DRINKING WATER INGESTION

Santodonato et al. (1981) estimated that a person ingests a relatively low amount of BaP per day through drinking water, about 1.1 nanograms per day (see Table 6). The authors derived this crude estimate by multiplying their estimate of the average concentration of BaP in U.S. drinking water (0.55 nanograms per liter) by a value for the average daily consumption of water

Table 6
ESTIMATED INGESTED DOSES OF BENZO[a]PYRENE (nanograms/day)

	Low est.	Average	High est.	References
Food	160	---	1600	a
	---	50	6000	b
	1.4	---	572	c
Water	---	1.1		a

Assumption: Two liters of drinking water are consumed per day.

References:
a. Santodonato et al. (1981)
b. Harris et al. (1982)
c. Lioy et al. (1988)

(two liters per day). The highest BaP concentration noted by the above authors was 2.1 nanograms per liter. Applying the same assumption, the upper range of the estimate would be 4.2 nanograms per day. There are insufficient data to estimate drinking water ingestion of BaP in California.

D. SUMMARY OF PRESENTED DAILY DOSE ESTIMATES

The major indoor sources of BaP inhalation exposures in California are environmental tobacco smoke, woodburning in stoves and fireplaces, and infiltration of polluted ambient air to the indoors. Indoor BaP exposures may also result from cooking and gas appliance use, although there are only limited data on these sources. Exposure to BaP also results from the ingestion of contaminated food or water. Based on U.S.-wide data, exposure to BaP from water ingestion appears to be minimal. However, exposure to BaP from eating certain cooked or contaminated foods can be substantial.

In homes and public buildings, estimated inhaled doses range from about 3 nanograms up to about 44 nanograms per day (see Table 5). In homes where residents smoke, the typical resident may receive an average estimated inhaled dose of about 6 to 27 nanograms daily. Additionally, a typical individual may be exposed to about 7 nanograms of BaP in indoor air during the eight hours that he or she works in buildings where smoking is permitted. Home-bound residents exposed to environmental tobacco smoke may receive inhaled doses of about 9 to 44 nanograms daily; in non-smoking homes (also referred to as "no source" homes) estimated 24-hour doses range from 4 to 17 nanograms of BaP per day. The upper end of the "no sources" estimate may be high due to the influence of polluted outdoor air filtering into the homes from which this estimate was derived; also, the presence of non-specified indoor combustion sources may have elevated BaP concentrations in these homes (Sheldon et al., 1993). The lower end of the smoking homes estimate may be low due to under-representation of smokers in the Riverside PTEAM study (Sheldon et al. (1992).

Woodburning in the home also increases indoor concentrations of BaP. The average resident could be exposed to an estimated inhaled dose ranging from about 4 nanograms up to 15 nanograms per day from the operation of woodstoves. Home-bound residents would likely receive higher doses, from an estimated 7 to 24 nanograms daily. Fireplace use is estimated to result in an inhaled dose of 12 nanograms BaP in a day; the home-bound resident would be exposed to 20 nanograms daily. Substantially higher presented doses can result from the use of woodstoves or fireplaces that are poorly designed, maintained or installed. However, data on such appliances are insufficient to support an estimate of inhaled dose.

The estimates of BaP ingested from eating food vary widely, ranging from about 1 to 6,000 nanograms (0.001 to 6.0 micrograms) per day. Eating foods that are smoked, grilled, or cooked at high temperatures can result in very high daily doses. Estimated doses from the ingestion of drinking water appear to be quite low, averaging about 1.1 nanograms per day.

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Appendix F

GLOSSARY OF TERMS

GLOSSARY

Catalytic Cracker: An oil refinery unit in which the cracking of petroleum takes place in the presence of a catalyst.

Coefficient of Haze Data: Data taken from a device often referred to as a "smoke sampler." In the "smoke sampler," a photometer detects the quantity of light absorbed by the particulate matter on a strip of paper tape that has been used to gather particles from the ambient air. The quantity of light absorbed (referred to as the "soiling index") is reported in the Coefficient of Haze (COH) scale.

Distillate Oil: Oil condensed from vapor during the petroleum distillation process.

Emission Factor: The rate of emission of a particular substance from an emission source.

"Hot Spot": An area of elevated concentrations of a substance, or a specific source impacting an area with concentrations of a substance at levels significantly higher than those found in unimpacted, ambient air.

Limit of Detection (LOD): The quantifiable limit (threshold) at and above which a substance can be accurately and precisely given a concentration value.

Mean Annual Exposure Estimate: The concentration of a airborne substance that a given population is exposed to, on the average, for a year.

PM_{10}: Particulate matter smaller than 10 microns.

Photolysis: Chemical decomposition induced by light or other radiant energy.

Polycyclic Aromatic Hydrocarbon (PAH): An organic compound (containing only carbon and hydrogen) having at least two fused benzene rings, and which may also contain additional fused rings not restricted to exclusively hexagonal rings. PAHs have a boiling point of greater than or equal to 100°C.

Polycyclic Organic Matter (POM): Organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100°C.

Population-weighted Exposure Estimate: An estimate of exposure to a substance that adds more weight (emphasis) to a site that represents a large population than it does to a site representing a smaller population.

Radical: A highly reactive substance having a charge (either positive or negative), that can act as an initiator or intermediate in combustion, oxidation, or polymerization.

Residual Oil: The low-grade oil products that remain after the distillation of petroleum.

Troposphere: The portion of the atmosphere (extending from ground level to around six kilometers above the ground) where weather occurs and pollutants are concentrated.