APPENDIX II

Historical Trends in Toxic Air Contaminants and Cancer Risks in the South Coast Air Basin and Vicinity

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Introduction

From 1986 to 1987, the District conducted a Multiple Air Toxics Exposure Study (MATES) to determine the Basin-wide risks associated with major airborne carcinogens (SCAQMD, 1987). A method to identify the magnitude of the air toxics impacts from individual chemical species and emission source categories was developed and applied to the Basin. The method integrated ambient concentrations, population distribution, and health risk data for individual chemical species into regional estimates of inhalation exposure, risk, and number of excess cancer cases. Of the 20 air toxics studied,[1] benzene emissions (primarily from mobile sources - 50 to 56 percent) and hexavalent chromium (primarily from stationary sources - 86 percent) appear to have had the greatest impact on the Basin's population at that time. One of the recommendations of the MATES study was to maintain ambient monitoring networks for selected gaseous organics and include ambient toxic metal compounds as well. The State of California Air Resources Board (ARB) has maintained such a network since the late 1980's. In this chapter, the eight years of toxic data collected by the ARB is analyzed. Looking at this rich historical data set provides perspective for the current monitoring and modeling efforts of MATES-II.

Data and Methods

Six of the approximately 20 sites in ARB's statewide toxics monitoring network are in the South Coast Air Basin (Basin) and vicinity as shown in Figure 1. Simi Valley is included in this analysis since it is just outside the western edge of the Basin and represents conditions in the western end of the San Fernando Valley. The measurements consist of 24-hour integrated samples collected once every 12 days. Table 1 lists the toxic air contaminants (TAC) sampled. The carcinogens in the table are identified with an asterisk. Tables 2 and 3 summarize the instrumentation and chemical methods used in ARB's sampling program.

For computational purposes, measurements below minimum detection levels (MDLs) are assumed to be one-half the respective MDL. The MDLs for the pollutants sampled are given in Table 4. Unit risk factors (URFs) for calculating cancer risks are the latest estimates from the State of California Office of Environmental Health Hazard Assessment (see also Table 4).

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[1] Organics - benzene, carbon tetrachloride, chloroform, ethylene dibromide, ethylene dichloride, methyl bromide, methylene chloride, perchloroethylene, toluene, 1,1,1-Trichloroethane, vinyl chloride, xylenes
Metals - arsenic, beryllium, cadmium, chromium, lead, mercury, nickel

Temporal Trends in Cancer Risks and Toxic Air Contaminants

Cancer risks from the individual species are estimated from the annual concentrations and their respective URFs. The trends in cancer risks for the five Basin stations and Simi Valley of the South Central Coast Air Basin are shown in Figure 2. Cancer risks are itemized by the six most important TACs (i.e., benzene, 1,3-butadiene, hexavalent chromium, carbon tetrachloride, perchloroethylene, and para-dichlorobenzene) and three lumped categories. The lumped category labeled "Other VOCs" consists of chloroform, ethylene dibromide, ethylene dichloride, methylene chloride, and trichloroethylene; the category called "Other PM" consists of arsenic, beryllium, cadmium, nickel, and lead; and lastly the category named "PAHs" consists of benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, and ideno(1,2,3-cd)pyrene. The cancer risks shown in Figure 2 are estimated from the TACs measured by the ARB. There are pollutants such as, diesel particulate matter that is now considered carcinogenic but was not measured in the past.

Cancer risks have decreased significantly at all stations since 1990. Specifically, risks have decreased by 63, 44, 56, 48, 56, and 48 percent at Burbank, Los Angeles, Long Beach, Rubidoux, Simi Valley, and Upland, respectively. The improvement is primarily from reductions in benzene and 1,3-butadiene concentrations (70 to 80 percent) and secondarily from decreases in hexavalent chromium concentrations (8 to 20 percent). However, ambient exposure to most of the measured TACs has decreased since 1990, as shown in Figure 3.

Figure 3 shows the network means[2] for each year along with its 90 percent two-tailed confidence interval. Statistically significant reductions in mean concentrations have occurred over the period 1990 to 1997 for the following TACs: 1,3 butadiene, benzene, carbon tetrachloride, methylene chloride, perchloroethylene, trichloroethylene, hexavalent chromium, lead, and nickel. State and District regulations that have contributed to these significant improvements are discussed in the last section of this chapter.

It is not clear from Figure 3 if there has been any reductions in the ambient concentrations of chloroform, para-dichlorobenzene, or selenium. However, the trends may be affected by the number of samples below detection levels. The frequency in which ambient concentrations have been detected is also an indicator of the concentration trends. Figure 4 shows the frequency of detection for each year for chloroform, para-dichlorobenzene, and selenium. Increasing frequency of detection implies increasing ambient concentrations, while decreasing frequency of detection iindicates decreasing concentrations. As shown in Figure, there has been a tendency for increasing frequency of detection of ambient chloroform over time, while para-dichlorobenzene has been detected less frequently recently. This implies increasing concentrations of chloroform and decreasing concentrations of para-dichlorobenzene. There is no discernible trend in selenium in Figure 4.

[2] The network means are an annual average of six sites consisting of Burbank, Los Angeles, Long Beach, Rubidoux, Upland, and Simi Valley. Rubidoux is missing from the 1997 network average since sampling did not take place there in that year.

