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Lifetimes and Fates of Toxic Air Contaminants in California's Atmosphere

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

AIR RESOURCES BOARD
Research Division

LIFETIMES AND FATES OF TOXIC AIR CONTAMINANTS IN CALIFORNIA'S ATMOSPHERE

Final Report
Contract No. 93-307

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Abstract

The staff of the California Air Resources Board (CARB) and the Office of Environmental Health Hazard Assessment (OEHHA) compiled summary sheets on each of the 244 substances on the CARB Toxic Air Contaminant Identification List as part of the State of California's air toxic program Assembly Bill (AB) 1807. As one specific task of this contract, the atmospheric chemists at the Statewide Air Pollution Research Center, University of California, Riverside, reviewed the draft data sheets and commented specifically on the atmospheric persistance of the Toxic Air Contaminants. The second task of this contract was to provide ambient concentration measurements for selected compounds including polycyclic aromatic hydrocarbons (PAH) and nitro-PAH for which potency equivalency factors (PEF) have been established by the OEHHA and for which few ambient measurements have been reported. In general, the PAH concentrations measured were significantly below those measured approximately 10 years ago at several locations throughout California (Final Report, CARB Contract No. A5-185-32, May 1988). A large range of ambient concentrations of PAH occur in California, varying geographically and seasonally. Because, unlike the nitro-PAH, there is no *in situ* formation of the PAH, maximum exposures occur in areas of maximum emission sources under meteorological conditions favoring atmospheric inversions. In contrast to the PAH data, the nitropyrene and 2-nitrofluoranthene concentrations measured in Riverside were within the range previously observed throughout California. An elevated nighttime level of 2-nitrofluoranthene, compared to 1- and 2-nitropyrene, suggested nighttime formation of 2-nitrofluorathene from the NO_3 radical-initiated reaction.

Executive Summary

Background

The staff of the California Air Resources Board (CARB) and the Office of Environmental Health Hazard Assessment (OEHHA) compiled summary sheets on each of the 244 substances on the CARB Toxic Air Contaminant Identification List as part of the State of California's air toxic program Assembly Bill (AB) 1807. As one specific task of this contract, the atmospheric chemists at the Statewide Air Pollution Research Center, University of California, Riverside, reviewed the draft data sheets and commented specifically on the atmospheric persistance of the Toxic Air Contaminants. The second task of this contract was to provide ambient concentration measurements for selected compounds including polycyclic aromatic hydrocarbons (PAH) and nitro-PAH for which potency equivalency factors (PEF) have been established by the OEHHA and for which few ambient measurements have been reported.

Methods

Ambient particulate samples were collected in Riverside using an ultra-high volume sampler in July and August, 1994. Twelve-hour daytime and 12-hr nighttime composited samples were solvent extracted, fractionated by high performance liquid chromatography and analyzed by combined gas chromatography/mass spectrometry. Deuterated PAH and and nitro-PAH standards were used for quantification.

Results and Conclusions

Ambient PAH Concentrations

In general, the PAH concentrations measured were significantly below those measured approximately 10 years ago at several locations throughout California (Final Report, CARB Contract No. A5-185-32, May 1988). Shown in Table i are our Riverside, 1994 PAH data compared to data from two sites in California from our 1986-1987 study. These sites from our earlier study, Concord and Mammoth Lakes, were chosen to represent an industrial site and a site impacted by wood smoke, respectively, and these sites experienced the highest PAH levels observed in our prior study.

Table i. PAH targeted for quantification. Results from Riverside, CA (day and night samples), together with highest ambient concentrations reported in California.

PAH	MW	Riverside day (pg m^{-3})	Riverside night[a] (pg m^{-3})	Concord[b] (pg m^{-3})	Mammoth Lakes,CA[c]
benz[*a*]anthracene	228	39	34	9,700	18,300
chrysene + triphenylene[d]	228	80	83	13,500	23,600
chrysene	228	61[d]	45[d]		
triphenylene	228	15[d]	15[d]		
benzo[*a*]pyrene	252	36	44	8,150	12,490
benzo[*e*]pyrene	252	130	170	5,760	8,000
Σbenzo[*b*+*j*+*k*]fluoranthenes[e]	252	360	400	15,530	23,200
perylene	252			1,670	2,760
indeno[1,2,3-*cd*]fluoranthene	276			750[f]	2,000[f]
indeno[1,2,3-*cd*]pyrene	276	87	84	6,240[f]	12,310[f]
benzo[*ghi*]perylene	276	98	124	7,670[f]	11,350[f]
dibenz[*a,h* + *a,c*]anthracene[g]	278	8.2	7.8	910[f]	3,550[f]
dibenz[*a,j*]anthracene	278	5.5	6.0	1,930[f]	2,030[f]
benzo[*b*]chrysene	278	3.0	2.9	580[f]	2,150[f]
benzo[*c*]chrysene	278	2.8	2.4	300[f]	740[f]
dibenzo[*a,e*]pyrene	302	1.7	3.6		
dibenzo[*a,h*]pyrene	302	<0.5	<0.5		
dibenzo[*a,i*]pyrene	302	<0.5	<0.5		
dibenzo[*a,l*]pyrene	302	18	18		

[a] Average of two separate determinations using two different quadrants of the megasampler.
[b] Data from Concord, industrial site with photochemical pollution (Atkinson *et al.*, 1988).
[c] Data from Mammoth Lakes woodsmoke impacted nighttime sample (Atkinson *et al.*, 1988).
[d] Isomers co-eluted on DB-5 column, separate quantifications made using a Smectic column.
[e] The benzofluoranthenes were not well resolved and their concentrations have been summed.
[f] Lower limit, deuterated internal standard not used to correct for < 100% recovery from HPLC.
[g] Dibenz[*a,c*]anthracene and dibenz[*a,h*]anthracene co-eluted; their concentrations were summed.

The strength of emission sources and meteorology (for example, whether an inversion is present) both will influence ambient PAH concentrations. It is of interest to compare our present Riverside data with the range of data previously obtained. Table ii compares ambient concentrations of selected PAH measured at Riverside with the minimum and maximum from our previous measurements at Glendora, Yuba City, Concord, Mammoth Lakes, Oildale and Reseda, and at the "clean" background site at Pt. Arguello. Clearly, a large range of ambient concentrations of PAH occur in California, varying geographically and seasonally. Because, unlike the nitro-PAH, there is no *in situ* formation of the PAH, maximum exposures occur in areas of maximum emission sources under meteorological conditions favoring atmospheric inversions. The highest PAH concentrations we have measured in California occurred in a Mammoth Lakes nighttime sample when woodsmoke was the dominant emission source. Another site where high ambient PAH concentrations were observed was Concord, CA, an area impacted by industrial emission sources. Aside from Pt. Arguello, where the winds are normally off the Pacific Ocean, the lowest ambient PAH concentrations previously measured were at Reseda and Oildale. Our Riverside 1994 PAH concentrations are up to a factor of four lower than those previously measured in Reseda and Oildale in 1987, suggesting that PAH emissions into the Los Angeles air basin may have decreased somewhat in the past decade.

Ambient Nitro-PAH Concentrations

Table iii lists the nitro-PAH targeted for analysis on the basis of their potency equivalence factors (PEF) as well as 2-nitrofluoranthene. While it is important to understand the concentrations of these nitro-PAH, the health implications of those nitro-PAH for which PEFs are not available, such as 2-nitrofluoranthene, should also be of concern. Nitro-PAH whose source is atmospheric formation dominated at Riverside and the other sites throughout California that were sampled. Significantly more abundant than the nitro-PAH listed in Table iii are 1- and 2-nitronaphthalene and the methylnitronaphthalenes (Arey *et al.*, 1987; Atkinson *et al.*, 1988; Gupta *et al.*, 1995).

Table ii. Comparison of selected PAH concentrations at Riverside with those previously measured throughout California.

PAH	MW	Riverside day (pg m^{-3})	Riverside night (pg m^{-3})	Range[a] (pg m^{-3})	Pt. Arguello[b] day, night
benz[*a*]anthracene	228	39	34	130-18,300	4, 10
chrysene + triphenylene	228	80	83	300-23,600	50, 50
benzo[*a*]pyrene	252	36	44	130-12,490	n.d.
benzo[*e*]pyrene	252	130	170	250-8,000	5, 8
Σbenzo[*b*+*j*+*k*]fluoranthenes	252	360	400	430-23,200	n.d.
indeno[1,2,3-*cd*]pyrene	276	87	84	110-12,310	n.d.
benzo[*ghi*]perylene	276	98	124	230-11,350	n.d., 2
dibenz[*a,c* + *a,h*]anthracene	278	8.2	7.8	8-3,550	n.d.

[a] The lowest and highest concentrations measured at Glendora, Yuba City, Concord, Mammoth Lakes, Oildale, or Reseda, CA. The highest values are all from Mammoth Lakes, the lowest values are generally from Reseda.

[b] Clean air site with winds normally off the Pacific Ocean.

Table iii. Nitro-PAH targeted for quantification. Results from Riverside, CA particle extract analysis, together with highest ambient concentrations reported in CA. Additionally, the probable source of the nitro-PAH are noted.

Nitro-PAH	M.W.	Riverside Sample[a] (pg m^{-3})	Ambient Sample (pg m^{-3}) CA Location[b]	Source[c]
5-Nitroacenaphthene	199	0.88		
3-Nitrobiphenyl	199	0.46	1,200[d] Glendora 6,000[d] Torrance[e]	A.R.
2-Nitrofluorene	211	none detected	≤20 Σ isomers Long Beach[f]	D.E.,A.R.[g]
9-Nitroanthracene	223	23, 49	660 Concord	D.E.
9-Nitrophenanthrene	223	none detected	180 Houston, TX[h]	D.E.[i]
2-Nitrofluoranthene	247	36, 116	2,000 Glendora	A.R.
1-Nitropyrene	247	4.4, 3.2	45 Concord 60 Torrance[e]	D.E.
2-Nitropyrene	247	4.2, 3.8	81 Concord 60 Torrance[e]	A.R.
4-Nitropyrene	247	≤1.6	<5 Torrance[e]	A.R.[g]
7-Nitrobenz[a]anthracene	273	≤5.8	44 Concord	D.E.
6-Nitrochrysene	273	≤5.4	none detected in CA	D.E.
1,6-Dinitropyrene	292	none detected	see text	D.E.
1,8-Dinitropyrene	292	none detected	see text	D.E.
6-Nitrobenzo[a]pyrene	297	none detected	only trace levels detected in CA	D.E.

[a] Quantified from filter sample.

[b] Data from Atkinson *et al.*, 1988, unless noted otherwise.

[c] D.E. = reported in diesel exhaust; A.R. = an atmospheric reaction product.

[d] Quantified in a gas-phase (PUF plug) sample.

[e] Torrance, CA (Arey *et al.*, 1987).

[f] Data taken during SCAQS study (Helmig *et al.*, 1992). No 2-nitrofluorene detected.

[g] Minor isomer formed from radical-initiated reaction.

[h] Mean value for Fall in Houston, TX; sum of vapor plus particle phase (Wilson *et al.*, 1995).

[i] Two unspecified nitrophenanthrene isomers reported (Paputa-Peck *et al.*, 1983).

In Tables iii and iv the data obtained on the Riverside particle extracts are given together with data mainly from our previous CARB contract (Contract No. A5-185-32, Atkinson *et al.*, 1988). It is clear that the pollution levels reached in Riverside were significantly less than the highest levels observed in our previous work (note that in our previous study we sampled only when the meteorology was most favorable for pollution). For example, in Concord, CA we measured 7-nitrobenz[a]anthracene levels more than seven times greater than we found in Riverside, and in Concord and Torrance we found 1-nitropyrene levels over an order of magnitude greater. If the maximum risk is to be calculated, the earlier data is more appropriate.

Table iv shows that the nitropyrene and nitrofluoranthene concentrations measured in Riverside were within the range previously observed throughout California. This may be contrasted with the PAH levels which were consistently lower than those measured in our previous study. In this study, as observed previously, the atmospherically formed nitro-PAH were more abundant than the directly emitted nitro-PAH. The elevated nighttime level of 2-nitrofluoranthene, compared to 1- and 2-nitropyrene, suggests nighttime formation of 2-nitrofluorathene from the NO_3 radical-initiated reaction. A more complete understanding of how present control strategies will affect ambient OH radical and NO_3 radical concentrations is needed to quantitatively understand the formation rates of those PAH, such as 2-nitrofluoranthene, 2-nitropyrene, the nitronaphthalenes and methylnitronaphthalenes, which are formed *in situ* in the atmosphere.

Table iv. Comparison of the ambient concentrations of 1- and 2-nitropyrene and 2-nitrofluoranthene measured at Riverside with previous measurements throughout California. 2-Nitrofluoranthene and 2-nitropyrene are expected to be the result of atmospheric formation, 1-nitropyrene is expected to be from direct emission sources.

Nitro-PAH	Riverside day, night	Range
2-nitrofluoranthene	36, 116	17-2,000
1-nitropyrene	4.4, 3.2	4.9-45
2-nitropyrene	4.2, 3.8	1.0-81

1. INTRODUCTION AND BACKGROUND TO THE PROJECT

Task 1 - Toxic Air Contaminant Data Sheets

The staff of the California Air Resources Board (CARB) and the Office of Environmental Health Hazard Assessment (OEHHA) compiled summary sheets on each of the 244 substances on the CARB Toxic Air Contaminant Identification List (see below) as part of the State of California's air toxic program Assembly Bill (AB) 1807. The atmospheric chemists at the Statewide Air Pollution Research Center were asked as one specific task of this contract to review the draft data sheets and comment specifically on the atmospheric persistance of the Toxic Air Contaminants.

