



**California Air Resources Board**

## **Technical Support Document**

# **Proposed Identification of Inorganic Arsenic as a Toxic Air Contaminant**

### **Part A Exposure Assessment**

**State of California  
Air Resources Board  
Stationary Source Division**

**May 1990**

REPORT TO THE AIR RESOURCES BOARD  
ON INORGANIC ARSENIC

PART A  
PUBLIC EXPOSURE TO AIRBORNE INORGANIC ARSENIC IN CALIFORNIA

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May 1990

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REPORT TO THE AIR RESOURCES BOARD  
ON INORGANIC ARSENIC

Part A

Public Exposure to, Sources of, and Atmospheric Fate of Airborne Inorganic Arsenic in California

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## INTRODUCTION AND SUMMARY

This report summarizes the Air Resources Board (ARB) staff investigation to determine whether inorganic arsenic should be identified as a toxic air contaminant pursuant to California law. A toxic air contaminant (TAC) is defined by state law as an air pollutant that may cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health.

Although arsenical skin treatments and other medical preparations containing arsenic have been used for centuries, it is the use of arsenic as a human poison that has given it such an infamous reputation. The acute and adverse health effects that have resulted from large doses of arsenic have been well documented in history and literature.

Our investigation of inorganic arsenic was prompted by a concern that low-level exposure to inorganic arsenic in ambient air may also cause adverse health effects. Additionally, identification of inorganic arsenic as a toxic air contaminant is required by Health and Safety Code Section 39655, since it has been identified as a hazardous air pollutant under Section 112 of the U.S. Clean Air Act.

"Part A" of this report presents an assessment of public exposure to inorganic arsenic in California's ambient air. Included in this assessment is an examination of the major arsenic sources in California, and the atmospheric fate of inorganic arsenic. "Part B," prepared by the Department of Health Services (DHS), presents a health assessment of public exposure to airborne inorganic arsenic. The public exposure levels presented in Part A of this report are used, in conjunction with potency values for inorganic arsenic (developed by DHS and other health agencies), to estimate the health risks posed to the people of California from exposure to airborne inorganic arsenic.

Arsenic exists in both the organic and inorganic form, as well as the gas and particulate matter phases. Inorganic arsenic is the predominant form in the atmosphere, and the majority of this is highly respirable particulate matter 2.5  $\mu\text{m}$  or smaller. Although other arsenic compounds are briefly discussed in Part A, primary emphasis is placed on inorganic arsenic in the trivalent (+3 or III) and pentavalent (+5 or V) oxidation states because these are the predominant oxidation states of inorganic arsenic present in the atmosphere. In the air, arsenic can exist as +3 or +5 oxides, oxyacids, or salts of the oxyacids.

Arsenic trioxide ( $\text{As}_2\text{O}_3$ ), a species with arsenic in the +3 oxidation state, is the predominant inorganic arsenic compound found in high temperature emissions from smelters and combustion sources. In the air, it can react with water to form a less volatile and more water-soluble oxyacid (e.g.,  $\text{H}_3\text{AsO}_3$ ) or can be oxidized to arsenic pentoxide ( $\text{As}_2\text{O}_5$ ), a species with arsenic in the +5 state. Arsenic pentoxide is not only an oxidation product of arsenic trioxide, but can be emitted directly from certain sources.



Inorganic arsenic is commonly present in the earth's crust as a component of sulfidic ores of metals such as copper, cobalt, and nickel. The smelting of these ores releases arsenic trioxide into the environment. In fact, most arsenic trioxide used commercially is produced and refined as a side product of primary smelting of other metals. Arsenic trioxide from smelters and other high-temperature processes is initially emitted predominantly as a gas ( $As_4O_6$ ) which cools and adsorbs to existing particles, primarily fine particles 2.5  $\mu m$  or smaller which are highly respirable. Gas-phase arsenic trioxide that has not adsorbed to particles may escape capture by particulate matter control devices.

Wood and fossil-fuel combustion sources (fireplaces, woodstoves, external combustion boilers, internal combustion engines, etc.) are the major emitters of inorganic arsenic in California. Other significant sources are geothermal steam usage and release (arsenic is present in the steam reservoir and is released with the steam by steam vendors and the utilities that use the steam for production of electricity) and pesticide usage (arsenicals are used in agriculture as pesticides and herbicides). Other sources of inorganic arsenic may include secondary lead smelting operations (where metal scraps such as lead-acid batteries are used as feed materials), mining and quarry operations, windblown dust from the dry lakebeds of eastern California, cement manufacturing, agricultural burning, waste incineration and resource recovery operations.

Total airborne inorganic arsenic emissions in California are estimated to have a minimum range of at least 7.4 to 24 tons per year. Emissions of inorganic arsenic are expected to increase in California due to anticipated increases in the amounts of residual oil, municipal waste, and firewood burned. An increase in the number of resource recovery facilities is also expected to increase emissions.

Although the focus of our report is on inorganic arsenic in the atmosphere, exposure to inorganic arsenic also occurs from consumption of drinking water, food, and tobacco smoke. The drinking of water in areas with high groundwater arsenic levels (e.g., the San Joaquin valley) will result in greater intake of inorganic arsenic than does inhalation of ambient air. Much of this exposure, however, is to pentavalent arsenic (V) which is generally considered to be less toxic than the trivalent form (III).

Arsenic is present in mainstream tobacco smoke. A smoker smoking one pack of cigarettes a day may inhale 0.8 to 2.4  $\mu g$  of arsenic. Arsenic has not been measured in sidestream smoke but is presumed to be a component. The chemical forms of arsenic in tobacco smoke are probably arsenic oxides.

Diet is also a source of arsenic intake. Arsenic in food occurs primarily as complex organo-arsenicals, although inorganic forms of arsenic may be present.

The sampling and analysis method used by the ARB for inorganic arsenic is a particulate matter sampling and analysis technique that cannot differentiate between inorganic and organic arsenic species and cannot detect arsenic present in the gas phase. This is not a problem since available information suggests that most arsenic present in the atmosphere is in

inorganic form (Johnson and Braman, 1975; Andreae, 1980), and the particulate arsenic represents the majority of inorganic arsenic in the ambient air (Walsh et al., 1979; Walsh et al., 1977; Germani et al., 1981; Appel et al., 1984). The ARB's inorganic arsenic method is considered scientifically valid. In this report, we assume that the ARB's monitoring network arsenic values are reasonably representative of inorganic arsenic concentrations present in the atmosphere. Unless otherwise noted in the text, airborne arsenic emissions and concentrations are assumed to be inorganic in form.

The statewide population-weighted exposure to inorganic arsenic for 1986 (based on an exposed population of 20,339,250 people) was estimated to be 1.9 ng/m<sup>3</sup>, with a lower bound of 1.5 ng/m<sup>3</sup> and an upper bound of 2.6 ng/m<sup>3</sup>.

The highest concentrations of ambient arsenic were found in the South Coast Air Basin where the population-weighted exposure for 1986 was 2.8 ng/m<sup>3</sup> with a lower bound of 2.1 ng/m<sup>3</sup> and an upper bound of 3.8 ng/m<sup>3</sup>. Some of the state's lowest ambient arsenic concentrations in 1986 were found in the San Francisco Bay Area Air Basin where the population-weighted exposure to inorganic arsenic was 0.8 ng/m<sup>3</sup> with a lower bound of 0.6 ng/m<sup>3</sup> and an upper bound of 1.1 ng/m<sup>3</sup>.

Although the annual means were relatively close among sites, there was a large amount of variability in monthly means among sites. Analysis of the peak-to-mean concentration ratios of the 19 monitoring network sites suggest the influence of intermittent sources of inorganic arsenic. There is insufficient information available at this time to associate specific activities with these observed variations in ambient concentration.

People living near stationary facilities with airborne arsenic emissions may be exposed to high localized concentrations of inorganic arsenic well above those concentrations found in air unimpacted by the facility. The resulting "hot spot" population exposure may significantly increase the opportunity for adverse health effects to occur.

A special ARB "hot spot" monitoring study (1986) demonstrated that over 1,000 Californians living near a secondary lead smelter in the South Coast Air Basin (SoCAB) have been exposed to inorganic arsenic concentrations of up to 392 ng/m<sup>3</sup>. Later studies (1988) have shown that inorganic arsenic concentrations in the area have been reduced, but still remain several times higher than the average ambient concentration monitored in the SoCAB. ARB modeling (1989) of the secondary lead smelter emissions indicate that the population in the study area are projected to be exposed to elevated levels of airborne inorganic arsenic above the basin-wide average.

## I. EXPOSURE TO INORGANIC ARSENIC

### A. EXPOSURE TO AMBIENT INORGANIC ARSENIC IN THE ATMOSPHERE

This chapter presents an analysis of inorganic arsenic exposure levels in California based on ARB measurements (January 1986 through December 1986) of atmospheric arsenic concentrations at 19 stations statewide. Sampling frequency was generally 1 sample at each of the 19 sites, every 6 days. Sampling duration was 24 hours for each sample. Samples from the 11 Northern California and 8 Southern California sites were analyzed for arsenic using atomic absorption/graphite furnace spectroscopy by the ARB's Southern Laboratory Branch (SLB) staff. Details of the analysis method are presented in Appendix A.

#### 1. Sampling and Analysis

The data used to estimate population exposure to inorganic arsenic represents total arsenic (principally inorganic compounds) in the solid phase. The sampling-and-analysis method employed by ARB staff is based on the collection of atmospheric particulate matter on glass fiber filters using a high-volume sampler, with subsequent analysis for arsenic by atomic absorption spectrophotometry. The use of glass fiber filters may slightly over-estimate particulate arsenic concentrations in the atmosphere, since gas-phase arsenic compounds may react with or be absorbed by the filter medium.

Because the compounds of concern from a health effects standpoint are the inorganic arsenic compounds, the accuracy of the health risk assessment depends upon the method's selectivity for inorganic arsenic. There are two aspects to this selectivity: (1) inclusivity, that is, does the method measure all of the inorganic arsenic present? and (2) exclusivity, that is, does the method measure only the inorganic compounds of arsenic, excluding organic compounds of arsenic?

The ARB sampling method is a particle collection technique and does not measure gas-phase inorganic arsenic. It has been shown (Johnson and Braman, 1975) that atmospheric inorganic arsenic exists primarily in the solid phase (that is, as a component of particulate matter). We believe that the ARB sampling method is inclusive because it collects almost all of the atmospheric inorganic arsenic borne by the sample volume. Since the method collects particulate matter, solid-phase organic arsenic compounds may be present in the sample and reported by the analysis. The relative amounts of organic and inorganic arsenic compounds present in the atmosphere have been studied (Johnson and Braman, 1975). The studies indicate that atmospheric arsenic (solid and gas phase) is a maximum of 20 percent organic, even in areas where high organo-arsenic concentrations are expected. Based on ambient measurements in marine and continental atmospheres (Walsh et al., 1979) it is believed that the fraction of solid-phase organic arsenic compounds are likely to be much less than 20 percent. On this basis, we have chosen to accept the possibility of a small bias, and consider the results of the sampling-and-analysis procedure to be reasonably representative of inorganic arsenic compound concentrations.

Inorganic arsenic in the atmosphere is predominantly a mixture of trivalent (III) and pentavalent (V) arsenic (As). Knowing the predominant valence of atmospheric inorganic arsenic is important from a biological perspective, since the biological activity of each valence state may vary.

A study of As(III) and As(V) in atmospheric particulate matter collected in Tucson, Arizona demonstrated that, although As(V) is the predominant valence in the atmosphere, the relative levels of these two arsenic chemical species can vary greatly (Solomon, 1984). The Solomon study found that the ratio of As(III) to As(V) varied from less than 0.04 to 1 to as much as 0.97 to 1 with an average ratio of 0.31 to one. A 16-day ARB study (see Appendix B) at a California site of relatively high prevailing ambient inorganic arsenic concentrations, located near a secondary lead smelter in the SoCAB's City of Industry, yielded As(III)-to-As(V) ratios ranging from about 0.5 to 1 to 2.9 to 1 with an average ratio for total particulate arsenic (the sum of fine and coarse) equal to 1.2 to 1.

## 2. ARB Inorganic Arsenic Monitoring Data

Particulate arsenic data were collected at widely separated sites in the San Francisco Bay Area Air Basin (SFBAAB), the San Joaquin Valley Air Basin (SJVAB), the South Coast Air Basin (SoCAB), as well as two sites in the South Central Coast Air Basin (SCCAB), and one each in the Sacramento Valley Air Basin (SVAB) and the San Diego Air Basin (SDAB). The monitoring sites were selected because they are established criteria-pollutant monitoring sites with roughly balanced geographic distribution, in locations of high population density, and unimpacted by known industrial sources of pollutant emissions. The locations of these sites are shown in Figure I-1. On the average, 4.6 samples per month were collected at the Southern and Northern California sites.

All samples were analyzed for arsenic using atomic absorption/graphite furnace spectroscopy by Monitoring and Laboratory Division's Southern Laboratory Branch (SLB). The lowest detectable concentration, or limit of detection (LOD) for the method used by SLB was  $0.4 \text{ ng/m}^3$ , with all concentrations reported to the nearest  $0.1 \text{ ng/m}^3$ . Less than one percent of the 1031 samples collected during the 1986 time period were below the LOD; the majority of the sites (63 percent) had at least one minimum concentration below the  $0.4 \text{ ng/m}^3$  LOD.

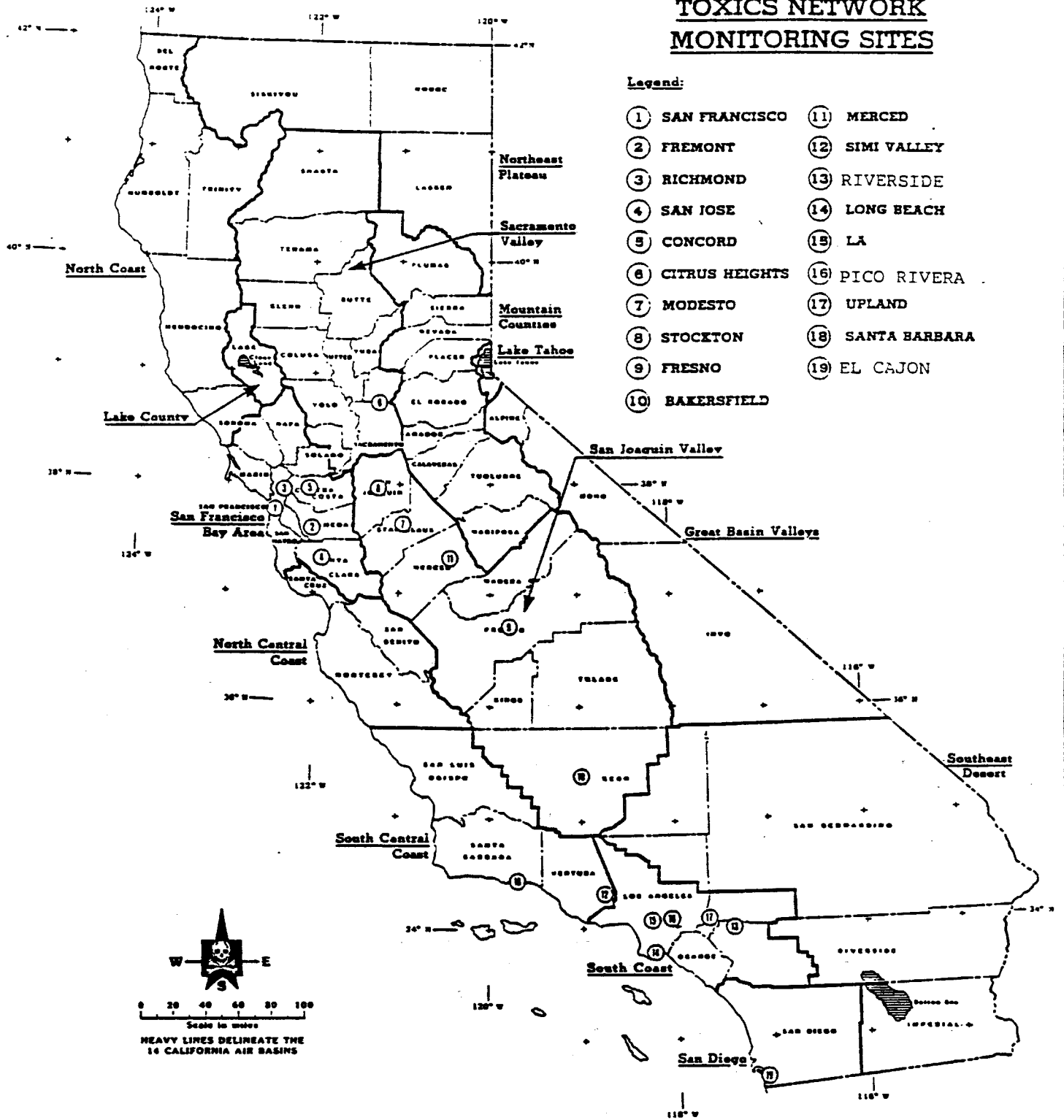
The ranges of concentrations measured at each site during 1986 are summarized in Table I-1. Maximum concentrations range from  $2.3 \text{ ng/m}^3$  at San Francisco to  $20.0 \text{ ng/m}^3$  at North Long Beach. In addition to the minimum and maximum concentrations, the means and standard deviations, as well as the estimated values and percentages of samples below the LOD are provided in Table I-1. The annual mean arsenic concentrations were calculated using the individual monthly means, providing an equal weighting for each of the 12 months.

FIGURE I-1

**AIR RESOURCES BOARD  
TOXICS NETWORK  
MONITORING SITES**

**Legend:**

- |                  |                 |
|------------------|-----------------|
| ① SAN FRANCISCO  | ⑪ MERCED        |
| ② FREMONT        | ⑫ SIMI VALLEY   |
| ③ RICHMOND       | ⑬ RIVERSIDE     |
| ④ SAN JOSE       | ⑭ LONG BEACH    |
| ⑤ CONCORD        | ⑮ LA            |
| ⑥ CITRUS HEIGHTS | ⑯ PICO RIVERA   |
| ⑦ MODESTO        | ⑰ UPLAND        |
| ⑧ STOCKTON       | ⑱ SANTA BARBARA |
| ⑨ FRESNO         | ⑲ EL CAJON      |
| ⑩ BAKERSFIELD    |                 |



Stationery Source Division

TABLE I-1  
 Summary of 1986 Inorganic Arsenic Data  
 (Units are nanograms per cubic meter)

AIR BASIN Site Location	Minimum Conc.	Maximum Conc.	Mean Conc.	Standard Dev.	Estimated Conc<LOD*	%below LOD	# of Samples
<b>SOUTHERN CALIFORNIA SITES</b>							
<b>SOUTH COAST AIR BASIN:</b>							
Los Angeles	0.4	11.0	2.4	1.5	0.4	0	56
No. Long Beach	0.5	20.0	2.2	2.2	0.4	0	55
Pico Rivera	1.0	18.4	5.0	2.3	0.4	0	58
Riverside	<0.4	7.0	1.6	0.4	0.3	3	59
Upland	0.4	6.0	1.9	0.4	0.4	0	61
<b>BASIN SUMMARY</b>	<b>0.5</b>	<b>12.5</b>	<b>2.6</b>	<b>1.4</b>	<b>0.4</b>	<b>1</b>	
<b>SOUTH CENTRAL COAST AIR BASIN:</b>							
Santa Barbara	<0.4	3.1	0.7	0.3	0.3	15	39
Simi Valley	<0.4	6.6	1.1	0.6	0.3	2	60
<b>BASIN SUMMARY</b>	<b>&lt;0.4</b>	<b>4.8</b>	<b>0.9</b>	<b>0.4</b>	<b>0.3</b>	<b>8</b>	
<b>SAN DIEGO AIR BASIN:</b>							
El Cajon	<0.4	3.0	1.1	0.5	0.3	4	51
<b>BASIN SUMMARY</b>	<b>&lt;0.4</b>	<b>3.0</b>	<b>1.1</b>	<b>0.5</b>	<b>0.3</b>	<b>4</b>	
<b>NORTHERN CALIFORNIA SITES</b>							
<b>SAN FRANCISCO BAY AREA AIR BASIN:</b>							
Concord	<0.4	2.6	0.7	0.4	0.3	28	60
Fremont	<0.4	3.3	0.8	0.4	0.3	18	61
Richmond	<0.4	3.0	0.8	0.5	0.3	17	54
San Francisco	<0.4	2.3	0.7	0.4	0.3	20	59
San Jose	<0.4	3.2	1.2	0.6	0.3	3	61
<b>BASIN SUMMARY</b>	<b>&lt;0.4</b>	<b>2.9</b>	<b>0.8</b>	<b>0.5</b>	<b>0.3</b>	<b>17</b>	
<b>SAN JOAQUIN VALLEY AIR BASIN:</b>							
Bakersfield	0.7	7.2	2.3	0.9	0.4	0	57
Fresno	<0.4	9.0	1.8	1.0	0.3	3	34
Merced	<0.4	3.4	1.3	0.4	0.3	2	56
Modesto	0.4	5.2	1.2	0.6	0.3	0	54
Stockton	0.4	5.2	1.5	0.4	0.3	0	48
<b>BASIN SUMMARY</b>	<b>0.5</b>	<b>6.0</b>	<b>1.6</b>	<b>0.7</b>	<b>0.3</b>	<b>1</b>	
<b>SACRAMENTO VALLEY AIR BASIN</b>							
Citrus Heights	<0.4	2.9	1.0	1.3	0.3	6	48
<b>BASIN SUMMARY</b>	<b>&lt;0.4</b>	<b>2.9</b>	<b>1.0</b>	<b>1.3</b>	<b>0.3</b>	<b>6</b>	

\* Gleit's method was used to estimate the concentration of samples below the LOD (Limit of Detection) of 0.4 nanograms per cubic meter.

The estimated mean arsenic concentrations calculated for the 1986 data range from 0.7 ng/m<sup>3</sup> at Santa Barbara, Concord, and San Francisco to 5.0 ng/n<sup>3</sup> at Pico Rivera. Several sites in the South Coast Air Basin (especially Pico Rivera) contributed to the higher overall mean concentration for that air basin.

Site-specific standard deviations for the arsenic data are relatively large, ranging from 21 to 130 percent of the estimated mean concentration. These large standard deviations indicate a high degree of variability among the data at a given site. Overall, standard deviations as a percentage of the mean are generally similar for both Northern and Southern California sites.

The statistical method developed by Gleit (1985) was used to calculate the means of the arsenic concentration values below the LOD. The values for samples below the LOD estimated by this method range from 0.3 to 0.4 ng/m<sup>3</sup> for the 1986 time period. The Gleit's method accounts for the concentrations below the LOD by setting them equal to the "below LOD mean," the mean of the portion below the LOD. The method had been shown statistically to provide a good estimate of values below the detection limit. A detailed description of the method developed by Gleit is provided in Appendix C.

Peak-to-mean ratios shown in Table I-2 were calculated to provide insight into the nature of arsenic emission release patterns. The technique is based on observations made for criteria pollutants. For example, carbon monoxide is an atmospherically inert pollutant with generally widespread emissions. Over an annual period, peak-to-mean ratios for carbon monoxide tend to be fairly low, generally less than 5 to 1. Another criteria pollutant, sulfur dioxide, is often emitted from localized point sources. Peak-to-mean ratios for sulfur dioxide at sites influenced by localized sources tend to be much greater than 5 to 1. Ratios between 50 to 1 and 90 to 1 have been seen at some locations.

Generally, a low peak-to-mean ratio (less than about 5 to 1) indicates either relatively constant and/or uniform emission sources or few emission sources but high, fairly constant background concentrations. A high peak-to-mean ratio (generally greater than about 6 to 1) usually indicates that there are either intermittent and/or scattered emissions sources or scattered emission sources with highly variable background concentrations. Peak-to-mean ratios can also be affected by meteorological influences.

As Table I-2 indicates, the ratios for the Southern California sites were generally higher than for the Northern California sites, having an average peak-to-mean ratio of 4.8 to 1 and 3.5 to 1, respectively. For the southern sites, the peak-to-mean ratio ranged from 2.7 to 1 at El Cajon to 9.1 to 1 at North Long Beach. The northern sites had a range of peak-to-mean ratios of 2.6 to 1 at Merced to 5.0 to 1 at Fresno. The low ratios tend to indicate fairly uniform emission patterns, both spatially and temporally, and the higher ratios tend to indicate non-uniform emission patterns. However, without more refined information regarding the spatial and temporal characteristics of arsenic emissions, we cannot determine the specific factors contributing to the ratios.

TABLE I-2  
**Summary of Inorganic Arsenic Peak-to-mean Ratios  
 1986**  
 (units are nanograms per cubic meter)

AIR BASIN Site Location	Peak Conc.	Mean Conc.	Peak-to-Mean ratio	Number of Samples
<b>SOUTHERN CALIFORNIA SITES</b>				
<b>SOUTH COAST AIR BASIN:</b>				
Los Angeles	11.0	2.4	4.6	56
No. Long Beach	20.0	2.2	9.1	55
Pico Rivera	18.4	5.0	3.7	58
Riverside	7.0	1.6	4.4	59
Upland	6.0	1.9	3.2	61
<b>SOUTH CENTRAL COAST AIR BASIN:</b>				
Santa Barbara	3.1	0.7	4.4	39
Simi Valley	6.6	1.1	6.0	60
<b>SAN DIEGO AIR BASIN:</b>				
El Cajon	3.0	1.1	2.7	51
<b>NORTHERN CALIFORNIA SITES</b>				
<b>SAN FRANCISCO BAY AREA AIR BASIN:</b>				
Concord	2.6	0.7	3.7	60
Fremont	3.3	0.8	4.1	61
Richmond	3.0	0.8	3.8	54
San Francisco	2.3	0.7	3.3	59
San Jose	3.2	1.2	2.7	61
<b>SAN JOAQUIN VALLEY AIR BASIN:</b>				
Bakersfield	7.2	2.3	3.1	57
Fresno	9.0	1.8	5.0	34
Merced	3.4	1.3	2.6	59
Modesto	5.2	1.2	4.3	54
Stockton	5.2	1.5	3.5	48
<b>SACRAMENTO VALLEY AIR BASIN:</b>				
Citrus Heights	6.0	1.0	2.9	48



### 3. Population-weighted Inorganic Arsenic Exposure Levels

Mean population-weighted exposure estimates were calculated using data from January through December 1986. For most of the air basins, it was assumed that all the people in each air basin were exposed to the same estimated air basin mean. Population exposures for the SoCAB and the SFBAAB were estimated by interpolating mean station values to census tract centroids. Population estimates were from the 1980 census data updated to 1985.

Three estimates (lower bound, mean, and upper bound) were calculated to show basinwide and statewide population-weighted exposure to inorganic arsenic. Figure I-2 depicts the cumulative population versus mean 1986 arsenic concentration, including the approximate upper and lower confidence limit bounds. All people in the represented air basins are estimated to be exposed to concentrations of at least  $0.5 \text{ ng/m}^3$ , while five percent (-1,017,000) are exposed to  $3.5 \text{ ng/m}^3$ .

The exposure data are summarized in Table I-3. The mean statewide population-weighted exposure for 1986 is estimated to be  $1.9 \text{ ng/m}^3$ , with a lower bound of  $1.5 \text{ ng/m}^3$  and an upper bound of  $2.6 \text{ ng/m}^3$ . An estimated 20,339,250 people are included in the overall exposure calculations.

