

HUMAN EXPOSURES TO ATMOSPHERIC ARSENIC

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HUMAN EXPOSURES TO ATMOSPHERIC ARSENIC

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I INTRODUCTION

The primary objective of this study has been to quantify the exposure of the United States population to arsenic in the atmosphere. The seven primary sources of atmospheric arsenic evaluated are coal-fired power plants; copper, lead, and zinc smelters; pesticide manufacturers; cotton gins; and glass manufacturers. In addition, general ambient background concentrations were analyzed to place the contributions by the seven sources in proper perspective. To estimate exposures, we have located and characterized plants for the seven sources, indicated atmospheric environmental concentrations of pollutants resulting from plant activities, and estimated the human population exposed to various levels of these pollutant concentrations.

Substantial evidence, both direct and indirect, indicates that arsenic is carcinogenic. Current U.S. Environmental Protection Agency (EPA) policy states that there is no zero risk level for carcinogens. To determine what regulatory action should be taken by EPA on atmospheric emissions of arsenic, three reports have been prepared: (1) a health effects assessment, (2) a population exposure assessment, and (3) a risk assessment document based on the data in the first two assessments. This is the document on population exposure assessment. On their review of earlier drafts of the three reports, the EPA Science Advisory Board, recommended that

... data essential for determining the potential hazard of arsenic emissions from certain point sources, such as glass manufacturing plants and cotton ginning operations, be collected and made available for critical analyses. There is also a need for additional monitoring data from regions with primary smelters.

II SUMMARY

Arsenic occurs in the atmosphere both as a result of man's activities and from natural sources. Anthropogenic sources can be divided into two groups: (1) from arsenic occurring naturally in many commercial raw materials and released when those materials are processed, and (2) from arsenic used to manufacture commercial products or from arsenic added to commercial products. Products such as arsenical pesticides may cause atmospheric contamination as a result of their manufacture and of their use. Examples of man-made sources include nonferrous smelters, pesticide manufacture and use, the combustion of fossil fuels (primarily coal), glass manufacturing, cotton ginning, and the lead alloy industry. Natural sources of atmospheric arsenic include volcanic action, hot springs, decay of plant matter and other microbial actions, and the weathering of minerals within soils.

Arsenic exists in several forms in the atmosphere. Some of these forms are more toxic than others. For example, trivalent arsenic is the most toxic form, whereas pentavalent arsenic is only slightly toxic. Arsine, a poisonous gas primarily associated with occupational hazards, is extremely toxic, whereas metallic arsenic is nontoxic.

Residence times for arsenic in the atmosphere have not (insofar as we have been able to determine) been reported in the literature. Arsenic absorbed onto particulate matter returns to earth with the particulates. It has been hypothesized that when volatile arsenicals are released to the atmosphere, they are oxidized in the presence of light and return to the earth by way of dry deposition or precipitation (Union Carbide, 1976).

Most compounds of arsenic, when heated in the presence of air, are converted to arsenic trioxide. Because arsenic trioxide sublimes at 193°C, it is easily suspended on small particles in the air (Sullivan, 1969). For this reason, atmospheric emission of arsenic from processes in which heat is involved are generally in the form of arsenic trioxide. This would include smelters, glass manufacturers, and coal-fired power plants. Because arsenic acid is used to desiccate cotton, the arsenic emissions from cotton gins are presumably the residues of the acid. The form of arsenic released during pesticide manufacturing depends on the stage in the manufacturing process at which it is released. Arsenic trioxide is used as raw material for their manufacture. More complex organic and inorganic compounds may be emitted at later stages in a process, depending on the product being manufactured.

This study characterizes human population exposures to seven major man-made arsenic emission sources. To assess the importance of the contributions of these human activities, it is necessary to estimate

the background concentrations for locations in which these activities are not present. Atmospheric arsenic concentration data for 1974 for 267 locations representing a resident population of more than 58,000,000 people were evaluated. The annual average concentrations for all sites ranged from below detection limit to 0.083 $\mu g/m^3$. The annual average concentration for all locations was 0.003 $\mu g/m^3$. The average concentration for eight locations near nonferrous smelters* was 0.030 $\mu g/m^3$, and the average concentration for eight locations in remote rural areas was 0.0004 $\mu g/m^3$ assuming a concentration of zero for samples reported as below detection limit. The lower detection limit for an individual arsenic sample is 0.001 $\mu g/m^3$.