Table 1. CALIFORNIA'S LIST OF POTENTIAL TOXIC AIR CONTAMINANTS

Acetaldehyde
Acetamide
Acetone
Acetonitrile
Acetophenone
2-Acetylaminofluorene
Acrolein
Acrylamide
Acrylic acid
Acrylonitrile
Allyl chloride
Aluminum compounds
4-Aminobiphenyl
Ammonia
Ammonium nitrate
Ammonium sulfate
Aniline
o-Anisidine
Antimony compounds
Arsenic compounds
Asbestos
Barium compounds
Benzene
Benzidine
Benzo[a]pyrene
Benzotrichloride
Benzoyl chloride
Benzyl chloride
Beryllium compounds
Biphenyl
Bis(2-ethylhexyl)adipate
Bis(2-ethylhexyl)phthalate
Bis(chloromethyl)ether
Bromine inorganics
Bromoform
1,3-Butadiene
Butyl acetate
n-Butyl alcohol
sec-Butyl alcohol
tert-Butyl alcohol
Butyl benzyl phthalate
Cadmium and compounds
Calcium cyanamide
Caprolactam
Captan
Carbaryl
Carbon black extracts
Carbon disulfide

Carbon tetrachloride
Carbonyl sulfide
Catechol
Chloramben
Chlordane
Chlorinated dioxins
Chlorinated fluorocarbons
Chlorine
Chlorine dioxide
Chloroacetic acid
2-Chloroacetophenone
Chlorobenzene
Chlorobenzilate
Chloroform
Chloromethyl methyl ether
Chlorophenols
Chloroprene
Chromium compounds
Cobalt compounds
Chromium VI
Coke Oven emissions
Copper compounds
Creosotes
Cresols/Cresylic acid
o-Cresol
m-Cresol
p-Cresol
Crystalline silica
Cumene
Cumene hydroperoxide
Cyanide compounds
Cyclohexane
2,4-D, salts and esters
DDE
Decabromodiphenyl oxide
Dialkylnitrosamines
Diaminotoluenes
Diazomethane
Dibenzofuran
1,2-Dibromo-3-chloropropane
Dibutylphthalate
1,4-Dichlorobenzene
3,3'-Dichlorobenzidene
Dichloroethyl ether
1,3-Dichloropropene
Dichlorvos
Dicofol
Diesel exhaust
Diethanolamine
Diethyl sulfate
3,3'-Dimethoxybenzidine
Dimethyl aminoazobenzene
N,N-Dimethylaniline
3,3'-Dimethyl benzidine
Dimethyl carbamoyl chloride
Dimethyl formamide
1,1-Dimethyl hydrazine
Dimethyl phthalate
Dimethyl sulfate
4,6-Dinitro-*o*-cresol, and salts
2,4-Dinitrophenol
2,4-Dinitrotoluene
1,4-Dioxane
1,2-Diphenylhydrazine
Environmental Tobacco Smoke
Epichlorohydrin
1,2-Epoxybutane
Ethyl acrylate
Ethylbenzene
Ethyl carbamate
Ethyl chloride
Ethylene dibromide
Ethylene dichloride
Ethylene glycol
Ethyleneimine
Ethylene oxide
Ethylene thiourea
Ethylidene dichloride
Fine Mineral Fibers
Formaldehyde
Gasoline Vapors
Glutaraldehyde
Glycol ethers
Heptachlor

Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclohexanes
Hexachlorocyclopentadiene
Hexachloroethane
Hexamethylene-1,6-diisocyanate
Hexamethylphosphoramide
Hexane
Hydrazine
Hydrochloric acid
Hydrogen fluoride
Hydrogen sulfide
Hydroquinone
Inorganic arsenic
Inorganic lead
Isophorone
Isopropyl alcohol
4,4'-Isopropylidenediphenol
Lead compounds
Lindane (all isomers)
Maleic anhydride
Manganese compounds
Mercury compounds
Methanol
Methoxychlor
Methyl bromide
Methyl chloride
Methyl chloroform
Methyl ethyl ketone
Methyl hydrazine
Methyl iodide
Methyl isobutyl ketone
Methyl isocyanate
Methyl methacrylate
Methyl *tert*-butyl ether
4,4-Methylene bis(2-chloroaniline)
Methylene chloride
Methylene diphenyl diisocyanate
4,4-Methylenedianiline
Molybdenum trioxide
Naphthalene
Nickel and compounds
Nitric acid
Nitrilotriacetic acid
Nitrobenzene
4-Nitrobiphenyl
4-Nitrophenol
2-Nitropropane
N-nitroso-*n*-methylurea
N-Nitrosodimethylamine
N-Nitrosomorpholine
Parathion
Pentachloronitrobezene
Pentachlorophenol
Peracetic acid
Phenol
p-Phenylenediamine
2-Phenylphenol
Phosgene
Phosphine
Phosphoric acid
Phosphorus
Phthalic anhydride
Polychlorinated Biphenyls
Polycyclic Organic Matter
1,3-Propane sultone
Propene
β-Propiolactone
Propionaldehyde
Propoxur
Propylene dichloride
Propylene oxide
1,2-Propylenimine
Quinoline
Quinone
Radionuclides (incl. Radon)
Selenium compounds
Silver compounds
Sodium hydroxide
Styrene
Styrene oxide
Sulfuric acid
Terephthalic acid
2,3,7,8-Tetrachloro-dibenzo-*p*-dioxin

1,1,2,2-Tetrachloroethane
Tetrachloroethylene
Thiourea
Titanium tetrachloride
Toluene
2,4-Toluene diamine
2,4-Toluene diisocyanate
o-Toluidine
Toxaphene
1,2,4-Trichlorobenzene
1,1,2-Trichloroethane
Trichloroethylene
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
Triethylamine
Trifluralin
1,2,4-Trimethylbenzene
2,2,4-Trimethylpentane
Vinyl acetate
Vinyl bromide
Vinyl chloride
Vinylidene chloride
Xylenes
m-Xylenes
o-Xylenes
p-Xylenes
Zinc compounds

Task 2 - Ambient Measurements of Polyclic Organic Matter

The second task of this contract was to provide ambient concentration measurements for selected compounds that are constituents of polycyclic organic matter (a class of compounds which appears as a single entry of the Toxic Air Contaminant list). The compounds selected included polycyclic aromatic hydrocarbons (PAH) and nitro-PAH for which potency equivalency factors (PEF) have been established by the OEHHA and for which few ambient measurements have been reported. The PAH targeted for analysis are listed in Table 2 and the targeted nitro-PAH are listed in Table 3. No PEF value has been established for 2-nitrofluoranthene, but it was included because it is generally the most abundant particle-associated nitro-PAH in ambient atmospheres (Final Report CARB Contract No. A5-185-32, May 1988). Additionally, 2-nitrofluoranthene is mutagenic and forms adducts with DNA (Herreno-Saenz *et al.*, 1992). Ambient particle extracts contain mutagenic compounds more polar than the nitro-PAH, including nitrophenanthrene lactones and nitropyrene lactones (Sasaki *et al.*, 1995). While nitrophenanthrene lactones have been shown to be genotoxic and to form DNA adducts (Watanabe *et al.*, 1995, 1996), PEF factors are not available for any nitro-PAH lactones and members of this compound class were not among the compounds targeted for analysis. Particle samples were collected in Riverside, CA during July and August, 1994 and analysis were conducted by gas chromatography/mass spectrometry (GC/MS) for the compounds listed.

Table 2. PAH Targeted for Quantification in Ambient Particles

PAH	M.W.[a]
Benz[a]anthracene	228
Chrysene	228
Triphenylene	228
5-Methylchrysene	242
Benzo[a]pyrene **(B[a]P)**	252
Benzo[e]pyrene	252
Benzo[b]fluoranthene	252
Benzo[j]fluoranthene	252
Benzo[k]fluoranthene	252
Perylene	252
7,12-Dimethylbenz[a]anthracene	256
3-Methylcholanthrene	268
Indeno[1,2,3-cd]fluoranthene	276
Indeno[1,2,3-cd]pyrene	276
Benzo[ghi]perylene	276
Dibenz[a,h]anthracene **(DB[a,h]A)**	278
Dibenz[a,c]anthracene	278
Benzo[b]chrysene	278
Benzo[c]chrysene	278
Dibenzo[a,e]pyrene	302
Dibenzo[a,h]pyrene	302
Dibenzo[a,i]pyrene	302
Dibenzo[a,l]pyrene	302

[a] M.W. = molecular weight.

Table 3. Nitro-PAH Targeted for Quantification in Ambient Particles

Nitro-PAH	M.W.[a]
5-Nitroacenaphthene	199
3-Nitrobiphenyl	199
2-Nitrofluorene	211
9-Nitroanthracene	223
9-Nitrophenanthrene	223
2-Nitrofluoranthene	247
1-Nitropyrene	247
2-Nitropyrene	247
4-Nitropyrene	247
7-Nitrobenz[a]anthracene	273
6-Nitrochrysene	273
1,6-Dinitropyrene	292
1,8-Dinitropyrene	292
6-Nitrobenzo[a]pyrene	297

[a] M.W. = molecular weight.

No standard was available for 5-methylchrysene and only an estimate based on earlier data on alkyl-PAH (Final Report CARB Contract No. A5-185-32, May 1988) could be made. Three azaarenes: *7H*-dibenzo[*c,g*]carbazole, dibenz[*a,j*]acridine and dibenz[*a,h*]acridine were also of interest to CARB because of their significant PEF values. Quantification of the azaarenes would require a substantially different analysis procedure from that employed for the PAH and azaarene analysis was not included in this task. The available literature data on the azaarenes was, however, examined.

2. COMMENTS ON DRAFT DATA SHEETS DEVELOPED ON POTENTIAL TOXIC AIR CONTAMINANTS

As one task of this CARB Contract, we provided comments to the CARB staff on the draft data sheets for the approximately 240 potential toxic air contaminants. We give below the introductory section of these comments, and three examples of our comments.

Introduction

There are a number of factors which influence the atmospheric behavior of chemical compounds in the atmosphere, and these are briefly discussed below:

Gas/Particle Partitioning. Chemical compounds emitted into the atmosphere, or produced *in situ* in the atmosphere by chemical reaction, can exist in the gas phase, in the particle phase (i.e., be associated with particulate matter by absorption into, adsorption onto, or inclusion in particles), or be partitioned between the gas- and particle- phases. The major factor determining partitioning of a chemical between the gas phase and particles is the liquid-phase vapor pressure P_L of the chemical (Bidleman, 1988, Odum *et al.*, 1996). The gas/particle partitioning ratio depends on temperature, with the chemical becoming more particle-associated at lower temperatures. While the gas/particle partitioning ratio is a smooth function of P_L, it also depends on the particle loading in the atmosphere, and more specifically on the surface area of the particulate matter in the atmosphere (Pankow, 1987; Bidleman, 1988; Odum *et al.*, 1996). As a useful approximation, a chemical will exist mainly in the particle phase for liquid-phase vapor pressures $<10^{-6}$ Torr at the temperature of the air-mass and will exist, at least partially, in the gas phase for values of $P_L > 10^{-6}$ Torr at the temperature of the air-mass. Odum *et al.* (1996, 1997) have shown that the formation of secondary organic aerosol can be explained by and modeled using gas/particle partitioning theory as described by Pankow (1987) and Bidleman (1988). Odum *et al.* (1997) have also shown that secondary organic aerosol formation from the photooxidation of whole gasoline can be explained by aerosol formation from the aromatic hydrocarbon constituents of gasoline.

Lifetimes and Half-lives of Chemicals in the Atmosphere. Chemical compounds (whether in the gas- or particle-phase) are removed from the atmosphere by physical processes (wet and dry deposition, see below) and chemical processes. For a gas-phase chemical, the major chemical loss processes include photolysis, reaction with the hydroxyl (OH) radical during daylight hours, reaction with the nitrate (NO_3) radical during nighttime hours, and reaction with ozone (O_3) [generally throughout the entire 24-hr period]. The lifetime, τ, of a gaseous chemical is the time for the concentration of the chemical to decrease to 37% (1/e) of its initial concentration, and the overall lifetime τ_{overall} is given by

$$1/\tau_{\text{overall}} = 1/\tau_{\text{physical}} + 1/\tau_{\text{chemical}}$$

where

$$1/\tau_{\text{physical}} = 1/\tau_{\text{wet dep.}} + 1/\tau_{\text{dry dep.}}$$

and

$$1/\tau_{\text{chemical}} = 1/\tau_{\text{OH}} + 1/\tau_{\text{NO3}} + 1/\tau_{\text{O3}} + 1/\tau_{\text{phot.}}$$

and, for example,

$$\tau_{\text{OH}} = (k_{\text{OH}}[\text{OH}])^{-1}$$

where k_{OH} is the rate constant for reaction of the chemical with the OH radical and [OH] is the OH radical concentration in the atmosphere, and similarly for the NO_3 radical and O_3 reactions.

The half-life, $t_{1/2}$, is the time for the concentration of the chemical to decrease by 50% (i.e., to 50% of its initial concentration) and is related to the lifetime, τ, by

$$t_{1/2} = 0.693\tau$$

Therefore, to calculate the overall lifetime or half-life of a chemical, or the lifetime or half-life due to each of the various loss processes, the reaction rate constants need to be known together with the ambient atmospheric concentrations of OH radicals, NO_3 radicals, and O_3.

All gaseous organic compounds except the chlorofluorocarbons (CFCs) react with the hydroxyl radical and for the majority of organic compounds reaction with the hydroxyl radical is the dominant chemical loss process in the atmosphere. To date, there are few direct measurements of the concentrations of OH radicals in the troposphere, and the apparently reliable measurements available are all at close to ground level. A diurnally, seasonally and annually averaged global tropospheric OH radical concentration has been derived by Prinn *et al.* (1992) from the emissions and atmospheric concentrations of methyl chloroform, of 8 x 10^5 molecule cm^{-3} as a 24-hr average. The OH radical concentration exhibits a diurnal cycle because a major production route involves the photolysis of ozone in the presence of water vapor, and OH radical concentrations peak during daylight hours, with peak concentrations of several x 10^6 molecule cm^{-3}. To date, few measurements have been made in polluted urban areas, but the limited information available indicate that OH radical concentrations in urban areas are similar to those in cleaner, more remote areas. This is consistent with the fact that in polluted urban areas, while the formation rates of OH radicals may be increased, so are the loss rates. Therefore, use of the global tropospheric average OH radical concentration is probably reasonably applicable to urban areas and will not underestimate urban airmass OH radical concentrations by more than a factor of ~2-3.

Wet and Dry Deposition of Particles and Particle-Associated Chemicals. Wet deposition refers to the removal of particles and particle-associated chemicals from the atmosphere by precipitation events (for example, rain- and snow- falls and precipitating fogs). Wet deposition of particles, and hence of particle-associated chemicals, is efficient. Dry deposition refers to the transport of gases and particles from the atmosphere to the Earth's surface, including to soil, vegetation, water surfaces (lakes, rives and oceans) and to snow-covered ground. Dry deposition of particles and particle-associated chemicals depends on the particle size, and the efficiency of dry deposition of particles is a minimum for particles of diameter ~0.1-2 μm. Therefore, the atmospheric residence time of particles depends on the particle size, and is a maximum for particles of this ~0.1-2 μm diameter size range.