FIGURE I-2  
Estimated Cumulative Inorganic Arsenic Exposure  
Statewide 1986

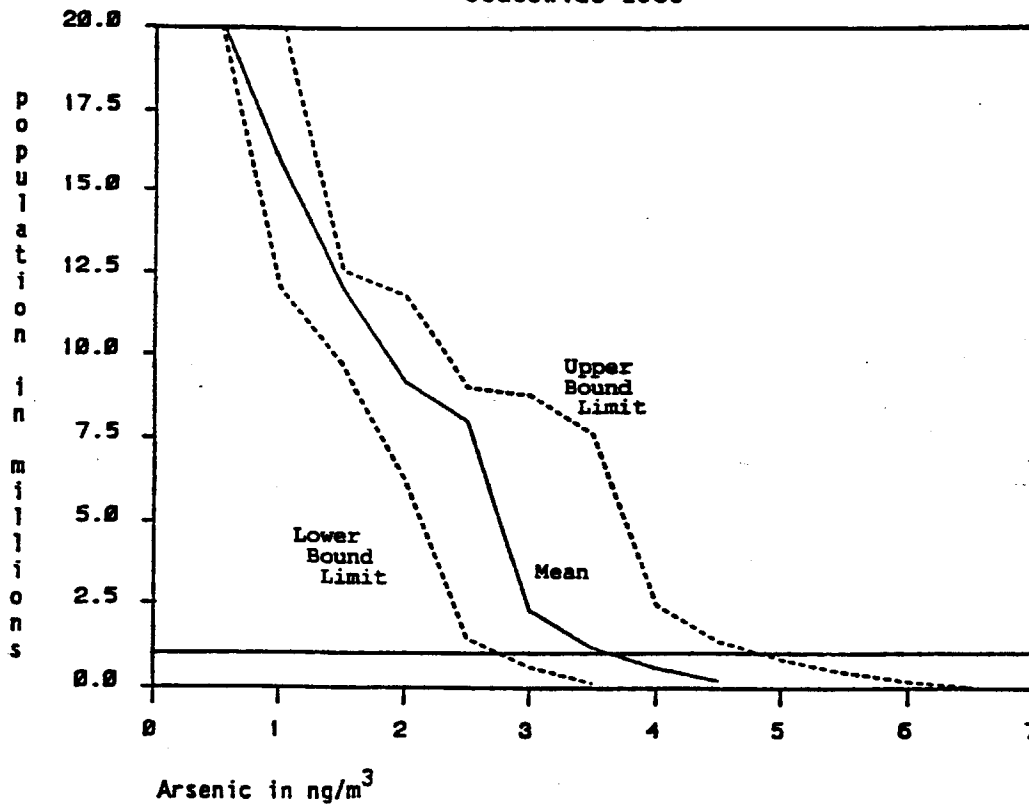


TABLE I-3  
 Range of Estimated Inorganic Arsenic Concentrations and Population-weighted  
 Exposure Estimates for 1986  
 (units are nanograms per cubic meter)

AIR BASIN Site Location	Lower Bound Estimate	Mean Estimate	Upper Bound Estimate	Total Population
<b>SOUTH COAST AIR BASIN (SoCAB):</b>				
Los Angeles	1.8	2.4	3.2	
No. Long Beach	1.4	2.2	3.3	
Pico Rivera	3.8	5.0	6.6	
Riverside	1.4	1.6	1.8	
Upland	1.7	1.9	2.2	
<b>POPULATION-WEIGHTED EXPOSURE FOR SoCAB</b>	<b>2.1</b>	<b>2.8</b>	<b>3.8</b>	<b>10,092,133</b>
<b>SOUTH CENTRAL COAST AIR BASIN (SCCAB):</b>				
Santa Barbara	0.6	0.7	0.9	
Simi Valley	0.8	1.1	1.4	
<b>POPULATION-WEIGHTED EXPOSURE FOR SCCAB</b>	<b>0.7</b>	<b>0.9</b>	<b>1.2</b>	<b>925,822</b>
<b>SAN DIEGO AIR BASIN (SDAB):</b>				
El Cajon	0.9	1.1	1.4	
<b>POPULATION-WEIGHTED EXPOSURE FOR THE CITY OF SAN DIEGO:</b>	<b>0.9</b>	<b>1.1</b>	<b>1.4</b>	<b>2,135,872</b>
<b>SAN FRANCISCO BAY AREA AIR BASIN (SFBAAB):</b>				
Concord	0.5	0.7	1.0	
Fremont	0.6	0.8	1.0	
Richmond	0.6	0.8	1.1	
San Francisco	0.6	0.7	1.0	
San Jose	0.9	1.2	1.6	
<b>POPULATION-WEIGHTED EXPOSURE FOR SFBAAB:</b>	<b>0.6</b>	<b>0.8</b>	<b>1.1</b>	<b>4,394,374</b>
<b>SAN JOAQUIN VALLEY AIR BASIN (SJVAB):</b>				
Bakersfield	1.9	2.3	2.8	
Fresno	1.2	1.8	2.6	
Merced	1.1	1.3	1.6	
Modesto	0.9	1.2	1.5	
Stockton	1.3	1.5	1.8	
<b>POPULATION-WEIGHTED EXPOSURE FOR SJVAB:</b>	<b>1.3</b>	<b>1.6</b>	<b>2.1</b>	<b>1,901,243</b>
<b>SACRAMENTO VALLEY AIR BASIN (SVAB):</b>				
	0.7	1.0	1.3	
<b>POPULATION-WEIGHTED EXPOSURE FOR SACRAMENTO COUNTY:</b>	<b>0.7</b>	<b>1.0</b>	<b>1.3</b>	<b>889,806</b>
<b>OVERALL POPULATION-WEIGHTED EXPOSURE:</b>				
	<b>1.5</b>	<b>1.9</b>	<b>2.6</b>	<b>20,339,250</b>

#### 4. Ambient Inorganic Arsenic Concentration Patterns

Figures I-4, -5, and -6 represent monitored arsenic concentrations statewide (Figure I-4), in the state's SoCAB (Figure I-5), and the SoCAB's Pico Rivera (Figure I-6) for the 29-month monitoring period of August 1985 through December 1987.

The graphs demonstrate the seasonal nature of inorganic arsenic concentrations by following the same general pattern typically found with particulate matter (i.e., high winter peaks). The high August 1985 concentrations monitored at Pico Rivera ( $8.6 \text{ ng/m}^3$ ) may have been the result of intensified industrial activity.

FIGURE I-3  
Statewide Monthly Inorganic Arsenic Concentrations  
August 1985 to December 1987

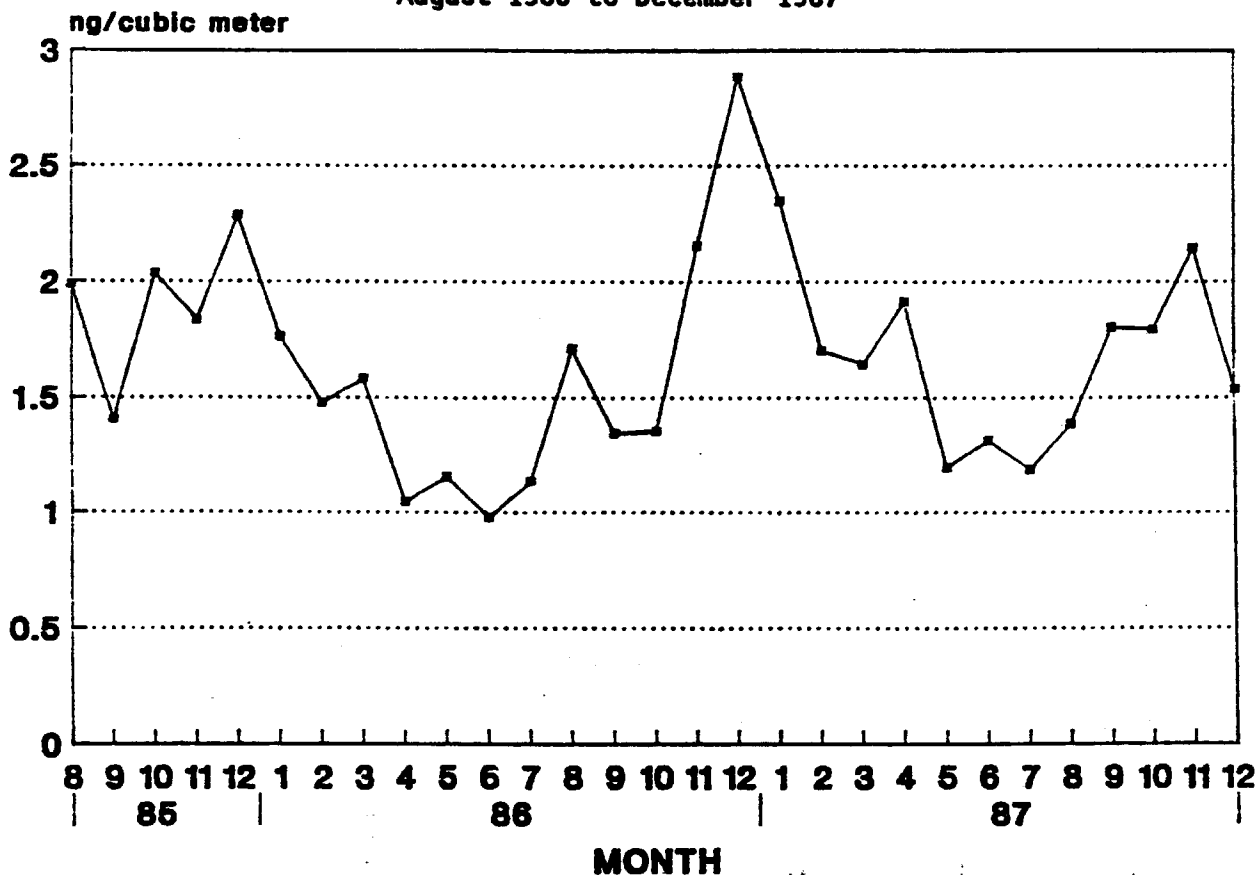


FIGURE I-4  
 South Coast Air Basin (SoCAB) Monthly Inorganic Arsenic Concentrations  
 August 1985 to December 1987

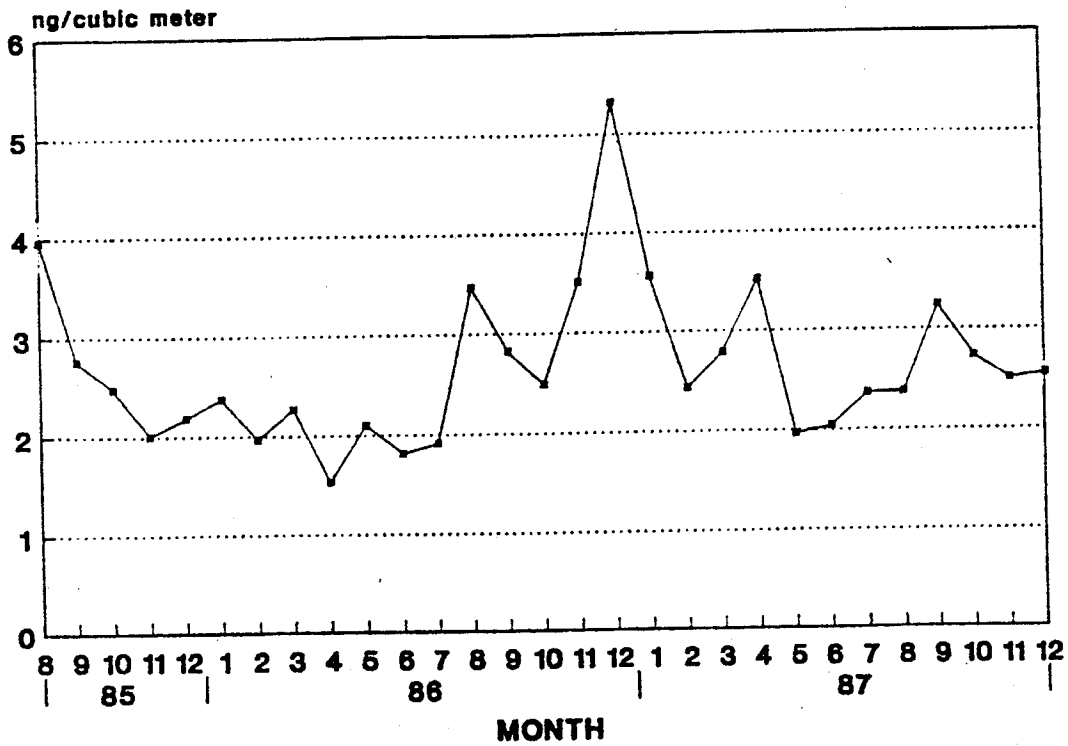
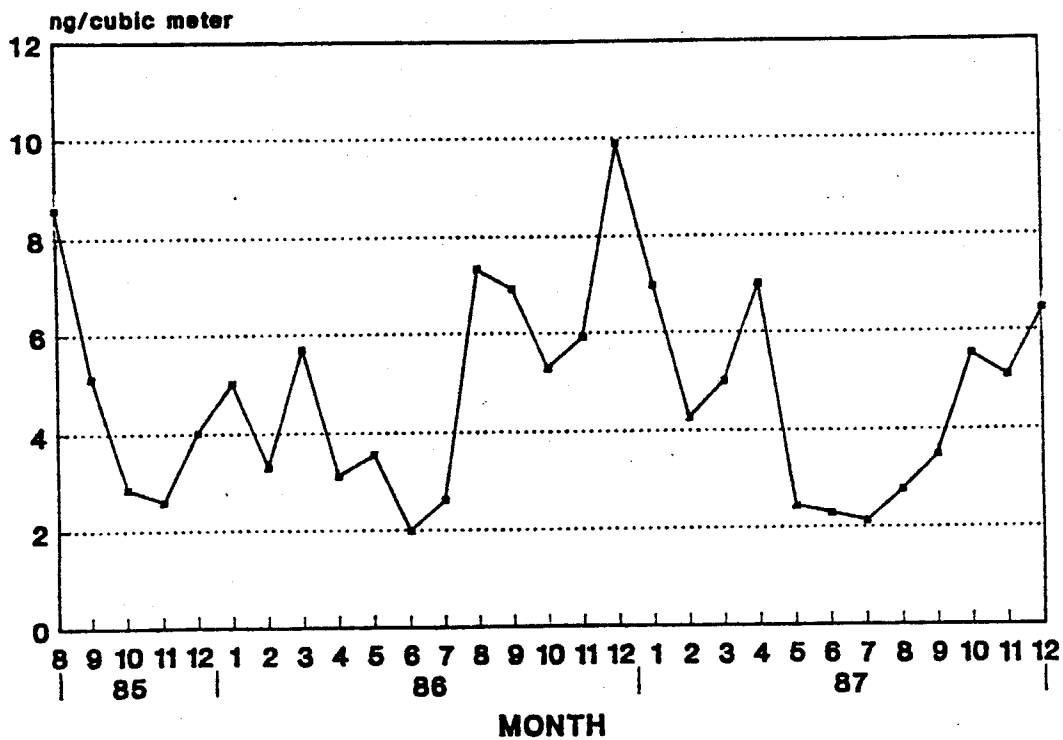


FIGURE I-5  
 Pico Rivera's Monthly Inorganic Arsenic Concentrations  
 August 1985 to December 1987



## B. ARSENIC "HOT SPOT" EMISSIONS TESTING

Although the monthly averages and peak-to-mean ratios are based on a limited amount of data, they suggest the influence of variable or intermittent emission sources. Contributing influences may also include the seasonal variability of the meteorology and concentrations of ambient particulate matter.

Stationary facilities with airborne arsenic emissions are capable of creating high localized ambient concentrations ("hot spots") of arsenic. These hot spot concentrations may be diluted by distance and air mass before they are sampled by a toxic air monitoring device. In an effort to identify hot spot airborne arsenic emissions in California, ARB staff used the Emission Data System (EDS) to do an analysis of arsenic sources in California. This analysis indicated that secondary lead smelters have the potential to emit arsenic because of the feed materials used.

There are four secondary lead smelters in California that are listed in ARB's EDS. The ARB selected one of the secondary lead smelters for a hot spot emissions study. What follows is a chronological account of this study.

In 1981, the ARB sponsored an SAI source test of a secondary lead smelter located in the SoCABs City of Industry. The test results yielded estimated total stack annual emissions of between 8 and 32 lbs per year, based upon proprietary information on the lead processing rate and the furnace operating hours (SAI, 1982). Only one of the facility stacks were tested, and inferences for the entire facility were based on the one stack's data. SAI estimated the fugitive arsenic emissions to be greater than the combined stack emissions, due to the nature of the smelting process and the facility design.

In 1986, a special study was performed to verify that the ambient air was being impacted by the secondary lead smelter. A hi-volume sampler was used to collect air samples at a point located approximately one-half kilometer from the projected point of maximum impact, and about one kilometer southwest of the source. The point of maximum impact had been predicted by a 1986 ARB ISCST model. Eleven 24-hour particulate matter samples were collected over the period of May 17 through June 15, 1986. A summary of the data is presented in Table I-4.

The samples collected over the one month sampling period had arsenic concentrations ranging from  $7 \text{ ng/m}^3$  to  $392 \text{ ng/m}^3$ . The monthly average at the impacted monitoring site was  $61 \text{ ng/m}^3$ , approximately 25 times greater than the annual unimpacted average. All of the arsenic values were well above the  $2.6 \text{ ng/m}^3$  SoCAB annual average observed in 1986.

The June 5, 1986 observation of  $392 \text{ ng/m}^3$  stands out as an extremely high 24-hour concentration. This value was extensively evaluated by the ARB's Haagen-Smit Laboratory and appears to be a valid observation.

Although the samples taken during the May 17 through June 15, 1986 study were not speciated, a 1987 non-source-impacted study in the SoCAB demonstrated As(III) was roughly equal to As(V) on both fine and course particulate matter (see Forms of Inorganic Arsenic in the Atmosphere in Chapter III).

TABLE I-4  
 South Coast Air Basin, Source-impacted Ambient Arsenic Monitoring Samples  
 5-17-86 to 6-15-86

Sample Date	Total Arsenic ng/m <sup>3</sup>
5-17-86	40
5-20-86	16
5-22-86	17
5-24-86	10
5-28-86	11
5-30-86	7
6-03-86	64
6-05-86	392
6-08-86	14
6-10-86	94
6-15-86	7

Monthly Average - 61 ng/m<sup>3</sup>

Results of the May 17 to June 15, 1986 air monitoring indicated the presence of elevated arsenic concentrations in the vicinity of the smelter. The smelter was the only major source of arsenic identified in this area by ARB's EDS, but it is possible that other unidentified sources were contributing to the unusually high arsenic concentrations monitored. If the period during which the monitoring occurred was a time of unusually high activity at the facility, the concentrations measured may not be representative of year-round activity. The South Coast Air Quality Management District (SCAQMD) reported that this facility is permitted to operate on a 24-hour continuous basis. This indicates that these values may be representative of normal activity at the facility (SCAQMD, 1986). If this smelter was the major source of arsenic emissions in the area and this was not a period of unusually high activity at the facility, then the monitoring data indicate that emissions must have been higher than estimated in the SAI test.

In 1988, the SCAQMD reevaluated the secondary lead smelter through a combined stack test and 9 week, 11 station monitoring study. Monitoring results indicated significantly elevated concentrations of both arsenic and lead downwind of the facility. The maximum arsenic concentration measured during the sampling study was 61.52 ng/m<sup>3</sup>, while the average arsenic concentration for the 9 week period was 19.18 ng/m<sup>3</sup>. Upwind concentrations of both arsenic and lead were approximately equivalent to concentrations measured at other locations in the SoCAB (SCAQMD, 1988).

In 1989, the ARB modeled the local population's exposure to arsenic emissions using the source test data provided by the 1988 SCAQMD stack test of the secondary lead smelter. The modeling analysis estimated the level of ambient arsenic exposure experienced by the population residing within a 20 by 20 kilometer grid. The smelter was in the center of the grid. The total population contained in the study area was 761,836.

Table I-5 reflects the results of an ISCST model of the facility using UNAMAP6 (dated 88348).

Fugitive emissions from the facility were not included in the modeling because recent estimates have not been made. Since meteorology was not available for the City of Industry, the ARB staff used meteorological data from the nearby city of Azusa.

TABLE I-5  
Cumulative Population Exposure Distribution Due to Arsenic Emissions from a  
Secondary Lead Smelter in the City of Industry (1981 Azusa Meteorology)

Annual Exposure Range (nanograms/m <sup>3</sup> )	Population Exposed (1985 Residential)	
	Incremental*	Cumulative**
0.0 - < 0.1	492,543	761,836
0.1 - < 0.5	240,662	269,293
0.5 - < 1.0	22,646	28,631
1.0 - < 1.4	3,282	5,985
1.4 - < 1.8	926	2,703
1.8 - < 3.0	1,231	1,777
3.0 - < 9.4	546	546

\* The Incremental list reflects the number of people that are predicted to be exposed to the concentration range immediately to the left (e.g., 546 people are predicted to be exposed to arsenic concentrations of 3.0 - 9.4 ng/m<sup>3</sup>).

\*\* The Cumulative list reflects the total number of people that are predicted to be exposed to the concentration to the left, as well as the preceding concentrations (e.g., 1,231 people are predicted to be exposed to 1.8 - 3.0 ng/m<sup>3</sup>; 546 additional people are predicted to be exposed to 1.8 - 3.0 ng/m<sup>3</sup> as well as a larger concentration of 3.0 to 9.4 ng/m<sup>3</sup>, making a cumulative exposure of 1,231 + 546 = 1,777 people exposed to the 1.8 - 3.0 ng/m<sup>3</sup> concentration of arsenic range).

Maximum predicted arsenic exposure from the facility for a small population (546 people) ranges from 3.0 ng/m<sup>3</sup> to 9.4 ng/m<sup>3</sup>. A larger population (1,777 people) is predicted to be exposed to arsenic concentrations near or slightly above the ambient SoCAB average of 2.6 ng/m<sup>3</sup>.

Results of the 1989 modeling study show that the local population is exposed to arsenic concentrations that are higher than other SoCAB populations living in unimpacted areas. Additionally, the study population may also be exposed to the ambient concentrations of arsenic experienced by the rest of the SoCAB.

Average ambient concentrations (like those developed during the 1986 and 1988 monitoring study) are based on data collected with air monitors and reflect the average concentrations impacting the toxic air monitors from a number of sources. Modeling results are "predicted" data (mathematically derived). The smelter study model considered the smelter to be the only source of arsenic in the area. That is unlikely, since arsenic is released from a variety of source types (e.g., combustion of fossil fuels and cement production) and people living near the source are probably exposed to greater concentrations than those predicted by the study.

### C. OTHER INORGANIC ARSENIC EXPOSURE ROUTES

Although this report concentrates on inorganic arsenic exposure from the ambient atmosphere, there are other routes of exposure to inorganic arsenic: drinking water, tobacco smoke, and food. The drinking water route of exposure is of particular interest because several areas in California contain unusually high levels of inorganic arsenic due to geochemical enrichment. Also, arsenic is often a component of mainstream tobacco smoke, and is likely to be a component of sidestream smoke as well. These sources are discussed in more detail below.

A summary of daily human inorganic arsenic intake is presented in Table I-6.

TABLE I-6  
Levels of Daily Human Inorganic Arsenic Intake

Route	Chemical Form	Concentration	Volume	Total Intake
Ambient Air	As(III)/As(V) compounds	.002 ug/m <sup>3</sup>	20 m <sup>3</sup>	.04 ug
Drinking Water	As(V) salts/As(III)	10 ug/liter	2 liters	20 ug
Cigarettes	arsenic oxides*	0.8-2.4 ug per pack**		0.8-2.4 ug

\* Presumed by nature of combustion conditions but not proven (USEPA, 1984).

\*\* (U.S. DHHS, 1989).



## 1. Water

The Safe Drinking Water Act set the Maximum Contaminant Level (MCL) for arsenic in public drinking water at 50 ug/l. The 50 ug/l standard was established earlier by the United States Public Health Service which also established a recommended limit of 10 ug/l. The majority of the drinking water consumed in California is below the 50 ug/l MCL.

Arsenic is present in ground water in some areas of California due to natural geochemical enrichment in localized areas (Green, 1986). The California Department of Water Resources (CDWR) conducted an extensive study of arsenic in well water in the San Joaquin Valley because arsenic levels which exceeded the Federal standard were detected in some wells. The results showed that many wells in the vicinity of Allensworth, California contained concentrations of arsenic exceeding the Federal standard, with concentrations of 1100 ug/l being reported (CDWR, 1970). Additional research found that the high concentrations of arsenic in some wells were the result of the high arsenic content of the local geology (Green, 1986).

In other parts of the San Joaquin Valley (outside of the Allensworth area), arsenic levels in well water were usually below the drinking water standards. Of 231 wells tested in the San Joaquin Valley, 4 wells exceeded the 50 ug/l MCL. Over 90 percent of the wells tested were below the 10 ug/l recommended standard with nearly 60 percent of the wells having arsenic concentrations below the detection limit of 5 ug/l (CDWR, 1970). The arsenic content of well water for the bulk of the wells was below 10 ug/l.

No special studies of arsenic in drinking water have been performed in other areas in the state, but the uniqueness of the San Joaquin Valley geology suggests arsenic levels in water in other parts of the state may be much lower. For purposes of this report, we assume that an arsenic level of 10 ug/l in drinking water (ground and/or surface water) represents an average conservative estimate of arsenic levels for the majority of California's population.

Assuming an adult consumes two liters of water per day with an arsenic concentration of 10 ug/l, arsenic intake from drinking water would be 20 ug/day. Arsenic (V) may be the predominant chemical form present in most drinking water supplies (USEPA, 1984), although arsenic (III) has been identified in surface water supplies in areas impacted by anthropogenic sources of arsenic. Andreae (1980) observed both As(III) and As(V) in most rainwater samples collected during a study along the eastern U.S. coast.

A map delineating water quality control regions in California is shown in Figure I-6.

The staff of the California Water Resources Control Board (CWRCB) retrieved additional test data on arsenic in California's ground and surface water from USEPA's Storage and Retrieval National Database (STORET). Table I-7 summarizes the STORET data and is broken down by water quality control regions. Region 5 is the Sacramento/San Joaquin Valley where elevated levels of ground and surface water contamination of arsenic have been observed. The majority of California's population lives in Regions 2, 4, 8, and 9 where surface water provides a large portion of the drinking water.

FIGURE I-6  
California Regional Water Quality Control Boards



1. North Coast Region
2. San Francisco Bay Region
3. Central Coast Region
4. Los Angeles Region
5. Central Valley Region
6. Lahontan Region
7. Colorado River Basin Region
8. Santa Ana Region
9. San Diego Region

TABLE I-7  
 Summary of Observations for Total (Suspended and Dissolved)  
 Arsenic (ug/l) in California Surface and Groundwater by Region

Region	SURFACE				GROUND			
	No. Obs.	Mean	Min.	Max.	No. Obs.	Mean	Min.	Max.
1	319	5.6	0	100	56	5.2	0	26
2	496	3.4	0	80	267	1.4	0	15
3	220	4.8	0	220	4	0.0	0	0
4	921	9.9	0	484	386	27.6	0	5000
5	3808	41.3	0	31000	3193	232.8	0	48000
6	164	21.6	0	250	473	106.4	0	4000
7	312	9.7	0	74	491	10.3	0	120
8	446	9.4	0	140	479	50.9	0	7000
9	139	7.0	0	110	143	5.1	0	160

(CDWR, 1970 and USEPA, 1988)

## 2. Tobacco Smoke / Indoor Air

a. Tobacco smoke - Arsenic levels of 1.5 ppm were measured in tobacco that had been grown in average (3 ppm arsenic concentration) soils (USEPA, 1984). Much of the arsenic measured in the tobacco in the past may have resulted from the use of arsenical pesticides on the tobacco crop (EPRI, 1981; IARC, 1986) which has been reduced in recent years. Approximately 10-15 percent of the total arsenic in the tobacco is present in the tobacco smoke, with the remaining 85-90 percent in the ash. The chemical forms of arsenic in cigarette smoke have not been determined, but are probably arsenic oxides.