Estimating human population exposures from the seven selected emission sources has necessitated reliance on very limited data. Because of the paucity of measured atmospheric arsenic data near emission sources, it was necessary to approximate concentrations through the use of dispersion modeling. The dispersion modeling used was developed by EPA for representative point source emissions; it is described in Appendix A. All estimates given in this report are subject to considerable uncertainty in regard to:

- (1) The quantity of arsenic emissions
- (2) Arsenic consumption levels
- (3) Source locations
- (4) Control technologies
- (5) Deterioration of installed control equipment over time
- (6) The physical characteristics (e.g., stack height) of arsenic emission sources
- (7) Inherent inaccuracies in the modeling approach.

As a result, the overall accuracy of the exposure estimates could not be directly assessed. However, the dispersion modeling results have been compared to ambient measured concentrations for nonferrous smelters and cotton gins. Generally, the modeling results agree with the measured concentrations within a factor of 3 to 4; however, variations for some results are much larger.

Several alternative exposure estimates were made for each of the seven arsenic sources evaluated. These alternatives are based on various assumptions designed to illustrate the uncertainties involved in such estimates. Table II-1 summarizes the results of this study for one selected set of exposure estimates for each of the sources evaluated. The exposure concentrations shown in the table are annual averages. Exposures for selected times may be much higher or lower than the annual averages. Population exposures for concentrations below 0.003 µg/m³ are

^{*}Smelter locations were separated because of their obviously high concentrations.

Table II-1
SUMMARY OF HUMAN POPULATION EXPOSURES TO ARSENIC
FOR SELECTED EMISSION SOURCES

| | Emission Source | | | | | | | | | |
|--|---------------------------------|-------------------------------|-------------------------------|-----------------------------|--|------------------------------------|--|--|--|--|
| Average Annual Concentration ^a (µg/m ³) | Copper Smelters ^b | Lead Smelters ^C | Zinc Smelters ^d | Cotton Gins ^e | Pesticide Manufacturer ^f | Glass Manufacturer ⁸ | | | | |
| 3.0-5.9 | | | | 5 | | | | | | |
| 1.0-2.9 | | | | 100 | | | | | | |
| 0.60-0.99 | 24,420 | | | 200 | | | | | | |
| 0.30-0.59 | 19,380 | | | 700 | | | | | | |
| 0.10-0.29 | 137,450 | 800 | 9,000 | 2,000 | | 1,440 | | | | |
| 0.060-0.099 | 119,860 | 2,600 | 18,000 | 3,000 | | 10,140 | | | | |
| 0.030-0.059 | 286,560 | 5,100 | 101,000 | 5,900 | | 75,180 | | | | |
| 0.010-0.029 | 313,380 | 38,000 | 170,000 | 20,000 | 60 | 212,040 | | | | |
| 0.005-0.009 | 8,810 | 46,000 | 110,000 | 56,000 | 800 | 363,870 | | | | |
| 0.003-0.004 | 12,960 | 67,000 | 13,500 | 135,000 | 11,900 | 583,360 | | | | |

Average omnidirectional concentrations. With the exception of cotton gin exposures, 24-hr worst-case exposures can be estimated by multiplying the annual averages by 12.5. The 24-hr worst-case exposures for cotton gins may be obtained by multiplying the concentrations by 81.

Based on EPA's estimate of stack emissions. Assumes fugitive emissions are 5% of input for all but Tacoma.

^CBased on an emission of 0.8 lb of arsenic per each ton of lead produced. Fugitive emissions are estimated to be 10% of stack emissions.

Based on an emission of 1.3 lb of arsenic per ton of zinc produced by pyrometallurgical smelters and no stack emissions at electrolytic smelters. Fugitive emissions assumed to be 10% of stack emissions.

Annual average exposure, assuming that ginning exposures occur during 15% of the year and that there are no exposures during the remainder of the year.

 $[\]mathbf{f}_{Assumes}$ that all large plant pesticide emissions are well controlled.

gassumes that 15% of pressed and blown glass is manufactured with arsenic, that only certain manufacturers use arsenic in all of their pressed and blown glass production, and that the size distribution of manufacturers who use arsenic is proportionate to the size output given in Table IX-1. It is assumed that 90% of the manufacturers are well-controlled and that 10% are poorly controlled.

not given because they are assumed to equal the average urban background concentration. Population exposures are not given for concentrations below 0.01 $\mu g/m^3$ for some copper smelter alternative estimates because to do so would have required extrapolation of modeling results beyond 20 km from the source. At these greater distances, the accuracy of the modeling results becomes increasingly uncertain.

Population exposures for coal-fired power plants are not shown in Table II-l because realistic worst-case annual average arsenic exposures for these plants have been estimated to be less than 0.003 $\mu g/m^3$ for the largest poorly controlled power plants and less than 0.001 $\mu g/m^3$ for most power plants.