From atmospheric observations and modeling of particle-associated ^{210}Pb, Balkanski *et al.* (1993) derive an average residence time (lifetime) for 0.1-1 μm size particles in the troposphere of 5-15 days due to wet and dry deposition. The lifetimes depend on latitude and altitude in the troposphere, with particles at 0.5 km altitude having a significantly shorter (by a factor of ~4) lifetime than those at 9 km altitude (Balkanski *et al.*, 1993).

Comments

We provided specific comments to the CARB on each of the draft data sheets for potential toxic air contaminants. In particular each sheet was edited to be consistent with regard to the phase distribution, dominant atmospheric loss processes and estimated lifetimes. The reaction rate constants were updated and where no rate data were available, the most recent estimation method for calculation of the OH radical reaction rate constant was applied (Kwok and Atkinson, 1995). Consistent estimates of ambient concentrations for the reactive species such as the hydroxyl radical (Prinn *et al.*, 1992) were used to estimate lifetimes and half-lives.

Three specific examples of our comments are given below, for acetaldehyde, acetamide, and bis(2-ethylhexyl)phthalate. The complete set of comments for the 244 toxic air contaminants has been provided on diskette.

Acetaldehyde

Acetaldehyde exists in the atmosphere in the gas phase. The dominant loss process for acetaldehyde in the troposphere is by reaction with the OH radical. The calculated lifetime, τ, and half-life, $t_{1/2}$, of acetaldehyde due to reaction with the OH radical are 22 hours and 15 hours, respectively, for an average OH radical concentration of 8 x 10^5 molecule cm^{-3} (Atkinson, 1994). The reaction products include formaldehyde and peroxyacetyl nitrate (PAN) [$CH_3C(O)OONO_2$].

Acetamide

Extrapolation of the vapor pressures cited at 105 °C and 222 °C to 298 K results in a sub-cooled liquid-phase vapor pressure of ~7 x 10^{-2} Torr. With this magnitude of vapor pressure, acetamide is expected to exist in the atmosphere in the gas phase, and undergo wet and dry deposition, and gas-phase reaction with the hydroxyl radical.

Bis(2-ethylhexyl)phthalate

Bis(2-ethylhexyl)phthalate partitions between the gas and particle phases in the atmosphere. In the gas phase, bis(2-ethylhexyl)phthalate will react with the OH radical, with an estimated rate constant of 2.0×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. With this rate constant, the calculated lifetime, τ, and half-life, $t_{1/2}$, of bis(2-ethylhexyl)phthalate due to gas-phase reaction with the OH radical are 17 hours and 12 hours, respectively, for an average OH radical concentration of 8×10^5 molecule cm^{-3}. Bis(2-ethylhexyl)phthalate in the particle-phase is subject to dry and wet deposition. The average lifetime (residence time) for particles and particle-associated chemicals in the troposphere is ~5-15 days (Balkanski *et al.*, 1993) [the half-life is then ~3.5-10 days].

An example of the draft compound summary for acetaldehyde in its entirety is given on pages 12-16.

ACETALDEHYDE

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

CAS Registry Number: 75-07-0 CH_3CHO

Molecular Formula: C_2H_4O

Acetaldehyde is a colorless, fuming liquid and at dilute concentrations has a fruity, pungent odor. As a liquid, it is lighter than water but the vapors are heavier than air. It is miscible in water, alcohol, acetone, gasoline, toluene, xylene, benzene, ether, paraldehyde and organic solvents. Acetaldehyde is volatile at ambient temperature and pressure. Both the liquid and the vapors are highly flammable and acetaldehyde is a dangerous fire hazard when exposed to heat or flames (Sax, 1989). It is highly reactive and a strong reducing agent which undergoes numerous condensation, addition and polymerization reactions. Acetaldehyde can react violently with acid anhydrides, alcohols, ketones, phenols, ammonia, hydrogen cyanide, hydrogen sulfide, halogens, phosphorus, isocyanates, strong alkalis and amines (Sax, 1989).

Physical Properties of Acetaldehyde

Synonyms: ethanal; acetic aldehyde; ethyl aldehyde; methyl formaldehyde

Molecular Weight:	44.06
Boiling Point:	20.8 °C
Melting Point:	-123.5 °C
Flash Point:	-38.0 °C
Vapor Density:	1.52 (air = 1)
Vapor Pressure:	740 mm Hg at 20 °C
Density/Specific Gravity:	0.79 at 18/4 °C
Log Octanol/Water Partition Coefficient:	0.43
Conversion Factor:	1 ppm = 1.8 mg/m^3

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

SOURCES AND EMISSIONS

A. Sources

Sources of acetaldehyde include emissions from combustion processes such as vehicular exhaust from mobile sources and fuel combustion from stationary internal combustion engines, boilers and process heaters. Combustion of gasoline containing the oxygenate additives ethanol or ethyl tert-butyl ether (ETBE) may also emit acetaldehyde (U.S. EPA, 1993b). Acetaldehyde is also a product of incomplete combustion in fireplaces and woodstoves, coffee roasting, burning of tobacco, and waste processing. Acetaldehyde is used as an intermediate in the production of acetic acid, acetic anhydride, ethyl acetate, peracetic acid, pentaerythritol, chloral, glyoxal, alkylamines and pyridines (ARB, 1993d). Acetaldehyde is also used as a fruit and fish preservative, flavoring agent, a denaturant for alcohol, for hardening gelatin fibers, and as a solvent in the synthetic rubber, paraldehyde, tanning and paper industries (Sittig, 1985; U.S. EPA, 1987a). It is also used in the manufacture of perfumes, butanol, aniline dyes, plastics, and silvering mirrors (Merck, 1989).

In California, photochemical oxidation is the largest source (as high as 41 to 67 percent) of acetaldehyde concentrations in the ambient air. Also in California, burning of wood in residential fireplaces and woodstoves, wildfires, and agricultural burning are also sources of emissions, followed by various stationary sources such as oil and gas extraction, refineries, cement kilns, and lumber and wood products (ARB, 1993d). The primary stationary sources that have reported emissions of acetaldehyde in California are crude oil and gas extraction and production, electric utilities, and cement production (ARB, 1995a).

B. Emissions

The total emissions of acetaldehyde from stationary source in California are estimated to be at least 130,000 pounds per year, based on data reported under the Air Toxics Hot Spots Program (AB 2588) (ARB, 1995a). In 1994, the Air Resources Board (ARB) also estimated that approximately 4 million pounds per year were emitted from on-road motor vehicles (ARB, 1995f). ARB also estimates that emissions from other mobile sources such as off-road recreational vehicles, boats, ships, and trains contributes an additional 1.6 million pounds per year of acetaldehyde into California's air (ARB, 1995f).

C. Natural Occurrence

Acetaldehyde occurs in nature as an intermediate product in the respiration of higher plants and can be found in ripening fruit such as apples. Also, acetaldehyde is an intermediate product of fermentation of alcohol and in metabolism of sugars in the body (ARB, 1993d).

AMBIENT CONCENTRATIONS

Acetaldehyde is routinely monitored by the statewide ARB air toxics network. When acetaldehyde was formally identified as a toxic air contaminant, the ARB estimated a population-weighted annual concentration of 4.19 micrograms per cubic meter ($\mu g/m^3$) or 2.33 parts per billion (ppb) (ARB, 1993d). The network's mean concentration of acetaldehyde from January 1994 through December 1994 is estimated to be 2.72 $\mu g/m^3$ or 1.52 ppb (ARB, 1995b).

Ambient air sampling of two rural regions, Point Barrow, Alaska and Whiteface Mountain, New York indicate 'background' acetaldehyde concentrations are from the limit of detection (LOD) to 1.4 $\mu g/m^3$ (LOD to 0.8 ppb) (ARB, 1993d). The United States Environmental Protection Agency (U.S. EPA) also reported concentrations of acetaldehyde from 14 study areas during 1989. The overall acetaldehyde mean concentrations in these areas was of 2.5 $\mu g/m^3$ (1.39 ppb) (U.S. EPA, 1993a).

INDOOR SOURCES AND CONCENTRATIONS

In general, concentrations are higher indoors than outdoors due in part to the abundance of combustion sources such as cigarettes, fireplaces, and woodstoves. Acetaldehyde can be emitted from cooking hamburgers and some building materials such as rigid polyurethane foams, and some consumer products such as adhesives, coatings, lubricants, inks, and nail polish remover. Other potential sources of indoor acetaldehyde concentrations are the infiltration of vehicle exhaust and the volatilization of acetaldehyde from certain foods (ARB, 1993d).

Residences with smokers have two to eight times higher acetaldehyde concentrations than the outdoor mean population-weighted statewide concentration of 4.19$\mu g/m^3$ (2.3 ppb). Limited surveys allow a crude estimate of an average acetaldehyde concentration inside residences of 5.4 $\mu g/m^3$ (3.0 ppb) to 27.0 $\mu g/m^3$ (15 ppb). Limited data suggest that the acetaldehyde concentrations in offices and public buildings are similar in magnitude to those inside residences. Higher levels may occur in some indoor environments; in the case of a tavern occupied by a number of smokers, levels of up to 203.4 $\mu g/m^3$ (113 ppb) were reported. Average and maximum in-vehicle acetaldehyde concentrations measured in southern California were similar in magnitude to those inside residences (ARB, 1993d).

ATMOSPHERIC PERSISTENCE

Acetaldehyde exists in the atmosphere in the gas phase. It also can be formed in the atmosphere as a result of photochemical oxidation of organic pollutants in urban atmospheres (ARB, 1993d). The dominant atmospheric loss process for acetaldehyde is by reaction with the hydroxyl radical. Based on this reaction, the atmospheric half-life and lifetime is estimated to be 15 hours and 22 hours, respectively (Atkinson, 1994). The products of this reaction include formaldehyde and peroxyacetyl nitrate (PAN) (Atkinson, 1995).

AB 2588 RISK ASSESSMENT INFORMATION

The Office of Environmental Health Hazard Assessment reviews risk assessments submitted under the Air Toxics Hot Spots Program (AB 2588). Of the risk assessments reviewed as of April 1995, acetaldehyde was the major contributor to the overall cancer risk in 1 of the approximately 450 risk assessments reporting a total cancer risk equal to or greater than 1 in 1 million and contributed to the total cancer risk in 87 of the these risk assessments. Acetaldehyde also contributed to the total cancer risk in 60 of the approximately 250 risk assessments reporting a total cancer risk equal to or greater than 10 in 1 million (OEHHA, 1995).

For non-cancer health effects, acetaldehyde contributed to the total hazard index in 17 of the approximately 70 risk assessments reporting a total chronic hazard index greater than 1. Acetaldehyde also contributed to the total hazard index in 3 of the approximately 70 risk assessments reporting a total acute hazard index greater than 1 (OEHHA, 1995).

HEALTH EFFECTS

Human exposure to acetaldehyde occurs primarily through inhalation (Howard, 1990).

Non-Cancer: Acute exposure to acetaldehyde vapor leads to eye, skin and respiratory tract irritation. Prolonged exposure of the skin to liquid acetaldehyde causes erythema and burns; repeated contact may lead to dermatitis due to primary irritation or sensitization. Long-term or chronic exposure has been shown to damage the respiratory tract in rats. In hamsters, chronic exposure to acetaldehyde has produced changes in the nasal mucosa and trachea, growth retardation, slight anemia, and increased kidney weight (U.S. EPA, 1994a).

The California Air Pollution Control Officers Association (CAPCOA) has established a chronic non-cancer Reference Exposure Level (REL) of 9.0 $\mu g/m^3$ for acetaldehyde. The toxicological endpoint considered for chronic toxicity is the respiratory system (CAPCOA, 1993). The U.S. EPA has established a Reference Concentration (RfC) of 0.009 milligrams per cubic meter (mg/m^3) based on degeneration of olfactory epithelium in rats, and has not determined a Reference Dose (RfD). No information is available regarding adverse reproductive or developmental effects of acetaldehyde in humans (U.S. EPA, 1994a). In studies with rodents, acetaldehyde has been shown to cross the placenta and cause growth retardation, to cause skeletal malformations, and to kill embryos. In vitro reproductive toxicity studies have shown that acetaldehyde is an inhibitor of testicular testosterone production (ARB, 1993d). Acetaldehyde is not listed by the State of California under Proposition 65 as a reproductive or developmental toxicant (CCR, 1994).

Cancer: Human data for carcinogenic effects of acetaldehyde are inadequate. An increased incidence of nasal tumors in rats and laryngeal tumors in hamsters has been observed following inhalation exposure to acetaldehyde. The U.S. EPA classified acetaldehyde in Group B2: Probable human carcinogen on the basis of sufficient evidence for carcinogenicity in animals and inadequate evidence in humans, and determined an inhalation potency value of 2.2×10^{-6} (micrograms per cubic meter)$^{-1}$. The U.S. EPA estimates that if an individual were to breathe air containing acetaldehyde at 0.5 $\mu g/m^3$ over a lifetime, that person would theoretically have no more than a 1 in 1 million increased chance of developing cancer (U.S. EPA, 1994a). The International Agency for Research on Cancer classified acetaldehyde in Group 2B: Possible human carcinogen based on sufficient evidence in animals and inadequate evidence in humans (IARC, 1987a).

The State of California Office has determined under Proposition 65 that acetaldehyde is a carcinogen (CCR, 1994). The recommended potency value for use in cancer risk assessment is 2.7×10^{-6} $(\mu g/m^3)^{-1}$. In other words, the potential excess cancer risk for a person exposed over a lifetime to one microgram per cubic meter of acetaldehyde is estimated to be no greater than 3 in 1 million (OEHHA, 1994).

3. AMBIENT MEASUREMENTS OF SELECTED PARTICLE-ASSOCIATED POLYCYCLIC AROMATIC HYDROCARBONS (PAH) AND NITRO-PAH

At the request of the California Air Resources Board (CARB), selected PAH and nitro-PAH were measured in ambient particle samples collected in Riverside. The targeted compounds for analysis were chosen by the CARB staff on the basis of their high potency equivalency factors and a lack of ambient air concentration data.

Experimental Methods

1. Sample Collection, Extraction and HPLC Separation

During the months of July and August, 1994 the SAPRC "megasampler" was used to collect large samples of ambient particles on Teflon-impregnated glass fiber (TIGF) filters. The "megasampler" has a capacity of 16 Hi-vol samplers and has a size selective inlet designed to exclude particles with an aerodynamic diameter of $> 20\mu m$. It has a total flow rate of approximately 640 SCFM through four quadrants each containing one 16 in. x 20 in. filter. Approximately 12-hr daytime and nighttime samples were collected as shown in Tables 4 and 5, respectively. The TIGF filters (Pallflex TX40HI20) used for particle collection were prewashed by sequential 16-hour soxhlet extractions with dichloromethane (CH_2Cl_2) and methanol (CH_3OH).