Species and Source Apportionment

Species apportionment of the 1997 cancer risks at the six sites is shown in Figure 5.[3] The pie charts shown also include risks from the carbonyls of formaldehyde and acetaldehyde. These species were first measured in 1996 and so were not shown in the cancer risk trends in Figure 2. Peak cancer risks occur at Burbank and Los Angeles with risks of 411 and 412 in one million, respectively. Lowest cancer risks occur in Simi Valley where risks are estimated to be 164 in one million. The sites of Long Beach, Rubidoux, and Upland have intermediate risks ranging from 274 (Rubidoux) to 316 (Long Beach) in one million. Generally, the source regions have the highest risks and the downwind sites have lower risks, although the Long Beach site has 23 percent lower risks than the other source region sites of Burbank and Los Angeles. Note that 60 to nearly 80 percent of the cancer risks at these six sites comes from ambient concentrations of benzene, 1,3 butadiene, formaldehyde, and acetaldehyde. On-road mobile sources are the primary source of these TACs as is shown in Chapter 4.

Regulatory Explanation

State and local rules and regulations that have contributed to the significant air quality improvements shown in Figures 2 and 3 are listed in Table 5. The table provides the assembly bill, senate bill, or District rule number; a brief description; and lists the TACs affected the rule or regulation.

The State of California LEV regulation has contributed to the continuous benzene reductions observed in the Basin and vicinity. On-road VOC emissions, which includes benzene, are estimated to have decreased 49 percent over the period 1990 to 1997 (SCAQMD, 1996). This has been accomplished inspite of a 9 percent increase in vehicle miles traveled and a 5 percent increase in vehicle trips (SCAQMD, 1996). District Rule 461 has also contributed to the improved benzene air quality.

California Phase 2 reformulated gasoline was fully in effect by April 1, 1996. Its effects on ambient cancer risks are clearly discernible from Figure 2 by the large reductions in risk at all six sites in 1996 and in Figure 3 by the large reductions in 1,3 butadiene and benzene. Total cancer risk reductions from 1995 to 1996 ranged from 19 percent at Los Angeles to 35 percent at Burbank. Norbeck et al. (1998) showed that 1995 gasoline was a transitional blend that met many of the ARB RFG Phase 2 fuel requirements, so to better assess the effects of RFG one should compare the 1994 and 1996 cancer risks. From 1994 to 1996, total cancer risk reductions ranged from 22 percent at Los Angeles to 41 percent at Burbank as a result of a 31 to 52 percent reduction in benzene and a 14 to 37 percent reduction in 1,3 butadiene, depending on the site considered (see Figure 3). ARB (1991, 1993) forecasted a nearly 50 percent reduction in benzene and 25 percent reduction in 1,3 butadiene with the introduction of Phase 2 RFG. These expectations agree quite well with the observations in the Basin and vicinity. The basinwide cancer risk reductions are estimated to be over 85 in one million as a result of the 1,3 butadiene and benzene emission reductions resulting from the introduction of reformulated gasoline.

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[3] The cancer risks in Figure 4 are for 1997 except at Rubidoux, which are 1996 cancer risks. Sampling did not take place in 1997 at Rubidoux.

The 66 percent reduction in hexavalent chromium concentrations in the Basin (see Figure 3) is equivalent to a 40 in one million reduction in cancer risk. District Rules 1401, 1404, and 1469 and Assembly Bill 2588 are responsible for these reductions. AB 2588 has had an indirect impact in the overall reduction of toxic pollutants in the Basin. Although not mandated by AB 2588 to reduce emissions or risks, many facilities have voluntarily instituted risk reduction activities before reaching the need for public notice. These permanent, verifiable, and enforceable emission and risk reductions may be incorporated into the final health risk assessment, thereby reducing the risks. Since July 1988 (the due date of the first inventories) and by virtue of all the risk reduction activities taken, the overall risk reduction in the Basin (of several toxic emissions) has been partially caused by AB 2588.

Finally, looking at Figure 3 and Table 5, Rules 1175, 1421, 1407, and 1420 contributed directly to the statistically significant reductions since 1990 in methylene chloride, perchloroethylene, nickel, and lead, respectively.

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Table 1. Toxic Air Contaminants Measured by the Air Resources Board.

Toxic VOCs		Toxic PM	
1,3 Butadiene*	Para-Dichlorobenzene*	Aluminum (Al)	Nickel (Ni)*
Benzene*	Para-Xylene	Antimony (Sb)	Phosphorous (P)
Carbon Tetrachloride*	Perchloroethylene*	Arsenic (As)*	Potassium (K)
Chlorobenzene	Styrene	Barium (Ba)	Rubidium (Rb)
Chloroform*	Toluene	Beryllium (Be)*	Selenium (Se)
Ethyl Benzene	Trichloroethylene*	Bromine (Br)	Silicon (Si)
Ethylene Dibromide*		Calcium (Ca)	Strontium (Sr)
Ethylene Dichloride*		Cadmium (Cd)*	Sulfur (S)
Meta-Dichlorobenzene		Chlorine (Cl)	Tin (Sn)
Meta-Xylene		Chromium (Cr)	Titanium (Ti)
Meta-, para-Xylene		Hexavalent Chromium*	Uranium (U)
Methyl Chloroform		Copper (Cu)	Vanadium (V)
Methyl Ethyl Ketone		Lead (Pb)*	Yttrium (Y)
Methylene Chloride*		Mercury (Hg)	Zinc (Zn)
Ortho-Dichlorobenzene		Manganese (Mn)	Zirconium (Zr)
Othro-Xylene		Molybdenum (Mo)	

* carcinogen

Table 2. Monitoring Methods of Organic TACs.