In using the EPA estimate of current stack emissions for copper smelters and assuming that fugitive emissions are 5% of input except for Tacoma, it is estimated that 923,000 people are exposed to annual average arsenic concentrations of 0.003 to $1~\mu g/m^3$. Another estimate of copper smelter exposures assumed an arsenic emission of 4.9 lb/ton of concentrate with fugitive emissions as 10% of stack emissions. These assumptions resulted in an estimated 950,000 people exposed to annual average concentrations of 0.01 to 1.0 $\mu g/m^3$.

It is estimated that 160,000 people are exposed to annual average concentrations of 0.003 to $0.3~\mu g/m^3$ due to lead smelter emissions. This estimate assumes an arsenic emission factor of 0.8~lb/ton of concentrate and that fugitive emissions are 10% of stack emissions. An alternative estimate assumed that 25% of the arsenic in the ore concentrate is emitted to the atmosphere as stack emissions with 10% additional fugitive emissions. This assumption resulted in an estimated 163,000 people exposed to annual average concentrations of 0.003 to $0.1~\mu g/m^3$.

It is estimated that 442,000 people are exposed to annual average concentrations of 0.003 to 0.3 $\mu g/m^3$ from zinc smelter emissions. This estimate assumes an arsenic emission factor of 1.3 lb/ton of concentrate for pyrometallurgical zinc smelter stacks and no emissions from electrolytic smelter stacks. Fugitive emissions for all smelters are assumed to be 10% of stack emissions.

Arsenic exposures from secondary smelters processing copper and zinc scrap are estimated to be insignificant by comparison with nominal urban background concentrations. Arsenic is added to lead used in batteries and battery cables. This lead is extensively recovered in blast furnace operations that can vaporize and release the arsenic content. The secondary lead industry is highly fragmented, and production figures for battery lead recovery by individual smelters are not available; however, it is estimated that such smelters might produce annual average environmental atmospheric concentrations on the order of 0.003 μg to 0.020 $\mu g/m^3$. Because most secondary smelters are located in fairly densely populated areas, an average of several thousand people could be exposed to emissions from each such smelter.

It is estimated that approximately 13,000 people are exposed to arsenic emissions from pesticide manufacturing. The annual average exposure concentrations range from 0.003 to 0.03 $\mu g/m^3$. These exposures are judged to be relatively minor because it is assumed that large pesticide manufacturers have already installed control equipment.

It is estimated that approximately 1.4 million people are exposed to atmospheric arsenic concentrations of 0.003 to 29 $\mu g/m^3$ during the cotton ginning session. Annual average population exposures, however, are much smaller because the ginning season occurs for only a few weeks a year. Based on annual average exposures, it is estimated that approximately 223,000 people are exposed to atmospheric arsenic concentrations of 0.003 to 6.0 $\mu g/m^3$. These exposure estimates assume that all Texas and Oklahoma machine-stripped cotton is desiccated with arsenic acid. During some years, however, it is not necessary to desiccate all machine-stripped cotton. For those years, the estimated number of exposed people should be proportionately reduced.

Because of uncertainties in determining which glass producers use arsenic and in estimating the amount of arsenic used, attempts to estimate the people exposed to arsenic from glass manufacturing are marked by considerable uncertainty. This uncertainty is illustrated by the several alternative exposure estimates based on different assumptions. However, all alternative estimates indicated that 15 thousand people or more are exposed to annual average arsenic concentrations in excess of 0.003 $\mu g/m^3$. The exposure estimate given in Table II-l shows approximately 1.2 million people exposed to arsenic concentrations of 0.003 to .30 $\mu g/m^3$.

As indicated in Table II-1, the exposures estimated in this report are subject to considerable uncertainty; they thus require further monitoring and sampling data and evaluation for a more complete assessment. Despite the insufficiency of data, however, the population exposure from these sources can be substantially greater than nominal background concentrations. Potential health effects from the estimated exposures will be addressed in another report being prepared by the EPA Cancer Assessment Group.

The primary purpose of this report was to estimate human inhalation exposures to atmospheric arsenic emissions. However, atmospheric emissions of arsenic are eventually deposited on the earth or in water. Deposits on the earth may enter waters through runoff. Plants may absorb this arsenic and they may in turn be consumed by humans or by animals that are eaten by humans. Humans may drink the arsenic-contaminated waters or consume aquatic organisms with an increased arsenic content caused by residing in such waters. Arsenic bioaccumulates in various organisms found in the environment, but the compound arsenic is not biomagnified in the food chain. Arsenic is ubiquitous in nature, and small amounts of it are found in most food and water supplies. Elevated levels of arsenic that appear to be unrelated to atmospheric emissions are found in seafood and local drinking waters. The effects of atmospheric fallout of arsenic

onto land from the sources evaluated in this report must be considered minor, in light of the fact that large quantities of arsenic are released on croplands as pesticides and are dissipated as wastes onto land or into water. Moreover, contamination of earth and water from the atmospheric sources evaluated in this report must accumulate over a relatively long period of time to reach significant levels. The most likely significant route of human exposure to arsenic from these secondary sources resulting from atmospheric arsenic emissions, is eating vegetables raised in arsenic-contaminated soils.