The arsenic content of mainstream cigarette smoke ranges from 40 to 120 ng of arsenic per cigarette (U.S. DHHS, 1989). A smoker who smokes one pack (usually 20 cigarettes) per day would inhale about 0.8 to 2.4 ug arsenic per day from the mainstream smoke. About 40 percent of the arsenic inhaled from mainstream smoke is deposited in the respiratory tract, and about 75 percent of that amount (or 30 percent of the inhaled portion) is believed to be absorbed (U.S. EPA, 1984).

Measurements of arsenic in sidestream smoke (smoke from the burning end of the cigarette) have not been made. However, it may be assumed that some amount of arsenic is emitted in sidestream smoke. Insufficient information is

available to permit any estimates of arsenic intake from exposure to sidestream smoke or to environmental tobacco smoke (ETS -- sidestream smoke plus exhaled mainstream smoke.)

b. **Indoor Air** - Few indoor sources of arsenic other than tobacco smoke have been identified. Acute toxic effects due to high inorganic arsenic exposures have been reported in buildings constructed on top of arsenic waste sites and in homes where wood treated with arsenic wood preservatives has been burned in fireplaces or woodstoves (Peters, et al., 1984). Less significant sources of arsenic in offices and residences of nonsmokers include indoor combustion of non-preserved wood or other fuels, and infiltration of street dust.

Indoor arsenic concentrations were measured in ten homes and two office buildings in Boston as part of a larger study in the late 1970s (EPRI, 1981). Indoor arsenic concentrations in homes where cigarette smoking occurred were generally equal to or greater than outdoor smoking concentrations measured simultaneously. However, only two of the six residences with smoking had indoor levels that were significantly higher than the outdoor concentrations (95 percent confidence.) Nonsmoking residences had indoor arsenic concentrations equal to or less than outdoor levels, and the indoor levels in the office buildings were much lower than outdoor levels. Measured indoor and outdoor concentrations ranged from less than  $1 \text{ ng/m}^3$  to about  $4 \text{ ng/m}^3$ ; however, the accuracy and precision of these measurements are uncertain. The investigators concluded that the indoor and outdoor levels of arsenic measured in their study were typical of or lower than outdoor nationwide averages. Since two of the six residences with smoking had significantly greater concentrations of arsenic, staff of the ARB conclude that tobacco smoking may contribute to elevated levels of arsenic indoors.

### 3. Diet

Food is a source of arsenic exposure, although it is generally in the form of complex organo-arsenicals which are not the focus of this report. Information regarding the arsenic species in food crops is limited.

It is known that growing plants will take up arsenic from the soil. In areas with high concentrations of arsenic in groundwater and soils, food crops may take up additional arsenic. The consumption of these plants will result in increased exposure to arsenic. "Part B" of this report discusses the significance of dietary arsenic exposure.

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## II. SOURCES OF ATMOSPHERIC ARSENIC

### A. PRODUCTION

Arsenic trioxide, the principal commercial arsenic raw material, is produced as a by-product of processing copper, lead, zinc, gold, and silver ores. In 1984, the United States produced approximately 5,500 tons of arsenic from domestic mines and imported ores (Edelstein, 1985). The major world producers of arsenic are the United States, France, the U.S.S.R., Mexico, and Sweden.

Imports are the major source of arsenic used in the United States. In 1984, the United States used approximately 15,000 tons of arsenic, while U.S. production was only 5,500 tons (Edelstein, 1985). The total amount of arsenic imported in 1984, including pure metal and other arsenic compounds such as sodium arsenate, arsenic acid and lead arsenate, was about 11,400 tons (USD0I, 1985b).

U.S. production of arsenic and arsenic compounds is on the decline. In 1973, U.S. production of contained arsenic was 10,000 tons; by 1984, this had declined to 5,500 tons (USD0I, 1985a and 1985b). No increase in U.S. arsenic production is expected (Edelstein, 1985).

### B. USAGE

Use of arsenic and its compounds by the year 2000 in the United States is estimated at 22,000 tons, representing an average growth rate of 1.1 percent per year for the years 1983-2000 (USD0I, 1985a). Historical production, imports, and use of arsenic nationally are shown in Figure II-1 (USD0I, 1985a, Edelstein, 1985). This figure estimates usage based on imports, stockpiling and production.

Arsenic trioxide serves as the raw material for about 97 percent of arsenic-containing products manufactured in the United States. Figure II-2 shows 1984 arsenic use by industry. The use pattern in recent years has been approximately 55 percent in industrial chemicals, primarily wood preservatives, 35 percent in agricultural pesticides and the remaining 10 percent divided among other uses (USD0I, 1985b). Pesticides were formerly the major use of arsenic, but the use of arsenic-containing pesticides has declined over the last decade because environmental concerns have led to the development of less toxic substitutes.

#### 1. Pesticides

Arsenicals (compounds containing arsenic) are used in agriculture as pesticides and herbicides. Inorganic arsenicals are regulated as restricted materials, but no permit is required for industrial or home use. Arsenicals are used in ant syrup or paste, industrial wood treatments, grape treatments for the control of dead arm and grape measles, and as a cotton defoliant.

During the 1930's and 1940's, sodium, lead, and calcium arsenate formed a major part of the pesticide industry, but their use is now limited

FIGURE II-1  
National Production, Imports, and Uses of Inorganic Arsenic

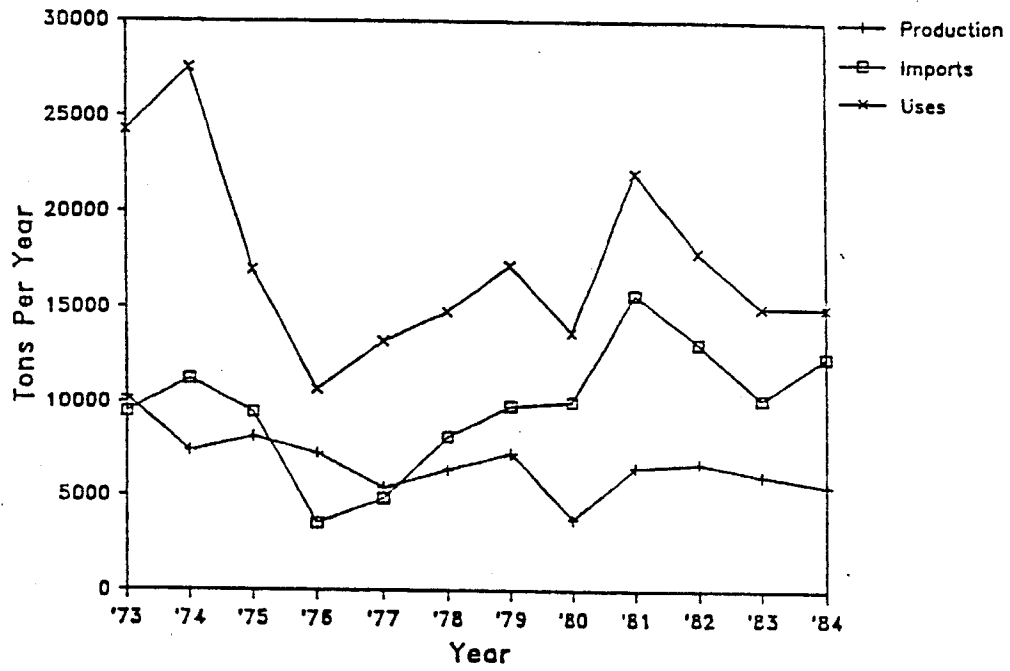
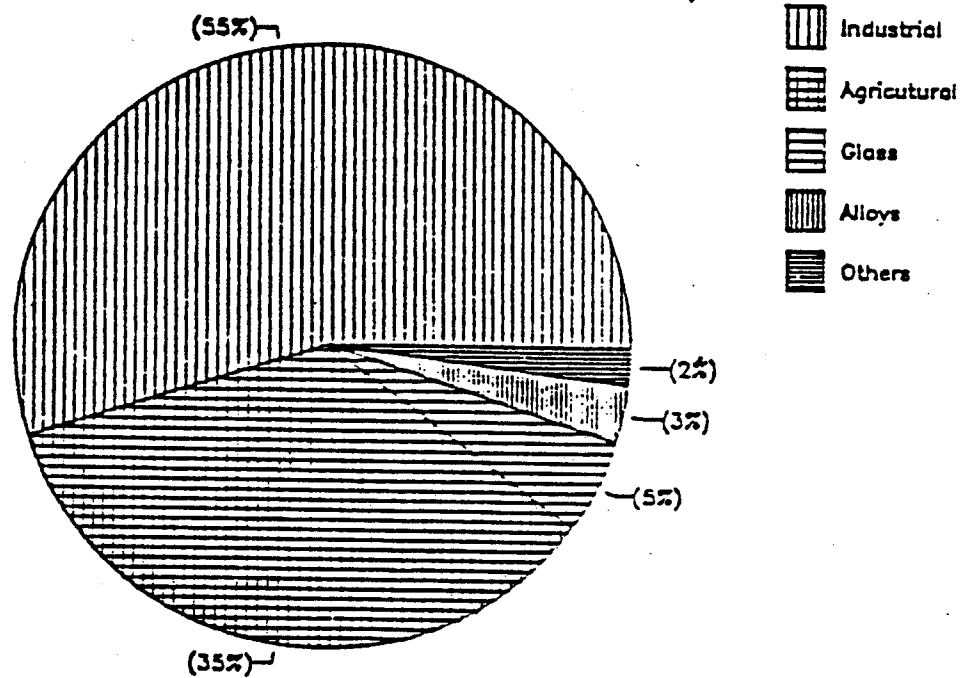


FIGURE II-2  
National Use of Inorganic Arsenic in 1984





to less than 3 million pounds per year nationwide (USDOl, 1985a). The major use of arsenical chemicals is in cotton production. In California, cacodylic acid is used as a cotton defoliant prior to mechanical harvesting (Lederer and Fensterheim, 1983). Monosodium methanearsonate (MSMA) and disodium methanearsonate (DSMA) are produced from arsenic trioxide and are used in the control of weeds. Many of these products are not inorganic arsenic compounds but organo-arsenic compounds and are under the control authority of the California Department of Food and Agriculture (CDFA). The remaining uses of arsenical pesticides include the use of sodium arsenite to fight grape measles, and lead arsenate to control grapefruit acidity (Lederer and Fensterheim, 1983). In 1984, over 226 tons of arsenicals were applied in California. A description of the uses and amounts of arsenical pesticides applied in California is given in Table II-1 (CDFA, 1984).

Commercial wood preservers use inorganic arsenic as an active ingredient in their treating solutions. When arsenic is used as a wood preservative, it is considered a pesticide. The California Occupational Safety and Health Administration's Carcinogen Registration List identified nine facilities which reported using inorganic arsenic-containing wood preservatives in 1985. Approximately 113 tons of elemental arsenic were used in California by wood preservers during the 1985 calendar year (ARB, 1986f). Wood preservatives containing chromated copper arsenate (CCA) or ammonical copper arsenate (ACA) are the inorganic arsenic-containing types most frequently used in California.

The majority of California wood preservers who utilize inorganic arsenic-containing wood preservatives use the CCA type. Two firms reported using the ACA type of inorganic arsenic-containing wood preservative. There does not seem to be any relationship between facility size and the type of wood preservative used, or the choice of on-site formulation used. Company locations are scattered between San Diego in the south, and Ukiah in the north. In 1985, usage of elemental arsenic at individual wood preserving facilities in California ranged from 10,631 lbs (5.32 tons) to 49,127 lbs (24.56 tons).

## 2. Glass Manufacturing

Arsenic trioxide or arsenic acid is used by glass manufacturers as a fining agent to remove tiny air bubbles, and as a decolorizing agent to oxidize divalent iron (greenish color) to trivalent iron (yellowish color). As a result of environmental concerns, glass companies have minimized this use of arsenic. Arsenic use in flat and container glass has been eliminated, but it is still used to a very limited extent in the manufacture of certain specialty glass products such as camera lenses, solar collector glass and in the pressed and blown glass industry (USEPA). Arsenic is also used in glass ceramics such as ceramic cookware and stove tops to control crystal growth rate (USDOl, 1985a).

## 3. Metallurgy

Arsenic is used in copper and lead-based alloys and in electronic applications. It is used as an additive to lead in storage batteries to

Table II-1: Use of Arsenical Pesticides in California (1984)

<u>Pesticide/Type</u>	<u>Amount Applied(lbs.)</u>	<u>Total Arsenic (lbs.)</u>	<u>Application</u>
DSMA (disodium methanearsonate)/Herbicide*	1,515	606	Cotton, Commercial Turf, Landscape
MSMA (monosodium methanearsonate)/Herbicide*	36,103	16,607	Commercial Turf, Landscape
Cacodylic Acid/Defoliant*	24,060	12,752	Cotton, right of ways
Sodium Arsenite/Herbicide	249,953	89,983	Grapes
Sodium Cacodylate/Defoliant* and Herbicide	140,863	64,797	Cotton, right of ways
<b>TOTAL</b>	<b>452,490</b> (226.25 tons)	<b>184,745</b> (92.37 tons)	

\* Organo-arsenic pesticides

improve the strength of the lead posts and grids. Arsenic-containing lead alloys are used in ammunition. Arsenical copper is used in plant piping, auto radiators, and admiralty brass (USD0I, 1985a). Gallium arsenide and its alloys are used in semiconductors, light-emitting diodes, solar cells, and room-temperature lasers. Arsine is used as a dopant to provide electron movements in many metal-oxide-semiconductor devices.

#### 4. Other Uses

Minor uses of arsenic include arsenical feed additives for poultry, chemical catalysts, veterinary medicines, and pharmaceuticals. Feed additives and other minor uses consume approximately 300 tons of arsenic per year nationwide (USD0I, 1985a).

### C. CURRENT AND PROJECTED EMISSIONS

There are a variety of point and area inorganic arsenic emission sources in California (see Table II-2 for arsenic emission source categories and emission estimates). These include the use of arsenic-containing pesticides, (which may contain either organic or inorganic arsenic), and emissions from the combustion of fuels containing trace amounts of arsenic.

TABLE II-2: Estimated Inorganic Arsenic Emissions in California

<u>Source</u>	<u>Type of Estimate</u>	<u>Emissions (tons/year)</u>	<u>Inventory Year</u>	<u>Ref.</u>
Fuel Combustion: Wood	Area	1.5-11	1981/1985	(USEPA, 1980; USDA, 1981; ARB, 1096f, USDOE, 1982)
Distillate Oil	Area	0.01-3	1984	
Residual Oil	Area	0.03-2.4	1984	
Waste Oil	Area	0.1-1	1983	
Coal gasification	Point	Not available		(ARB, 1986a; ARB, 1986b; Menczel, 1984; SCE, 1986)
Diesel Oil	Area	Not available		
Gasoline	Area	Not available		
Geothermal Steam Operations	Area	2.7	1984	(ARB/GAMP, 1988)
Pesticide Use	Area	2.3	1984	(ARB, 1985a; Roberts, 1980)
Cement Production <sup>1,2</sup> and Coal Combustion	Point	0.004-0.76	1984	(ARB, 1984b; Haynes, 1982; ARB, 1986g; Edwards, 1980)
Sewage Sludge Incineration	Point	0.18	1983	(ARB, 1985d, Bennett, 1982)
Glass Manufacturing	Area	0.16	1984	(ARB, 1985e; ARB, 1985f)
Secondary Lead <sup>2</sup> Smelting	Point	0.13	1987	(ARB, 1989)
Cotton Ginning <sup>3</sup>	Area	0.04	1978	(USDOE, 1982)
Waste-to-Energy Facilities	Point	0.002	1989	(ARB, 1989c)
Pesticide Manufacturing	Point	Not Available		
Wood Preservative Manufacturing	Point	Not Available		
Electronics Manufacturing	Point	Not Available		
Windblown Soil and Dust	Area	Not Available		

1 The majority of California's coal combustion is associated with cement production.

2 Estimates do not include fugitive emissions.

3 Estimate for Fresno County only. Data from other counties are not available.

Other sources include glass manufacturing, secondary lead smelting, mining, windblown dust from dry lakebeds and playas, and commercial use of geothermal steam. The first two sources emit primarily arsenic trioxide, while the other sources may release a variety of arsenic compounds.

Statewide inorganic arsenic emissions are estimated to have a minimum range of at least 7.4 to 24 tons per year. However, emissions data are not available for pesticide use, wood preservative manufacturing, electronics manufacturing, or windblown dust from dry lakebeds and playas.

### 1. Geothermal Steam

Deposits of arsenic are geologically associated with sulfidic ores or serpentine formations, and can be concentrated in crust that has been chemically altered by geothermally-heated water and steam. As a result, inorganic arsenic is present in geothermal steam and may be in varying combinations of the following forms: suspended particulate matter, arsenic trioxide vapor, arsenous acid gas, and arsine. The concentrations and forms of inorganic arsenic will be highly dependent on the geology of the resource reservoir, which may vary from well site to well site.

Geothermal steam vendors and the electrical utilities that use the steam to drive their turbines are sources of inorganic arsenic emissions. As of February 1989, California had 47 geothermal power plants with a combined generating capacity of 2,694 MW of electricity. Over half of the power plants are located at the Geysers in northern California's Sonoma and Lake Counties (CEC, 1989). In 1986, 235 billion pounds of steam were used to produce 1,823 MW of electricity from the Geysers-Calistoga Known Geothermal Resources Area (KGRA) (California Dept. of Conservation, 1986), the world's largest developed "dry steam" geothermal resource.

Inorganic arsenic present in geothermal steam, along with other gases and particulate matter that may be present in the steam (e.g., hydrogen sulfide, boron, ammonia, chlorides, fluorides, hydrocarbons, nitrates, radon 222, methane, selenium and heavy metals) can become airborne during the production, transportation, and use of the steam for electrical production.

Two major factors influence the amount of arsenic emitted from power plant cooling towers: 1) Very little water is reinjected during hot weather, and virtually all of the geothermal steam drawn from the wells is condensed and used for cooling water makeup, ultimately being released to the atmosphere, and 2) arsenic is concentrated in the cooling tower basin due to evaporation of the cooling water. Concentrations of arsenic in the cooling tower blowdown are often 10 times higher than in the condensate (PG&E, 1982). Measurements of the arsenic concentration in the condensed geothermal steam, the cooling tower and Stretford-process sludges, the cooling tower blowdown, and the water reinjected into the ground indicate that the arsenic present in the incoming geothermal steam is not all released to the atmosphere (PG&E, 1982).

From a power plant, the major route of arsenic emission is via cooling tower drift. Arsenic from this drift will influence local ambient particle-sampling monitors while gas-phase emissions of arsenic may not, unless sufficiently rapid condensation onto airborne particulate matter occurs.

Attempts to perform a mass balance for arsenic have provided inconclusive results. Because of the lack of complete information on other routes of arsenic effluence at geothermal plants, the worst-case assumption that all arsenic contained in the geothermal steam is emitted into the atmosphere is used. We recognize that actual emissions may be lower; however, arsenic loading measured in the condensed steam may also under-represent the actual concentrations of arsenic in the steam due to incomplete condensation of arsenic or escape of soluble gas-phase arsenic that the particle-sampling monitors will not detect. While studies of copper smelter emissions have indicated that most gas-phase arsenic undergoes rapid condensation onto airborne particulate matter, we do not know that the same conditions exist to make a parallel determination for geothermal cooling tower emissions.

In addition to the condensate drift that is released from the power plant cooling towers, geothermal steam and particulate matter are released directly into the atmosphere at the individual well sites during steam exploration, drilling operations, cleanout, testing, well rework, and steam stacking during power outages. Steam emissions also result from "wild" wells, standby well bleeds, and transmission line venting. All of these releases result in direct emissions of arsenic contained in the steam. Untreated steam venting has been estimated at up to 5 percent of the total steam field production, although steam field management techniques have improved since the estimate and the percentage is probably less (Lake County AQMD, 1988). It is important to note that these emissions result in the release of untreated steam (as opposed to the "treated" emissions of the cooling towers) and represent a larger arsenic emission than would result from an equal amount of steam being used by a power plant.

Ambient air monitoring data from the Geysers Air Monitoring Program (GAMP) has demonstrated monthly concentrations ranging from 1 to 4 ng/m<sup>3</sup>, while annual averages ranged from 1 to 2 ng/m<sup>3</sup> (Lake County AQMD, 1988). Concentrations at the two monitoring sites located east of the developed steam field have shown maximum 24-hour averages (taken once every six days) up to 14 ng/m<sup>3</sup> of fine (<2.5 um) particulate matter arsenic during 1983-1984, and 4 ng/m<sup>3</sup> for 1986-1987 (GAMP, 1987). In the study, 95 percent of the reported values were at or below the GAMP LOD of 3 ng/m<sup>3</sup>. Since the samples were taken with a size-selecting dichotomous particle sampler, the gas-phase arsenic was not collected or quantified. Additionally, the fine and coarse (>2.5 um and <10 um) arsenic particles were analyzed separately. The coarse arsenic concentrations fell below the LOD. As a result, arsenic levels in the ambient air may be higher than those reported by the ongoing study.

Area emissions of arsenic from California's geothermal power plant operations were estimated by ARB staff at 2.7 tons in 1988, based on the number of power plants and wells, steam production, arsenic concentrations in the steam, and steam usage. Arsenic emission factors for unmitigated (direct) steam release from the steam vendors will be required before point source-specific estimates can be made.

Arsenic emissions from power plants using geothermal steam are not expected to increase due to improved steam management, however, arsenic emissions from steam field operations may increase as a result of "make up" well drilling. As the steam reservoir servicing a well becomes less productive, new wells are needed to maintain power plant production capacity. The number of wells that each plant will require is dependent on the megawatt capacity of the power plant and the steam production of the wells. The number of wells per power plant range from as few as 5 to as many as 60 over the life of the plant (Lake County AQMD, 1989).

## 2. Pesticides

Several industrial facilities use arsenic in California for the manufacture of arsenic-containing pesticides. Inorganic arsenic emissions from these facilities are expected to be small. At most of these facilities the arsenic is in nonvolatile form, or the use of arsenic is limited to a closed system process.

Two companies in the South Coast Air Quality Management District (SCAQMD) have been reported to manufacture arsenical pesticides (Suta, 1979). As of 1985, the Automated Emission Inventory System (AEIS) of the SCAQMD did not list these companies as currently manufacturing arsenical pesticides (SCAQMD, 1985). A 1982 report sponsored by EPA also reported that one of the SCAQMD companies had discontinued arsenic pesticide production (Pedco, 1982). Small-scale manufacture of arsenical pesticides would not be reported in either of these data bases.

The use of arsenical pesticides and herbicides also results in arsenic emissions. During application, some of the applied pesticides and herbicides are lost to the atmosphere. This loss averages about 5 percent of the total amount sprayed. The amount of arsenic emissions associated with this loss was estimated to be about 6.0 tons in 1984, of which 2.3 tons are in the form of inorganic arsenic (ARB, 1985a; Roberts, 1980; and CDFA, 1984). Additionally, agricultural burning of biomass that had been previously treated with organic or inorganic arsenic compounds will result in inorganic arsenic emissions. Pesticidal emissions of arsenic in California are under the regulatory authority of the Department of Food and Agriculture rather than the ARB; however, arsenic emissions from agricultural burning are under ARB's regulatory authority.

Air sampling data from an agricultural burn of vineyard cuttings in Northern Sonoma County (ARB, 1989b) demonstrated extreme hot spot concentrations of unspiciated arsenic up to  $12,639 \text{ ng/m}^3$ . Possible use of arsenical pesticides on the vines prior to the burn would not account for the unusually high concentrations of arsenic. The high arsenic concentrations were the result of copper arsenate-treated vine support posts being burned with the vine cuttings (observed by the air monitoring technicians). Metals analysis of the air sample filters demonstrated high concentrations of copper up to  $2,680 \text{ ng/m}^3$ , supporting the case that arsenical pesticide-treated vine

support posts had been included in the vine burn. The Northern Sonoma County Air Pollution Control District (NSCAPCD) does not typically allow agricultural burning of vine support posts, and this disposal method is recommended against by the wood treatment industry.

### 3. Fuel Combustion

a. **Wood Combustion** - The combustion of arsenical pesticide-treated wood is a demonstrated source of arsenic emissions. One incidence of poisoning attributed to the burning of treated wood in a woodstove has been reported (Peters, et al., 1984). Chromate-copper-arsenate (CCA)-treated wood was identified as the source of the contamination because arsenic pentoxide, copper oxide and chromium oxide were in the ash, and the proportion of these metals in the ash were the same as in commercial wood treatment solutions. In this instance, only arsenic (V) oxide was detected.

McMahon, et al., (1985) examined the release of copper, chromium, and arsenic from burning wood treated with preservatives. The amount of arsenic released depended on the duration and temperature of heating of the residual ash. Approximately 22 percent of the arsenic was emitted under smoldering (400°C) or flaming (800°C) with little residual ash heating. Up to 77 percent of the arsenic was emitted when the ash was heated for six hours at 800°C to 1000°C. The forms of arsenic emitted were a mixture of inorganic arsenic (III) and (V) compounds, with the (III) form favored by a factor of 6 to 1.

The industry has taken action to inform customers about the proper use of arsenical pesticide-treated wood. Each shipment of arsenical pesticide-treated wood contains a Consumer Information Sheet (CIS) which informs the consumer that the wood has been treated with inorganic arsenic and gives handling and use precautions such as a warning against burning. In the previously mentioned case of poisoning attributed to the burning of arsenical pesticide-treated wood, old scrap wood from a marine facility was the source of the treated wood. This scrap wood no longer had any visible warning about its use.

There is no information available about the amount of arsenical pesticide-treated wood which is eventually burned. In a study of pentachlorophenol wood preservatives, Bridle (1984) estimated that 1-10 percent of the treated wood was burned with wood wastes. Based on this assumption, potential arsenic emissions from the combustion of treated wood would result in an estimated 0.32 tons per year of arsenic emissions.

Wood stoves and fireplaces are sources of inorganic arsenic emissions because arsenic is naturally present in wood. Trees and other plants absorb the arsenic that is present in the soil through their root systems (Lederer and Fensterheim, 1983). The combustion of firewood results in state-wide emissions of 1.5 to 11 tons of arsenic per year.

b. **Oil Combustion** - Trace metals, such as arsenic, have been found in distillate, residual, and waste oils (Pedco, 1984; Menczel, et al., 1984; USEPA, 1984; Krishnan, 1982; and Surprenant, 1983). Combustion of these oils results in emissions estimated at 0.14 ton to 6 tons of arsenic per year in California (see Appendix D). Power plants contribute approximately 7 to 15 percent of this total (ARB, 1986a and ARB, 1986b). Other sources such as oil fields, refineries, chemical manufacturers, and ships are responsible for the rest of the emissions from fuel oil combustion.