	Volatile Organic Compounds (VOCs)			Carbonyl Compounds	Polynuclear Aromatic Hydrocarbons (PAHs)
Parameter measured	Aromatic & Halogenated Compoundas	1,3 Butadiene	Oxygenates (MTBE, ETBE, & TAME)	Acetaldehyde, Formaldehyde, & Methyl ethyl ketone	Benzo(a)pyrene Benzo(b)fluoranthene Benzo(k)fluoranthene Dibenzo(a,h)anthracen eBenzo(g,h,I)perylene Indeno(1,2,3-cd)pyrene
Sampling Schedule	Every 12 days			Every 12 days	Every 12 days
ARB Collection Method	XonTech 910A Gaseous Sampler			XonTech 920 TAC Sampler	High Volume Size Selective Inlet Sampler
Sampling Media	Polished Stainless Steel Canister			DNPH-Coated Silica Gel Cartridges	Quartz Microfiber Filter 8 x 10 inches
ARB Analysis Method	Method 052 Crygenic Trap Preconcentration Capillary GC/PID-ECD	Method 051 Cryogenic Trap Preconcentration Capillary GC/PID	Method 050 Cryogenic Trap Preconcentration Capillary GC/FID	Method 022 HPLC/Ultraviolet Detector	Method 028 HPLC/Fluorescence Detector
Data Availability	Technical Support Division, Air Quality Data Branch, (916) 322-6076: U.S. EPA Aerometric Information Retrieval System (AIRS)				

Table 3. Monitoring Methods of Toxic Metals.

Parameter Measured	Al, As, Ba, Br, Ca, Cl, Co, Cr, Cu, Fe, Hg, K, Mn, Mo, Ni, P, Pb, Rb, S, Sb, Se, Si, Sn, Sr, Ti, U, V, Y, Zn, Zr	Chromium VI	Arsenic (As) Beryllium (Be) Cadmium (Cd)
Sampling Schedule	Every 12 Days		Every 12 Days
ARB Collection Method	XonTech 920 TAC Sampler		High Volume Total Particulate Sampler
Sampling Media	Teflon Filter, 37 mm	Cellulose Filter, 37 mm	Glass Fiber Filter, 8 x 10 inch
ARB Analysis Method	Method 034 X-ray Fluorescence	Method 039 Ion Chromatography	Method 005 Graphite Furnace Atomic Absorption/ ZEEMAN
Data Availability	Technical Support Division, Air Quality Data Branch, (916) 322-6076: U.S. EPA Aerometric Information Retrieval System (AIRS)		

Table 4. Minimum Detection Levels and Unit Risk Factors.

Toxic Air Contaminant	Minimum Detection Level	Unit Risk Factor $(\mu g/m^3)^{-1}$
1,3 Butadiene	0.04 ppb	1.7×10^{-4}
Acetaldehyde	N/A	2.7×10^{-6}
Benzene	0.5 ppb	2.9×10^{-5}
Carbon Tetrachloride	N/A	4.2×10^{-5}
Chloroform	0.02 ppb	5.3×10^{-6}
Ethylene Dibromide	0.01 ppb	7.1×10^{-5}
Ethylene Dichloride	0.2 ppb	2.2×10^{-5}
Formaldehyde	N/A	6.0×10^{-6}
Methylene Chloride	1 ppb	1.0×10^{-6}
Para-Dichlorobenzene	0.2 ppb	1.1×10^{-5}
Perchloroethylene	N/A	5.9×10^{-6}
Trichloroethylene	0.02 ppb	2.0×10^{-6}
Arsenic (As)	0.2 ng/m^3	3.3×10^{-3}
Beryllium (Be)	0.02 ng/m^3	2.4×10^{-3}
Cadmium (Cd)	0.2 ng/m^3	4.2×10^{-3}
Hexavalent Chromium	0.2 ng/m^3	1.5×10^{-1}
Nickel (Ni)	2 ng/m^3	2.6×10^{-4}
Lead (Pb)	4 ng/m^3	1.2×10^{-5}
Selenium (Se)	2 ng/m^3	N/A
Benzo(a)pyrene	0.2 ng/m^3	1.1×10^{-3}
Benzo(b)fluoranthene	0.2 ng/m^3	1.1×10^{-4}
Benzo(k)fluoranthene	0.2 ng/m^3	1.1×10^{-4}
Dibenzo(a,h)anthracene	0.2 ng/m^3	3.9×10^{-4}
Indeno(1,2,3-cd)pyrene	0.2 ng/m^3	1.1×10^{-4}

Table 5. Summary of ARB and District Rules and Regulations Controlling TACs.