Two daytime replicate composite samples were made by combining the Quadrant I particle-laden filters from the 7 daytime samples (Day Quadrant I Composite) and the Quadrant II filters from the 7 daytime samples (Day Quadrant II Composite). Analogously, two nighttime replicate composite samples were made by combining the Quadrant I particle-laden filters from the 7 nighttime samples (Night Quadrant I Composite) and the Quadrant II filters from the 7 nighttime samples (Night Quadrant II Composite). The total volumes of air represented by each composite sample are also listed in Table 4 and 5. After spiking with deuterated internal standards as noted in Table 6, the filters were Soxhlet extracted with CH_2Cl_2 for 24 hours, concentrated by rotary evaporation to 15 ml, filtered to remove any particles (Acrodisc PTFE, 0.2 μ), and concentrated to 400 μl under a gentle stream of dry nitrogen at 25°C.

Table 4. Daytime U.C. Riverside Megasampler Samples, Summer 1994

DATE	DAY/NIGHT	TIME ON	TIME OFF	TOTAL HRS
7/27/94	DAY	0920	1852	9.53
7/28/94	DAY	0712	1903	11.85
8/3/94	DAY	0825	1904	10.65
8/4/94	DAY	0717	1904	11.78
8/24/94	DAY	1017	1858	8.68
8/25/94	DAY	0713	1912	11.98
8/26/94	DAY	0715	1915	12.00
Total Volume Sampled on Quadrant I, 7 Days Composited				21,000 m^3
Total Volume Sampled on Quadrant II, 7 Days Composited				21,300 m^3

Table 5. Nighttime U.C. Riverside Megasampler Samples, Summer 1994

DATE	DAY/NIGHT	TIME ON	TIME OFF	TOTAL HRS
7/27/94	NIGHT	1900	0704	12.07
7/28/94	NIGHT	1913	0707	11.9
8/3/94	NIGHT	1908	0713	12.08
8/4/94	NIGHT	1908	0715	12.12
8/24/94	NIGHT	1905	0707	12.03
8/25/94	NIGHT	1916	0709	11.88
8/26/94	NIGHT	1945	0708	11.38
Total Volume Sampled on Quadrant I, 7 Nights Composited				23,400 m^3
Total Volume Sampled on Quadrant II, 7 Nights Composited				23,500 m^3

Table 6. Amount (μg) of Deuterated Internal Standards Spiked on Composited Filters

Soln. Code	Compound	Quadrant I Daytime Composite	Quadrant I Nighttime Composite	Quadrant II Daytime Composite	Quadrant II Nighttime Composite
	PAH	μg	μg	μg	μg
P1	Dibenz[a,h]anthracene-d_{14}	4.08	4.08	3.91	3.91
P2	Benzo[a]pyrene-d_{12}	6.45	6.45	6.88	6.88
P3	Perylene-d_{12}	1.69	1.69	1.69	1.69
P4	Benz[a]anthracene-d_{12}	3.85	3.85	3.91	3.91
P5	Chrysene-d_{12}	18.48	18.48	18.07	18.07
	Nitro-PAH	μg	μg	μg	μg
N1	2-Nitrofluorene-d_9	0.45	0.45	0.52	0.52
N2	9-Nitroanthracene-d_9	3.58	3.58	3.70	3.70
N3	1-Nitropyrene-d_9	0.81	0.81	0.86	0.86
N4	2-Nitrofluoranthene-d_9	5.54	16.62	5.60	5.60
N5	6-Nitrochrysene-d_{11}	0.45	0.45	0.43	0.43
N6	7- + 9-Nitrobenz[a]anthracene-d_{11}	0.44	0.44	0.53	0.53
N7	1,3-/1,6-/1,8-Dinitropyrenes-d_8	0.44	0.44	0.47	0.47
N8	6-Nitrobenzo[a]pyrene-d_{11}	0.40	0.40	0.50	0.50

Dichloromethane was chosen as the extraction solvent because it provides good recoveries of PAH and nitro-PAH without extracting large amounts of polar material which then must be removed prior to analysis (Final Report CARB Contract No. A5-183-32, May 1988). The extracts were initially fractionated by open column silica chromatography to remove aliphatic hydrocarbons (eluted with pentane) from the PAH/nitro-PAH fraction (eluted with CH_2Cl_2). The polar fraction (eluted with methanol) was not analyzed.

The PAH/nitro-PAH fractions were further fractionated by normal-phase high-performance liquid chromatography (HPLC) on silica (Spherisorb, 5μ, 250 x 10mm, Phase Separations, Inc.). The HPLC system consisted of a Hewlett-Packard Model 1050 Series HPLC with a UV-Visible detector. The mobile phase program employed, at a rate of 3 ml min^{-1}, was as follows: 100% *n*-hexane for 10 minutes, followed by a 5-min linear gradient to 95% *n*-hexane and 5% CH_2Cl_2. The solvent was programmed over the next 25 minutes to 100% CH_2Cl_2, where it was held for 10 minutes, then programmed to 100% acetonitrile (CH_3CN) over 10 minutes, held isocratic for an additional 10 minutes and then programmed back to the initial conditions.

For the Quadrant I extracts, nine 9-minute HPLC fractions of increasing polarity were collected beginning at one minute. With this fractionation scheme, the PAH were collected in fraction 3 (19-28 min) and the nitro-PAH were collected in fraction 4 (28-37 min).

In an attempt to isolate the dinitropyrenes in a single fraction containing fewer interfering compounds, a modification of the above fraction collection program was applied to the Quadrant II filter extracts. A mononitro-PAH fraction, fraction 4A, was collected from 28-36 min and a dinitropyrene fraction, fraction 4B, was collected from 36-40 min (thus shortening fraction 5 to six minutes).

2. PAH GC/MS Analysis

PAH identifications and quantifications were made using a Hewlett-Packard 5890 Gas Chromatograph (GC) interfaced to a 5970 Mass Selective Detector (MSD). The GC was equipped with a cool on-column injection system and a 60-m DB-5MS fused silica capillary column (0.25 mm i.d. and 0.25 μm film thickness) eluting directly into the MS ion source. HPLC fractions analyzed for PAH were dissolved in CH_2Cl_2 for injection by the 7673A

Automatic Sampler. The GC conditions were as follows: cool on-column injections with initial column temperature at 40°C. The column was programmed at 20°C min^{-1} to 220°C and then at 2°C min^{-1} to 320°C, where it was held for approximately 10 minutes.

The following molecular ions, corresponding to the PAH listed in Table 7, were monitored in the Selective Ion Monitoring (SIM) mode: m/z 228, 252, 256, 268, 276, 278, 302. Molecular ions of the deuterated internal standards were monitored as follows: m/z 240 for benz[a]anthracene-d_{12} and chrysene-d_{12}, m/z 264 for benzo[a]pyrene-d_{12} and perylene-d_{12}, and m/z 292 for dibenz[a,h]anthracene-d_{14}. Identifications were based on retention time matching with authentic standards, and response factors relative to the appropriate deuterated internal standard (*i.e.,* the standard most closely matched in retention time) were determined from calibration solutions of authentic standards (see Table 7). The response factors (R.F.) reported in Table 7 are equal to the (area counts per ng for the deuterated internal standard)/(area counts per ng for the compound). Injections for GC/MS-SIM analyses were made in triplicate.

To maximize sensitivity of the labile PAH, the samples were introduced onto the GC column using on-column injection. As a result, the pre-column and often the front meter of the column had to be removed every few sample injections to due degrading peak shapes. Retention times for specific compounds were determined from standards analyzed on the column when it was the same length. The retention times given in Table 7, therefore, may not be used to determine the relative elution order of PAH of different molecular weights which may have been analyzed at different times (i.e., with slightly different column lengths).

In addition to analysis on the DB-5MS column, a 50 m SB-Smectic (liquid crystalline polysiloxane, 0.2 mm i.d., 0.15 μm film thickness, Dionex Inc.) column was used to separate and identify the chrysene and triphenylene (which co-eluted on the DB-5 column) present in the ambient sample. Cool on-column injections were made with an initial column temperature of 120°C followed by temperature programming at 50°C min^{-1} to 250°C, held isothermal for 20 min and then programmed at 20°C min^{-1} to 270°C where it was held for ~30 minutes.

There will be no differentiation between the PAH and their deuterated analogues in terms of losses during the analysis procedures. Therefore, any losses which occur due to, for example, volatilization or degradation on the HPLC or GC column will be compensated for.

Table 7. PAH Targeted for Quantification by GC/MS-SIM Analysis and Response Factors Measured Relative to Deuterated Compounds Employed as Internal Standards

PAH	M.W.[a]	Retention Time (min)	Deuterated Internal Standard	R.F.[a]
Benz[a]anthracene	228	21.5	Chrysene-d_{12}[b]	1.24
Chrysene	228	21.7[c]	Chrysene-d_{12}	1.21
Triphenylene	228	21.6[c]	Chrysene-d_{12}	1.46
5-Methylchrysene	242	no std.[d]		
Benzo[a]pyrene (**B[a]P**)	252	32.0	B[a]P-d_{12}	1.37
Benzo[e]pyrene	252	31.6	B[a]P-d_{12}	1.37
Benzo[b]fluoranthene	252	29.5[e]	B[a]P-d_{12}	1.30[e]
Benzo[j]fluoranthene	252	29.5[e]	B[a]P-d_{12}	1.30[e]
Benzo[k]fluoranthene	252	29.5[e]	B[a]P-d_{12}	1.30[e]
Perylene	252	32.6	Perylene-d_{12}	1.72
7,12-Dimethylbenz[a]anthracene	256	29.5	B[a]P-d_{12}	0.21[f]
3-Methylcholanthrene	268	35.1	B[a]P-d_{12}	0.56
Indeno[1,2,3-cd]fluoranthene	276	38.9	DB[a,h]A-d_{14}	4.70
Indeno[1,2,3-cd]pyrene	276	41.6	DB[a,h]A-d_{14}	(4.70)[g]
Benzo[ghi]perylene	276	42.9	DB[a,h]A-d_{14}	6.66
Dibenz[a,h]anthracene (**DB[a,h]A**)	278	41.3[h]	DB[a,h]A-d_{14}	5.69
Dibenz[a,c]anthracene	278	41.2[h]	DB[a,h]A-d_{14}	5.59
Benzo[b]chrysene	278	42.1	DB[a,h]A-d_{14}	4.64
Benzo[c]chrysene	278	39.5	DB[a,h]A-d_{14}	3.22
Dibenzo[a,e]pyrene	302	54.0	DB[a,h]A-d_{14}	6.76
Dibenzo[a,h]pyrene	302	55.5	DB[a,h]A-d_{14}	5.81
Dibenzo[a,i]pyrene	302	55.0	DB[a,h]A-d_{14}	6.21
Dibenzo[a,l]pyrene	302	51.4	DB[a,h]A-d_{14}	5.00

[a] M.W. = molecular weight; R.F. = response factor (see text for definition).
[b] Chrysene-d_{12} used because benz[a]anthracene-d_{12} standard had apparently degraded.
[c,h] Compounds co-elute.
[d] No standard available.
[e] Compounds not resolved. R.F. for benzo[j]fluoranthene used to quantify all three.
[f] Standard not pure.
[g] Used R.F. for indeno[1,2,3-cd]fluoranthene.

The only deuterated standard available for the higher molecular weight (276 and greater) species was the deuterated analogue of dibenz[*a,h*]anthraene (DB[*a,h*]A). As noted above, response factors relative to DB[*a,h*]A-d_{14} were measured for these high molecular weight PAH (see Table 7) and the assumption was made that recoveries would be comparable to that of DB[*a,h*]A-d_{14}. No volatilization losses are expected, but potential losses in the HPLC separation cannot be ruled out without conducting extensive recovery studies.

3. Nitro-PAH GC/MS Analysis

Identifications of the nitro-PAH by GC/MS-SIM were made on the basis of the presence of the molecular ion and several characteristic major fragment ions as well as retention time matching. A 60-m DB-5MS fused silica capillary GC column was again utilized to separate the nitro-PAH, which were analyzed by GC/MS-SIM. Cool on-column injections with different temperature programs (as described below) were employed to achieve separation and identification of various nitro-PAH. Table 8 lists the targeted nitro-PAH, their molecular weights, retention times (note that because different GC temperature programs were used, the retention times of different molecular weight nitro-PAH do not necessarily reflect their elution order), the deuterated internal standards employed and the response factors determined from calibration solutions of authentic standards. The HPLC fractions to be analyzed for the presence of nitro-PAH were dissolved in CH_2Cl_2, and injections for nitro-PAH quantifications were made in triplicate.

Nitrofluoranthenes and Nitropyrenes: Cool on-column injections made with the initial column temperature at 40°C. The GC was programmed at 20°C min^{-1} to 240°C and then at 2°C min^{-1} to 300°C where it was held for approximately 10 minutes. The molecular ion and fragment ions monitored were: $[M]^+$, m/z 247; $[M-NO]^+$, m/z 217; $[M-NO_2]^+$, m/z 201 and the corresponding ions for the deuterated species: m/z 256, 226, and 210.

Nitrobenz[a]anthracenes and Nitrochrysenes: Cool on-column injections made with the initial column temperature at 40°C. The GC was programmed at 20°C min^{-1} to 200°C and then at 4°C min^{-1} to 300°C where it was held for approximately 10 minutes. The molecular ion and fragment ions monitored were: $[M]^+$, m/z 273; $[M-NO]^+$, m/z 243; $[M-HNO_2]^+$, m/z 226; $[M-NO-CO]^+$, m/z 215 and the corresponding ions for the deuterated standards at 10 or 11 amu higher.