There is a large variation in the reported arsenic content of distillate, residual, and waste oils. Southern California Edison (SCE) reported concentrations of less than 0.01 ppm for the distillate and residual oils burned at its plants in the South Coast Air Basin (SCE, 1986); however, other sources have reported concentrations of up to 3.1 ppm (Menczel et al., 1984). Fuel oils burned at power plants in the South Coast are lower in arsenic concentration due to the South Coast Rule 431.2 which limits the sulfur content of any liquid fuel burned at power plants and refineries to 0.25 percent (SCAQMD, undated). A 0.50 percent sulfur limit applies to liquid fuels burned in the Bay Area (BAAQMD, 1984). The ARB staff has considered the different arsenic content of oils in estimating the range of arsenic emissions from fuel oil combustion.

Both distillate and residual oil use is predicted to increase in the next decade (CEC, 1986a). The California Energy Commission (CEC) forecasts a slight increase for distillate oil, including diesel (CEC, 1986a). The CEC also forecasts a three-fold increase in residual oil used by the utility industry from 1985 to 1997 (CEC, 1986a and CEC, 1986b). By 2005, residual oil used by the utility industry is expected to return to the low 1984 level due to increased use of alternative energy sources (CEC, 1986b). The use of residual oil by other sectors, such as industrial users, is forecast to remain about the same from 1985 to 2005 (CEC, 1986a). There are no data available on the future levels of waste oil use. Because arsenic emissions from fuel oil combustion are directly proportional to the amount of fuel used, arsenic emissions from fuel oil combustion are expected to correspondingly increase in the next decade.

c. **Coal Combustion** - Arsenic is present in coal as a trace contaminant, and when coal is burned, arsenic can be emitted to the atmosphere. There is considerable variation in the arsenic content of coal, ranging from 2.3 ppmw in western coal to 25 ppmw in eastern coal (ARB, 1984b and Edwards et al., 1980). Because the cement industry is the source category that is the largest coal user in California, it is expected that arsenic emissions resulting from coal combustion come largely from this industry. In this report, arsenic emissions from coal combustion in the cement industry are included in the cement production category because the combustion of coal during the cement manufacturing process is the major use of coal in California. Coal combustion is also the major source of arsenic emissions in the cement production process.

Eight coal-fired cogeneration plants have received authorization for construction in California. Six other plants have been proposed.



Together, these plants would provide approximately 476 mw (megawatts) of electricity (ARB, 1986d). Assuming a heat content of 12,000 btu/lb for coal and a 30 percent efficiency of heat input, the eight approved plants would use approximately 1.2 million tons of coal. The six additional plants would use approximately 678 thousand tons of coal per year. If all these plants were to become operational, arsenic emissions in California would increase by an estimated 0.06 tons of inorganic arsenic per year.

d. **Coal Gasification** - Even though a number of coal gasification programs have been, or are being considered by the utility industry, only one plant is currently known to gasify coal in Southern California. This plant used 108,000 tons of coal from June 1984 through January 1985 (Wolk, 1985). The coal gasification process is also a potential source of arsenic emissions which will become more important if the use of this process becomes more widespread.

#### 4. Cement Production

Arsenic is a trace contaminant of feed materials such as limestone, gypsum, clay, shale, and sandstone used in cement production. Therefore, arsenic is emitted along with other particulate matter during processes such as crushing, grinding, mixing and blending, clinker cooling, cement distribution, and kilning. Data are not available on the arsenic concentration of the feed materials (although believed to be low). Even at low concentrations in the feed materials, total emissions could be significant due to the large volume of feed materials processed (approximately 13.9 million tons in 1984)(USD0I, 1985d). The ARB Emission Data System (EDS) reports that California cement manufacturers emitted approximately 6,500 tons of particulate matter in 1985 (ARB, 1988b). This level of PM emission would result in arsenic emissions of up to 0.76 tons per year (which includes the 0.56 tons per year of arsenic emitted from coal combustion during cement production).

In 1985, the Department of the Interior forecasted U.S. cement production in 1990 and 2000 to be 77 million tons and 87 million tons, respectively (USD0I, 1985c). Based on the United States and California production data for 1980 through 1984, California accounted for an average of 11.2 percent of U.S. cement production (USD0I, 1985c and 1985d). Assuming the ratio of California cement production to the United States is the same in the future, California is forecast to produce approximately 8.6 million tons and 9.7 million tons in 1990 and 2000, respectively. If the arsenic emissions are directly proportional to the amount of cement produced, arsenic emissions from cement manufacturing would be expected to increase slightly to the year 2000.

#### 5. Secondary Smelters

Secondary smelters are resource recovery facilities that use scrap metal for a feedstock. Arsenic emissions from secondary smelters result from the arsenic present in the feedstock. Processes for reclaiming metals from

secondary smelters, such as sweating, smelting and refining, emit arsenic as particulate arsenic. Although arsenic emissions are possible from secondary copper, brass and zinc smelters, secondary lead smelters are of particular concern because arsenic-lead alloys are used in lead-acid batteries. The percent arsenic content of lead-acid batteries peaked in the early 1970's. At that time, arsenic content averaged 0.2 to 0.3 percent of process lead and occasionally reached 0.8 percent. With the introduction of maintenance-free calcium-lead batteries which contain no arsenic, the overall arsenic content of process lead at secondary lead smelters has dropped to approximately 0.15 percent (Radian, 1985b).

Secondary lead smelters differ from lead melting facilities such as foundries. In a secondary lead smelter, metal scraps such as lead-acid batteries are used as feed material, while lead ingots are used in foundries. Lead ingots used by foundries are relatively cleaner and contain smaller amounts of trace metals such as arsenic than does scrap metal. Based on data retrieved from the Emission Data System (EDS) for inventory year 1985, and surveys conducted by the ARB in 1988 (ARB, 1988a; and ARB, 1988b), four secondary lead smelters and four lead foundries were operating in California during 1987.

Secondary lead smelters employ three basic steps: 1) pretreatment such as sweating to remove low melting-point metals, 2) smelting in different furnaces to obtain a certain type of lead, and 3) refining such as alloying to modify the final products.

The primary form of arsenic usually identified in smelter emissions is arsenic trioxide (Eatough, 1979). At some battery recyclers, arsenic chloride ( $AsCl_3$ ) has also been detected (Radian, 1985b). This occurs at secondary lead smelters which do not separate the plastic battery cases from the metal prior to smelting.

Secondary lead smelters use scrubbers, baghouses, or combinations of baghouses and scrubbers to control airborne emissions from battery crushers, smelting furnaces, and refining or alloying kettles. Particulate matter (including trace metals and total organic gases) can be released in fugitive emissions from sorting bins, sorting areas, and roadways. Fugitive emissions can also occur during the process operations of charging, slag tapping, and lead tapping. Gas-phase arsenic may not be controlled by particulate matter control devices.

The ARB staff estimates that the four secondary lead smelters in California emitted 257 lbs (0.13 tons) of arsenic from their exhaust stacks in 1987, based on source tests performed by the South Coast Air Quality Management District and information received from the facilities themselves. This emission estimate does not include fugitive emissions. The emission estimate accounts only for those emissions released from exhaust stacks of smelting furnaces and the emissions from the alloying or refining kettles. Other sources of emissions such as sorting / charging operations and roadways have not been estimated due to insufficient information.

Although the total amount of non-fugitive arsenic being emitted from secondary lead smelters is estimated at 0.13 ton and may not seem significant

when compared to larger "tons per year" sources, a significant "hot spot" exposure to the local population near a secondary lead smelter has been demonstrated (see Table I-4 and the accompanying text).

#### 6. Glass Manufacturing

As of 1984, no glass manufacturing plants in California are known to use arsenic in their production processes. However, test results from four glass plants in the State show arsenic emissions (ARB, 1985f). Arsenic emissions from these glass plants are thought to originate through the use of feed materials which naturally contain arsenic as a trace constituent.

The EDS identified 22 glass plants in California with production of approximately 7 million tons in 1981 (ARB, 1985e). Assuming arsenic emissions from each glass plant are approximately the same, based on test results from four facilities (ARB, 1985c and 1985f); arsenic emissions from glass manufacturing plants are estimated to be 0.16 tons per year.

#### 7. Waste Combustion

a. **Sewage Sludge Incineration** - Arsenic has been found in municipal sewage sludge of many U.S. cities, including Los Angeles and San Francisco (Furr, 1976 and Gerstle, 1982). Some industrial wastewater disposal of arsenic compounds is known to occur, and would contribute to the arsenic burden in the sewage sludge. When the sludge is incinerated, arsenic can be emitted. Sewage sludge incinerators in California are estimated to have emitted approximately 360 pounds (0.18 tons) of arsenic in 1983 (ARB, 1985d and Bennett, 1982). Although the statewide arsenic emissions from sewage sludge incinerators are not expected to be a significant part of the total emission inventory, the potential for hot spot exposure to a small localized population does exist.

b. **Waste-to-Energy Projects** - Facilities that incinerate waste to produce electricity are potential sources of arsenic emissions. Three waste-to-energy facilities are operating in California (Commerce, Long Beach, and Modesto) processing approximately 2400 tons of waste per day. Another facility (in San Diego) was in the later stage of the permitting process as of November 1989. Arsenic emissions from the operating waste-to-energy facilities are estimated to be less than 5 pounds per year (ARB, 1989c).

#### 8. Cotton Ginning

Arsenic emissions may result from the ginning or incineration of cotton or cotton wastes which have been treated with arsenical defoliants. Emission factors as high as 0.02 lb. of arsenic per bale of cotton have been estimated (Roberts, 1980). In 1980, the ARB estimated there were 233 cotton gins operating in California; however, not all gins would emit arsenic since cotton defoliation in California is predominantly done with nonarsenicals. The ARB estimated arsenic emissions from Fresno County gins to be 88 lbs in 1978 based

on the assumptions that all the arsenicals applied went into the gin and that the arsenic composition in the gin's cyclone is the same as in the feed (Roberts, 1980). All cotton defoliants reported used in California are organo-arsenicals. Any emissions from ginning would be organic arsenic. Incineration of cotton gin trash previously treated with arsenic compounds will result in the emission of inorganic arsenic. Several cotton gins in California presently incinerate gin trash in a resource recovery process to provide fuel for dryers. No information on emissions from the incineration of gin trash is available at this time.

#### 9. Wood Preservatives

Arsenic is used in wood preservatives as a pesticide. Although the largest use of arsenic is in wood preservatives, the emissions from their use are negligible. Over 95 percent of the preservatives are supplied to treatment plants in liquid form and are handled in a closed system operation in which the liquid concentrate and dilution water are meter-mixed. Air monitoring data detected no elevated ambient levels of arsenic around these plants under normal operating conditions (Lederer and Fensterheim, 1983).

A San Mateo-based company uses arsenic acid to produce arsenical wood preservatives in Weed, California. Arsenic acid from this company is also sold to a Stockton company to manufacture arsenical wood preservatives. Wood preservatives at these two plants are produced for internal use to treat wood (Morgan, 1985). No information is available to estimate arsenic emissions for these two plants at this time.

A Burbank company intermittently produces sodium arsenite in small 1- to 5-lbs batches. Total annual production is less than 100 lbs. Because of the low production rate, their contribution to annual arsenic emissions can be considered negligible (Cruse, 1981).

#### 10. Semiconductor Industry

The semiconductor industry uses a variety of inorganic arsenic-containing compounds in the manufacture of printed circuits and microchips. Arsine gas, arsenic trioxide, elemental arsenic, gallium arsenide, and arsenic trichloride are used by semiconductor manufacturers in California, predominantly in Santa Clara and San Mateo Counties. The nature of the manufacturing process suggests that arsenic emissions into the atmosphere should be low and intermittent.

Table II-3 shows the number of companies using various arsenic compounds in the two counties (MacKay et al., 1987, ARB, 1987b).

Arsine is the most widely used arsenic compound in the semiconductor industry. It is not very water soluble, and does not respond well to traditional pollution control devices. Consequently, many arsine users do not have arsine emission control devices. Because it is considered an "extremely toxic poison" (Alexeeff, 1987) it is tightly controlled in the manufacturing process and is not expected to be released under normal circumstances.

TABLE II-3

**Arsenic Compounds Used in the Semiconductor Industry  
in Santa Clara and San Mateo Counties, 1987**

<u>Compounds</u>	<u>Companies Reporting Use</u>
Arsine gas	26
Gallium arsenide	7
Arsenic trioxide	2
Elemental arsenic	1
Arsenic trichloride	1

Arsine is typically used in the ion implantation and epitaxy processes. Arsine gas is used to change the electrical properties of microchip wafers. There is no available information on the use of pure arsine at semiconductor facilities. Typical arsine concentrations in the gas mixture for the ion implantation process is approximately 10 vol percent to 15 vol percent. In the epitaxy process, arsine concentrations range from 35 to 50 ppmv (parts per million by volume).

In 1984, over 18,500 cubic feet of arsine-containing gas was used in Santa Clara County (BAAQMD, 1985). It is not known how much, if any, of the gas escaped into the atmosphere in either fugitive or stack emissions. A source test of a semiconductor manufacturing facility failed to detect arsine emissions from the emission stacks, however, arsine gas use in the production process is intermittent and may account for the inability to detect the gas.

In 1987, the Bay Area Air Quality Management District (BAAQMD) reported that there were 46 semiconductor manufacturing facilities in Santa Clara County (BAAQMD, 1987). Several electronics manufacturers in San Diego County were also reported to use arsine (Lake, 1988).

There is only one arsine manufacturer in California, which produces approximately 3,000 lbs or an equivalence of 26,280 standard cubic feet of pure arsine per year (Lake, 1988). It is not known if this arsine is used only in California.

Gallium arsenide is used in LED (light-emitting-diode) circuits and other special electronic applications. No emissions of this solid material would be expected with the exception of dust from cutting and milling of the material. Small arsenic emissions may be possible during the manufacture of gallium arsenide. This involves the heating of elemental arsenic to a vapor and allowing it to react with gallium to form gallium arsenide crystals. The manufacture of gallium arsenide crystals accounts for the single reported use of elemental arsenic in Table II-3.

No information was available on the amounts (or the nature of the use) of arsenic trioxide and arsenic trichloride although it appears to be quite limited.

## 11. Disturbance of the Earth's Crust

Arsenic is present in 245 mineral species found in the earth's crust. Disturbance of the earth's crust (e.g., mining, quarrying, road building) may result in airborne particulate matter emissions that include emissions of inorganic arsenic. In addition to the arsenic that may become airborne because of geologic disturbances, arsenic trioxide that is used in micro-recovery of precious metals in open pit mining operations may be emitted to the atmosphere during use. Open pit mining emissions of arsenic trioxide have not been quantified but may be significant.

Dry lakebeds in California's central and southeastern desert regions are sources of windblown inorganic arsenic. Saline lakes that are lowering as a result of inflow water diversion (e.g., Mono Lake) provide arsenic salts from newly-exposed lakebed and are sources for additional arsenic emissions.

Windblown dust analysis studies conducted downwind of Owens and Mono Lake have indicated that there are a number of toxic elements present in the dust, including selenium, mercury, lead, and arsenic. Results of the study have shown that the arsenic concentrations in the airborne dust downwind of Owens and Mono Lake were an estimated  $30 \text{ ng/m}^3$  and  $25 \text{ ng/m}^3$ , respectively. "Dust events" responsible for the arsenic emissions occurred on 11 percent of the study period days (Kusko and Cahill, 1984). Therefore, dust events may result in hot spot arsenic exposure to local populations.

Water from the Owens Lake/Mono Lake watershed region feeds the Los Angeles Aqueduct and provides a significant portion of the water for the people living in the Los Angeles Basin. The Los Angeles Department of Water and Power (1990) reports an average waterborne arsenic concentration in the aqueduct of  $10 \text{ ug/l}$ , and attributes the majority of the arsenic in the water to the contribution of Hot Creek rather than airborne arsenic deposition. (Hot Creek, one of the contributing tributaries, is naturally high in arsenic and fluorides because of its unique geology.) This concentration is well below the Federal Safe Drinking Water Act Maximum Contaminant Level of  $50 \text{ ug/l}$ , and equal to the U.S. Public Health Service recommended arsenic limit of  $10 \text{ ug/l}$ . (For more information on arsenic concentrations in California's drinking water, please see Water in Chapter I.)

Windblown dust, mining operations, road building and other natural or anthropogenic activities represent potentially significant sources of airborne arsenic. Emission factors and estimated arsenic concentrations from geologic sources (natural and anthropogenically induced) need to be developed and should be the focus of additional research.

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### III. PROPERTIES OF INORGANIC ARSENIC IN THE ATMOSPHERE

#### A. PHYSICAL AND CHEMICAL PROPERTIES

Arsenic is the twentieth most abundant element in the earth's crust and is present in 245 mineral species. Rarely found as the free element, arsenic is found in a variety of minerals, with arsenopyrite (FeAsS) being the most common. Heating of most arsenic-containing compounds in the presence of air results in the oxidation of the arsenic bound in the mineral. The product of this oxidation is primarily arsenic trioxide.

The chemistry of arsenic is complex due to the stability of three oxidation states (-3, +3, +5) and also because of the ability of arsenic compounds to undergo complexation, precipitation, absorption, and biotransformation. Inorganic arsenic is most commonly present in the oxidized trivalent (+3 or III) and pentavalent (+5 or V) forms. Arsenic compounds are generally nonvolatile, except for gaseous arsines and arsenic trioxide.

Most commercial arsenic products are manufactured using arsenic trioxide as the raw material. This raw material serves as the basis for approximately 50 other arsenic compounds produced in the United States. Table III-1 lists some physical and chemical properties of arsenic compounds with environmental significance (USEPA, 1982).

Arsenic trioxide is a relatively volatile metal oxide. It sublimes at 193°C. Thermodynamic data indicates that at the temperatures 10°C, 25°C, and 40°C, up to 0.04 ug/m<sup>3</sup>, 0.45 ug/m<sup>3</sup>, and 4.03 ug/m<sup>3</sup>, respectively, of arsenic could be in the gas phase as arsenic trioxide (As<sub>2</sub>O<sub>3</sub>) (Murray, et al., 1974 and Pupp, et al., 1974). However, these levels of arsenic have not been observed in the atmosphere. This may be because the thermodynamic calculations of Murray et. al. and Pupp et. al. do not consider the reaction of water with As<sub>2</sub>O<sub>3</sub> to form the less volatile and more water soluble species oxyacid or the oxidation of As(III) to As(V).

Arsenic trioxide in the gas phase can pass through particulate matter control and monitoring equipment.

#### B. FORMATION AND FATE IN THE ATMOSPHERE

##### 1. Introduction

As a result of its complex chemistry, a key factor in understanding the behavior of inorganic arsenic is determining the physical state and chemical form of inorganic arsenic in the atmosphere. This is made difficult because the standard sampling and analytical methods for measuring arsenic in the atmosphere can only measure total arsenic in the particle phase. Our investigation indicates that arsenic in the atmosphere is predominantly a variable mixture of arsenic trioxide and arsenic pentoxide (or as the oxyacid or salt of the oxyacid). These inorganic arsenic oxides are primarily present in the atmosphere on particles less than 2.5 um.

TABLE III-1  
CHEMICAL PROPERTIES OF ARSENIC COMPOUNDS

Chemical Name and Formula	Synonyms	Oxidation State	Transition Points	Water Solubility (per liter)	Specific Properties
Arsenic pentoxide $As_2O_5$	Arsenic oxide; arsenic acid; arsenic anhydride	+5	Decomposes at 315 C to $As_4O_6$ vapor	1.5 kg (16 C)	Forms arsenic acid, $H_3AsO_4$ , in water; the salts of which are known as arsenates.
Arsenic acid $H_3AsO_4 \cdot 1/2 H_2O$	Orthoarsenic acid, hemihydrate	+5	mp 35.5 C bp 160 C	170g (20 C)	Forms a triprotic acid in water with pKa values of 2.2, 7.0 and 11.5.
Calcium arsenate $Ca_3(AsO_4)_2$	Arsenic acid ( $H_3AsO_4$ ), calcium salt (2:3)	+5	—	0.13 g (25 C)	
Lead arsenate $PbHAsO_4$	Arsenic acid ( $H_3AsO_4$ ), lead (+2) salt (1:1); schultenite	+5	Decomposes at 720 C	V. sl. soluble	Occurs in mineral form as schultenite.
Sodium arsenate $Na_3AsO_4$	Arsenic acid ( $H_3AsO_4$ ), sodium salt	+5	—	389g (16 C)	Also available as the potassium salt, $KH_2AsO_4$ . The name "sodium arsenate" is applied to both the disodium and trisodium salts.
Arsenic trioxide $As_2O_3$ , crystalline or glass; $As_4O_6$ , gas	Arsenous oxide; arsenous acid; white arsenic	+3	Sublimes at 193 C mp 315 C bp 457 C	21g (25 C) Rate of dissolution is very slow	Forms arsenous acid $As(OH)_3$ in water; the salts of which are known as arsenites.
Sodium arsenite $NaAsO_2$	Arsenous acid ( $HAsO_2$ ), sodium salt	+3	—	V. sol.	Available as the potassium salt, $KH(AsO_2)_2$ .

Table III-1 (continued)

Arsenic sulfide $As_2S_3$	Arsenic yellow; orpiment	+3	mp 320 C bp 707 C	0.5 mg (18 C)	Burns in air forming $As_4O_6 + SO_2$ . Occurs naturally as orpiment.
Arsenic As	Arsenic black; metallic arsenic	0	Sublimes at 613 C	Insoluble	When heated in air, sublimes and is oxidized to $As_4O_6$ .
Arsine $AsH_3$	Arsenic hydride; hydrogen arsenide	-3	bp -55 C	200 ml (20 C)	Faint garlic odor. Vapor density is 2.7 times that of air.
Monosodium methylarsenate $CH_3AsO_3Na$	Methane arsonic acid, monosodium salt; arsonic acid, methyl-, monosodium salt; MSMA	Organo- metallic	mp 115-119 C	570g (25 C)	Also available as disodium salt, disodium methyl- arsenate (DSMA).
Cacodylic acid $(CH_3)_2AsO_2H$	Dimethyl-arsinic acid; arsine oxide, hydroxydimethyl-	Organo- metallic	mp 200 C	830g (22 C)	Available as the sodium salt, sodium cacodylate.
Arsanilic acid $C_6H_4NHAsO_3H_2$	Arsonic acid (4-aminophenyl)	Organo- metallic	mp 232 C	Sol. (hot)	Available as the sodium salt, sodium arsanilate.

Source: (EPA, 1982; corrections by Solomon)

## 2. Inorganic Arsenic in the Gas Phase

Arsenic trioxide and arsine ( $AsH_3$ ) are two forms of inorganic arsenic with sufficient volatility to be present in the gas phase (either completely or to some extent present) under atmospheric conditions. Other forms of arsenic are much less volatile and are not expected to be present in significant amounts in the gas phase. Arsine is a gas under atmospheric conditions. Because of arsine's high acute toxicity, anthropogenic emissions of arsine are expected to be small. Arsine emissions are strictly regulated, and should not significantly contribute to ambient arsenic exposure. At the present time, arsine gas exposure is of concern only in the work environment or in the event of accidental release to the ambient air.

Arsenic trioxide, on the other hand, is the primary form of inorganic arsenic expected to be emitted from high temperature industrial sources (Eatough et al., 1979). It is a solid at room temperature, but sublimates at  $193^{\circ}C$ . Thermodynamic studies and experiments with selenium oxides, which have similar properties to arsenic oxides, indicate that a potentially significant portion of arsenic trioxide could be present in the atmosphere in the gas phase (Davison, et al., 1974). In-stack monitoring of  $130^{\circ}C$  copper smelter effluent for arsenic, conducted by Germani, et al., (1981) found 10 to 30 percent of the arsenic in the gas phase. These results suggest that arsenic (probably as arsenic trioxide) is present in the gas phase when emitted from a high temperature source. Despite the evidence for the presence of a significant portion of arsenic trioxide in the gas phase, it has not been detected in the ambient air as a gas. Johnson and Braman (1975) performed total air sampling (both particle and gas phase) sampling for arsenic. All of the inorganic arsenic was found in the particulate matter phase. Walsh et al. (1979) measured gas and particle phase arsenic in close proximity (500 m) to a large copper smelter. The source primarily emitted arsenic in the gas phase, probably as  $As_4O_6$  (As III oxide). Walsh and co-workers observed that greater than 90 percent of the arsenic that they collected near the source was in the particle phase. Test results indicate that gas-phase arsenic from high temperature sources quickly condenses onto existing particles (preferring the fine particulate matter) and will not be present to any great extent in the gas phase under normal atmospheric conditions.

In contrast, methyl arsines, a biologically generated arsenic byproduct (see the following section on biochemical transformations), are the only arsenic forms normally detected in the gas phase in ambient air.

Based on consideration of the previously mentioned studies, we will make the assumption that arsenic trioxide in the atmosphere is present almost entirely in the particle phase.

## 3. Inorganic Arsenic in the Particle Phase

Arsenic-containing particles in urban aerosols and from high temperature sources are significantly enriched in arsenic relative to the geological



background (which can range from as little as 1 ppm to as much as 40 ppm in soils) (USEPA, 1984). The greatest levels of arsenic enrichment are found with fine particulate matter, which indicates that the origin of most arsenic in the air is due to anthropogenic sources and not surface erosion. The level of enrichment varies with the nature of the arsenic source. This can range from a factor of 100 for coal fired power plants to a factor of a million (essentially pure arsenic trioxide) for copper smelters (Germani, et al., 1981). The geometric mean of arsenic concentration in urban aerosols from 29 cities in U.S., Europe, and Japan showed an enrichment factor of 136 above geological background (Davidson, et al., 1981).

Studies of particle size distribution of arsenic-containing particles indicate that the arsenic concentration of airborne particles increases with the inverse of particle size (Davison, 1974; Natusch, 1974; and Germani, et al., 1981). Davison, et. al., (1974) hypothesized that arsenic trioxide is volatilized in high temperature processes and condenses or adsorbs onto the surface of entrained particles with the greatest amount of arsenic per unit weight on the smaller particles. Paciga and Jervis (1976) estimated that 37 percent of the mass of arsenic in urban aerosols was on particles of 1.1 micron or less with the average particle size being 1.5 micron. These results are consistent with the results of an ARB monitoring study which showed the bulk of the inorganic arsenic on particles less than 2.5  $\mu\text{m}$  (see Table III-2).

#### 4. Forms of Inorganic Arsenic in the Atmosphere

Our study of inorganic arsenic indicates that high-temperature processes such as smelting and combustion are the largest sources of emissions to the atmosphere. Trivalent arsenic, particularly arsenic trioxide, is the predominant inorganic arsenic compound found in emissions from many of these processes. The formation of arsenic trioxide in high temperature processes (Germani et al., 1981; Davison et al., 1974) is so chemically preferred that extremely pure arsenic trioxide is recovered commercially from the effluent gases from copper ore smelting. Although arsenic trioxide is usually the major form emitted, exceptions to this have been reported. In cases where the combustion temperature is not high enough, pentavalent arsenic may not be converted to arsenic trioxide (Peters, et al., 1984). Arsenic chloride ( $\text{AsCl}_3$ ) has been detected at secondary lead smelters where large amounts of plastics are present in the feed stock (Radian, 1985).

The major chemical transformation that As(III) undergoes in the atmosphere is oxidation to As(V). Due to a lack of an accepted methodology for measuring trivalent and pentavalent levels, there has been a considerable debate concerning the rate of oxidation of trivalent arsenic in the atmosphere. Braman (1984) suggested that rapid oxidation of trivalent to pentavalent arsenic in the atmosphere seems likely to occur and concludes that only arsenic pentoxide should be present in the atmosphere. Other researchers (Cherry, et al., 1979 and Tallman, et al., 1980) have found that arsenic trioxide oxidizes slowly in aqueous solutions even under experimental conditions where oxidation would be thermodynamically favored. Additionally,

arsenic trioxide may first undergo (or be very competitive with) a reaction with water to form the As(III) oxyacid before oxidation to As(V).