AB/SB/Rule	Description	Affetced TACs
LEV	Implemented in 1990, it established four categories of vehicle classes and associated tailpipe standards applicable to future automobiles sold in California.	VOCs
CGB	Required the sale of clean burning gasoline in California beginning April 1, 1996. Clean burning gasoline significantly reduced emissions of the toxic compounds of 1,3 butadiene and benzene.	1,3 butadiene, benzene
AB 2588	Air Toxics "Hot Spots" Information and Assessment Act of 1987 – requires facilities to inventory the TACs that they emit, assess its local impact, and notify the affected population.	Many TACs
SB 1731	Airborne Toxics Risk reduction Audit and Plan Act – requires facilities to perform an audit and plan for risk reduction based on the risks presented in a health risk assessment.	Many TACs
Rule 461	Gasoline Transfer and Dispensing – requires all gasoline transfer devices be equipped with Phase I and Phase II vapor recovery systems and to institute good operating, reporting, and recordkeeping practices	Benzene
Rule 1175	Control of Emissions from the Manufacture of Polymeric Cellular (Foam) Products – prohibits the use of chlorofluorocarbons, methylene, chloride, and volatile organic compounds (VOCs) as the blowing agent in the production of foam products.	Methylene chloride
Rule 1401	New Source Review of Toxic Air Contaminants – limits the maximum individual cancer risk, cancer burden, and noncanmcer acute and chronic indices of new permit units, relocations, or modifications to existing permit units.	Many TACs
Rule 1402	Control of Toxic Air Contaminants from Existing Sources - reduces the health risk associated with emissions of toxic air contaminants from existing sources by establishing specific risk thresholds.	Many TACs
Rule 1403	Asbestos Emissions from Demolition/Renovation Activities, requires the proper survey, notification, removal, handling, disposal, and recordkeeping of asbestos-containing materials during building demolition and renovation.	Asbestos
Rule 1404	Hexavalent Chromium Emissions from Cooling Towers - prohibits the use of hexavalent chromium as a water treatment chemical in cooling towers.	Hexavalent chromium
Rule 1405	Control of Ethylene Oxide and Chlorofluorocarbon Emissions from Sterilization or Fumigation Processes - requires facilities that use ethylene oxide as a sterilizing or fumigating agent to use appropriate controls and to institute good operating and recordkeeping practices, and prohibits sterilizing or fumigating facilities from using chlorofluorocarbons as diluents.	Ethylene oxide
Rule 1406	Control of Dioxin Emissions from Medical Waste Incinerators - requires facilities that use medical waste incinerators to use appropriate controls.	Dioxins

Table 5. Concluded.

AB/SB/Rule	Description	Affetced TACs
Rule 1407	Control of Emissions of Arsenic, Cadmium and Nickel from Non-Ferrous Metal Melting Operations - requires facilities that own or operate non-ferrous metal melting equipment to use appropriate emission collection systems at all emission points and to institute good operating, reporting, and recordkeeping practices.	Arsenic, cadmium, nickel
Rule 1414	Asbestos-Containing Serpentine Material in Surfacing Applications, prohibits the use of asbestos-containing serpentine material for surfacing applications.	Asbestos
Rule 1420	Emissions Standard for Lead, requires facilities that use or process lead-containing materials to use appropriate emission collection systems at all emission points.	Lead
Rule 1421	Control of Perchloroethylene Emissions from Dry Cleaning Systems - requires perchloroethylene dry cleaning facilities to use appropriate controls; phase out old equipment; and institute good operating, reporting, and recordkeeping practices.	Perchloroethylene
Rule 1469	Hexavalent Chromium Emissions from Chrome Plating and Chromic Acid Anodizing Operations, requires chrome plating and chromic acid anodizing facilities to use appropriate controls, and institute good operating, reporting, and recordkeeping practices.	Hexavalent chromium

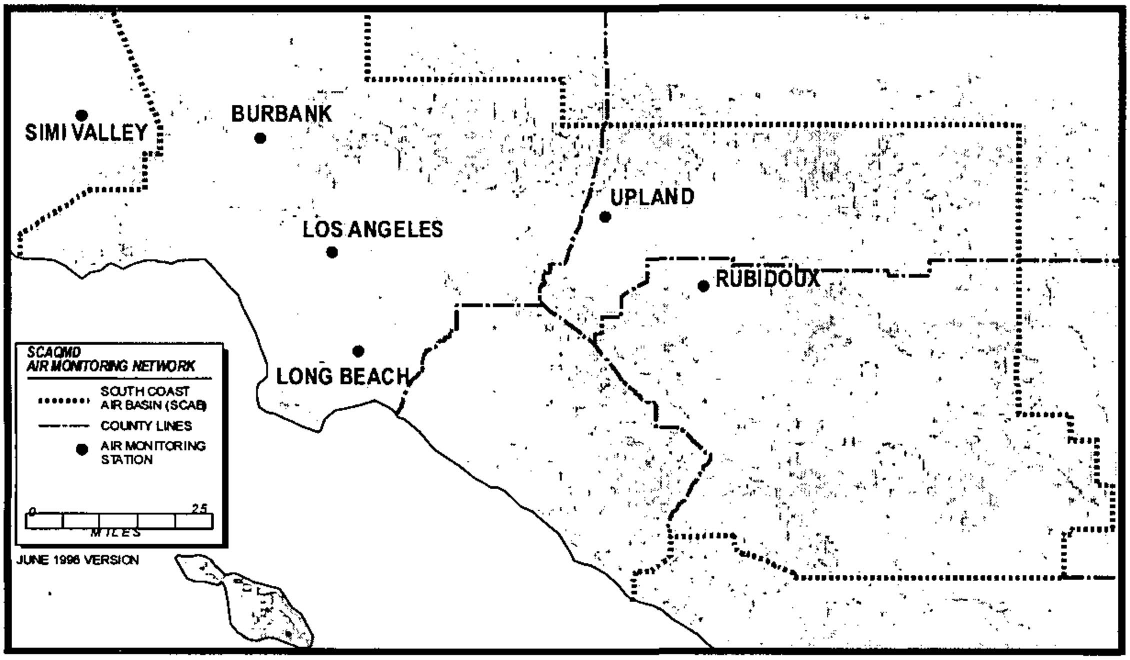


Figure 1. ARB toxic monitoring sites in the South Coast Air Basin and vicinity.