Table 8. Nitro-PAH Targeted for Quantification by GC/MS-SIM Analysis and Response Factors Measured Relative to Deuterated Compounds Employed as Internal Standards

Nitro-PAH	M.W.[a]	Retention Time (min)	Deuterated Internal Standard	R.F.[a]
5-Nitroacenaphthene	199	20.1	2-Nitrofluorene-d_9	0.78
3-Nitrobiphenyl	199	15.9	2-Nitrofluorene-d_9	0.88
2-Nitrofluorene	211	22.2	2-Nitrofluorene-d_9	b
9-Nitroanthracene	223	22.3	2-Nitrofluorene-d_9	1.06
9-Nitrophenanthrene	223	24.1	2-Nitrofluorene-d_9	0.28
2-Nitrofluoranthene	247	24.6	2-Nitrofluoranthene-d_9	1.9[c]
1-Nitropyrene	247	25.7	1-Nitropyrene-d_9	1.4
2-Nitropyrene	247	26.1	1-Nitropyrene-d_9	2.04
4-Nitropyrene	247	24.9	1-Nitropyrene-d_9	1.06
7-Nitrobenz[a]anthracene	273	27.4	7-Nitrobenz[a]anthracene-d_{11}	1.44
6-Nitrochrysene	273	28.9	6-Nitrochrysene-d_{11}	1.00
1,6-Dinitropyrene	292	d	1,3-/1,6-/1,8-Dinitropyrenes-d_8	
1,8-Dinitropyrene	292	d	1,3-/1,6-/1,8-Dinitropyrenes-d_8	
6-Nitrobenzo[a]pyrene	297	d	6-Nitrobenzo[a]pyrene-d_{11}	

[a] M.W. = molecular weight; R.F. = response factor (see text for definition).

[b] Not found in ambient sample.

[c] Response Factor calculated relative to m/z 210, $[M-NO_2]^+$, fragment of internal standard.

[d] Deuterated internal standards not recovered from HPLC.

Nitroanthracenes, Nitrophenanthrenes, Nitrofluorenes, Nitroacenaphthenes and Nitrobiphenyls: Cool on-column injections made with the initial column temperature at 40°C. The column was initially programmed at 20°C min^{-1} to 150°C and then at 4°C min^{-1} to 280°C where it was held for approximately 10 minutes. The molecular ion and fragment ions monitored were as follows, for nitroanthracenes and nitrophenanthrenes: $[M]^+$, m/z 223; $[M-HNO_2]^+$, m/z 176; for nitroacenaphthenes and nitrobiphenyls: $[M]^+$, m/z 199; $[M-NO_2]^+$, m/z 153; $[M-HNO_2]^+$, m/z 152; for nitrofluorenes: $[M]^+$, m/z 211; $[M-NO_2]^+$, m/z 165. The deuterated standard used for quantifications was 2-nitrofluorene-d_9 and the corresponding molecular ion and fragment ion monitored were: $[M]^+$, m/z 220; $[M-NO_2]^+$, m/z 174.

Nitrobenzo[a]pyrenes, Nitroperylenes and Dinitropyrenes: Cool on-column injections were made with the initial column temperature at 40°C. The column was initially programmed at 20°C min^{-1} to 240°C and then at 2°C min^{-1} to 300°C where it was held for approximately 10 minutes. The molecular ion and fragment ions for nitrobenzo[a]pyrenes and nitroperylenes were: $[M]^+$, m/z 297; $[M-HNO]^+$, m/z 268; $[M-HNO_2]^+$, m/z 250 and the corresponding ions for the deuterated standard, 6-nitrobenzo[a]pyrene-d_{11} at 10 or 11 amu higher. The molecular ion and fragment ions monitored for the dinitropyrenes were: $[M]^+$, m/z 292; $[M-(NO_2)_2]$, m/z 200 and the corresponding ions for the deuterated standards at 8 amu higher.

Results

PAH

Table 9 lists the PAH quantified in the Day Quadrant II Composite (the HPLC Fraction #3 of the Day Quadrant I Composite was inadvertantly lost), and the Night Quadrant I and Quadrant II composites. No dramatic day/night differences are seen in the PAH concentrations. In general, judging from the benzo[a]pyrene and benzo[e]pyrene levels observed in Riverside, these samples contained significantly lower levels of the PAH than previously reported samples (Final Report to CARB Contract No. A5-185-32). Targeted PAH that were not detected in the Riverside sample were: perylene, 7,12-dimethylbenz[*a*]anthracene, 3-methylcholanthrene, indeno[1,2,3-*cd*]fluoranthene, dibenzo[*a,h*]pyrene and dibenzo[*a,i*]pyrene. At the request of the CARB, an upper limit for the concentration of dibenzo[*a,h*]pyrene and dibenzo[*a,i*]pyrene was estimated. Based on the GC/MS-SIM traces for the molecular ion peak at m/z 302, the

Table 9. PAH Quantified (pg m^{-3}) by GC/MS-SIM Analysis in Riverside Ambient Particle Samples

PAH	Day Quadrant II Composite (pg m^{-3})	Night Quadrant I Composite (pg m^{-3})	Night Quadrant II Composite (pg m^{-3})
Benz[a]anthracene	39	38	31
Chrysene + Triphenylene[a]	80	100	66
Benzo[*a*]pyrene	36	52	35
Benzo[*e*]pyrene	130	200	140
Σ Benzo[*b*+*j*+*k*]fluoranthenes[b]	360	400	400
Indeno[1,2,3-*cd*]pyrene	87	99	68
Benzo[*ghi*]perylene	98	160	88
Dibenz[*a,h* + *a,c*]anthracene[b]	8.2	8.5	7.0
Dibenz[*a,j*]anthracene	5.5	6.8	5.1
Benzo[*b*]chrysene	3.0	2.9	2.9
Benzo[*c*]chrysene	2.8	2.4	2.3
Dibenz[*a,e*]pyrene	1.7	3.6	-
Dibenz[*a,h*]pyrene	<0.5	<0.5	
Dibenz[*a,i*]pyrene	<0.5	<0.5	
Dibenz[*a,l*]pyrene	18	20	15

[a] Isomers co-eluted on DB-5 column. Analysis using a Smectic column for separation: chrysene: 61 pg m^{-3} day, 45 pg m^{-3} night; triphenylene: 15 pg m^{-3} day, 15 pg m^{-3} night.

[b] Isomers co-eluted on DB-5 column.

concentrations of dibenzo[*a,h*]pyrene and dibenzo[*a,i*]pyrene in the Riverside POM samples were <0.5 pg m^{-3}. However, this assumes 100% recovery of these PAH during the HPLC fractionation step. Because the sample matrix may influence the HPLC recovery and deuterated standards of these PAH are not available, this upper limit should be viewed with caution.

As noted earlier, CARB was also interested in ambient concentrations of 5-methylchrysene and three azaarenes. A procedure used for estimating 5-methylchrysene ambient concentrations is discussed below.

5-Methylchrysene

Benz[*a*]anthracene, chrysene and triphenylene, three PAH of molecular weight 228 have been quantified at numerous sites throughout California. Although a standard of 5-methylchrysene was available for retention time matching, ions characteristic of methyl derivatives of benz[*a*]anthracene, chrysene and triphenylene at m/z 242 have been monitored in various ambient samples (Final Report CARB Contract No. A5-185-32). Generally, the loss of a methyl group from a methylsubstituted PAH does not result in a significant fragment ion peak in the electron impact gas chromatography/mass spectrometry (GC/MS) spectra. As is the case for the non-substituted parent PAH, the molecular ion is the base peak in the spectra of the methyl-PAH, including 5-methylchrysene (EPA/NIH Mass Spectral Data Base). Therefore, by comparing the area of the molecular ion peak of the methyl-PAH with that of the parent, unsubstituted PAH which has been quantified, an estimate can be made of the methyl-PAH concentration.

Because no information is available on the exact retention time of 5-methylchrysene, an upper limit to the 5-methylchrysene concentration has been estimated by using the largest peak (in the approximate retention time window) in the m/z 242 ion trace for ambient samples collected in Yuba City, Concord and Oildale, CA under conditions of maximum photochemical pollution (Final Report CARB Contract No. A5-185-32). The resulting estimates for the upper concentration limits for 5-methylchrysene are given in Table 10. With the exception of retene (1-methyl-7-isopropylphenanthrene), alkyl-PAH are generally less abundant than the nonsubstituted parent PAH.

The upper limit for 5-methylchrysene was estimated to be between 10-30% of the chrysene + triphenylene concentration. Therefore, an upper limit of 24 pg m^{-3} (0.3 x 80 pg m^{-3}) would be reasonable for Riverside during our summer 1994 sampling period.

Table 10. Estimated upper limits for the 5-methylchrysene concentration in ambient air samples collected at three sites in California (Data from Final Report CARB Contract No. A5-185-32).

SITE	Σ Chrysene + Triphenylene[a] (ng m^{-3})	Upper Limit for 5-Methylchrysene (ng m^{-3})
Yuba City (Daytime composite)	1.1	0.1
Concord (Nighttime composite)	13.5	3.9
Oildale (Nighttime composite)	1.1	0.2

[a] Chrysene and triphenylene co-eluted on the 5% phenyl-methylsilicone phase used in the GC separation and are, therefore, reported as their sum.

Azaarenes

Azaarenes, the nitrogen heterocycle analogues of PAH are basic compounds, which like the PAH, are products of incomplete combustion. The concentrations of azaarenes have been reported to be generally one to two orders of magnitude lower than those of the PAH (Nielsen *et al.*, 1986). In Table 2 below, the dibenzacridine concentrations measured during the month of February in Copenhagen, Denmark in the years 1976-1982 are given, along with the concentrations of several other azaarenes and PAH. The authors noted the higher concentrations of the dibenzacridines observed in the residential area and suggested that the heating of buildings by furnaces and stoves may be a major source of dibenzacridines. Note that the concentration of benzo[*e*]pyrene and most of the PAH and other azaarenes measured were higher in the busy street suggesting car exhausts were their major source. No literature data on the ambient air concentration of 7*H*-dibenzo-[*c,g*]carbazole was found.

Table 11. The average amount of selected azaarenes and PAH measured in a suburban residential area and in a busy street in Copenhagen in February in the years 1976-1982 (Data from Nielsen *et al.*, 1986).

Compound	Residential Area (ng m^{-3})	Busy Street (ng m^{-3})
Dibenz[*a,h*]acridine	0.2	0.08
Dibenz[*a,j*]acridine	0.2	0.07
Quinoline	0.11	0.4
7,8-Benzoquinoline	0.2	0.3
3,4-Benzacridine	0.09	0.17
Σ Chrysene + Triphenylene	1.8	2.3
Benzo[*e*]pyrene	1.2	1.8
Benzo[*ghi*]perylene	1.7	3.2

Nitro-PAH

Table 12 lists the nitro-PAH quantified in the replicate day (Quadrant I and II) and replicate nighttime (Quadrant I and II) samples. The nighttime level of 2-nitrofluoranthene (2-NF) was significantly higher than the daytime level and the ratio of 2-NF/2-nitropyrene was also elevated at night, suggesting nighttime NO_3 radical-initiated formation of 2-nitrofluoranthene. The sources of the nitro-PAH observed and the relative importance of atmospherically-formed nitro-PAH *vs* nitro-PAH directly emitted from combustion sources is discussed in Section 4. Based upon the data presented in Section 4 below, artifactual formation of nitro-PAH during the ambient sample collection on filters was negligible.

Table 12. Nitro-PAH Quantified (pg m^{-3}) by GC/MS-SIM Analysis in Riverside Ambient Particle Samples

Nitro-PAH	Day Quadrant I Composite (pg m^{-3})	Day Quadrant II Composite (pg m^{-3})	Night Quadrant I Composite (pg m^{-3})	Night Quadrant II Composite (pg m^{-3})
3-Nitrobiphenyl		0.46		
5-Nitroacenaphthene		0.88		
2-Nitrofluorene	none detected	none detected	none detected	none detected
9-Nitroanthracene		23		49
2-Nitrofluoranthene	39	33	100	132
1-Nitropyrene	4.1	4.6	2.0	4.4
2-Nitropyrene	4.8	3.6	2.6	4.9
4-Nitropyrene	1.6			
7-Nitrobenz[a]anthracene			5.8	
6-Nitrochrysene			5.4	

4. SOURCES OF NITRO-PAH IN AMBIENT AIR - INCLUDING ATMOSPHERIC FORMATION

Interest in the nitro-PAH present in ambient air followed findings of direct-acting bacterial mutagens (not requiring microsomal activation) in ambient particle extracts and the facile formation of nitro-PAH from reactions of filter-adsorbed benzo[*a*]pyrene and perylene when exposed to NO_2 and traces of nitric acid (Pitts *et al.*, 1978). This "facile nitration" suggested the possible formation of nitro-PAH during sample collection on filters, in exhaust effluents and in the atmosphere (Pitts *et al.*, 1978). The finding of 1-nitropyrene and dinitropyrenes as important contributors to the direct-acting mutagenic activity of diesel exhaust particles (Schuetzle, 1983) enhanced interest in the health implications, and in particular, in the potential carcinogenic risks from nitro-PAH. There are now two well-documented sources of nitro-PAH in ambient air: (1) direct emission from combustion sources (Rosenkranz and Mermelstein, 1983; Tokiwa and Ohnishi, 1986; IARC, 1983, 1984, 1989) resulting from probable electrophilic nitration mechanisms and (2) *in-situ* atmospheric formation from radical-initiated reactions of the parent PAH (Atkinson and Arey, 1994). A summary of the important findings regarding the sources of ambient nitro-PAH, the data available on ambient concentrations of nitro-PAH in California, and suggested assumptions that can be made regarding nitro-PAH concentrations from a knowledge of the chemistry of their formation are given below.

Electrophilic Nitration

The reactivities of 25 PAH toward electrophilic nitration (Nielsen, 1984) are given in Table 13. Also listed in the table are the major electrophilic nitration products of selected PAH (Ruehle, 1985), which include many of the nitro-PAH identified in diesel exhaust extracts (Paputa-Peck *et al.*, 1983).

Artifactual Formation of Nitro-PAH During Sampling of Particles on Filters

The potential for artifactual formation of nitro-PAH during high-volume sampling of ambient air has been evaluated (Arey *et al.*, 1988a). Fully deuterated fluoranthene, pyrene, benzo[*a*]pyrene and perylene were coated onto filters loaded with previously collected particles and exposed to ambient gases during additional high-volume sampling. The nitro-PAH expected to form artifactually from reaction of NO_2 and/or nitric acid during the sampling of particles on filters are the electrophilic nitration products of the PAH. It was verified that the electrophilic

Table 13. Relative reactivities of 25 PAH toward electrophilic nitration (Nielsen, 1984) and major electrophilic nitration product of selected PAH (Ruehle *et al.*, 1985).