Andreae (1980) measured arsenic levels in rainwater samples collected in various areas of the United States and detected both inorganic As(III) and As(V) arsenic in most samples. The ratio of these arsenic species in the samples varied widely. This variation was attributed to several factors, including the presence of industrial sources of trivalent arsenic, the age of the aerosol, the effective oxidation-reduction potential of the aerosol, and sources contributing As(V). Elevated As(III) levels in rainwater were detected at long distances from a large industrial source of arsenic trioxide emissions. These findings suggest that arsenic trioxide may not rapidly oxidize to arsenic pentoxide in the atmosphere.

Solomon (1984) developed a new analytical method capable of measuring trivalent arsenic and pentavalent arsenic levels in atmospheric samples. His analysis of air samples gave similar results to what Andreae observed in rainwater. Trivalent arsenic was present above the detection limit

(approximately  $1 \text{ ng/m}^3$ ) in only half of the samples, whereas, As(V) was present in all samples analyzed. A wide variation also was observed in the relative amounts of trivalent and pentavalent arsenic in the samples. The ratio of As(III) to As(V) in samples collected in the Tucson, Arizona area varied from less than 0.04 to 0.97 with an average of 0.31. Solomon concluded that the fluctuations in the As(III)/As(V) ratio suggest that either the rate of As(III) oxidation in the atmosphere varies, the age of the aerosol differed from sample to sample, or there may be other arsenic sources contributing to the variations in the ratio. Although these results suggest that trivalent arsenic can persist in the atmosphere, the factors influencing trivalent arsenic levels in the atmosphere after emission from an industrial source are presently unknown and are the subject of future research (Solomon, 1984).

The ARB's Southern Laboratory Branch used the arsenic speciation method developed by Solomon to investigate the composition of airborne arsenic in Los Angeles near a known high temperature source of arsenic (see Appendix B). The results of this study reinforce the assertion that inorganic arsenic is present in both the (III) and (V) forms in the ambient air.

Atmospheric sampling was conducted in the City of Industry on 16 days during the period January 12, 1987 to February 3, 1987. A high-volume dichotomous virtual impactor (HVDVI) collected both coarse particle ( $>2.5 \text{ } \mu\text{m}$ ) and fine particle ( $<2.5 \text{ } \mu\text{m}$ ) samples. These samples were analyzed using the arsenic speciation method developed by Solomon: selective reduction to arsine followed by flame atomic absorption spectroscopy (FAAS). Parallel sampling at the same site was conducted with a high-volume (hi-vo) sampler. These samples were analyzed with the analytical method for total particulate arsenic used in the toxic air contaminant monitoring network described in Appendix A. The results of this study are presented in Table III-2.

On the average, in both the fine and coarse particle size ranges, the concentrations of As(III) measured were approximately equal to those measured for As(V) (i.e., an As(III)/As(V) ratio of about 1 to 1). The highest As(III) concentration observed (sum of fine plus coarse) was  $48.8 \text{ ng/m}^3$ , which

TABLE III-2

**Fine- and Coarse-particle As(III) and As(V) Concentrations  
and Total As Concentrations in TSP**

(All reported concentrations are in  $\text{ng}/\text{m}^3$ )

Sampling Date (1987)	As(III) found		As(V) found		As(III) + As(V) by HVDVI/FAAS	Total As by Hi-vol/GFAAS
	Fine	Coarse	Fine	Coarse	Fine + Coarse	Total
1/12	44.0	4.8	18.7	6.6	74.1	69.4
1/13	10.9	1.8	6.6	3.0	22.3	24.4
1/14	4.2	<1.8	4.6	2.2	11.0	5.5
1/15	2.0	<1.1	1.9	1.4	6.2	4.4
1/19	2.9	1.4	3.4	2.2	9.9	16.2
1/20	5.3	1.2	2.4	<1.0	8.9	12.1
1/21	4.5	1.5	2.9	<1.2	8.9	11.8
1/22	14.1	4.1	4.9	1.7	24.8	34.0
1/25	<1.2	<0.9	<1.0	<1.0	<1.1	2.8
1/26	10.2	2.2	5.9	4.3	22.6	35.9
1/27	1.5	<1.0	1.8	0.9	4.2	15.0
1/28	6.3	<2.4	12.0	3.9	22.2	21.2
1/29	2.2	<0.9	<0.9	1.6	3.8	6.8
2/1	3.7	1.0	3.4	1.3	9.4	12.7
2/2	<1.7	<1.7	7.0	2.3	9.3	14.4
2/3	4.2	<1.1	6.1	1.5	11.8	15.8

comprised 66 percent of the total As(III) and As(V). The As(III) concentration observed in the fine particles was below the detection limit on 2 out of the 16 days sampled, and on one of those days the As(V) concentration was also below the detection limit. Most of the arsenic, both (III) and (V), was measured on the fine particles; As(III) and As(V) concentrations averaged  $7.4 \text{ ng/m}^3$  and  $5.2 \text{ ng/m}^3$ , respectively, on fine particles and  $1.8 \text{ ng/m}^3$  and  $2.2 \text{ ng/m}^3$  on coarse particles for the 16 sampling days. (The concentrations that were detectable but not quantifiable were considered to be at the level of detection for the averages reported in this paragraph.)

The results of the parallel sampling with the sampling and analytical methods used in the toxic monitoring network are also presented in Table III-2. The concentrations of "total" arsenic measured were generally greater than the sum of the As(III) and As(V) concentrations measured using the HVDVI and the Solomon analytical method. This occurred on 12 of the 16 monitoring days. The 16-day average concentrations were  $18.9 \text{ ng/m}^3$  measured for total arsenic and  $15.7 \text{ ng/m}^3$  measured for As(III) and As(V). Considering the differences in the sampling and analytical techniques involved, the results are surprisingly comparable, having a correlation coefficient of 0.95.

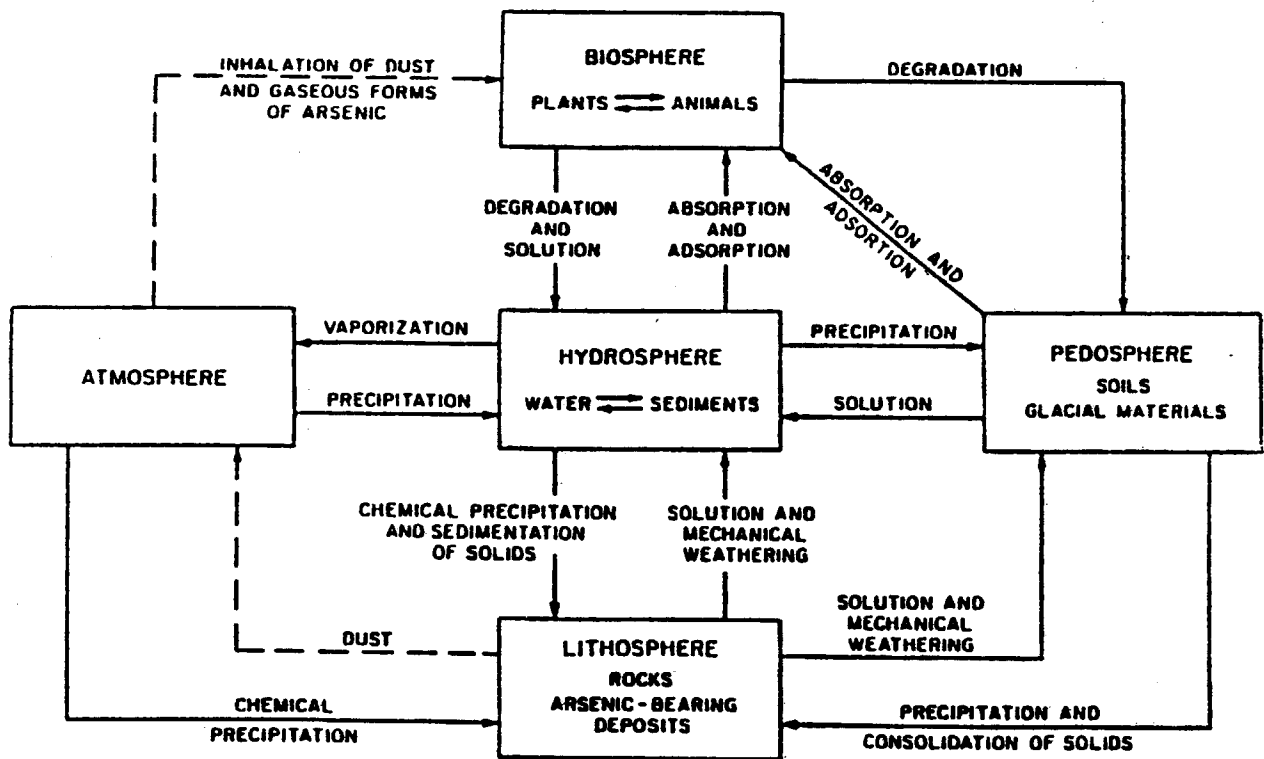
The higher arsenic total measured with the toxic monitoring network method can possibly be explained by a number of factors. Polytetrafluoroethylene (PTFE) filters were used in the HVDVI sampler, while glass microfiber filters were used in the hi-vol sampler. PTFE filters are virtually inert; however, gas-phase oxyacids of arsenic (most likely  $\text{As}_4\text{O}_6$ ) may be adsorbed and even oxidized by the more reactive glass-fiber filter substrate. This results in a positive artifact for aerosol arsenic undertotal-arsenic GFAAS analysis. Also, about one third of the arsenic (III) or (V) values observed on coarse particles were above the reagent blank level but below the quantitation limit. If the concentrations in those samples could be quantified and added to the As(III)-and-As(V) total, the values from the HVDVI sampling and the hi-vol sampling would probably be closer.

## 5. Environmental Mobility

Inorganic arsenic released from combustion sources is usually in the form of arsenic trioxide. Arsenic trioxide adsorbed onto airborne particles settles as dry deposition or is washed out with precipitation (NAS, 1977 and Andreae, 1980). In many cases, a portion of the arsenic trioxide may be emitted in the gaseous phase, but can later be adsorbed onto particulate matter in the atmosphere. The residence time for inorganic arsenic in air is estimated to be about nine days (Woolson and Kearney, 1973).

Arsenic is highly mobile in the environment, and it is subject to a complex cycle of chemical and biochemical transformations. These transformations can convert arsenic into water soluble, water insoluble, or volatile forms. Figure III-1 presents the geochemical cycling of arsenic through various environmental media. Once deposited on soils or water from the air, arsenic may still be moved between various environmental compartments by ground or surface waters.

FIGURE III-1: The Generalized Geochemical Cycle for Arsenic



(U.S. EPA, 1984)

In terms of the relative amounts of arsenic partitioned among the various environmental compartments, Suta (1980) calculated that land is the major sink for arsenic, accounting for approximately 90 percent of the dissipation. The atmosphere accounted for 7 to 8 percent with the remainder in waterborne effluents.

## 6. Geochemical Transformations

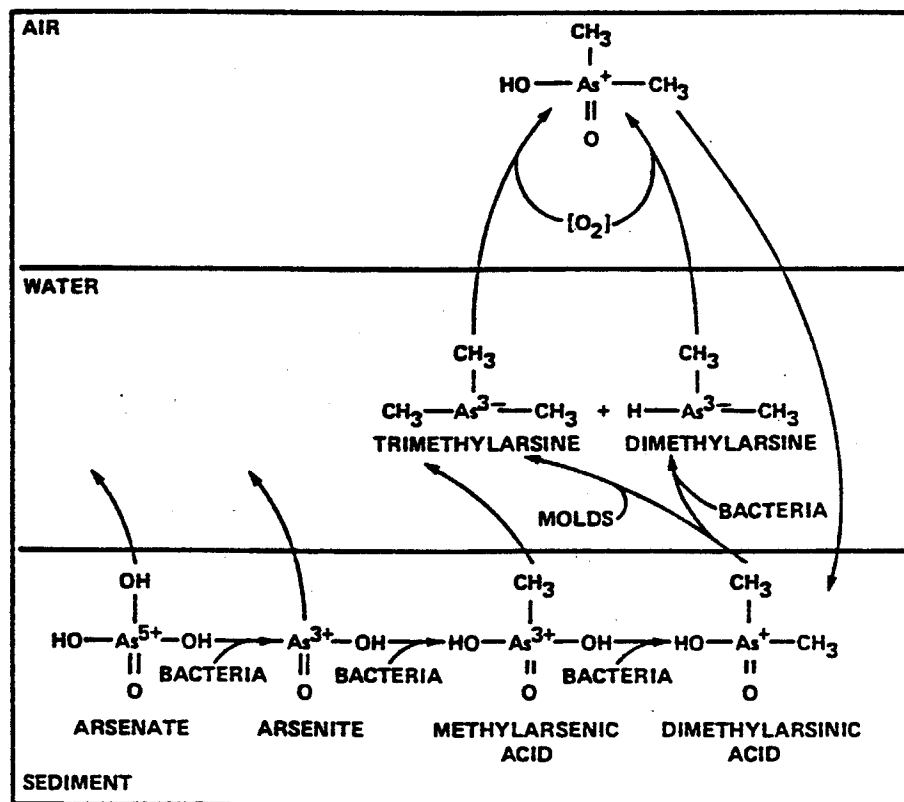
Arsenic emissions can undergo a variety of reactions in the environment. Trivalent arsenic in the atmosphere can undergo oxidation to the pentavalent state. This conversion can also occur in aerated surface waters. Conversely, pentavalent arsenic, under certain conditions, can be converted to trivalent arsenic in aqueous medium (NAS, 1977). Arsenic also reacts with iron, aluminum, calcium, and magnesium ions in the soil to produce insoluble arsenates which are biologically inactive. This transformation usually removes arsenic from further transformations in the cycle.

## 7. Biochemical Transformations

Arsenic may also undergo biochemical transformations according to a cycle presented in Figure III-2. Biochemical cycling of anthropogenic arsenic may begin with deposited arsenic oxides being converted to arsenate ( $\text{AsO}_4^{3+}$ ). The arsenate is reduced and methylated by bacterial action in the soil which can lead to the production of volatile arsines. Reduction and methylation of inorganic arsenic appears to occur only to a limited extent in soils, with one to two percent transformed over a period of months having been reported (USEPA, 1984).

Formation of insoluble arsenates is the fate for the majority of deposited arsenic (Woolson, 1984). However, soils that are re-exposed to arsenicals liberate volatile arsines more readily than soil that is subject to arsenic deposition for the first time (Woolson and Kearney, 1973). This presumably is a result of a microbial population better adapted to arsenic metabolism. This suggests the potential for a shift in the biogeochemical cycle of arsenic towards reduction and methylation on a local level (Wood, 1974 and Woolson, 1984) and may result in higher concentrations of volatile arsenicals being released from areas of constant deposition.

FIGURE III-2: The Proposed Biological Cycle for Arsenic



Source: Wood (1974)

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**APPENDIX A**

**ARB PROCEDURE FOR THE SAMPLING AND  
ANALYSIS OF ATMOSPHERIC INORGANIC ARSENIC**

June 1986  
(Revised September 1987)

**AIR RESOURCES BOARD  
PROCEDURE FOR THE SAMPLING AND ANALYSIS  
OF ATMOSPHERIC ARSENIC (Inorganic)**

**Method 107  
Revision 3**

**Monitoring and Laboratory Division  
State of California  
Air Resources Board  
9528 Telstar Avenue  
El Monte, CA 91731**

Procedure for the Sampling and Analysis  
of Atmospheric Arsenic

Method 107

1 Introduction

- 1.1 This procedure describes a method of sampling and analyzing ambient arsenic (As).
- 1.2 Particulate arsenic concentrations from 3.0 ng/mL to 50.0 ng/mL As can be analyzed by this method. Higher concentrations of arsenic can be diluted to within this range prior to analysis.

2 Method

- 2.1 Suspended particulates in ambient air are collected on a glass fiber filter for 24 hours using a high volume sampler.
- 2.2 The arsenic in the particulates on the glass fiber filter is dissolved in dilute nitric acid (HNO<sub>3</sub>).
- 2.3 The soluble arsenic is analyzed by flameless atomic absorption spectroscopy.

3 Apparatus

- 3.1 The hi-volume sampler used to collect the sample is described in Appendix D, "Procedure for use of High-Volume Sampler" (Air Resources Board Ambient Toxics Sampling and Analytical Procedures.)
  - 3.1.1 An EPM Whatman 2000 glass fiber filter (8 x 10 inch) is used to collect the samples.
- 3.2 Heated ultrasonic water bath: 450 watts minimum cleaning power and capable of being heated to about 75°C.
- 3.3 Atomic absorption (AA) spectrophotometer equipped with deuterium background correction, an autosampler with provisions for use of a matrix modifier, a graphite furnace; pyrocoated graphite tubes with L'vov platform, and an arsenic electrodeless discharge lamp.
  - 3.3.1 A PE-3030 AA spectrophotometer, AS-40 autosampler, HGA-400 graphite furnace and a printer were used in this procedure.

- 3.4 Glassware: Volumetric flasks and pipets, 100 mL graduated mixing cylinders (large mouth opening), short stem powder funnels (about 0.5 in. i.d. stem suitable for use with the 100 mL mixing cylinders), short stem filtration funnels (55 mm diameter), and 30 mL glass beakers.
- 3.5 Polyethylene bottles for sample storage, 60 or 125 mL.
- 3.6 Lead donuts, 640 g (from: Instruments for Research and Industry, P.O. Box 159M, Cheltenham, PA 19012, Catalog # LD-5C).
- 3.7 Stainless steel scissors, forceps, plastic gloves and glass stirring rods.
- 3.8 Whatman filter paper #40, 9 cm dia, medium retention.

#### 4 Reagents

- 4.1 Metal-free distilled deionized water or double distilled water is used for preparing all reagents, standards, and sample dilutions.
  - 4.1.1 The Millipore Corporation's Milli-Q Type I reagent grade water system using deionized feed water is used for atomic absorption work in this procedure.
- 4.2 Nitric acid, HNO<sub>3</sub>, concentrated (16 N), ACS reagent grade quality or redistilled HNO<sub>3</sub> is used to prepare the nitric acid solutions.
  - 4.2.1 Nitric acid, diluted, 0.50 N. Add 31.0 mL concentrated HNO<sub>3</sub> to metal-free water in a 1 liter volumetric flask. Mix well and make up to volume.
  - 4.2.2 Nitric acid, diluted, 0.25 N. Add 15.6 mL concentrated HNO<sub>3</sub> to metal-free water in a 1 liter volumetric flask. Mix well and make up to volume.
- 4.3 Argon gas: 99.999% purity.
- 4.4 Arsenic (As) stock standard solution, NBS standard reference material 3103, 10.00 mg/mL in 15% HCl.
  - 4.4.1 Arsenic standard solution I (1.0 mL = 40.0 ug As): Dilute 2.0 mL As stock standard solution (10.00 mg As per mL) with 0.25 N HNO<sub>3</sub> to 500.0 mL. Mix well. Prepare this solution every twelve months.
  - 4.4.2 Arsenic standard solution II (1.0 mL = 1.00 ug As ): Dilute 25.0 mL As standard solution I to 1000.0 mL with 0.25 N HNO<sub>3</sub>. Mix Well. Prepare this solution every six months.

- 4.4.3 Arsenic calibrating standard solutions: 15.0, 30.0, and 50.0 ng/mL As.
- 4.4.3.1 15.0 ng/mL As: Dilute 3.0 mL of 1.0 ug/mL As standard solution to 200 mL with 0.25 N HNO<sub>3</sub>. Mix well.
- 4.4.3.2 30.0 ng/mL As: Dilute 6.0 mL of 1.0 ug/mL As standard solution to 200 mL with 0.25 N HNO<sub>3</sub>. Mix well.
- 4.4.3.3 50.0 ng/mL As: Dilute 10.0 mL of 1.0 ug/mL As standard solution to 200 mL with 0.25 N HNO<sub>3</sub>. Mix well.
- 4.4.3.4 The calibrating standard solutions mentioned in 4.4.3 should be prepared every two weeks.
- 4.5 EPA quality control check samples or NBS standard reference material solutions: concentrated solutions are diluted so as to fall within the calibrated linear range of the instrument.
- 4.6 Nickel nitrate solution, 4.0 mg Ni per mL:  
Weigh 19.81 g Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Puratronic Grade from Alfa Products, Danvers, MA) and dissolve in metal-free water. Make up to 1.0 liter mark in volumetric flask. This is used as a matrix modifier for the arsenic analysis.

## 5 Procedures

- 5.1 Sampling is performed as described in Appendix D, "Procedure for Use of High Volume Sampler". The sampling period is 24 hours at a flow rate of 40 cubic feet per minute (cfm).
- 5.2 The analysis is performed with an emphasis on the prevention of reagent and sample contamination.
- 5.3 The sample is prepared for instrumental analysis:
- 5.3.1 Thoroughly clean all glassware and sample containers with a metal-free nonionic detergent solution, rinse with tap water, soak in 1:1 HNO<sub>3</sub>/H<sub>2</sub>O and then rinse several times with metal-free water.
- 5.3.2 Remove filter from storage envelope using clean stainless steel forceps.
- 5.3.3 Using stainless steel scissors, remove one-quarter of the filter for analysis. (The remainder of the sample may be used for replicate analyses.)
- 5.3.4 For a blank (background measurement), two or more clean unexposed quartered glass fiber filters should be prepared and analyzed in the same manner as the samples and standards.

- 5.3.5 Fold the filter into halves on the long axis and cut one-half inch (or less) strips parallel to the long axis, leaving the strips uncut at the top with a one-half inch margin.
- 5.3.6 Place a powder funnel (wide mouth, wide stem) into a 100 mL graduated cylinder and, while holding the filter sample at the margin, cut the strips at right angles at 1/4 inch (or less) intervals while the filter sample is directly over the funnel. The cut filter pieces should fall through the filter stem into the cylinder. Use clean plastic gloves to hold the filter during the cutting process. If the cut pieces do not fall through the stem of the funnel, push the pieces gently through using a clean glass stirring rod.
- 5.3.7 Add 25 mL 0.50 N HNO<sub>3</sub> to the cut filters. The acid solution must cover all the filter pieces. Note the volume of the acid solution containing the cut filters. It is recommended that the filters be allowed to soak in the nitric acid solution for about 24 hours before the extraction procedure.
- 5.3.8 Cover the cylinders with inverted 30 mL beakers to prevent liquid evaporation and contamination of the samples.
- 5.3.9 Put enough deionized water in a clean ultrasonic bath so that the water level is above the acid level in the cylinder. Heat the water in the bath to about 75°C.
- 5.3.10 Place the cylinders in the ultrasonic bath using flexible lead weights to hold the cylinders down.
- 5.3.11 Ultrasonicate the samples for 1 hour at the highest possible level.
- 5.3.12 Remove the cylinders from the bath and add 25 mL water to each of the cylinders. The volume may be increased if additional elements are to be analyzed but an adjustment of the acidity of the standards used for calibration must be made to match the sample.
- 5.3.13 Cover the cylinders and ultrasonicate for another hour.
- 5.3.14 Mix the contents of the cylinder by inverting the stoppered cylinder several times. If evaporative losses have occurred, replace the lost liquid with metal-free water.

- 5.3.15 Prerinse the Whatman filter paper with 0.25 N nitric acid and allow most of the nitric acid solution to drain from the filter. Using the prerinsed filter, filter the contents of the cylinders into the plastic sample storage bottles. Discard the first few milliliters of the filtrate. Use the filtrate for analysis. The final concentration of the nitric acid should be 0.25 N.
- 5.4 The instruments are prepared for the analysis:
- 5.4.1 Prepare the AA spectrophotometer, graphite furnace and auto-sampler for the flameless atomic absorption analysis following the manufacturer's recommended operating conditions.
- 5.4.2 Install an arsenic electrodeless discharge lamp and use the recommended number of watts to operate the lamp. Install a pyrocoated graphite tube with L'vov platform in the furnace (other tubes might give lower sensitivities).
- 5.4.3 Adjust the wavelength to 193.7 nm and set the slit to 0.7 nm (low).
- 5.4.4 Turn on the graphite furnace, autosampler, AA instrument and printer. Enter the program to be used for the analysis in the AA instrument: (enter peak area mode for signal measurement and the concentration of the calibrating standards).
- 5.4.5 Turn on the deuterium lamp for background correction and allow the instrument to warm up until the energy source stabilizes (usually within one hour). Align the lamp and furnace according to the manufacturer's recommended procedure.
- 5.4.6 Turn on the argon gas flow and adjust the flowrate according to the manufacturer's recommendation. The argon gas is used to purge the graphite tube prior to and after atomization.
- 5.4.7 Turn on the water used to cool the graphite tube and condition the tube before starting the analysis.
- 5.4.8 Program the drying, charring, atomizing and graphite-tube-cleanup conditions in the graphite furnace.
- 5.4.9 The following procedure has been used for the arsenic analysis using the pyrocoated tube with the L'vov platform: The sample is dried at 110°C for 25 seconds, going from room temperature to 110°C in 20 seconds (ramp rate). The temperature is then raised to 1300°C with a ramp rate of 20 seconds. Char at this temperature for 20 seconds. After charring, the sample is atomized for 4 seconds at 2400°C using the maximum power mode or the fastest possible heating rate (0 ramp rate). Stop the argon flow during atomization.

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- 5.4.10 Condition (clean) the graphite tube at 2600 °C for 3 seconds with a ramp rate of 1 second.
- 5.4.11 Program the autosampler to perform the following: (1) single injections per standard and sample, (2) calibrate with three standards, (3) inject 20 uL of the samples or standards and 5 uL of the nickel nitrate matrix modifier containing 0.02 mg Ni for every injection.
- 5.4.12 Fill the matrix modifier cup with the nickel nitrate solution.
- 5.4.13 Load the autosampler with the reagent blank (0.25 N HNO<sub>3</sub>) used to zero the instrument, the calibrating standards and the samples. The AS-40 autosampler automatically calibrates the instrument using one or more calibration standards. The calibration standards must be within the linear range of the instrument. For quality control, use an EPA quality control check sample or an NBS standard reference material solution to check the accuracy of the calibration. The concentration of these solutions must be within the range of the calibration standards.
- 5.5 The AA spectrophotometer is calibrated for the sample analysis:
- 5.5.1 Start the analysis run by pressing the program START button. When the program is started, an aliquot of blank solution is dispensed into the furnace to auto-zero the instrument. At the completion of the atomization, the spectrophotometer performs the autozero. An aliquot of each of the calibrating standard solutions is then dispensed into the furnace. At the completion of this analytical phase, the spectrophotometer performs a calibration procedure, and then computes the standard calibration plot.
- 5.5.2 The samples, sample blank, EPA quality control check samples and other standards are then analyzed in sequence under the conditions selected on the HGA programmer. Place an arsenic standard solution in the analysis cycle after every seven samples to determine if the instrument is giving correct values. Recalibrate the instrument if the value of the standard is greater than ±15% of the true value.
- 5.5.3 Samples that exceed the linear concentration of the instrument should be diluted with 0.25 N HNO<sub>3</sub> to bring them into the linear range. They should be analyzed after dilution.

6. Calculations



6.1 If the instrument was calibrated in ng As per mL, the amount of As found in the samples is reported by the instrument in ng/mL concentration units. The amount of As present in the sample is calculated as follows:

$$\frac{\text{ng As}}{\text{m}^3} = \frac{\text{ng As}}{\text{mL}} \times \frac{50.0 \text{ mL}}{\text{volume of sample (in m}^3\text{)}} \times \text{diln factor (if any)} \times \frac{4}{1}$$

\*ng As = ng As as found in the sample less the  
mL mL ng As/mL found in the blank.