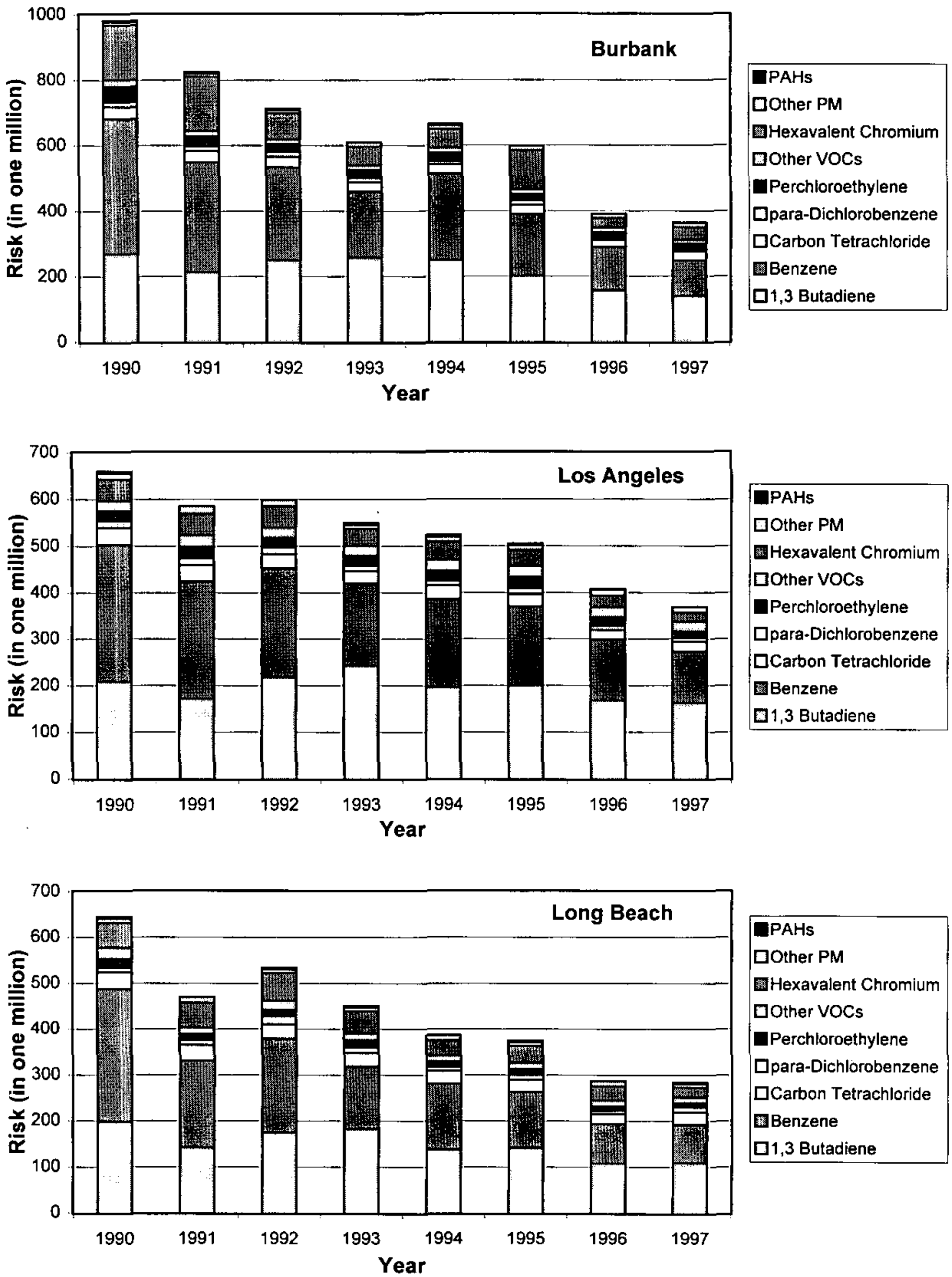
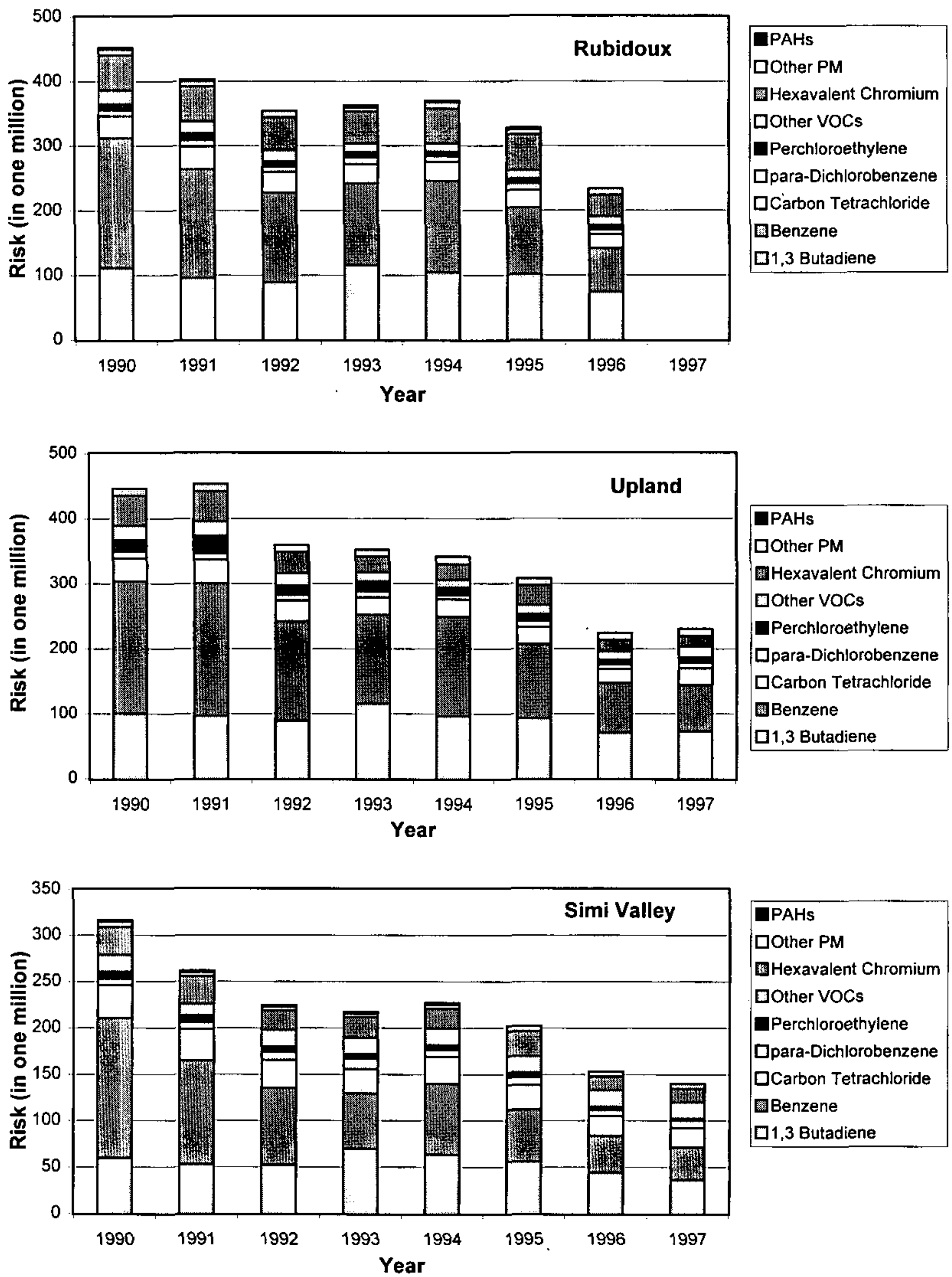