PAH	Relative Reactivity	Nitro-PAH
anthanthrene	100,000[a]	6-nitroanthanthrene
perylene	73,000	3-nitroperylene
9,10-dimethylanthracene	21,000	
9-methylanthracene	6,500	
picene	2,100	
2-methylanthracene	1,600	
anthracene	1,200	9-nitroanthracene[b]
benzo[*a*]pyrene	1,100	6-nitrobenzo[*a*]pyrene[b]
1-methylanthracene	860	
benzo[*ghi*]perylene	28	
pyrene	27	1-nitropyrene[b]
coronene	6.8	
chrysene	6.3	6-nitrochrysene[b]
dibenz[*a,h*]anthracene	5.3	
benz[*a*]anthracene	4.5	7-nitrobenz[*a*]anthracene[b]
benzo[*e*]pyrene	<1	
benzo[*b*]fluorene	<0.9	
benzo[*ghi*]fluoranthene	<0.6	
benzo[*b*]fluoranthene	<0.5	
benzo[*k*]fluoranthene	<0.5	
triphenylene	<0.5	
phenanthrene	<2	9-nitrophenanthrene
fluoranthene	<0.4	3-nitrofluoranthene[b]
benzo[*j*]fluoranthene	<0.2	
indeno[1,2,3-*cd*]pyrene	<0.2	

[a] The relative reactivity of anthanthrene was set at 100,000.

[b] Reported in diesel exhaust; 2-nitrofluorene also abundant in exhaust (Paputa-Peck *et al.*, 1983; Sawyer and Johnson, 1995).

nitration products of the PAH were formed and that the amount of nitro-PAH formed artifactually followed the relative reactivities of the PAH listed in Table 13. Deuterated nitro-PAH were formed from pyrene (up to 40 ng of 1-nitropyrene-d_9), benzo[*a*]pyrene (up to 200 ng of 6-nitrobenzo[*a*]pyrene-d_{11}) and perylene (up to 1000 ng 3-nitroperylene-d_{11}) during 7-10 hr exposure/sampling periods in Torrance, CA, during a wintertime high-NO_x episode. No formation of nitrofluoranthenes was observed, and it was calculated that <3% of the 1-nitropyrene collected during such a pollution episode was formed during collection (Arey *et al.*, 1988a).

The potential problem of 1-nitropyrene formation during filter sampling of diesel emissions from dilution tubes has also been assessed (Schuetzle and Perez, 1983). It was found that on average 12% of the 1-nitropyrene found in particles collected from light duty and heavy-duty diesels was due to formation on the filter under average sampling conditions of 10-15/1 dilution at 44 °C with 3 ppm NO_2 for 23 min (Schuetzle and Perez, 1983).

Nitro-PAH Emitted in Combustion Sources

The nitro-PAH emitted from combustion sources such as diesel exhaust are the electrophilic nitration products of the PAH (Schuetzle, 1983; HEI, 1995 and references therein). The most abundant nitro-PAH in diesel exhaust are 1-nitropyrene and 2-nitrofluorene (Schuetzle and Perez, 1983; Beije and Möller, 1988 and references therein). Emission rates of these and other nitro-PAH vary with engine type, operating conditions and fuels (Schuetzle and Frazier, 1986; IARC, 1989). Nitro-PAH have been shown to contribute 20-55% of the direct-acting mutagenicity of diesel exhaust particle extracts, with 1-nitropyrene and 1,3-; 1,6-; and 1,8-dinitropyrenes (DNP) being the major contributors (Schuetzle, 1983; IARC, 1989 and references therein).

Tables 14-16 summarize recent data on nitro-PAH in vehicle emissions. As seen from Table 14, 1-nitropyrene is generally more abundant in diesel exhaust than the dinitropyrenes (Schuetzle and Perez, 1983), but under conditions of increased speed and load, 1-nitropyrene was significantly reduced with a concurrent increase in partially oxidized nitro-PAH and in dinitro-PAH (Schuetzle and Perez, 1983). Table 15 suggests dinitropyrene emission levels range above those of 1-nitropyrene (Sawyer and Johnson, 1995), while the data in Table 16 shows 1-nitropyrene consistently higher than the dinitropyrenes in diesel and gasoline engine-powered vehicles (Hayakawa *et al.*, 1994).

Table 14. The effect of engine operating conditions on the concentration of nitro-PAH in heavy-duty diesel particulates (adapted from Schuetzle and Perez, 1983).

	Concentration in Particulates (ppm)[a]			
Nitro-PAH	HDD38 (idle)	HDD34 (high speed - no load)	HDD4 (high speed -full load)	NIST SRM 1650[b]
2-nitrofluorene	84(164)	62(134)	1.9(15)	0.27
3-nitro-9-fluorenone	18(35)	7.9(17)	8(63)	
9-nitroanthracene	94(184)	16(35)	5.1(40)	
1-nitropyrene	14(28)	3(6.5)	0.13(1)	19 ± 2
1,3-dinitropyrene	<0.8(<1.6)	0.6(1.3)	0.4(3.1)	
1,6-dinitropyrene	<0.8(<1.6)	1.2(2.6)	0.8(6.3)	
1,8-dinitropyrene	<0.8(<1.6)	1.2(2.6)	0.8(6.3)	
7-nitrobenz[*a*]anthracene				2.8
6-nitrobenzo[*a*]pyrene	<3.2(<6.5)	1.6(3.5)	0.3(2.4)	1.6

[a] Number in parentheses is ppm concentration in extract. Extraction of samples HDD38, HDD34 and HDD4 gave 51, 45.9 and 12.7% extractables, respectively.

[b] National Institute of Standards and Technology, Standard Reference Material (SRM) 1650, heavy-duty diesel engine particulate matter.

Table 15. Nitro-PAH emissions as a function of time period and engine type[a] (adapted from Sawyer and Johnson, 1995).

	Emissions (ng/m^3)	
Nitro-PAH	1980s 4S-NA, 4S-TC, 2S-DI	1990s 4S-NA, 4S-TC, 2S-DI
2-nitrofluorene	5-600	100-3,100
1,6- and 1,8-dinitropyrene	400-800	20-400
1,3-dinitropyrene	200-600	10-150
1-nitropyrene	6-180	10-80
7-nitrobenz[*a*]anthracene	1-30	<17
6-nitrochyrsene	2-25	<15

[a] Abbreviations: 4S-NA = four-stroke, naturally aspirated; 4S-TC = four-stroke, turbocharged; 2S-DI = two-stroke, direct-injected.

Table 16. Concentrations (pmol/mg particles) of 1-nitropyrene and dinitropyrenes in particles from gasoline engine vehicles and diesel engine vehicles (adapted from Hayakawa *et al.*, 1994).

Nitro-PAH	Gasoline engine vehicles[a] (pmol/mg) mean ± SD	Diesel engine vehicles[b] (pmol/mg) mean ± SD
1-nitropyrene	1.8 ± 0.85	51 ± 53
1,3-dinitropyrene	0.22 ± 0.15	0.23 ± 0.15
1,6-dinitropyrene	0.44 ± 0.36	0.23 ± 0.16
1,8-dinitropyrene	0.35 ± 0.18	0.21 ± 0.14

[a] Five sedans, 1 van, 1 coupe, 1 hatchback.
[b] Two trucks, 1 hatchback, 1 land cruiser, 1 bus, 2 sedans.

Ambient air data from Japan where diesel-powered vehicles are 18% of all vehicles, showed 1-nitropyrene levels 2 orders of magnitude higher than that of the dinitropyrenes (see Table 17, data from Murahashi *et al.*, 1995). Based on the ratios of the (Σ ([1,3-DNP] + [1,6-DNP] + [1,8-DNP])/ 1-nitropyrene) in ambient particles (0.014), in gasoline exhaust particles (0.56) and in diesel exhaust particles (0.013), the authors estimated that diesel engine vehicles contributed 94.3% and 99.8% to the three DNPs and 1-nitropyrene concentrations in ambient air, respectively (Murahashi *et al.*, 1995). In a sample collected in Santiago, Chile, researchers reported the Σ 1,6-DNP + 1,8-DNP and 1-nitropyrene to be 0.2 and 0.15 μg/g of particulate matter, respectively (Tokiwa *et al.*, 1983). The mechanism of formation of dinitropyrenes in diesel exhaust has been the subject of considerable debate (Ross *et al.*, 1987 and references therein) and it seems likely that under various diesel engine operating conditions, different mechanisms may be responsible for nitro-PAH formation.

Table 17. Ambient concentrations of 1-nitropyrene, dinitropyrenes and benzo[*a*]pyrene in downtown Kanazawa, Japan (Murahashi *et al.*, 1995).

Nitro-PAH[a]	fmol/m^3 mean ± SD[b]
1-nitropyrene	920 ± 410
1,3-dinitropyrene	4.3 ± 2.8
1,6-dinitropyrene	3.5 ± 2.1
1,8-dinitropyrene	4.7 ± 2.4
benzo[*a*]pyrene	9900 ± 5000

[a] Measured by HPLC with chemiluminsecence detection after reduction to the corresponding amines.

[b] Mean concentrations for 24 hr samples (collected in 2 hr sampling intervals). Sampling was performed once a month from July 1993 to February, 1994 (n = 8).

Nitro-PAH Formed in the Atmosphere

2-Nitrofluoranthene is not the electrophilic nitration product of fluoranthene and (unlike isomeric 1-nitropyrene) has generally not been observed in combustion emission sources like diesel exhaust (Atkinson and Arey, 1994 and references therein). However, in numerous samples collected worldwide, we and other researchers have found 2-nitrofluoranthene levels in ambient air generally exceed 1-nitropyrene levels (Pitts *et al.*, 1985; Nielsen and Ramdahl, 1986; Ramdahl *et al.*, 1986; Arey *et al.*, 1988; Atkinson *et al*, 1988; Nishioka *et al.*, 1988; Zielinska *et al.*, 1989; Ciccioli *et al.*, 1995). The source of the 2-nitrofluoranthene observed in ambient air has been demonstrated to be *in situ* formation from radical-initiated reactions of gas-phase fluoranthene (Atkinson *et al.*, 1990; Atkinson and Arey, 1994 and references therein).

Numerous laboratory studies have demonstrated that the products of the atmospheric reactions of gas-phase PAH include nitro-PAH (Atkinson *et al.*, 1990; Atkinson and Arey, 1994 and references therein). Hydroxyl (OH) radical-initiated formation reactions take place during daylight hours (with the OH radical being formed mainly from the photolysis of O_3 [Atkinson, 1988]) and are expected to occur in both clean and polluted atmospheres. In contrast, NO_3

radical reactions are expected to be important at night because the NO_3 radical rapidly photolyzes. Additionally, because both O_3 and NO_2 are required for the formation of NO_3 radicals, the NO_3 radical concentration is expected to be highly variable (Atkinson, 1988). Table 18 lists the specific nitro-PAH isomers and their yields obtained from laboratory reactions simulating OH and NO_3 radical-initiated reactions of selected PAH. These PAH are all abundant in ambient air (Atkinson *et al.*, 1988) and, as noted in Table 18, nitro-isomers of these PAH have been reported in diesel exhaust (Paputa-Peck *et al.*, 1983).

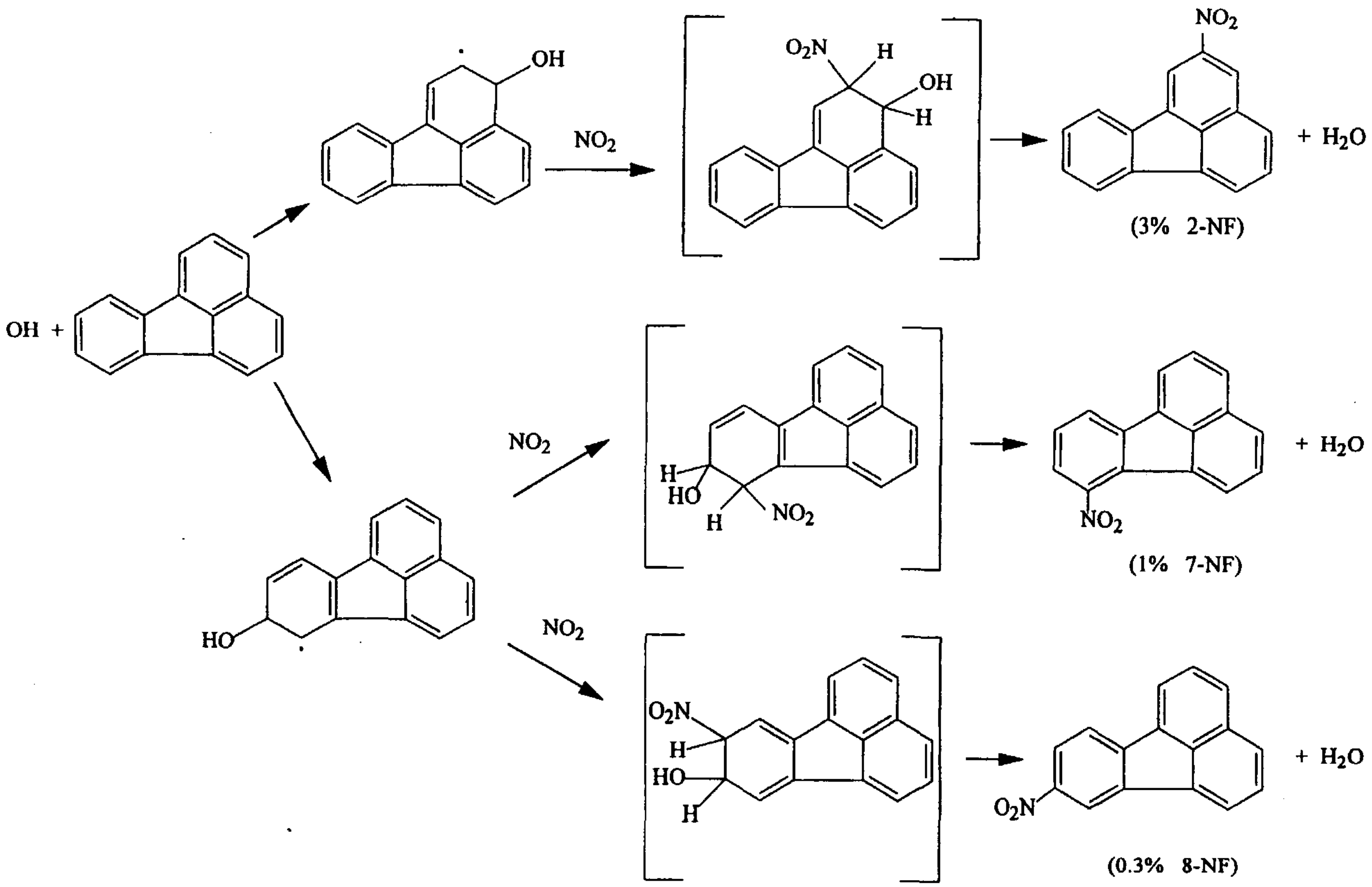
Daytime OH radical-initiated reaction of the PAH is expected to control their atmospheric lifetimes (Atkinson and Arey, 1994). However, although OH radical-initiated reaction is expected to be the major atmospheric loss process for gaseous PAH (Arey *et al.*, 1989), because the NO_3 radical-initiated reactions of certain PAH produce nitro-PAH in high yields (see Table 18), both OH radical-initiated and NO_3 radical-initiated reactions can be important in the secondary formation of nitro-PAH.