\*\*

final volume of the extract solution

\*\*\*

if 1/4 of the glass fiber filter is taken for analysis

6.2 The Minimum Detection Limit (Cl), expressed in laboratory units of ng/mL of solution, is calculated as follows (based on the IUPAC definition):<sup>9.1</sup>

$$Cl (\text{ng/mL}) = k \cdot Sb$$

Where:

k = 3 for a confidence level of 99.86%

Sb = standard deviation of the blank absorbance measurements. This is equal to 0.6 ng/mL As (See Table 8.3.1) or Cl = (3)(0.6 ng/mL As) = 1.8 ng/mL As.

6.2.1 The Monitoring and Laboratory Division (Southern Laboratory Branch) reports a higher limit of detection (3.0 ng/mL As) than the above mentioned limit of 1.8 ng/mL As. There are other factors that can affect the limit of detection (e.g. age of lamp, number of times the graphite tube has been fired, temperature used during firing, etc).

6.3 The Minimum Detection Limit Cl (in ng/mL As) is converted to ambient concentrations in ng/m<sup>3</sup> and thus becomes a variable dependent on the air volume sampled. It is calculated as shown below:

$$\text{Minimum Detection Limit (ng/m}^3\text{)} = \frac{Cl (\text{ng/mL})}{V (\text{m}^3)} \times \frac{E (\text{mL})}{F}$$

Where:

E = extraction volume in mL, usually 50.0 mL

V = sampled air volume in m<sup>3</sup>

F = fraction of the filter used in the analysis,  
usually 1/4 of the filter

## 7 Quality Control

- 7.1 Analyze EPA quality control check samples or NBS standard reference material samples after every calibration procedure to ensure that the instrument is operating properly and that the calibration is valid. If the results are greater than  $\pm 15\%$  of the true values, stop the analysis and determine the cause of the discrepancy. Recalibrate and proceed with the analysis when the problem has been identified and corrected.
- 7.2 Dilute samples when the concentration of arsenic is found to be outside the linear range of the instrument. Reanalyze the diluted sample.
- 7.3 Analyze two or more blanks, using one-quarter of a clean unexposed Whatman EPM 2000 glass fiber filter. The entire procedure should be followed to determine the presence of arsenic in the filters and/or reagents. Subtract the amount of arsenic found in the blank from the sample values. This procedure is followed every time a batch of samples is extracted and analyzed.
- 7.4 Spike two or more quartered clean Whatman EPM 2000 glass fiber filters with known amounts of an arsenic standard solution. The amount of arsenic added to the filter should not be greater than 2.0 ug As, so that the concentration of As in the final extract solution (50.0 mL volume) is within the calibration range of the instrument. Dry, then cut the filter, extract and analyze the arsenic solution according to the above procedure. If the amount of arsenic recovered is not at least 85% of the known amount, stop the analysis and identify the problem. When the problem has been resolved, proceed with the analysis. This is done every time there is a change in extraction procedure.
- 7.5 If possible, run duplicate samples every tenth sample. The results must not exceed  $\pm 15\%$  of each other. If the limits are exceeded, stop the analysis and identify the problem. When the problem has been corrected, proceed with the analysis.

- 7.6 Record the EPA quality control check sample results (or standard reference material sample results) in a notebook along with the date of the analysis. Plot the values on a quality control chart. If a bias appears to be developing in the results or if the results are not within  $\pm 15\%$  of the true value, stop the analysis. Determine the cause of the deviation and proceed with the analysis when the problem has been resolved.
- 8 Minimum Detection Limit and Recovery Efficiency
- 8.1 The Minimum Detection Limit (CL) of As is the concentration in ng/mL at which the sample can be distinguished from a blank at a given percentage of time; this percentage of time must be specified and is designated as the level of uncertainty,  $k$ , where  $k = 3$  for a 99.86% confidence level.
- 8.2 The atomic absorption spectrophotometer instrument was calibrated using a reagent blank and three (3) standard solutions. The slope ( $m$ ) and the  $y$ -intercept ( $b$ ) of the calibration curve were determined by a linear regression analysis of the calibration points. A quadratic fit can be applied if the calibration curve is not linear.
- 8.3 Eleven blanks (clean, 1/4 Whatman 2000 8" X 10" filter) were cut, extracted and analyzed for As using the Method 107 procedure. These blank solutions were analyzed to determine the variability of the instrument response at or near the zero concentration levels. This variability is mathematically expressed as the standard deviation ( $S_b$ ) of a number of blank absorbance measurements.
- 8.3.1 Table 8.3.1 lists the variabilities of the instrument response (in ng/mL) to the blank samples.
- 8.4 The limit of detection is 3 ng/mL As. If 1500 cubic meters of air are sampled, the limit of detection is 0.4 ng/M<sup>3</sup> under the following conditions: one-quarter of the filter is used in the analysis and the final volume of the extract solution is 50.0 mL.
- 8.5 The greater the volume of air sampled, the lower the detection limit in nanograms per cubic meter of arsenic e.g. if 2000 m<sup>3</sup> of air is sampled, the detection limit becomes 0.3 ng/m<sup>3</sup> As.

- 8.6 Single laboratory, single operator data have been collected for As using an automated flameless atomic absorption technique (graphite furnace) with background correction. Twelve quartered glass fiber filters (Whatman EPM 2000) were spiked with 1.0 mL of a 1.0 ug/mL As standard, air dried, cut into small pieces and extracted according to the procedure given above. The final concentration of As in the recovery extract was 20.0 ng/mL. Recovery from these filters averaged  $97\% \pm 10\%$ .

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**APPENDIX B**

**SPECIATION OF ARSENIC IN AMBIENT AIR**

Speciation of Arsenic in Ambient Aerosols  
Collected in Los Angeles

Final Report

1182R/0214A

May 19, 1987

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# Speciation of Arsenic in Ambient Aerosols Collected in Los Angeles

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First-time measurements of the potentially toxic inorganic species of arsenic (arsenite and arsenate) have been obtained in fine (<2.5  $\mu\text{m}$  AD) and coarse (>2.5  $\mu\text{m}$  AD) atmospheric particles in the Los Angeles area. A recently developed method that includes procedures for sample collection, preparation, and analysis was used in this study. Size-fractionated aerosol samples were collected with a high-volume dichotomous virtual impactor that employed polytetrafluoroethylene filters. Results were obtained for the recovery of arsenic standards added to unexposed and collected filters. Data from this study, indicated that the recently developed speciation method can be used to determine concentrations of As(III) and As(V) in atmospheric particulate matter samples.

Size-fractionated aerosol samples were collected in the city of industry during January and February 1987. In most samples, As(III) and As(V) were above the detection limit (approximately  $1 \text{ ng m}^{-3}$  of either species) in both aerosol size fractions. A greater portion (about 75 percent) of the two species were observed in the fine particles. The As(III)/As(V) ratio for both particle sizes was close to 1 (i.e., an equal mixture of both species). Comparison of total suspended particulate arsenic measured by the speciation method to that measured by a routine California Air Resources Board-approved procedure showed good agreement ( $r = 0.94$ ), indicating both methods were approximately equivalent for the collection and analysis of aerosol arsenic.

California's air toxic law became effective in January 1985, and defines California's air toxic program (Health and Safety Code Sections 39650 et seq.).<sup>1</sup> Under this legislation, a statutory mandate was created for the identification and control of toxic air contaminants found in California.

One of the mandated criteria used in the identification process to prioritize compounds that are believed to be hazardous to human health is ambient concentration. The California Air Resources Board (ARB) has developed a list of potentially toxic substances based on the mandated ambient criteria. One such element under consideration is arsenic. The measurement of individual species of this element is particularly important because of the variations in toxicity and carcinogenicity of the different arsenic compounds found in the environment. Arsenic(III) is not only more toxic, but also may represent a greater carcinogenic hazard than As(V).<sup>2-5</sup>

Arsenic is emitted into the atmosphere from both anthropogenic and natural sources and is present in the atmosphere in trace amounts. Its atmospheric concentration ranges from about  $0.01$  to  $0.1 \text{ ng m}^{-3}$  in clean areas such as Antarctica<sup>6</sup> and up to  $500 \text{ ng m}^{-3}$  near certain industrial environments such as copper smelters.<sup>7</sup> The average measured arsenic level in U.S. urban areas is approximately  $20 \text{ ng m}^{-3}$ .<sup>8</sup> The primary source of arsenic in the Los Angeles area, approximately  $33 \text{ kg}$  per day, is from stationary high-temperature combustion processes (e.g., glass furnaces, primary metallurgical processes, and fuel oil combustion).<sup>9</sup> This is important, since several researchers<sup>10,11</sup> suggest  $\text{As}_4\text{O}_6$  ( $\text{As}_2\text{O}_3$  sublimates to form the gas phase species  $\text{As}_4\text{O}_6$ ) is the predominant arsenic species emitted into the atmosphere from these types of industrial sources.

A variety of analytical methods currently exist for measuring total arsenic at concentrations present in the atmosphere. However, Solomon has proposed a method for determining the inorganic species of arsenic [arsenite, As(III); arsenate, As(V)] in atmospheric particulate matter.<sup>12</sup> In that study, particular attention was given to the measurement of these species, while maintaining the initial As(III)/As(V) ratio during the sample collection, preparation, and analysis steps. An analytical detection limit of  $25 \text{ ng}$  was obtained for each species in a given sample aliquot. An average As(III)/As(V) ratio of about  $0.31 \pm 0.29$  with a range from less than  $0.04$  to  $0.97$  was reported for total suspended particulate matter (TSP) collected in Tucson, Arizona. The average atmospheric concentrations of As(III) and As(V) were about  $1.6 \pm 1.4 \text{ ng m}^{-3}$  and  $5.4 \pm 3.3 \text{ ng m}^{-3}$ , respectively.

To help assess the impact of these potentially toxic species on human health, size-fractionated samples of atmospheric particulate matter should be obtained, with an emphasis on particles that are most efficiently collected in the lungs (i.e., particles less than  $2.5 \mu\text{m}$  aerodynamic diameter).<sup>13,14</sup> A preliminary study, employing the commercially available low-volume virtual dichotomous sampler (VDS) (Model 241, Sierra-Andersen Corp., Inc.), indicated this sampler collected an insufficient amount of material for the analysis of As(III) and/or As(V) by the sensitive analytical method reported by Solomon. In addition, replicate analysis could not be performed, since the entire filter sample was used to obtain maximum sensitivity. To help overcome these problems, a high-volume dichotomous virtual impactor (HVDVI) was employed.<sup>15</sup> This sampler can collect up to 30 times the mass of efficiently size-fractionated material and has a sample-to-blank ratio that is twice that of the VDS.

The objective of this work is to verify the method reported by Solomon<sup>12</sup> for the collection and analysis of inorganic species of arsenic (arsenite and arsenate) in size-fractionat-

HVDVI and a collocated standard high-volume sampler. The latter is used for routine monitoring of TSP by the ARB. Experiments also were carried out to examine the efficiency of recoveries of aqueous arsenite and arsenate standards added both to unexposed filters and to filters containing aerosol particles.

## Experimental

### Atmospheric Particulate Matter Collection

Atmospheric particulate matter samplers were sited on the roof of the two-story U.S. Post Office building located in the middle of an industrial area in the City of Industry, Los Angeles County, California. Previous routine monitoring by the ARB indicated high ambient concentrations of total arsenic can typically be found in this area.

Two samplers were employed at this site. One was a standard high-volume aerosol sampler (hi-vol)<sup>16</sup> that employed 8 × 10-inch Whatman glass microfiber filters and operated at a flow rate of about 1.1 m<sup>3</sup> min<sup>-1</sup>. This sampler collected total suspended particulate matter (TSP) and is currently employed by the ARB for routine aerosol monitoring of many atmospheric species. The other sampler was a high-volume dichotomous virtual impactor<sup>15</sup> (HVDVI) that collected atmospheric particles in two size ranges (fine and coarse) on 102-mm polytetrafluoroethylene (PTFE) filters (Zefluor, 2.0 μm, Gelman Sciences). This particular filter type required several rinsings in deionized, metal-free water prior to sample collection to obtain reliable, reproducible results.

The HVDVI, when operated at about 400 L min<sup>-1</sup>, has a cutpoint (50 percent collection efficiency) of about 2.5 μm aerodynamic diameter (AD). Thus, the fine particle filter collected particles smaller than 2.5 μm AD, whereas the coarse particle filter collected particles larger than 2.5 μm AD.

Immediately following sample collection, the loaded filters were removed from the sampler and brought to the lab. The HVDVI filters were placed individually into glass petri dishes, sealed, and then placed into plastic ziplock bags. The samples were then stored in a freezer for one day to several weeks, until they were analyzed.

### Sample Preparation and Analysis

The semimicro sample preparation procedure developed by Solomon<sup>12</sup> was used in this study for determining the inorganic species of arsenic (arsenite and arsenate) collected on PTFE filters. A second preparation method was employed for the analysis of total arsenic collected on glass fiber filters.

**Arsenic speciation.** In the speciation method, one-eighth of the 102-mm Zefluor filter was sectioned and placed in a 7-mL Teflon vial fitted with a threaded screw cap (Saville Corporation). For PTFE filters, 0.05 mL of 100 percent ethanol was pipetted directly onto the filter surface. This was done to reduce the hydrophobic nature of the PTFE material and to allow for the interaction of the leaching solution with the sample.<sup>12,17</sup> A PTFE rod (3/8 × 1/2-inch) was then placed on top of the filter pieces to keep them submerged, and 2.0 mL of 10<sup>-4</sup> N HCl was added. The Teflon container was closed tightly and placed in an oven at 85 to 90°C for one hour. The vial and sample were allowed to cool to room temperature before analysis. A 1.0-mL aliquot of the sample leachate was then analyzed for As(III) and As(V) by the Zn-NaBH<sub>4</sub> method described below.

In the Zn-NaBH<sub>4</sub> analysis procedure, As(III) and As(V) were efficiently separated in a two-step reduction process

reduction step, a slurry of Zn metal powder was used to reduce As(III) to arsine (AsH<sub>3</sub>). Immediately following the first reaction, NaBH<sub>4</sub> was used to reduce As(V) to AsH<sub>3</sub>. The arsine produced during each step was detected in the N<sub>2</sub>-H<sub>2</sub> air-entrained flame of an atomic absorption spectrophotometer (Model 3030, Perkin-Elmer Corporation). A complete description of the apparatus and the experimental conditions used can be found in the literature.<sup>12</sup> The procedure resulted in a routine (day-to-day) analytical detection limit of about 20 to 25 ng for each species. The direct analysis of aqueous arsenite and arsenate mixed standards by this method resulted in an analytical measurement precision for As(III) and As(V) of 11 and 9 percent, respectively, at 100 ng of each species, and 2 and 4 percent, respectively, at 500 ng of each species.

**Total arsenic.** A procedure developed by the ARB's Haagen-Smit Laboratory (Method 107) was used for the analysis of total arsenic.<sup>16</sup> In this procedure, one-quarter of a glass fiber filter was sectioned and placed into a 100-mL graduated mixing cylinder to which 50 mL of 0.5 N HNO<sub>3</sub> was added. The cylinder and contents were placed in an ultrasonic bath (450 watts) for one hour at about 70°C. After that time, 50 mL of deionized, metal-free water were added, and the contents were leached for a second hour. The sample was filtered and a 0.02-mL aliquot was analyzed for total arsenic by graphite furnace atomic absorption spectroscopy (Model 3030, Perkin-Elmer Corporation).

**Standards and reagents.** Arsenic(III) standards were diluted daily from a 1000-mg L<sup>-1</sup> stock solution of As(III) that was prepared from As<sub>2</sub>O<sub>3</sub> and obtained directly from VWR Scientific (arsenic reference standard solution, VWR Scientific). The As(V) standards were diluted daily from a 1000-mg L<sup>-1</sup> stock solution of As(V) that was prepared from As<sub>2</sub>O<sub>5</sub> and obtained directly from EM Reagents (1000 ± 0.002 gm L<sup>-1</sup> of As in water). Sodium tetrahydridoborate pellets (NaBH<sub>4</sub>, 99 percent purity, 5/16-inch, Alpha Products), each weighing approximately 0.25 gm, and Zn metal powder (8 micron, 99.9 percent pure, Aesar) were used as the reductants. Concentrated hydrochloric acid (reagent grade with no measurable arsenic blank was obtained from Bakers Chemical Company. All solutions were prepared in deionized, metal-free water (Milli-Q, Millipore Corporation).

## Results and Discussion

The effect of the amount of ethanol pipetted directly onto the PTFE filter surface, prior to leaching the sample for speciation analysis, was studied. Improved recoveries for both arsenic species (about equal to the amount of arsenic added to the filter) were observed when ethanol (0.05 or 0.10 ml) was added to unexposed filters, relative to recoveries when no ethanol was employed. These were similar to results observed by Solomon.<sup>12</sup>

A limited number of experiments were performed to study the recovery of standards added to unexposed PTFE filters. In each case, an aqueous standard containing equal amounts of As(III) and As(V) (in the range of 200 to 600 ng) was pipetted directly onto the filter surface after the surface was wet with ethanol (100 percent). The additions were allowed to dry and then analyzed by the arsenic speciation method. Excellent recoveries were obtained for both As(III) and As(V) (95 ± 7 and 100 ± 8 percent, respectively).

Aqueous standards, similar to those added to the unexposed filters, also were directly pipetted onto the particles of collected filters after the filter surface was wet with ethanol (100 percent). These filter samples were allowed to dry and then analyzed by the speciation method. The average recovery of As(III) and As(V) (including both the fine and coarse aerosol fractions) was 79 ± 22 and 97 ± 23 percent, respectively. These results suggested that the complex matrix collected particulate matter may slightly affect the measure-



**Table I.** Comparison of two methods for the collection and analysis of total arsenic<sup>a</sup> (concentrations in ng m<sup>-3</sup>).

Date collected	Collected by HVDVI <sup>b,d</sup>	Collected by standard hi-vol <sup>c</sup>
12 Jan 87	74.1	69.4
13 Jan 87	22.3	24.4
14 Jan 87	12.8	5.5
15 Jan 87	6.4	4.4
19 Jan 87	9.9	16.2
20 Jan 87	8.9	12.1
21 Jan 87	8.9	11.8
22 Jan 87	24.8	34.0
25 Jan 87	4.1	2.8
26 Jan 87	22.6	35.9
27 Jan 87	5.2	15.0
28 Jan 87	24.6	21.2
29 Jan 87	5.6	6.8
1 Feb 87	9.4	12.7
2 Feb 87	12.7	14.4
3 Feb 87	12.9	15.8

<sup>a</sup> Total arsenic equals the sum of As(III) and As(V) in total suspended aerosol.

<sup>b</sup> Employed Zefluor (PTFE) filters and was analyzed by the arsenic speciation method.

<sup>c</sup> Employed Whatman glass fiber filters and was analyzed by the ARB-HSL Method 107, see Reference 18.

<sup>d</sup> Sum of both arsenic species in the fine and coarse particle fractions. Less than values in Table II were set equal to the detection limit for this calculation.

ment of individual arsenic species. Similar results (i.e., a slight change up to about 20 percent) have been previously reported.<sup>12</sup> Therefore, to obtain the most accurate results, the method of standard additions can be used to compensate these small changes.

Results obtained from the two types of recovery experiments (i.e., recoveries from unexposed and collected filters) can be used to estimate the precision for the combined sample preparation and analysis procedure employed for the determinations of the inorganic species of arsenic. The estimated error for As(III) and As(V) ranged from about 8 percent for unexposed filters to about 23 percent for filters containing particles. The larger error obtained for the arsenic species determined on the loaded filters was most likely due to the effect that variations in the complex matrix of the collected particles can have on the analysis of As(III) and As(V).

Concentrations of arsenic [sum of As(III) and As(V)] measured in total suspended aerosol (TSA) collected by the HVDVI (sum of fine and coarse fractions) and in TSP collected by the standard high-volume sampler are presented in Table I. Samples collected by the HVDVI were analyzed according to the arsenic speciation method, whereas those collected by the standard high-volume sampler were analyzed by the total arsenic procedure (ARB Method 107).<sup>18</sup> The method of standard additions was not applied to the arsenic speciation results presented in this paper (Tables I and II) because the possible sample matrix effect due to particles is believed to be small, certainly less than 20 percent (see Reference 12 and this paper). In addition, data presented by Solomon<sup>12</sup> indicate that TSA arsenic results (Table I) should not be affected, since the effect due to collected atmospheric particles is most likely the oxidation of As(III) to As(V); that is, total arsenic is conserved.

As can be seen in Table I, the concentration of total arsenic observed in samples collected by the HVDVI ranged from 4.1 to 74.1 ng m<sup>-3</sup> with a mean and standard error of the mean of 16.6 ± 4.2 ng m<sup>-3</sup> (this is an upper limit which includes less than values as equal to the detection limits indicated in Table II). Values reported for samples collected by the hi-vol sampler range from 2.8 to 69.4 ng m<sup>-3</sup> with a

mean and standard error of the mean of 18.9 ± 4.1 ng m<sup>-3</sup>. The average ratio of total arsenic collected by the HVDVI to that of the hi-vol sampler was 0.88. Linear regression analysis [hi-vol (x) versus HVDVI (y)] of these data yielded a slope and intercept of 0.97 and -1.7, respectively, and a correlation coefficient (r) of 0.95 (n = 16). This agreement was very good considering the two samplers employed different collection substrates, the samples were prepared and analyzed by different methods, and the samplers probably have different inlet collection efficiencies.

With respect to the collection by different filter substrates, it should be noted that while PTFE filters are virtually inert, gas phase oxides or oxyacids of arsenic (most likely As<sub>2</sub>O<sub>3</sub>)<sup>10,11</sup> may be adsorbed and even oxidized by the more reactive glass fiber filter substrate. This would result in a positive artifact for aerosol arsenic. Similar results of positive artifact formation on glass fiber filters have been reported for the collection of aerosol nitrate and sulfate. In these cases, the oxides or oxyacids of nitrogen and sulfur (e.g., NO, NO<sub>2</sub>, HNO<sub>3</sub>, SO<sub>2</sub>, and H<sub>2</sub>SO<sub>4</sub>) are adsorbed, or adsorbed and oxidized by the reactive filter material.<sup>19-21</sup>

Table II presents the As(III) and As(V) concentrations (ng m<sup>-3</sup>) measured in the fine and coarse particle fractions collected in the City of Industry from January 12 to February 3, 1987. All analyses were performed using the arsenic speciation method. Once again, these data were not corrected for the small but possible sample matrix effect discussed previously. Arsenic(III) was observed on all but two filters in the fine particle fraction and was above the detection limit on about half the collected coarse particle samples. Arsenic(V) was measured on about 85 percent of the collected coarse and fine particle samples. On the average, approximately 13 to 20 percent of the As(III) and 29 to 30 percent of the As(V) were observed in the coarse particle fraction. The range of values indicates an upper and lower limit (see Table II, footnotes b and c).

The coarse particle fraction for As(III), and especially for As(V) observed in this study, is larger than one would typically expect if the major source of arsenic, in the Los Angeles

**Table II.** Arsenic(III) and As(V) concentrations (ng m<sup>-3</sup>) and the As(III)/As(V) ratio observed in fine and coarse particles collected at the City of Industry in Los Angeles.<sup>a</sup>

Date collected	As(III) ng m <sup>-3</sup>		As(V) ng m <sup>-3</sup>		As(III)/As(V)	
	Fine	Coarse	Fine	Coarse	Fine	Coarse
12 Jan 87	44.0	4.8	18.7	6.6	2.4	0.7
13 Jan 87	10.9	1.8	6.6	3.0	1.7	0.6
14 Jan 87	4.2	<1.8	4.6	2.2	0.9	—
15 Jan 87	2.0	<1.1	1.9	1.4	1.1	—
19 Jan 87	2.9	1.4	3.4	2.2	0.9	0.6
20 Jan 87	5.3	1.2	2.4	<1.0	2.2	—
21 Jan 87	4.5	1.5	2.9	<1.2	1.6	—
22 Jan 87	14.1	4.1	4.9	1.7	2.9	2.4
25 Jan 87	<1.2	<0.9	<1.0	<0.8	—	—
26 Jan 87	10.2	2.2	5.9	4.3	1.7	0.5
27 Jan 87	1.5	<1.0	1.8	0.9	0.8	—
28 Jan 87	6.3	<2.4	12.0	3.9	0.5	—
29 Jan 87	2.2	<0.9	<0.9	1.6	—	—
1 Feb 87	3.7	1.0	3.4	1.3	1.1	0.8
2 Feb 87	<1.7	<1.7	7.0	2.3	—	—
3 Feb 87	4.2	<1.1	6.1	1.5	0.7	—
$\bar{x} \pm \sigma^b$	7.4	1.8	5.2	2.2		
	±10.4	±1.1	±4.6	±1.5		
$\bar{x} \pm \sigma^c$	7.3	1.1	5.1	2.1	1.4	0.9
	±10.6	±1.5	±4.7	±1.7	±0.7	±0.7

<sup>a</sup> Values not corrected for 10 percent flow through coarse particle filter. see Reference 15.

<sup>b</sup> Upper limit, includes less than values (indicated by <) in the average as equal to the detection limit indicated.

<sup>c</sup> Lower limit, includes less than values in the average as equal to zero.

these sources predominantly emit As(III) as gas phase  $As_2O_3$ <sup>9,10</sup> and if only gas-to-particle conversion processes were occurring. However, arsenic(III) oxide (most likely  $As_2O_3$ ), a Lewis acid and the most probable precursor for particulate As(III) and As(V) species, may be behaving similar to the gas phase precursors of particle nitrate and sulfate [i.e., the oxyacids of nitrogen (e.g., NO, NO<sub>2</sub>, HNO<sub>3</sub>) and sulfur (e.g., SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>), respectively] both of which exhibit coarse particle modes in the South Coast Air Basin.<sup>22-24</sup> This hypothesis simply considers the same type of acid-base chemistry, gas-to-particle transformations, and oxidation process that can occur in the formation of coarse particle NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> (i.e., similar to the reactions of the gas phase weak acids NO, NO<sub>2</sub>, and SO<sub>2</sub> with alkaline coarse particles to form coarse particle nitrate and sulfate). Obviously, this hypothesis does not completely extend itself to reactions of the strong acids, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> with coarse particles, since the oxyacids of arsenic are only weak acids (e.g., oxyacids of arsenic would be incapable of displacing HCl from large sea-salt or NaCl particles, however, both the strong and weak acids are capable of sitting down on or reacting with alkaline coarse particles, e.g., coarse particles derived from crustal material).

The ratio of As(III)/As(V) also is presented for each sample in Table II. The average of this ratio was greater than one for the fine particles and slightly less than one for the coarse particles. For samples where both species were above their minimum detectable level, the As(III)/As(V) ratio ranged from about 0.5 to about 2.9 in both the fine and the coarse particle fractions. These results are somewhat different from those obtained in Tucson, Arizona.<sup>12</sup> In that study, the average As(III)/As(V) ratio observed in TSP collected by a high-volume sampler employing quartz fiber filters, was about 0.3, with a range from less than 0.04 to 0.97. These differences were most likely due to the impact of the various sources in the surrounding areas, on the age of the aerosol measured at the sampling sites, and/or on the rate at which As(III) was oxidized in the atmosphere (i.e., variations in the effective oxidation potential of the atmospheric environment).