Figure 2. Trends in cancer risk in the South Coast Air Basin and vicinity.



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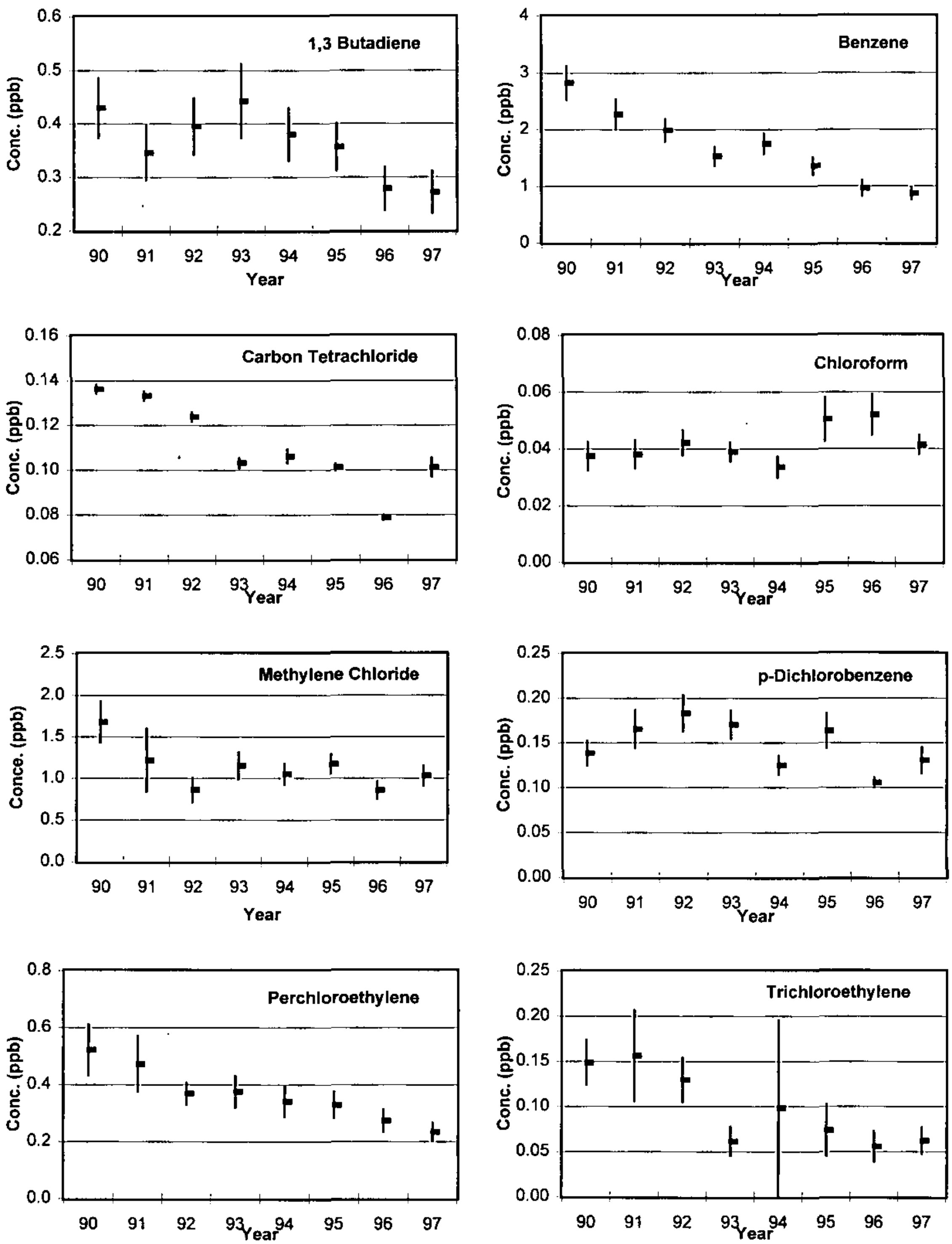
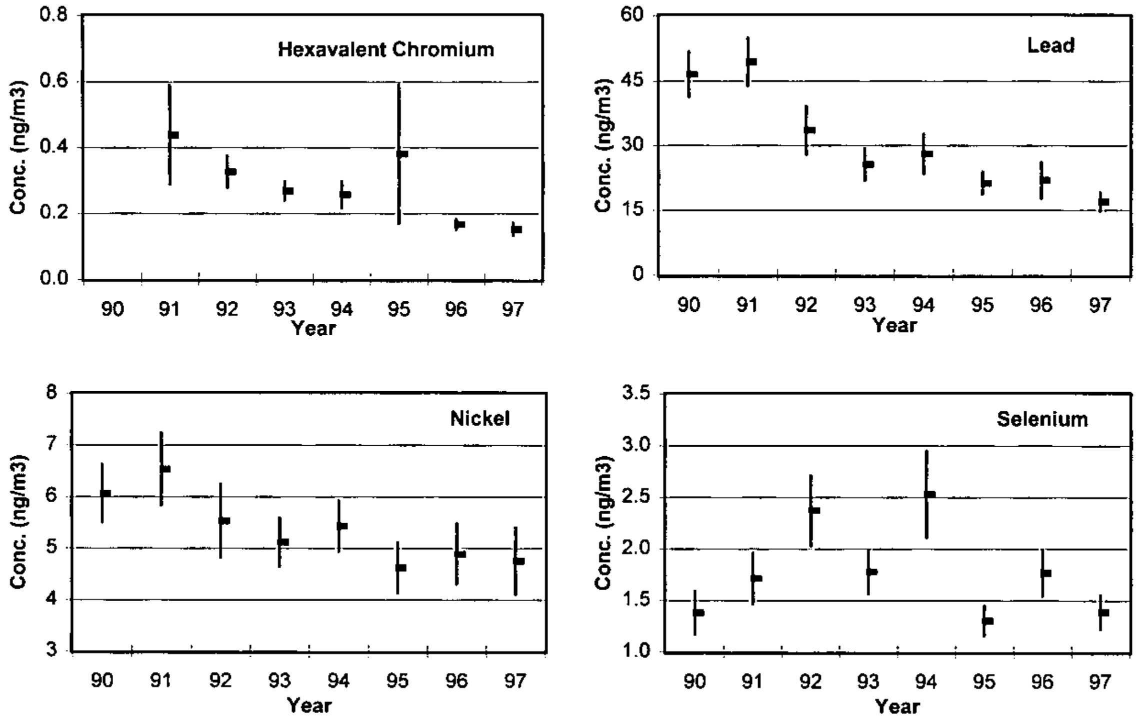