The specific nitro-isomers observed in ambient measurements and their relative abundances suggest that *in-situ* atmospheric formation of nitro-PAH, *i.e.*, as secondary reaction products of the PAH, dominates over direct nitro-PAH emissions (Arey *et al.*, 1987; 1988b; 1989; Zielinska *et al.*, 1989; Atkinson and Arey, 1994; Sasaki *et al.*, 1995; Gupta *et al.*, 1996). For example, fluoranthene and pyrene (both m.w. 202) are generally present in diesel exhaust and in ambient samples in similar amounts. However, while 1-nitropyrene (1-NP) is one of the most abundant nitro-PAH observed in diesel exhaust, 2-nitrofluoranthene (2-NF) has been found to be the most abundant isomer in ambient samples collected throughout the world (Ramdahl *et al.*, 1986; Arey *et al.*, 1988b; Atkinson *et al.*, 1988; Zielinska *et al.*, 1989; Ciccioli *et al.*, 1995). Scheme I shows the OH radical-initiated reaction of fluoranthene producing low yields of nitrofluoranthene (NF) isomers (the other products formed have not been identified). Note that the radical attack on the aromatic ring is expected to occur mainly at the positions of highest electron density, and the hydroxycyclohexadienyl-type radical formed adds NO_2 in the *ortho* position. Although for monocyclic aromatics reactions of the hydroxycyclohexadienyl radicals with O_2 are expected to dominate, for the polycylic aromatics reaction as shown with NO_2 may occur under ambient conditions (Atkinson and Arey, 1994). Note that the electrophilic nitration product of fluoranthene, 3-NF, is not formed and also that 2-nitrofluoranthene has not been

Table 18. Nitro-PAH isomers formed and their yields from the gas-phase reactions of selected PAH with OH radicals and NO_3 radicals (each in the presence of NO_x) and the nitro-PAH isomers identified in diesel exhaust.

	Nitro-PAH Formed (Yield) in Reaction with		Nitro-PAH present
Parent PAH	OH	NO_3	in Diesel Exhaust[a]
Naphthalene	1-Nitronaphthalene (0.3%) 2-Nitronaphthalene (0.3%)	1-Nitronaphthalene (17%) 2-Nitronaphthalene (7%)	1-Nitronaphthalene
1-Methylnaphthalene	(Total Yield ~0.4%) Most abundant: 1-Methyl-5-nitronaphthalene 1-Methyl-4-nitronaphthalene 1-Methyl-6-nitronaphthalene	7 Isomers (Total Yield 30%) Most abundant: 1-Methyl-3-nitronaphthalene 1-Methyl-5-nitronaphthalene 1-Methyl-4-nitronaphthalene	None Reported
2-Methylnaphthalene	(Total Yield ~0.2%) Most abundant: 2-Methyl-5-nitronaphthalene 2-Methyl-6-nitronaphthalene 2-Methyl-7-nitronaphthalene	7 Isomers (Total Yield 30%) Most abundant: 2-Methyl-4-nitronaphthalene 2-Methyl-1-nitronaphthalene 2-Methyl-5-nitronaphthalene	2-Methyl-1-nitronaphthalene
Fluorene	3-Nitrofluorene (~1.4%) 1-Nitrofluorene (~0.6%) 4-Nitrofluorene (~0.3%) 2-Nitrofluorene (~0.1%)		2-Nitrofluorene
Fluoranthene	2-Nitrofluoranthene (~3%) 7-Nitrofluoranthene (~1%) 8-Nitrofluoranthene (~0.3%)	2-Nitrofluoranthene (~24%)	3-, 8-, 7-, and 1-Nitrofluoranthene
Pyrene	2-Nitropyrene (~0.5%) 4-Nitropyrene (~0.06%)	4-Nitropyrene (~0.06%)	1-Nitropyrene

[a]From: Paputa-Peck *et al.* (1983).



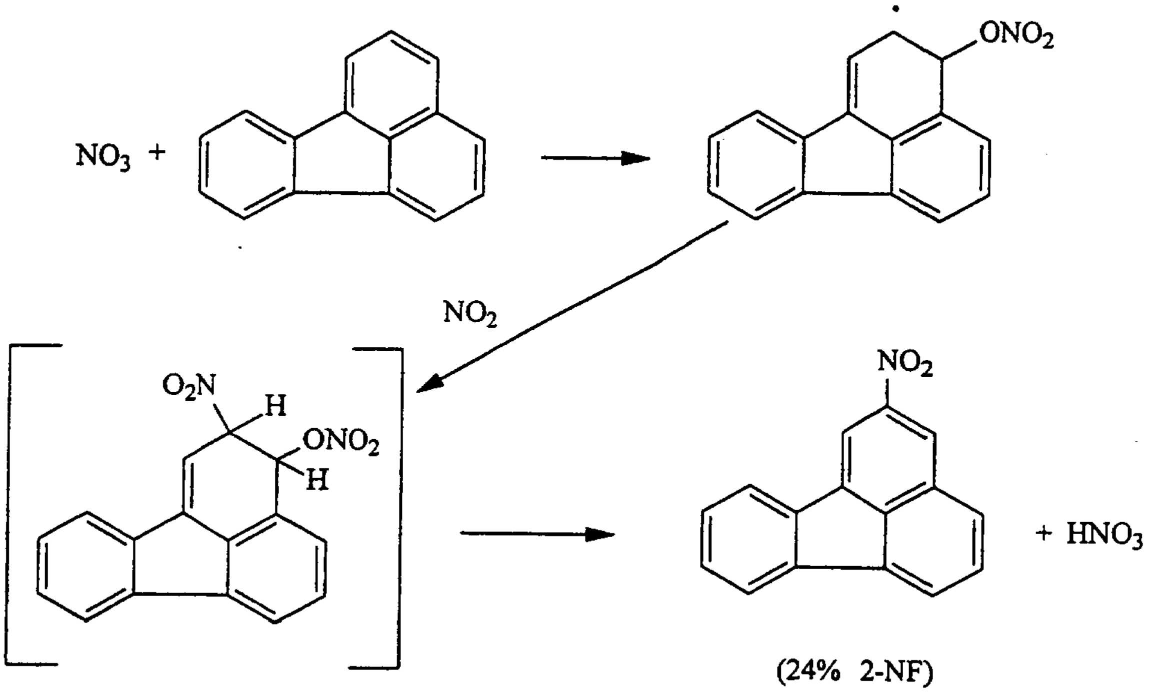
Scheme 1. Hydroxyl radical-initiated reaction of fluoranthene (with the OH radical adding mainly in the 3-position and to a lesser extent in the 7-position) leading to the formation of 2-nitrofluoranthene (3% yield), 7-nitrofluoranthene (1% yield) and 8-nitrofluoranthene (0.3% yield). An analogous reaction scheme can be postulated for the OH radical-initiated reaction of pyrene (with the OH radical adding mainly in the 1-position and to a minor extent in the 4-position) leading to the formation of 2-nitropyrene (0.5% yield) and 4-nitropyrene (0.06% yield).

reported in diesel exhaust. Similar reaction schemes for OH radical-initiated reaction of pyrene and fluorene are consistent with the observed formation of predominantly 2-nitropyrene and 3-nitrofluorene, respectively. Thus the isomers formed in the radical-initiated reactions are distinct from the 1-nitropyrene and 2-nitrofluorene reported in diesel emissions (see Table 18).

An analogous reaction scheme can be postulated for NO_3 radical-initiated reaction of fluoranthene (Scheme II). Note that only 2-NF is formed, suggesting that the NO_3 radical is more selective in the position of addition, and it is formed in almost an order of magnitude higher yield than from the OH radical-initiated reaction. Recent work has shown that the NO_3 radical and not N_2O_5 is the species which reacts with the PAH (Atkinson *et al.,* 1990) and that the nitratocyclohexadienyl-type radical formed is expected to react with NO_2 and not with O_2 under ambient conditions (Atkinson and Arey, 1994; Atkinson *et al.*, 1994).

Figure 1 shows mass chromatograms from gas chromatography/mass spectrometry (GC/MS) selected ion monitoring (SIM) analysis of an ambient particle extract for the molecular ion (m/z 247) of the nitrofluoranthenes (NF), nitropyrenes (NP) and nitroacephenanthrylenes (NAc). The ambient particles, collected in Torrance, CA using a high-volume sampling technique, were spiked prior to extraction with deuterated 2-NF and 1-NP (molecular ion at m/z 256) to serve as internal standards. After Soxhlet extraction of the particle-laden filters, HPLC fractionation on a semi-preparative scale silica column allowed separation of a fraction enriched in the nitro-PAH. Initial reports on ambient sample analyses mistakenly identified the major isomer present as 3-NF (Nielsen *et al.*, 1984; Wise *et al.*, 1985). Following the identification of 2-NF in ambient air samples (Pitts *et al.*, 1985) these misidentifications were corrected (Nielsen and Ramdahl, 1986; Nishioka *et al.*, 1988). Distinction between the closely eluting 2-NF and 3-NF isomers is possible with the resolution achieved by using a 60 m 5% phenyl-methylsilicone column, and the elution of the deuterated internal standards just prior to the normal isotopes on this column provides further confirmation that 2-nitrofluoranthene is the dominant isomer (see Figure 1). By applying response factors determined for the various isomers relative to the deuterated standards, quantification may be accomplished by GC/MS-SIM analysis.

In California, levels of 2-NF as high as 2 ng m^{-3} have been observed, while maximum 1-NP levels reported were $\sim$50 pg m^{-3} (Arey *et al.*, 1988; Atkinson *et al.*, 1988). Thus, the gas-phase reaction of fluoranthene leads to a less volatile product which condenses onto particles becoming the major nitro-PAH observed in ambient air particulate sample extracts.



Scheme II. Nitrate radical-initiated reaction of fluoranthene (with the NO_3 radical adding exclusively in the 3-position). Note the high nitro-PAH yield (24% of 2-nitrofluoranthene). The analogous reaction of the NO_3 radical with pyrene does not give 2-nitropyrene under ambient atmospheric conditions (Atkinson *et al.*, 1990). Thus, OH radical-initiated reaction of pyrene is the sole known source of ambient 2-nitropyrene.

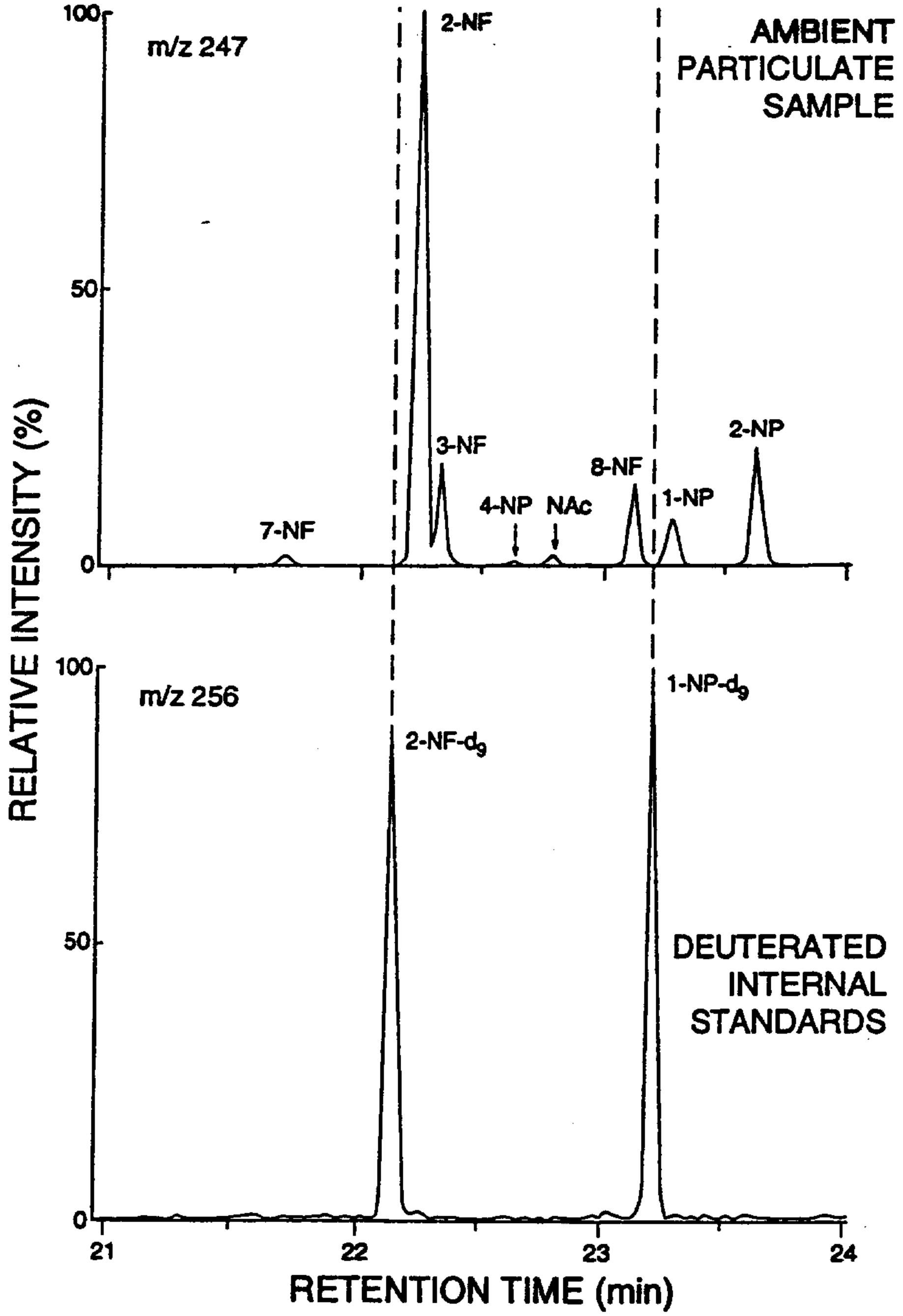


Figure 1. Mass chromatogram of the molecular ion (m/z 247) of nitrofluoranthenes (NF), nitropyrenes (NP) and nitroacephenanthrylenes (NAc) [top] from the GC/MS-SIM analysis of an HPLC fraction of an extract of ambient particles collected in Torrance, CA. Deuterated internal standards of 2-NF-d_9 and 1-NP-d_9 were added prior to extraction and the lower mass chromatogram shows the molecular ion of these internal standards (m/z 256).