## Conclusion

A recently developed method<sup>12</sup> for the determination of inorganic species of arsenic (arsenite and arsenate) in atmospheric particulate matter was applied to aerosols collected in the Los Angeles area. Fine (<2.5 μm AD) and coarse (>2.5 μm AD) particle samples were collected in the City of Industry by a high-volume dichotomous virtual impactor (HVDVI). The use of this sampler allowed for the collection of a sufficient amount of sample so that both As(III) and As(V) could be routinely detected in both particle size fractions. In addition, use of the HVDVI, instead of the commercially available low-volume virtual dichotomous impactor, allowed for replicate analyses on individual filter samples. This is important since more accurate results for the analysis of As(III) and As(V) can be obtained by applying the method of standard additions.

Results obtained from recovery experiments, where arsenic standards were directly added to unexposed and collected filters, indicated that the arsenic speciation method can be used to determine concentrations of As(III) and As(V) in atmospheric particulate matter samples collected in the Los Angeles area. In addition, comparison of total suspended aerosol arsenic determined by the speciation method to that measured by a routine ARB-approved method showed good agreement. These results indicated the two methods were approximately equivalent for the monitoring of aerosol arsenic.

Size-fractionated aerosol samples were collected in the City of Industry and analyzed for their concentrations of

were found in the fine particle fraction of the aerosol. The average As(III)/As(V) ratio observed in both the fine and coarse particle fractions was close to 1 (i.e., an equal mixture of the two species). For both particle size ranges, the As(III)/As(V) ratio varied from about 0.5 about 2.9.

This study should be helpful in assessing the potential adverse health effects due to public exposure of inorganic arsenic in ambient air in California. This is especially true since the data presented here indicate that both As(III) and As(V) species are present in ambient aerosols. Thus, by assuming all arsenic in atmospheric particulate matter is As(III), the health risk assessment of inhaled inorganic arsenic may over-estimate the unit risk for public exposure to populations in California. In addition, the chemical and physical information obtained from speciation measurements of this type will certainly help to evaluate source and sink strengths more thoroughly and to gain a better understanding of the complex geochemical cycles of arsenic and other related species in the environment.

## Acknowledgments

The authors would like to thank Pat Harrington of the California Air Resources Board for his valuable contribution in conducting the sampling phase of this project. The authors would also like to thank the U.S. Postal Service for allowing the aerosol sampling equipment to be sited on the roof of its building in the City of Industry. This work was fully supported by ARB.

## Disclaimer

This report has been reviewed by the staff of the California Air Resources Board and has been approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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# High-Volume Dichotomous Virtual Impactor for the Fractionation and Collection of Particles According to Aerodynamic Size

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A prototype dichotomous virtual impactor (DVI) using a single acceleration nozzle, operating at approximately 500 l/min, and having an aerodynamic particle cutpoint diameter of about 2–3  $\mu\text{m}$  has been constructed and tested. Under these conditions the flow through the acceleration nozzle is calculated to be turbulent. This sampler was calibrated with a monodisperse aerosol, and the measured particle size-dependent collection efficiencies demonstrate that the sampler size fractionates atmospheric particulate matter as efficiently as the low-volume dichotomous virtual impactors. Analysis of test data indicates that the high-volume sampler can be described by classical impaction theory. These data also indicate that over the range of Reynolds numbers from 24,000 to

81,000 there is little, if any, dependence of inferred acceleration nozzle turbulence on the performance characteristics of the sampling system. A comparison of the concentration of atmospheric particulate matter, sulfate, and calcium on the fine filter samples collected with colocated high- and low-volume virtual impactors also shows that the two samplers are operating with similar performance characteristics. Additionally, the high-volume DVI collects at least 10–30 times the mass of particulate matter that the presently available virtual impactors collect and thus allows one to obtain improved precision in the measurement of those airborne species that are near the minimum detectable level of current analytical methods.

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## NOMENCLATURE

$C$  Cunningham's slip correction factor (dimensionless)  
 $D_c$  diameter of the collection probe (cm)  
 $D_j$  diameter of the acceleration nozzle (cm)  
 $D_p$  diameter of the particle (cm)  
 $D_{p50}$  diameter of the particle at 50% collection efficiency (cm)  
 $f$  large particle air flow transport ratio (%)  
 $J$  nozzle-to-probe spacing (cm)  
 $Q$  total flow rate (l/min)  
 $Re_j$  Reynolds number calculated for the acceleration nozzle (dimensionless)  
 $St$  Stokes number (dimensionless)  
 $T$  throat length of the acceleration nozzle (cm)

$V_j$  particle velocity at the acceleration nozzle exit plane (cm/sec)  
 $\theta$  one-half the entrance angle of the acceleration nozzle (deg)  
 $\mu$  viscosity of the air ( $1.81 \times 10^{-4}$  g/sec cm)  
 $\rho_a$  density of the air ( $1.2 \times 10^{-3}$  g/cm<sup>3</sup>)  
 $\rho_p$  density of the particle (g/cm<sup>3</sup>)  
 $\psi$  impaction parameter (dimensionless)  
 $\psi_{50}$  impaction parameter at 50% collection efficiency (dimensionless)

## INTRODUCTION

Suspended particulate matter in the atmosphere exists primarily in two size ranges. The large or coarse particles are considered to have an aerodynamic diameter of greater

than about 2–3  $\mu\text{m}$ . Willeke and Whitby (1975), Dzubay and Stevens (1975), and others have shown that the large particles are primarily produced by mechanical processes (e.g., soil erosion or disruption). The small or fine particles are considered to have an aerodynamic diameter of less than a few micrometers and are composed primarily of nonvolatile gas phase reaction products and the more volatile chemical compounds and elements. Fine particles have long atmospheric residence times, typically on the order of weeks, and therefore they can be transported over long distances (Jaenicke, 1980). Middleton (1952), Charlson (1969), and Jaenicke (1980) indicate that fine particles have the potential to affect visibility and climate, since they efficiently scatter and absorb solar radiation. Brown et al. (1950) and Perera and Karim Ahmed (1979) have studied or reviewed the collection characteristics of atmospheric particulate matter in the human respiratory tract; their work indicates that fine particles are most efficiently collected deep in the lungs, where they have the potential to cause adverse health effects.

For these reasons, many air samplers have been designed to collect size-fractionated samples of atmospheric particulate matter. One class of particle size fractionators, originally developed by May (1945), is the impactors, where particle size fractionation is performed by inertial separation. Ranz and Wong (1952), Mitchell and Pilcher (1959), Cohen and Montan (1967), and others have described the real, or classical, impactor, for which size fractionation of the particles takes place at a surface. In classical impaction a small plate is placed such that the surface is perpendicular to the air flow at the exit of a particle acceleration nozzle. The large particles are impacted on the plate, while the small particles, having smaller inertia, follow the air streamlines around the plate. Lundgren (1967) and Dzubay et al. (1976) have demonstrated that this method of collecting size-fractionated samples can suffer from large-particle bounce or reentrainment

problems, which result in contamination of the small particles by large particles.

The virtual impactor, first developed by Hounam and Sherwood (1965) and later modified by Conner (1966), Dzubay and Nelson (1975), and Loo et al. (1976), eliminates the particle bounce problem associated with classical impactors. In a virtual impactor a collection probe replaces the plate, and the size fractionation of the particles occurs in the space between the nozzle and probe. Typically, 90% of the air is removed perpendicular to the acceleration nozzle, and 10% flows down through the large particle collection probe. In this type of system the fine particles follow the streamlines of the major air flow and are collected on a fine-particle filter, while the coarse particles, with greater inertia, are accelerated across the space between the nozzle and probe and are collected on a coarse-particle filter. The use of filters and the replacement of the impaction surface with a collection probe in a virtual impactor eliminates the particle bounce problem associated with real impaction surfaces. As a result of the air flow design of the virtual impactor, 10% of the small particles are collected on the large-particle filter. However, the fine-particle sample is essentially free from large-particle contamination.

The present day commercial low-volume dichotomous virtual impactor (LVDVI), using a single acceleration nozzle and operating under laminar flow conditions, separates particles into two size ranges (Loo et al., 1979). In these samplers the coarse particles have an aerodynamic diameter greater than about 2.5  $\mu\text{m}$ , while the fine particles are those with an aerodynamic diameter of less than 2.5  $\mu\text{m}$ . The LVDVI typically collects suspended atmospheric particulate matter on polytetrafluoroethylene (PTFE) membrane filters, operates at low flow rates (less than 20 l/min), and, depending on the concentration of atmospheric particulate matter, collects from less than 10 to several hundred micrograms of sample in a 24-hr period. This

results in particulate matter filter loadings (defined here as the volume of air collected in 24 hr per unit area of filter collecting surface) of about  $4 \text{ m}^3/\text{cm}^2$ . Because of the use of the PTFE membrane filter medium with its smooth collection surface, these samples are well-suited for analysis by x-ray fluorescence techniques. In addition to elemental analysis by x-ray fluorescence, these filters can also be analyzed for mass and various ionic species (Stevens and Dzubay, 1978). However, these samplers still collect relatively small amounts of particulate matter mass, and for this reason, when these low-volume samplers are used, many chemical species of interest are at or near the minimum detectable limit (MDL) of the analytical method. For example, it is difficult to analyze for individual organic species,  $^{14}\text{C}$ , and several trace elements (Se, As, Sb, etc.) by present analytical methods. Additionally, contamination or blank problems associated with these low-volume samplers often limit the sampling time resolution to longer than desirable for many investigations. Loo et al. (1976) developed a medium-volume dichotomous virtual impactor (MVDVI) that uses three acceleration nozzles, operates at 50 l/min, and has a filter loading of  $11.7 \text{ m}^3/\text{cm}^2$ . The MVDVI provides great improvement relative to situations where the analytical measurement is limited by contamination or blank problems. However, the MVDVI still collects relatively small amounts of particulate matter.

In order to overcome some of the situations where the analysis of size-fractionated samples is limited by the small amount of particulate mass collected (i.e., measurements at or near the MDL of the analytical method) a single-jet high-volume dichotomous virtual impactor (HVDVI) has been developed. In addition to the advantages obtained when more sample is collected, the HVDVI also provides for an increased filter loading advantage relative to the LVDVI while maintaining essentially the filter loading obtained with the multijet MVDVI. The

HVDVI was calibrated by two methods: (1) a laboratory calibration was obtained using a monodisperse aerosol, and (2) a field test was obtained by comparing the chemistry of the small-particle fraction of atmospheric particulate samples collected with colocated HVDVI and LVDVI samplers. In this paper the design and performance characteristics of the HVDVI sampler are presented and discussed.

## EXPERIMENT

### Laboratory Calibration

A monodisperse aerosol was generated by a Berglund-Liu vibrating orifice monodisperse particle generator from Thermal Systems Inc., model No. 3050<sup>1</sup> (Berglund and Liu, 1973). This generator produces solid or liquid monodisperse particles of a known size from approximately 0.50 to 50  $\mu\text{m}$  in diameter with a standard deviation of approximately 1%. In this work, the aerosol was generated from an ethanol solution of oleic acid and fluorescein. The aerodynamic diameter of particles greater than 3  $\mu\text{m}$  was determined by measuring their terminal velocity in still air and calculating the diameter using the Stokes equations. These particle diameters are accurate to about  $\pm 2\%$ . The diameter of particles less than 3  $\mu\text{m}$  was calculated based on the dilution of solutions used to generate larger particles of specified diameter, with the accuracy being better than  $\pm 5\%$ . All particle sizes were monitored on-line for an estimate of the particle size distribution by using an optical particle counter (Climate model No. 208) equipped with a multichannel analyzer (Tracor, Northern Inc., model No. TN 1705).

<sup>1</sup>Certain commercial equipment, instruments, and materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Circular Whatman 41 filter paper (10-cm diameter) was used in the sampler to collect the generated particles. The fluorescein dye was leached from the filters using 0.1N  $\text{NH}_4\text{OH}$ , and the absorbance of the resulting solution was measured at 490 nm using a standard laboratory spectrophotometer. The fine-particle collection efficiency was determined by measuring the ratio of fine-particle absorbance to the sum of the fine and coarse or total absorbance. An approximate value for wall losses was determined by disassembling the impactor and wiping the exposed surfaces with a piece of Whatman 41 filter paper wet with 0.5 ml of 0.1N  $\text{NH}_4\text{OH}$ .

#### Chemical Analysis of Airborne Particles

An empirical calibration of the sampler was obtained by comparing various chemical species on samples collected with colocated LVDVI and HVDVI samplers. The LVDVI uses 37 mm 2.0- $\mu\text{m}$ -pore-size PTFE membrane filters (Membrana Corp.), and the HVDVI sampler uses 10.0-cm-diam quartz filters (Pallflex Corp., Pallflex 2500 QAST).

The concentrations of the mass of collected particulate matter were determined by gravimetric analysis. The quartz filters were weighed on an analytical balance and the PTFE filters on a microanalytical balance. For sulfate analysis a section of each quartz filter was placed in a Teflon bomb with distilled/deionized water and extracted at 90°C for 2 hr. A microprocedure developed by Derrick and Moyers (1981) was used to extract sulfate from the PTFE filters. In this procedure one-half of each PTFE filter is placed in a Teflon bomb, "wet" with ethanol, and then extracted with  $5 \times 10^{-5}\text{N}$   $\text{HClO}_4$  at 90°C for 2 hr. The extraction solutions were analyzed for  $\text{SO}_4^{2-}$  by ion chromatography (Mulik et al., 1976). For metal analysis, the quartz filters were extracted with 6N nitric acid at 90°C for 2 hr while the PTFE filters were first "wet" with ethanol and extracted with 6N nitric acid at 90°C for 2 hr. These solutions were then analyzed by flame atomic absorption spectroscopy.

## RESULTS AND DISCUSSION

### Impaction Theory and Design Parameters

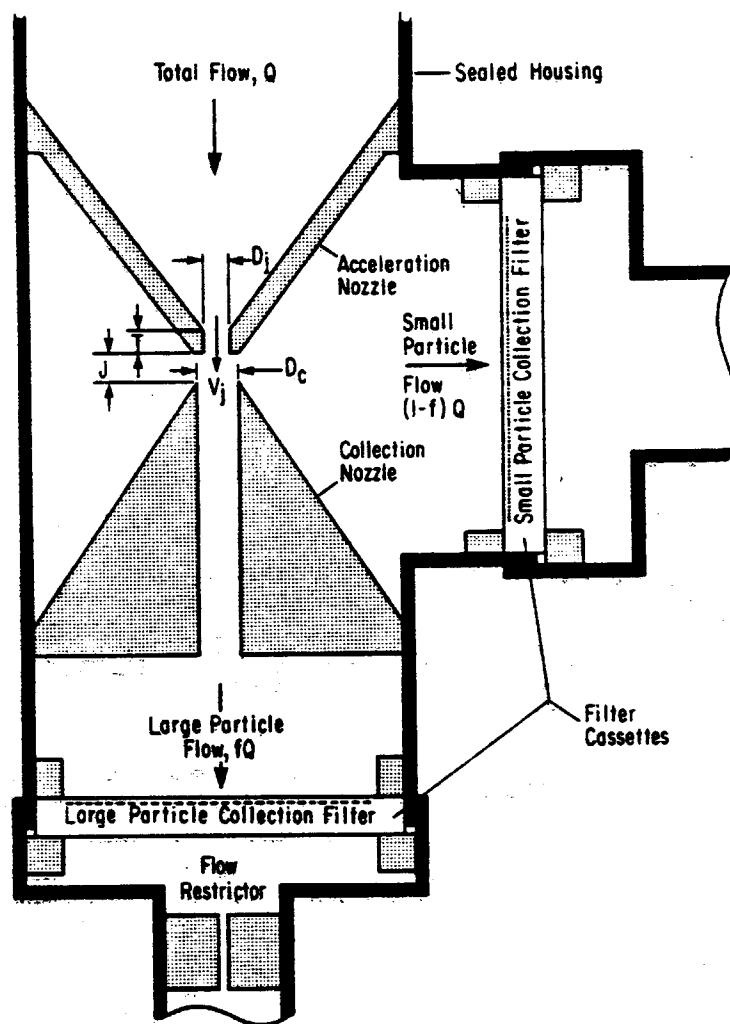
There have been numerous studies of both real and virtual impactors, including experimental and theoretical studies designed to measure or define the motion of particles in this type of sampling system (Ranz and Wong, 1952; Mitchell and Pilcher, 1959; Cohen and Montan, 1967; Marple and Liu, 1974; Marple et al., 1974; Marple and Chien, 1980).

Assuming that the gravitational and electrical effects are small compared with the inertial effects, the classical impaction process can be characterized by a single dimensionless parameter  $\psi$ , as defined by Ranz and Wong (1952):

$$\psi = C\rho_p V_j D_p^2 / 18\mu D_j \quad (1)$$

The Stokes number  $St$  as defined by Fuchs (1964), also a dimensionless parameter, is equal to  $2\psi$  and is the ratio of the stopping distance of the particle to  $D_j/2$ . Each of these dimensionless parameters is used throughout the literature to describe the performance characteristics of impactors. The collection efficiency curve is a plot of the efficiency of collection (number collected/number incident) versus either the aerodynamic particle diameter or  $\psi^{1/2}$ . Experimental values of  $\psi_{50}$  (impaction parameter for 50% collection efficiency) range from about 0.06 (Swartz et al., 1973) to about 0.4 (Mercer, 1963), with most values falling between  $0.1 \leq \psi_{50} \leq 0.3$  (Ranz and Wong, 1952; Cohen and Montan, 1967; McFarland, 1978).

Based on the classical impaction theory of Ranz and Wong (1952) and the design of the present day dichotomous virtual impactor, an HVDVI was constructed and is illustrated in Figure 1. It is approximately 50 cm in height and about 11.5 cm in diameter. The HVDVI uses two 10-cm diameter filters supported in individual filter cassettes, leaving a sample collection diameter of just under 9 cm. Approximately 90% of the total air flow ( $Q-f$ ) is removed perpendicular to the acceleration nozzle and collection probe



through the small-particle filter, while the remaining 10% ( $f$ ) passes through the large-particle filter. Presently, the HVDVI uses the same high-volume pump that is used with the standard high-volume sampling system. When such a pump is used, the sampler can operate at a flow rate of up to approximately 500 l/min.

Table 1 compares some sampling flow rates, filter loadings, and particulate matter masses obtained with the LVDVI, MVDVI, HVDVI, and standard high-volume (HV) sampling systems. The HVDVI sampler, when operated at 500 l/min for 24 hr, collects about 10 and 30 times the mass of the MVDVI and LVDVI samplers, respectively,

FIGURE 1. Physical design parameters of the HVDVI.

and about 40% of the mass collected by the HV sampler. Under standard operating conditions, the LVDVI and the HV sampler have filter loadings of about  $4 \text{ m}^3/\text{cm}^2$ , while the MVDVI and HVDVI have filter loadings of about  $11.5 \text{ m}^3/\text{cm}^2$ . Therefore, the HVDVI and the MVDVI have obtained an increase in the sample-to-blank ratio of about 3 over the LVDVI and HV samplers. It should be noted that with higher loadings filter clogging becomes more important and may become a serious problem in highly polluted



**TABLE 1.** Comparison of Typical Collection Parameters for the HVDVI, MVDVI, LVDVI, and Standard HV Samplers

	HVDVI	MVDVI	LVDVI	Standard HV Sampler
flow rate (m <sup>3</sup> /hr)	30	3	1	70
volume per day (m <sup>3</sup> )	720	72	24	1700
mass per day <sup>a</sup> (μg)	43,200	4320	1440	102,000
filter area (cm <sup>2</sup> )	62	6.1	6.1	400
filter loading (m <sup>3</sup> /cm <sup>2</sup> )	11.6	11.7	3.9	4.2

<sup>a</sup>Assuming an atmospheric particulate concentration of 60 μg/m<sup>3</sup>.

areas. However, the advantages obtained by collecting more mass and having the higher filter loadings make the HVDVI especially favorable for collecting size-fractionated samples in remote areas where particulate concentrations are very low or where the required time resolution is too short to obtain a sufficient sample by other virtual impactors.

#### Laboratory Calibration

Calibration and evaluation of the system was performed by varying the parameters of known or suspected importance (i.e.,  $D_j$ ,  $Re_j$ ,  $D_c$ ,  $J$ ). For all the experimentally determined cutpoints of this sampler the impaction parameter,  $\psi_{50}$ , was calculated; it ranged from about 0.1 to 0.36. These values fall within the range found in the literature for laminar flow real and virtual impactors. Figure 2 illustrates three typical collection efficiency curves for the HVDVI. Table 2 lists the operating conditions and physical

**FIGURE 2.** Comparison of HVDVI and DVI collection efficiency curves.

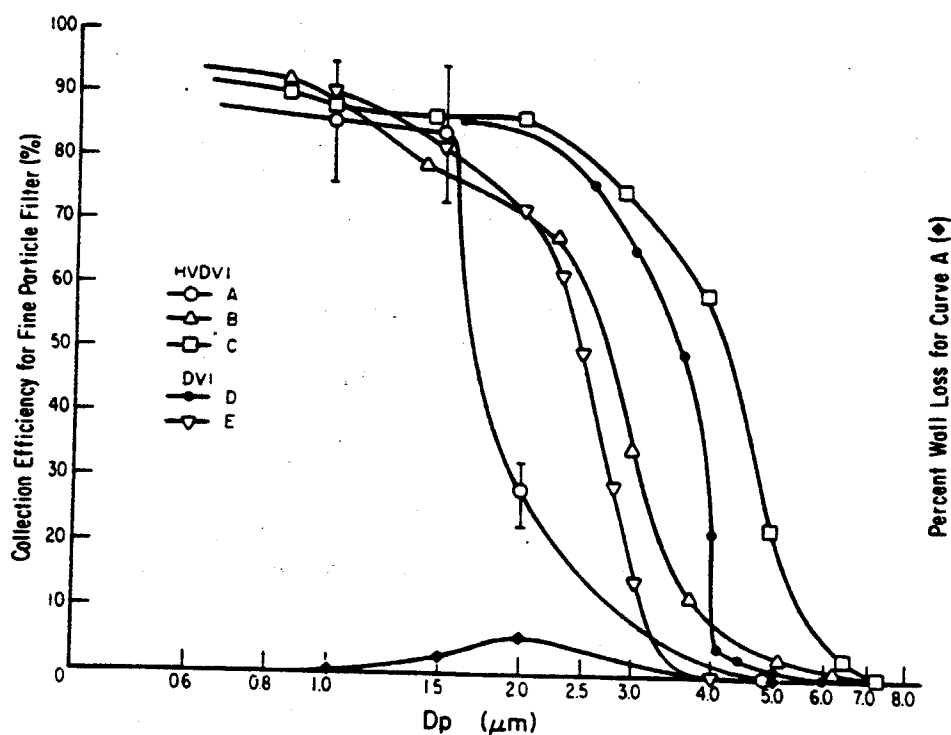


TABLE 2. Operating Conditions and Physical Design Parameters for the Efficiency Curves in Figure 2

	HVDVI			DVI <sup>a</sup>	
	Curve A <sup>b</sup>	Curve B <sup>b</sup>	Curve C <sup>b</sup>	Curve D <sup>c</sup>	Curve E <sup>d</sup>
$Q$ (l/min)	420	500	200	14.0	16.7
$D_{p50}$ ( $\mu\text{m}$ )	1.8	2.6	4.3	3.6	2.5
$Re_j$	78,000	81,000	32,000	4900	7700
$D_j$ (cm)	0.76	0.87	0.87	0.40	0.31
$D_c/D_j$	1.33	1.33	1.33	1.31	1.38
$J/D_j$	1.43	1.25	1.25	0.89	1.04
$f$ (%)	-9	-7	-11	10	10
$T$ (cm)	0.75	0.85	0.85	0.89	0.32
$\theta$ (deg)	42.5	42.5	42.5	45	45

<sup>a</sup>Low-volume dichotomous virtual impactor.

<sup>b</sup>This work.

<sup>c</sup>McFarland (1978).

<sup>d</sup>Loo et al. (1979).

design parameters for the efficiency curves shown in Figure 2. Curve A, with a cutpoint of 1.8  $\mu\text{m}$ , was obtained at a flow rate of 420 l/min and a nozzle diameter of 0.76 cm. Curves B and C, with cutpoints of 2.6  $\mu\text{m}$  and 4.3  $\mu\text{m}$ , were obtained at flow rates of 500 and 200 l/min, respectively, using an acceleration nozzle diameter of 0.87 cm. The Reynolds number is a parameter used to describe the flow through a pipe as either laminar or turbulent and is subsequently discussed. The Reynolds numbers calculated for the above acceleration nozzle diameters and flow rates are 78,000, 81,000, and 32,000, respectively. The error bars in curve A of Figure 2 represent the relative standard deviation associated with the measurement of the collection efficiency based on four individual determinations. In general, the measured relative standard deviation in the fine-particle collection efficiency was less than 5% near the 0% collection efficiency, about 15% near the cutpoint (the steepest slope), and about 10% when the particle collection efficiency was greater than about 75%. Curves D and E in Figure 2 are reported collection efficiency curves for two low-volume virtual impactors. Curve D was obtained by McFarland (1978), and Curve E was obtained by Loo et al. (1979). For each of the LVDVI systems, the Reynolds numbers are approximately 5000. As can be seen in Figure 2, the slope and

shape of the efficiency curves determined for the HVDVI are qualitatively similar to those of the LVDVI.

#### Wall Losses

The wall losses obtained for each particle size for curve A are also plotted in Figure 2. As can be seen, the maximum wall loss occurs near the cutpoint and under these operating conditions is about 6%. Depending on the operating conditions, wall losses for the HVDVI sampler at the cutpoint ranged from approximately 5% to 20%. Wall losses obtained near the cutpoint for the DVI samplers were 10.7% and less than 1%, as reported by McFarland (1978) and Loo et al. (1979), respectively.

The nozzle-to-probe distance was optimized based on the amount and location of the internal wall losses. The wall loss was found in three locations: on the bottom of the acceleration nozzle, on the inside lip of the collection probe, and on the inside circumference of the main body of the sampler. The wall loss in this last area was located in a plane parallel to and equal in width to the spacing between the nozzle and probe. This type of wall loss occurred for most experiments when  $D_j$  was greater than or equal to 0.87 cm. Wall loss was eliminated on the bottom of the acceleration nozzle by increas-

ing the nozzle-to-probe distance to greater than 1 cm. For nozzle diameters greater than 0.85 cm, the nozzle-to-probe distance can fall in the range from  $1.0D_j$  to at least  $1.5D_j$ , as described for real impactors by Marple and Liu (1974) and for virtual impactors by Marple and Chien (1980).

### Reynolds Number

The Reynolds number  $Re$ , as discussed by Schlichting (1968), is a dimensionless parameter used to describe the flow of a fluid (liquid or gas) through a pipe as either laminar or turbulent. The Reynolds number  $Re_j$  within the acceleration nozzle can be defined as

$$Re_j = \rho_a V_j D_j / \mu. \quad (2)$$

Experiments reviewed by Schlichting (1968) have shown that the flow is laminar when the Reynolds number is less than about 2000. Above 2000 the flow can either be laminar or turbulent, depending on the flow characteristics of the system. For Reynolds numbers above about 10,000, it becomes increasingly difficult to maintain laminar flow, and for most situations turbulent flow exists. It is important to note that most previous real and virtual inertial-type impactors have been designed for particle size fractionation to be

applied to laminar flow or assumed laminar flow conditions (i.e.,  $Re_j$  typically less than about 9000).