Figure 3. Trends in selected toxic air contaminants. The tick mark represents the mean and the bars represent the 90 percent confidence interval about the mean.



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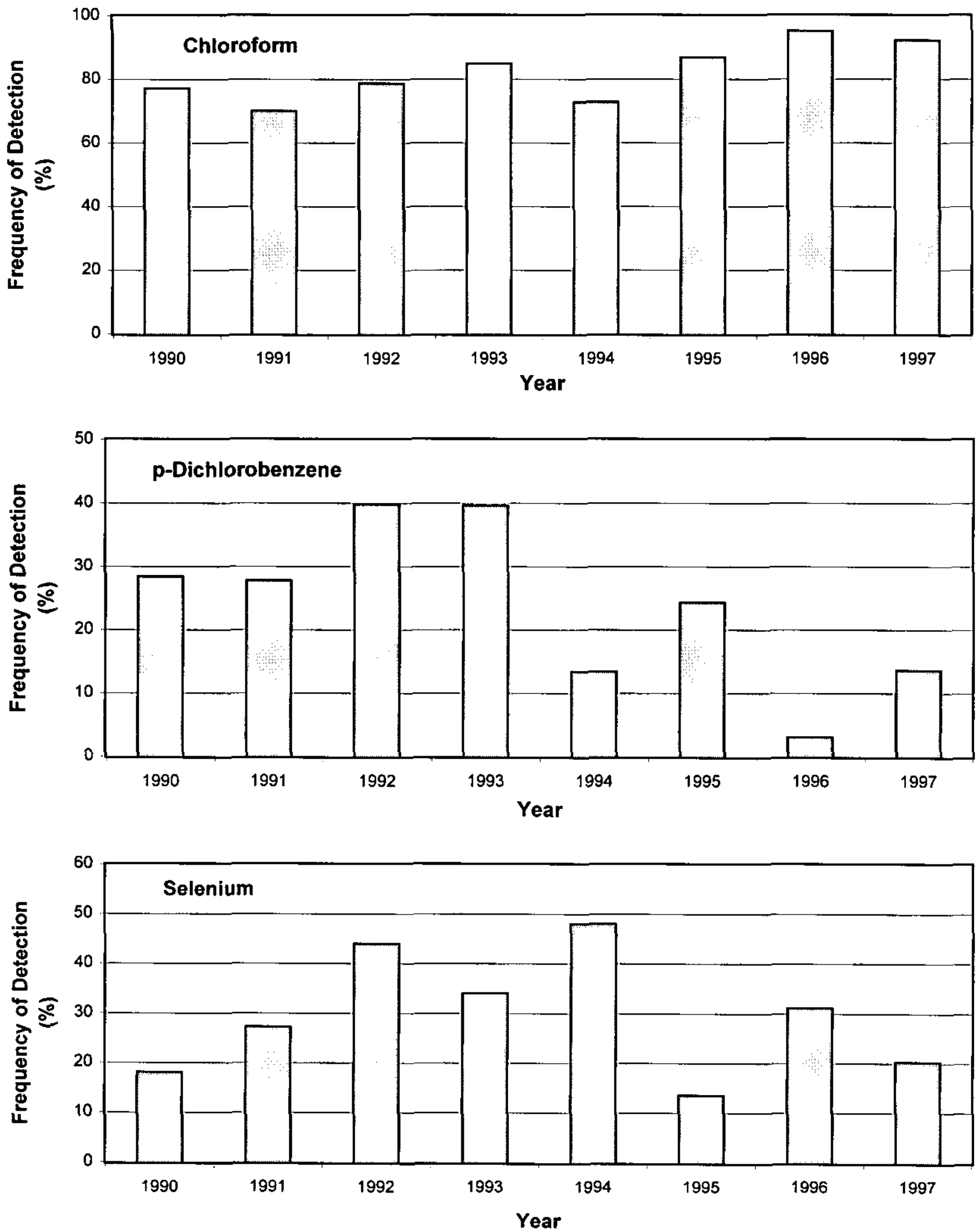