4-Nitropyrene. 4-Nitropyrene is generally considered more potent than 1-nitropyrene, and a PEF value is available for this nitro-PAH. Thus, 4-nitropyrene is more mutagenic and more tumorigenic than 1-nitropyrene in the newborn mouse assay (Fu, 1990). 4-Nitropyrene has been detected in ambient samples (Zielinska *et al,* 1989; Korfmacher *et al.*, 1987) and not in diesel exhaust. Atmospheric formation from the OH radical-initiated reaction of gas-phase pyrene is expected to be the main source of the 4-nitropyrene observed in ambient air. Additionally if NO_3 radicals are present, small amounts of 4-nitropyrene are expected to be formed. One means of estimating the maximum 4-nitropyrene to which Californians are exposed would be to scale the 2-nitropyrene (only due to OH radical-initiated reaction) concentrations by the yield data obtained in the laboratory (Atkinson *et al.*, 1990, see Table 18). As noted in Table 18, the ratio of 2-nitropyrene/4-nitropyrene from the OH radical-initiated reaction of pyrene is 8. Thus, using the maximum 2-nitropyrene measured (81 pg m^{-3} at Concord), the estimated 4-nitropyrene would be ~10 pg m^{-3}.

Similarly, if it is assumed that most of the 2-nitrofluoranthene measured at Glendora when 2000 pg m^{-3} was observed was the result of NO_3 radical-initiated reaction of fluoranthene, the corresponding 4-nitropyrene (2-nitrofluoranthene yield/4-nitropyrene yield = 400) would be 5 pg m^{-3}. Thus, a maximum 4-nitropyrene concentration of 10 pg m^{-3} is a reasonable estimate.

Nitro-PAH in Diesel Emissions. Not surprisingly, the nitro-PAH whose source is diesel exhaust are significantly higher in areas of the world more impacted by diesel use than California. Thus, ambient concentrations of 2-nitrofluorene as high as 5.2 ng m^{-3} have been reported for ambient air samples collected in Berlin, Germany (Beije and Möller, 1988 and references therein). 6-Nitrochrysene concentrations as high as 0.27 ng m^{-3} in Tokyo, Japan air have been reported (Matsushita and Iida, 1986) and, dinitropyrene concentrations (Σ 1,3-DNP + 1,6-DNP + 1,8-DNP) of 3.6 pg m^{-3} (see Table 17) have been reported in Kanazawa, Japan (Murahashi *et al.*, 1995).

Either direct sampling of diesel exhaust or sampling in traffic where diesel vehicles are most prevalent in California will be required to estimate the maximum exposure to these combustion-emitted nitro-PAH.

4. CONCLUSIONS

Ambient PAH Concentrations

As was noted in the results section above, several of the targeted PAH were not observed in the ambient samples from Riverside. In general, the PAH concentrations measured were significantly below those measured approximately 10 years ago at several locations throughout California (Final Report, CARB Contract No. A5-185-32, May 1988). Table 19 repeats our Riverside data and shows data from two sites in California from our earlier study. These sites, Concord and Mammoth Lakes, were chosen to represent an industrial site and a site impacted by wood smoke, respectively, and these sites experienced the highest PAH levels in our prior study. Our inability to detect perylene and indeno[1,2,3-*cd*]fluoranthene in our Riverside samples is consistent with the relatively low levels of these two PAH found in Concord and at Mammoth Lakes where, for example, benzo[*a*]pyrene was 5-10 fold higher in ambient concentration.

The strength of emission sources and meteorology (for example, whether an inversion is present) both will influence ambient PAH concentrations. It is of interest to compare our present Riverside data with the range of data previously obtained. Table 20 compares ambient concentrations of selected PAH measured at Riverside with the minimum and maximum from our previous measurements at Glendora, Yuba City, Concord, Mammoth Lakes, Oildale and Reseda, and at the "clean" background site at Pt. Arguello. Clearly, a large range of ambient concentrations of PAH occur in California, varying geographically and seasonally. Because, unlike the nitro-PAH, there is no *in situ* formation of the PAH, maximum exposures occur in areas of maximum emission sources under meteorological conditions favoring atmospheric inversions. The highest PAH concentrations we have measured in California occurred in a Mammoth Lakes nighttime sample when woodsmoke was the dominant emission source. Another site where high ambient PAH concentrations were observed was Concord, CA, an area impacted by industrial emission sources. Aside from Pt. Arguello, where the winds are normally off the Pacific Ocean, the lowest ambient PAH concentrations previously measured were at Reseda and Oildale. Our Riverside PAH concentrations are up to a factor of four lower than those previously measured in Reseda and Oildale, suggesting that PAH emissions into the Los Angeles air basin may have decreased somewhat in the past decade.

Table 19. PAH targeted for quantification. Results from Riverside, CA (day and night samples), together with highest ambient concentrations reported in California.

PAH	MW	Riverside day (pg m^{-3})	Riverside night[a] (pg m^{-3})	Concord[b] (pg m^{-3})	Mammoth Lakes,CA[c]
benz[*a*]anthracene	228	39	34	9,700	18,300
chrysene + triphenylene[d]	228	80	83	13,500	23,600
chrysene	228	61[d]	45[d]		
triphenylene	228	15[d]	15[d]		
benzo[*a*]pyrene	252	36	44	8,150	12,490
benzo[*e*]pyrene	252	130	170	5,760	8,000
Σbenzo[*b*+*j*+*k*]fluoranthenes[e]	252	360	400	15,530	23,200
perylene	252			1,670	2,760
indeno[1,2,3-*cd*]fluoranthene	276			750[f]	2,000[f]
indeno[1,2,3-*cd*]pyrene	276	87	84	6,240[f]	12,310[f]
benzo[*ghi*]perylene	276	98	124	7,670[f]	11,350[f]
dibenz[*a,h* + *a,c*]anthracene[g]	278	8.2	7.8	910[f]	3,550[f]
dibenz[*a,j*]anthracene[h]	278	5.5	6.0	1,930[f]	2,030[f]
benzo[*b*]chrysene	278	3.0	2.9	580[f]	2,150[f]
benzo[*c*]chrysene	278	2.8	2.4	300[f]	740[f]
dibenzo[*a,e*]pyrene	302	1.7	3.6		
dibenzo[*a,h*]pyrene	302	<0.5	<0.5		
dibenzo[*a,i*]pyrene	302	<0.5	<0.5		
dibenzo[*a,l*]pyrene	302	18	18		

[a] Average of two separate determinations using two different quadrants of the megasampler.
[b] Data from Concord, industrial site with photochemical pollution (Atkinson *et al.*, 1988).
[c] Data from Mammoth Lakes woodsmoke impacted nighttime sample (Atkinson *et al.*, 1988).
[d] Isomers co-eluted on DB-5 column, separate quantifications made using a Smectic column.
[e] The benzofluoranthenes were not well resolved and their concentrations have been summed.
[f] Lower limit, deuterated internal standard not used to correct for <100% recovery from HPLC.
[g] Dibenz[*a,c*]anthracene and dibenz[*a,h*]anthracene co-eluted; their concentrations were summed.
[h] Dibenz[*a,j*]anthracene was not on targeted list of PAH.

Table 20. Comparison of selected PAH concentrations at Riverside with those previously measured throughout California.

PAH	MW	Riverside day (pg m^{-3})	Riverside night (pg m^{-3})	Range[a] (pg m^{-3})	Pt. Arguello[b] day, night
benz[*a*]anthracene	228	39	34	130-18,300	4, 10
chrysene + triphenylene	228	80	83	300-23,600	50, 50
benzo[*a*]pyrene	252	36	44	130-12,490	n.d.
benzo[*e*]pyrene	252	130	170	250-8,000	5, 8
Σbenzo[*b*+*j*+*k*]fluoranthenes	252	360	400	430-23,200	n.d.
indeno[1,2,3-*cd*]pyrene	276	87	84	110-12,310	n.d.
benzo[*ghi*]perylene	276	98	124	230-11,350	n.d., 2
dibenz[*a,c* + *a,h*]anthracene	278	8.2	7.8	8-3,550	n.d.

[a] The lowest and highest concentrations measured at Glendora, Yuba City, Concord, Mammoth Lakes, Oildale, or Reseda, CA. The highest values are all from Mammoth Lakes, the lowest values are generally from Reseda.

[b] Clean air site with winds normally off the Pacific Ocean.

Ambient Nitro-PAH Concentrations

Table 21 lists the nitro-PAH targeted for analysis on the basis of their potency equivalence factors (PEF) as well as 2-nitrofluoranthene. While it is important to understand the concentrations of these nitro-PAH, the health implications of those nitro-PAH for which PEFs are not available, such as 2-nitrofluoranthene, should also be of concern. Nitro-PAH whose source is atmospheric formation dominated at Riverside and the other sites throughout California that were sampled. Significantly more abundant than the nitro-PAH listed in Table 21 are 1- and 2-nitronaphthalene and the methylnitronaphthalenes (Arey *et al.*, 1987; Atkinson *et al.*, 1988; Gupta *et al.*, 1995).

In Tables 21 and 22 the data obtained on the Riverside particle extracts are given together with data mainly from our previous CARB contract (Contract No. A5-185-32, Atkinson *et al.*, 1988). It is clear that the pollution levels reached in Riverside were significantly less than the highest levels observed in our previous work (note that in our previous study we sampled only when the meteorology was most favorable for pollution). For example, in Concord, CA we measured 7-nitrobenz[a]anthracene levels more than seven times greater than we found in Riverside, and in Concord and Torrance we found 1-nitropyrene levels over an order of magnitude greater. If the maximum risk is to be calculated, the earlier data is more appropriate.

Table 22 shows that the nitropyrene and nitrofluoranthene concentrations measured in Riverside were within the range previously observed throughout California. This may be contrasted with the PAH levels which were consistently lower than those measured in our previous study. The elevated nighttime level of 2-nitrofluoranthene, compared to 1- and 2-nitropyrene, suggests nighttime formation of 2-nitrofluorathene from the NO_3 radical-initiated reaction. A more complete understanding of how present control strategies will affect ambient OH radical and NO_3 radical concentrations is needed to quantitatively understand the formation rates of those PAH, such as 2-nitrofluoranthene, 2-nitropyrene, the nitronaphthalenes and methylnitronaphthalenes, which are formed *in situ* in the atmosphere.

Table 21. Nitro-PAH targeted for quantification. Results from Riverside, CA particle extract analysis, together with highest ambient concentrations reported in CA. Additionally, the probable source of the nitro-PAH are noted.

Nitro-PAH	M.W.	Riverside Sample[a] (pg m^{-3})	Ambient Sample (pg m^{-3}) CA Location[b]	Source[c]
5-Nitroacenaphthene	199	0.88		
3-Nitrobiphenyl	199	0.46	1,200[d] Glendora 6,000[d] Torrance[e]	A.R.
2-Nitrofluorene	211	none detected	≤20 Σ isomers Long Beach[f]	D.E.,A.R.[g]
9-Nitroanthracene	223	23, 49	660 Concord	D.E.
9-Nitrophenanthrene	223	none detected	180 Houston, TX[h]	D.E.[i]
2-Nitrofluoranthene	247	36, 116	2,000 Glendora	A.R.
1-Nitropyrene	247	4.4, 3.2	45 Concord 60 Torrance[e]	D.E.
2-Nitropyrene	247	4.2, 3.8	81 Concord 60 Torrance[e]	A.R.
4-Nitropyrene	247	≤1.6	<5 Torrance[e]	A.R.[g]
7-Nitrobenz[a]anthracene	273	≤5.8	44 Concord	D.E.
6-Nitrochrysene	273	≤5.4	none detected in CA	D.E.
1,6-Dinitropyrene	292	none detected	see text	D.E.
1,8-Dinitropyrene	292	none detected	see text	D.E.
6-Nitrobenzo[a]pyrene	297	none detected	only trace levels detected in CA	D.E.

[a] Quantified from filter sample.

[b] Data from Atkinson *et al.*, 1988, unless noted otherwise.

[c] D.E. = reported in diesel exhaust; A.R. = an atmospheric reaction product.

[d] Quantified in a gas-phase (PUF plug) sample.

[e] Torrance, CA (Arey *et al.*, 1987).

[f] Data taken during SCAQS study (Helmig *et al.*, 1992). No 2-nitrofluorene detected.

[g] Minor isomer formed from radical-initiated reaction.

[h] Mean value for Fall in Houston, TX; sum of vapor plus particle phase (Wilson *et al.*, 1995).

[i] Two unspecified nitrophenanthrene isomers reported (Paputa-Peck *et al.*, 1983).

Table 22. Comparison of the ambient concentrations of 1- and 2-nitropyrene and 2-nitrofluoranthene measured at Riverside with previous measurements throughout California. 2-Nitrofluoranthene and 2-nitropyrene are expected to be the result of atmospheric formation, 1-nitropyrene is expected to be from direct emission sources.

Nitro-PAH	Riverside day, night	Range	Pt. Arguello[a] day, night
2-nitrofluoranthene	36, 116	17-2,000	3.6, 5.6
1-nitropyrene	4.4, 3.2	4.9-45	0.65, 0.33
2-nitropyrene	4.2, 3.8	1.0-81	0.29, n.d.

[a] Clean air site with winds normally of the Pacific Ocean.

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Glossary of Terms, Abbreviations and Symbols

fmole	Femtomole
GC	Gas chromatography
GC/MS	Gas chromatography with mass spectrometric detection
Hi-vol	High-volume sampler
HPLC	High performance liquid chromatography
ng	Nanogram (10^{-9} g)
Nitro-PAH	Nitrated polycyclic aromatic hydrocarbons
NO_2	Nitrogen dioxide
NO_3	Nitrate radical
OH	Hydroxyl radical
O_3	Ozone
PAH	Polycyclic aromatic hydrocarbons
PEF	Potency equivalency factor
pg	Picogram (10^{-12} g)
SIM	Selected ion monitoring