A major objective of this study was to evaluate the potential effect on impactor performance of high Reynolds numbers (suggesting turbulent air flow conditions) as calculated for the acceleration nozzle. Marple and Chien (1980) provide a computer simulation of the performance characteristics of the LVDVI indicating that for Reynolds numbers between 5000 and 15,000 there is little effect on the particle size-dependent collection efficiency of the sampling device. McFarland's (1978) empirical study of the LVDVI also shows little effect on the shape and slope of the collection efficiency curve for values of the Reynolds number from 2000 to 9000.

Since the HVDVI operates at a much higher Reynolds number, an extensive set of experiments were conducted to evaluate the possible effect of turbulent air flow in the acceleration nozzle. Table 3 presents a summary of the measured  $D_{p50}$  values and calculated  $\psi_{50}$  values for different Reynolds numbers and various values of the design parameters  $Q$ ,  $V_j$ , and  $D_j$ . In Table 3 one can observe that there is no apparent or systematic effect of  $Re_j$  on impactor performance, where the impactor performance can

TABLE 3. Particle Diameter at 50% Collection Efficiency ( $D_{p50}$ ) and Impaction Performance Parameter ( $\psi_{50}$ )

Design parameter			Performance parameter		Parameter approximate constant
$D_j$ (cm)	$V_j$ (cm/sec)	$Re_j$	$D_{p50}$ ( $\mu\text{m}$ )	$\psi_{50}$	
0.87	5,600	32,000	4.3	0.33	$D_j$
0.87	9,200	52,000	2.7	0.24	
0.87	13,000	74,000	2.8	0.32	
0.87	14,000	81,000	2.6	0.36	
0.52	8,000	27,000	2.0	0.19	$V_j$
0.56	8,300	31,000	2.1	0.20	
0.87	8,000	45,000	2.5	0.17	
1.03	7,700	52,000	3.3	0.25	
0.56	14,000	53,000	1.6	0.20	$Re_j$
0.64	12,000	52,000	1.8	0.19	
0.76	10,000	50,000	2.2	0.20	
0.87	9,200	52,000	2.7	0.24	
1.15	6,600	51,000	3.9	0.27	

be evaluated from the calculated values of the dimensionless impactor parameter  $\psi_{50}$ . The use of linear and nonlinear multiple regression analysis on these data indicates that  $D_{p50}^2$  is dependent on the same design parameters that describe laminar flow impactors (i.e.,  $D_j$  and  $V_j^{-1}$ ). The average  $\psi_{50}$  determined from these data is  $0.24 \pm 0.06$ . Thus, for the system configuration studied in this work,  $\psi_{50}$  falls within the range that has been demonstrated for laminar flow real and virtual impactor designs. This, of course, implies that for these types of systems classical impaction theory may be used in the design of systems even when apparently highly turbulent conditions would be expected to occur in the acceleration nozzles.

#### Field Comparison

A field comparison of the concentration of fine suspended particulate matter, fine sulfate, and fine Ca for 12 samples collected with colocated LVDVI and HVDVI samplers was made. These results are presented in Table 4. As can be seen in Table 4, the average concentrations of fine suspended particulate matter and fine sulfate (90% of the sulfate is found on particles less than  $2.5 \mu\text{m}$ ) agree within 5%, while the average fine Ca concentrations (10% of the calcium is found on particles less than  $2.5 \mu\text{m}$ ) agrees within 10%. The high standard deviation for Ca observed with the LVDVI samplers is a result of the Ca concentrations' being close to the detection limit of the analytical measurement method. The LVDVI is designed with a size-selective inlet, which theoretically allows only particles of less than  $15 \mu\text{m}$

aerodynamic diameter to enter the sampler. The HVDVI has no such inlet. Therefore, no comparison can be made for the collection of coarse particles by the two sampling systems.

The increase in sample size and the analyte-to-blank ratio available with the HVDVI makes it especially promising for use with atmospheric organic chemistry investigations, including the newly developing area of  $^{14}\text{C}$  measurements (Currie and Klouda, 1982). Any desired sampling media (e.g., quartz or PTFE) can be used, and thus the analytical methodology developed for the other sampling systems should be directly applicable to samples collected with the HVDVI.

#### CONCLUSION

These results provide convincing evidence that the dichotomous virtual impactor using a single acceleration jet can be operated as a high-volume sampler. Under these conditions, the HVDVI operates in the turbulent flow region (as calculated for the acceleration nozzle) but can still separate particles according to aerodynamic diameter as efficiently as the state-of-the-art laminar flow dichotomous virtual impactor. The analysis also indicates that the performance characteristics of this turbulent flow impactor can be described by the same theory that describes both real and virtual laminar flow impactors. The HVDVI sampler not only collects greater than 10–30 times the mass of particulate matter the MVDVI and LVDVI samplers collect, but it also has a sample-to-blank ratio that is about three times greater than the LVDVI or standard high-volume air

TABLE 4. Comparison of the HVDVI and the LVDVI Samplers for Observed Mass, Sulfate, and Calcium Concentrations

Measurement <sup>a</sup>	LVDVI ( $\bar{x} \pm \sigma \mu\text{g}/\text{m}^3$ )	HVDVI ( $\bar{x} \pm \sigma \mu\text{g}/\text{m}^3$ )	HVDVI/LVDVI ( $\bar{x} \pm \sigma$ )
Mass	$9.2 \pm 1.9$	$10.1 \pm 3.0$	$0.95 \pm 0.15$
Sulfate	$3.8 \pm 0.8$	$3.8 \pm 0.6$	$1.01 \pm 0.17$
Calcium	$0.07 \pm 0.03$	$0.08 \pm 0.01$	$0.88 \pm 0.42$

<sup>a</sup>Fine particles (12 individual sampling periods).

sampler. The HVDVI and MVDVI have similar sample-to-blank ratios. The use of this sampler maintains the advantages of the LVDVI and MVDVI, but it will also allow for the analysis of size-fractionated samples for many atmospheric species that presently are near or below the minimum detectable level of present analytical techniques and cannot be determined using currently available size-fractionating virtual impactors. A potential disadvantage of this system is that more pronounced clogging problems will occur in these sampling situations where the particulate matter loading is high. This sampler is especially attractive for use in remote areas or for obtaining improved time resolution information on particulate species present in the atmosphere.

The HVDVI is a prototype sampler in its early stages of development. Future research should be directed toward the optimization of the sampler for both performance and convenience of operation. Additionally, the development of a size-selective inlet to operate at these flow rates would greatly enhance the comparability of the HVDVI to other thoracic or inhalable-type particulate matter samplers.

The authors would like to thank Dr. Harry Rook, Dr. Raymond McKenzie, and Dr. Dave Bright of the National Bureau of Standards for their support, space, and equipment, which helped make the calibration of this air sampler possible. We would also like to thank Dr. William Zoller and Dr. Glen Gordon at the University of Maryland for their support and suggestions in building and calibrating the HVDVI.

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APPENDIX C

DESCRIPTION OF THE STATISTICAL METHOD DEVELOPED BY GLEIT

## DESCRIPTION OF GLEIT'S METHOD

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

The below-LOD mean of a normal distribution of a variable with a limit of detection  $L$  is given, in terms of  $L$  and the mean  $\mu$  and the standard deviation  $\sigma$  of the distribution, by equation 1:

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

In equation (1),  $f$  and  $F$  are, respectively, the probability density function and cumulative distribution function of the standard normal distribution. The "Estimated Concentrations for Samples Below the LOD" reported in Table II-2 are the below-LOD means of the assumed lognormal distributions of the concentrations. These below-LOD means are computed from equation (2) in terms of parameters of the associated normal distribution: the LOD  $L$ , the mean concentration from Table II-2, and the estimated standard deviation (which is not tabulated).

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

We now describe how Gleit's method estimates the mean and variance of the assumed normal distribution. The mean and variance cannot be estimated by merely substituting into standard formulas, if below-LOD concentrations are to be set to the below-LOD mean. On the one hand, the mean and variance must be known in order to calculate the below-LOD mean from (1); on the other hand,

the below-LOD mean must be known if it is to be used in the calculation of the mean and variance. Statistical theory, by asserting that a "best-fitting" mean and variance for the distribution exist, provides a way out of this dilemma. Gleit uses a simple iterative procedure to compute these best-fitting parameters. Since his procedure can be simply described in words, a written description is given, supplemented where necessary by equations written in a notation more convenient than Gleit's.

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

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

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

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

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

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

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



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

$$\sigma^2_{\text{BLOD}(K+1)} = \sigma^2(K) \cdot [1 - Z(K) \cdot (f(Z(K)) / F(Z(K))) ],$$

where  $Z(K) = (L - \mu(K)) / \sigma(K)$ .

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

**APPENDIX D**  
**INORGANIC ARSENIC EMISSION RATE CALCULATIONS**

**Note:** The following calculations were used by ARB staff to make some of the emission estimates found in Section II of this report.

1. Pesticide Use:

The inorganic arsenic content of arsenical pesticides applied in 1985 was calculated to be 16.3 tons (ARB, 1985a and CDFA, 1987). ARB reported an estimated 5% loss from actual spraying of arsenical pesticides due to the drift (Roberts, 1980). Arsenic emissions from pesticidal use are estimated as follows:

$$\begin{aligned} \text{Ems} &= \text{Use} * \text{Drift Loss} \\ &= 16.3 \text{ tons/yr} * 0.05 = 0.815 \text{ tons/yr} \end{aligned}$$

2. Distillate Oil:

California used approximately 352.6 million gallons of distillate oil in 1984 (ARB, 1986a and 1986b). Various devices such as baghouses, electrostatic precipitators (ESP) and scrubbers are used to control particulate matter (PM) emissions from the combustion of distillate oil. Based on the percentage of oil used in equipment with PM-controls and the average control efficiency of various control devices (ARB, 1986c and 1986d), it was assumed that 30 percent of distillate oil was used in equipment with control devices having 90 percent control efficiency and 70 percent was used in equipment without control. Arsenic emissions from distillate oil combustion are estimated using Equation 1:

$$\text{EMS} = \text{PR} * [\text{PRF}_1 * (1-\text{CNTL}_1) + \text{PRF}_2 * (1-\text{CNTL}_2)] * \text{D} * \text{C}_{\text{As}} * \text{U}_f^{-1} \quad (7)$$

Where:

- EMS = Arsenic emissions, tons per year
- PR = Amount of oil used million gallons per year
- PRF = Fraction of oil burned subject to emission control
- CNTL = Control fraction, unit-less
- D = Density of distillate oil, lbs per gallon
- C<sub>As</sub> = Arsenic concentration, ppm
- U<sub>f</sub> = Unit conversion factor (2000), lbs per ton

Arsenic concentrations in distillate oil are reported to range from less than 0.01 ppm to 3.1 ppm (Menczel, et al., 1984 and SCE, 1986). Using equation (1) the arsenic emissions from distillate oil combustion are estimated below:

$$\text{EMS} = (352.6 \text{ million gals/yr}) * [0.30 (1-.90) + 0.70 (1-0)] * (7.2 \text{ lbs/gal}) * (0.01 \text{ ppm}) * (2,000 \text{ lbs/ton})^{-1}$$

	<u>Lower</u> (TPY)	<u>Upper</u> (TPY)
EMS	0.01	2.9

3. Residual Oil:

California used approximately 1,442 million gallons of residual oil in 1984 (ARB, 1986a and 1986b). It was assumed that 55 percent of the residual oil was used in boilers equipped with control devices having 90 percent control efficiency and 45 percent was used in boilers without control devices (ARB, 1986c and 1986d). A residual oil arsenic concentration of 0.01 ppm (SCE, 1986) was used to calculate the lower emission estimate while a concentration of 0.8 ppm (USEPA, 1984) was used to calculate the upper number. Equation 1 was also used to estimate arsenic emissions from residual oil combustion. Arsenic emissions from residual oil combustion are estimated as follows:

$$\begin{aligned} \text{EMS} &= (1,331 \text{ million gal/yr}) * [0.55 (1-.9) + 0.45 (1-0)] * \\ &\quad (8.2 \text{ lb/gal}) * 0.01 \text{ ppm} (2,000 \text{ lb/ton})^{-1} \\ &= 0.03 \text{ ton/yr} \end{aligned}$$

	<u>Lower</u> (TPY)	<u>Upper</u> (TPY)
EMS	0.03	2.4

4. Waste Oil:

California used approximately 13 million gallons of waste oil in 1983 (ARB, 1985). Arsenic concentrations in waste oil are reported to range from 1.5 ppm to 19.5 ppm (Pedco, 1984; Menczel, et. al., 1984; USEPA, 1984; Krishnan and Hellwig, 1982; and Surprenant and Battye, 1983). Assuming all arsenic in waste oil is emitted upon combustion, arsenic emissions from waste oil are estimated as follows:

$$\text{EMS} = \text{PR} * D_W * C_{As} * U_f^{-1} \quad (8)$$

Where:

- EMS = Arsenic emissions, tons per year
- PR = Amount of oil used, million gallons per year
- $D_W$  = Density of waste oil, lbs per gallon
- $C_{As}$  = Arsenic concentration in waste oil, ppm
- $U_f$  = Unit conversion (2,000), lbs per ton

$$\text{EMS} = (13 \text{ million gal/yr}) * (7.5 \text{ lb/gal}) * (1.5 \text{ ppm}) * (2,000 \text{ lb/ton})^{-1}$$

	<u>Lower</u> (TPY)	<u>Upper</u> (TPY)
EMS	0.07	0.95

5. Cement Manufacturing:

The Emission Data System (EDS) shows that California Cement manufacturers emitted approximately 6,500 tons of particulate matter in 1985 (ARB, 1988b). These emissions are itemized:

- a. Raw material preparation (primary crushing, grinding and homogenizing)..... 2,780 tons
- b. Calcining and clinkering (including fuel combustion)..... 1,490 tons
- c. Cement preparation (clinker cooling, finish grinding, and distribution)..... 2,250 tons

Arsenic concentration in California kiln dust range from 2.8 ppmw to 509 ppmw.

Emission calculations are as follows:

$$EMS = PM * C_{As} \quad (10)$$

Where:

EMS = Arsenic emissions, tons per year

PM = Particulate matter emissions from cement manufacturing, tons per year

$C_{As}$  = Arsenic concentration, ton As/ $10^{-6}$  ton PM.

Applying PM emissions and the arsenic concentrations in the equation, arsenic emissions from cement kilns (including coal combustion) range from 0.004 to 0.76 ton in 1985.

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APPENDIX E

INORGANIC ARSENIC INFORMATION REQUEST LETTER

## AIR RESOURCES BOARD

1102 Q STREET

P.O. BOX 2815

SACRAMENTO, CA 95812



June 4, 1985

Dear Sir or Madam:

Request for Information Regarding Inorganic Arsenic

I am writing to request information on the health effects of inorganic arsenic as part of our toxic air contaminant program. This program is based on Health and Safety Code Sections 39650, et seq. which require the ARB to identify compounds as toxic air contaminants and once identified to develop and adopt control measures for such compounds. After consultation with the staff of the Department of Health Services (DHS), we have selected inorganic arsenic as a candidate toxic air contaminant to be evaluated in accordance with the provisions of Health and Safety Code Sections 39650, et seq. During our evaluation of inorganic arsenic, we will consider all available health information regarding this compound. Additionally, we are soliciting information regarding possible biological transformations of inorganic arsenic.

Before the ARB can formally identify a compound as a toxic air contaminant, several steps must be taken. First, the ARB must request the Department of Health Services to evaluate the health effects of candidate compounds. Second, the ARB staff must prepare a report which includes the health effects evaluation and then submit the report to a Scientific Review Panel for its review. The report submitted to the Panel will be made available to the public. Information submitted in response to this request will be considered in the ARB report to the Panel. Although any person may also submit information directly to the Panel for its consideration, I urge you to submit all information at this time for our consideration in the development of the report for the Panel. The Panel reviews the sufficiency of the information, methods, and data used by the DHS in its evaluation. Last, after review by the Scientific Review Panel,

June 4, 1985

the report with the written findings of the Panel will be considered by the Air Resources Board and will be the basis for any regulatory action by the Board officially to identify a compound as a toxic air contaminant.

Prior to formally requesting the DHS to prepare a health effects evaluation of inorganic arsenic, we are providing, pursuant to the provisions of Section 39660(e) of the Health and Safety Code, an opportunity to interested parties to submit information on the health effects of inorganic arsenic which he or she believes would be important in DHS's evaluation of inorganic arsenic as a candidate toxic air contaminant.

In May 1985, we received a reference search on inorganic arsenic health effects using the MEDLINE and TOXLINE Information Services. These information services include material available to the public in late 1984. The attached bibliography lists the references from this information search. We are requesting pertinent information on inorganic arsenic health effects, including any material that may not be available to the public, that is not included in the attached bibliography.

Pursuant to the provisions of the Public Records Act (Government Code Sections 6280 et seq.), the information you provide will be a public record and subject to public disclosure, except for trade secrets which are not emission data or other information which is exempt from disclosure or the disclosure of which is prohibited by law. The information may also be released to the Environmental Protection Agency, which protects trade secrets and confidential information in accordance with federal law, and to other public agencies, which are also required to protect such information.

To expedite the review process, we ask that any information which you believe should be regarded as "trade secret" be clearly marked and separated from other information. You may identify portions of the information you submit as "trade secret" in accordance with Health and Safety Code Section 39660(e). The claim of trade secrecy must be supported upon the request of the Air Resources Board. Other information claimed to be trade secret and information otherwise claimed to be exempt from disclosure may be identified as confidential in accordance with Section 91011, Title 17, California Administrative Code. Section 91011 requires that the claim of confidentiality be accompanied by specified supporting information.

I would appreciate receiving any relevant information you wish to submit by July 12, 1985. Your help in expediting our review will be greatly appreciated. Please send the information to the attention of:

June 4, 1985

William V. Loscutoff, Chief  
Toxic Pollutants Branch  
Re: Inorganic Arsenic  
California Air Resources Board  
P. O. Box 2815  
Sacramento, CA 95812

If you have any further questions regarding health effects information, please contact Mr. John Batchelder at (916) 323-1505. For any other questions, please contact Mr. Robert Barham at (916) 322-7072.

If you are not the person to whom this request should be addressed, please forward it to the appropriate person in your organization. Also, please let us know whether you would like to continue to receive information inquiries for other candidate compounds, and if not, if there is anyone in your organization to whom such requests should be sent.

Sincerely,



Peter D. Venturini, Chief  
Stationary Source Division

cc: Alex Kelter, DHS  
Lori Johnston, DFA  
Wayne Morgan, President, CAPCOA  
Jan Bush, Executive Secretary, CAPCOA  
David Howekamp, EPA Region IX  
Assemblywoman Sally Tanner, Chairwoman, Committee on Toxic  
Materials  
Senator Ralph Dills, Chairman, Committee on Governmental  
Organization  
Senator Art Torres, Chairman, Committee on Toxics and  
Public Safety Management  
Emil Mrak, Chairman and Scientific Review Panel  
Members  
APCOs

Attachment

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APPENDIX F

INORGANIC ARSENIC HEALTH EFFECTS REQUEST TO DHS

# Memorandum

To : Kenneth Hizer, M.D., Director  
Department of Health Services  
714 P Street  
Sacramento, CA 95814

Date : August 6, 1985

Subject: Evaluation of  
Inorganic  
Arsenic

James D. Boyd  
Executive Officer

From : Air Resources Board

I am writing to formally request that the Department evaluate the health effects of inorganic arsenic as a candidate toxic air contaminant in accordance with Assembly Bill 1807 (Tanner). According to Health and Safety Code Sections 39660-62, your Department has ninety days to submit a written evaluation and recommendations on the health effects of inorganic arsenic to the Air Resources Board and may request a thirty day extension.

Attached for your staff's consideration in evaluating inorganic arsenic are: Attachment I - a list of references on inorganic arsenic health effects which were identified in an ARB letter of public inquiry or received in response to the inquiry letter; and Attachment II - ambient inorganic arsenic concentration data which should be used to estimate the range of risk to California residents as required in Health and Safety Code Section 39660(c).

My staff is available for consultation in conducting this health effects evaluation. We look forward to continuing to work closely with you and your staff in carrying out this legislative mandate. If you have any further questions regarding this matter, please contact me at 445-4383 or have your staff contact Peter D. Venturini, Chief of the Stationary Source Division, at 445-0650.

## Attachments

cc: Jananne Sharpless  
Alex Kelter, DHS, w/attachments  
Raymond Neutra, DHS, w/attachments  
Peter D. Venturini, ARB  
Assemblywoman Sally Tanner  
Claire Berryhill, DFA  
Emil Mrak, Chairman and Members  
of the Scientific Review Panel  
Senator Ralph Dillis  
Senator Art Torres  
John Holmes, ARB

Doc. #2415W/Arch. 1344

ATTACHMENT I

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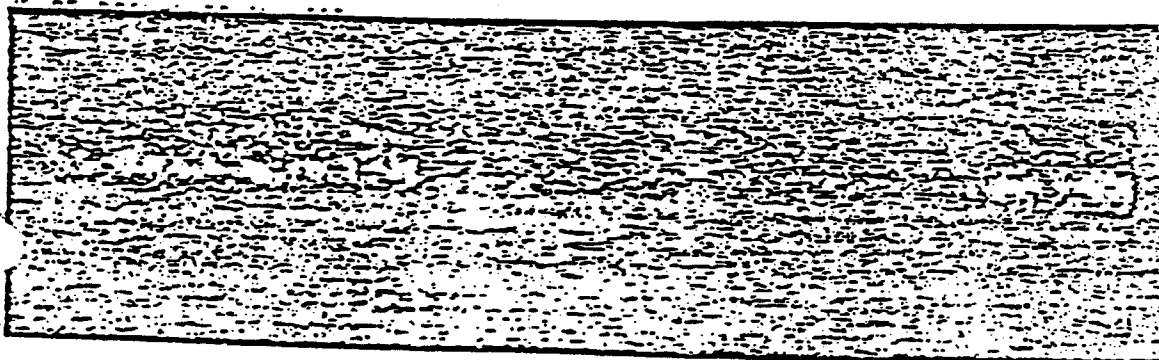
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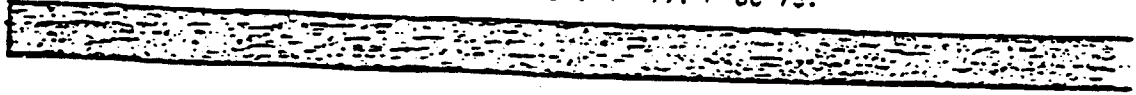
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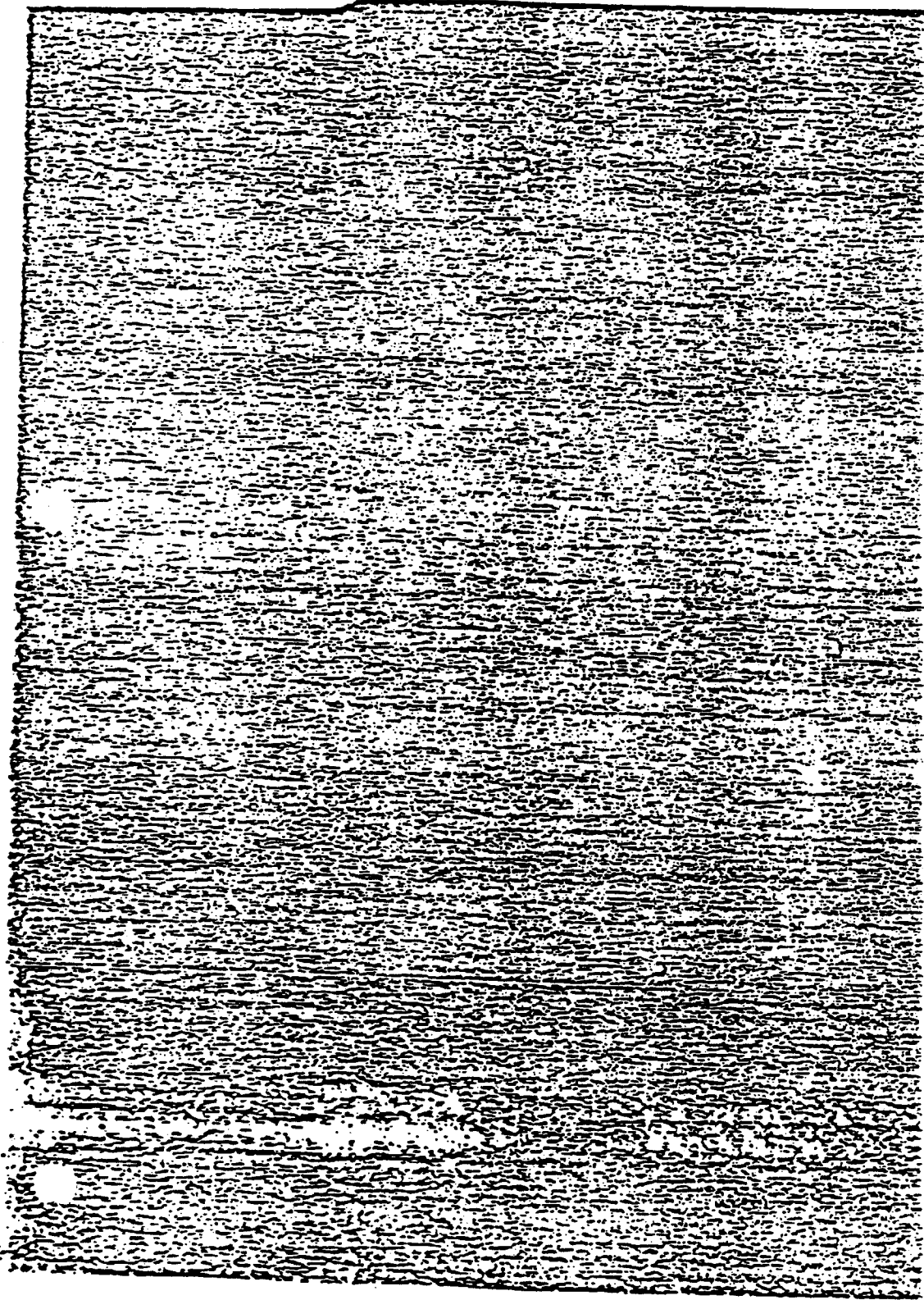
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RS SEARCH MODE - ENTER QUERY

9 :2 and biotransformation.de. and human.ce.

RESULT 8 DOCUMENTS

10 :9 not (3 7 8)

RESULT 2 DOCUMENTS

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RESULT 5851 DOCUMENTS

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END OF DOCUMENTS IN LIST  
PLEASE REAPPLY - ENTER QUERY

0.978 DEC 1975 SESSION 0014  
C-ARS DE-ROY CIT-ROY COMM TOTAL  
514.67 55.87 521.75 57.82 550.11  
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## ATTACHMENT II

### AMBIENT ARSENIC CONCENTRATIONS AND EMISSION TRENDS

Data from the U.S. Environmental Protection Agency's National Aerometric Data Bank for the period 1977-1981 shows annual average concentrations of arsenic in California ranging between 7.2 ng/m<sup>3</sup> and 2.7 ng/m<sup>3</sup>. These data represent total particulate arsenic 50 um and smaller collected from ambient air at sites throughout California.

Inorganic arsenic and its compounds are used in pesticides, and to a limited extent in glass manufacture. The use of inorganic arsenic has been declining and this trend is expected to continue. Potential sources of inorganic arsenic in the air are emissions from nonferrous primary smelters, fossil fuel combustion, municipal incinerators, and secondary nonferrous smelters. Investigations are under way to determine the magnitude of emissions in California from these and other types of sources.