Figure 4. Frequency of detectable concentrations for selected toxics.

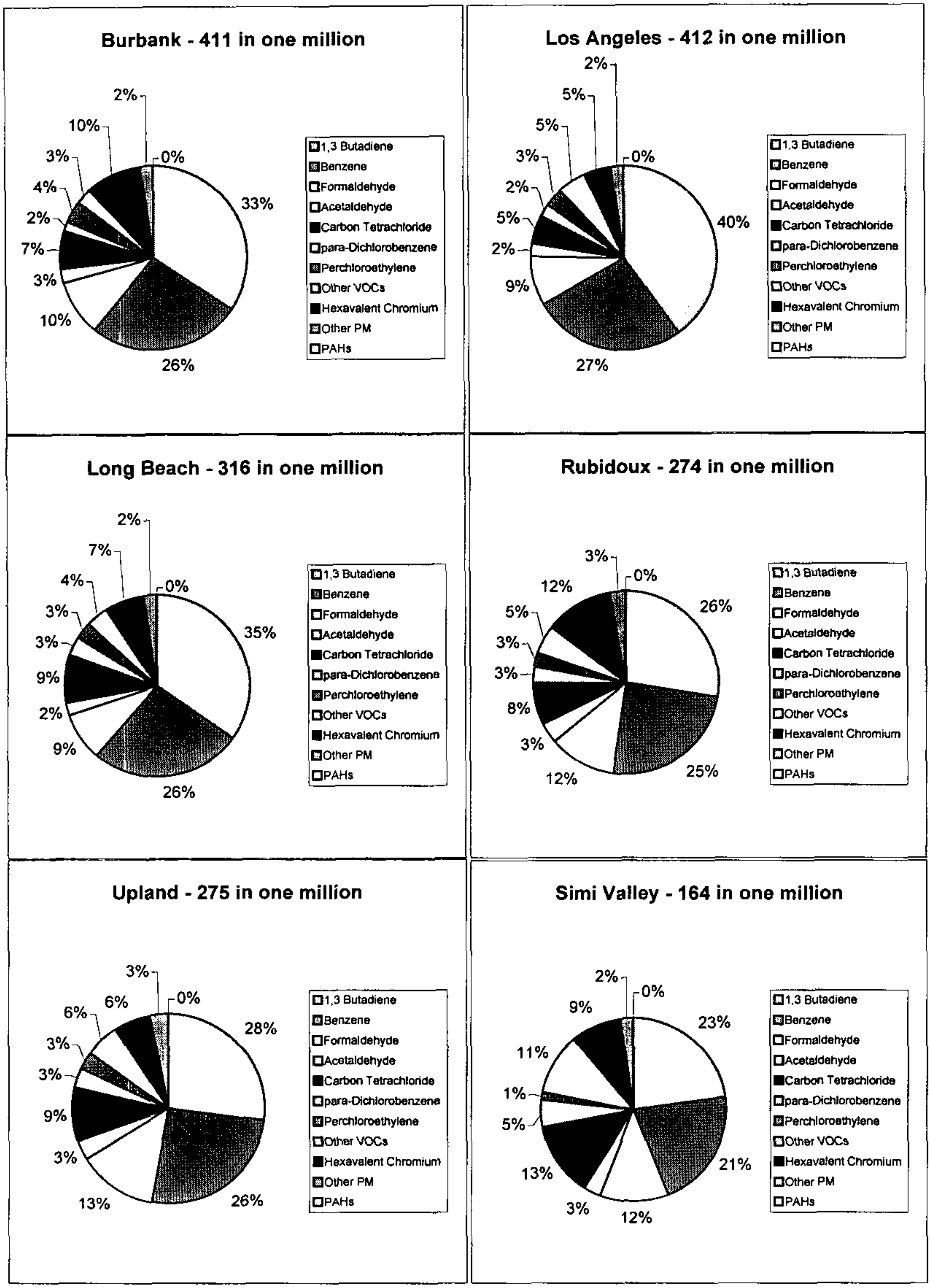

Figure 5. Species apportionment of 1997 cancer risk in the South Coast Air Basin and vicinity.