III SOURCES AND BEHAVIOR OF ARSENIC IN THE ENVIRONMENT

Arsenic occurs in the atmosphere both as a result of man's activities and from natural sources. Man-made sources include nonferrous smelters, pesticide manufacture and use, the combustion of fossil fuels (primarily coal), glass manufacturing, cotton ginning, and the lead alloy industry. Tables III-1 and III-2 provide rough estimates of all environmental contribution from these and other sources. The estimates given on these two tables were made by different authors and differ considerably for some sources. Natural sources of arsenic include volcanic action, hot springs, decay of plant matter and other microbial actions, and the weathering of minerals within the soils.

Arsenic is mobile in the environment. Microbes in the soils, waters, and sediments methylate and reduce arsenic to arsine, which is volatile and can enter the atmosphere. The arsines may then be oxidized to less toxic products, that can return to the earth and may be recycled. Most foods and beverages contain small arsenic concentrations. Seafoods, particularly marine invertebrates, usually contain more arsenic than other foods. Although arsenic is bioaccumulated by various organisms, especially in marine environments, there appears to be no significant biomagnification of this element within food chains (Union Carbide, 1976).

The geochemical cycle for arsenic is presented in Figure III-1. As arsenic cycles through the environment, it is converted from one oxidation state to another. Because of multiple oxidation states and the tendency to form soluble complexes, arsenic geochemistry is intricate and not well characterized (Boyle and Jonasson, 1973).

The biological cycle for arsenic (Figure III-2) is understood more completely than the geochemical cycle. In sediments, arsenate is microbially reduced to arsenite, which is then methylated to methylarsenic acid. Methylarsenic acid is reduced and methylated to form dimethylarsinic This acid is reduced to dimethylarsine, which is methylated to yield trimethylarsine. Arsines, which are volatile and very toxic, leave the sediments to pass through the water. When the arsines enter the atmosphere, they are readily oxidized to less toxic products such as cacodylic acid (CA) (McBride and Wolfe, 1971; Wood, 1974). If the CA returns to water (by way of dry fallout or precipitation), it can be reduced by microbes, repeating the latter portion of the cycle, or it can return to sediment either by precipitation with or by adsorption on hydrous oxides (Ferguson and Gavis, 1972). If the CA returns to land, soil organisms can alter it to arsine and recycle it to the atmosphere, or they can convert it to CO_2 and AsO_4^{3-} . The AsO_4^{3-} is then bound to hydrous oxides in the soil. Thus, the environmental fate of arsenic appears to be metabolization to inorganic arsenate which is bound in insoluble compounds in the soil (Woolson and Kearney, 1973).

Table III-1

ARSENIC POLLUTANT SOURCES

| Source | Annual Environmental Release (ton) | Percent of Total Release |
|---|---|------------------------------------|
| Mining | 2 | 0.03 |
| Phosphate rock | Negligible | Negligible |
| Primary copper Roasting Reverberatory furnaces Converters Material handling | 900 400 1150 250 | 9.71 4.32 12.41 2.70 |
| Primary zinc Roasting | 1390 | 15.00 |
| Primary lead Sintering Blast furnace Reverberatory furnace | 285 80 11 | 3.08 0.87 0.12 |
| Gray iron foundry | 97 | 1.05 |
| Cotton ginning and burning | :345 | 3.73 |
| Nonferrous alloys | Negligible | Negligible |
| Phosphoric scid | Negligible | Negligible |
| Glass manufacture | 638 | 6.89 |
| Wood preservatives | Negligible | Negligible |
| Miscellaneous arsenic chemicals | 3 | 0.04 |
| Arsenic pesticide production | 196 | 2.12 |
| Pesticide, herbicide, fungicide use | 2925 | 31.56 |
| Power plant boilers Pulverized coal Stoker coal Cyclone coal | 429 49 15 | 4.63 0.53 0.17 |
| Industrial boilers Pulverized coal Stoker coal Cyclone coal All oil | 19 67 9 Negligible | 0.21 0.73 0.10 Negligible |
| Residential/commercial coal | 6 | 0.07 |
| Incineration | 2 | 0.03 |
| Total | 9268 | 100.00* |

^{*}Sum exceeds 100% because of rounding error.

Source: Union Carbide (1977)

Table III-2

ENVIRONMENTAL DISSIPATIONS OF ARSENIC (1974)

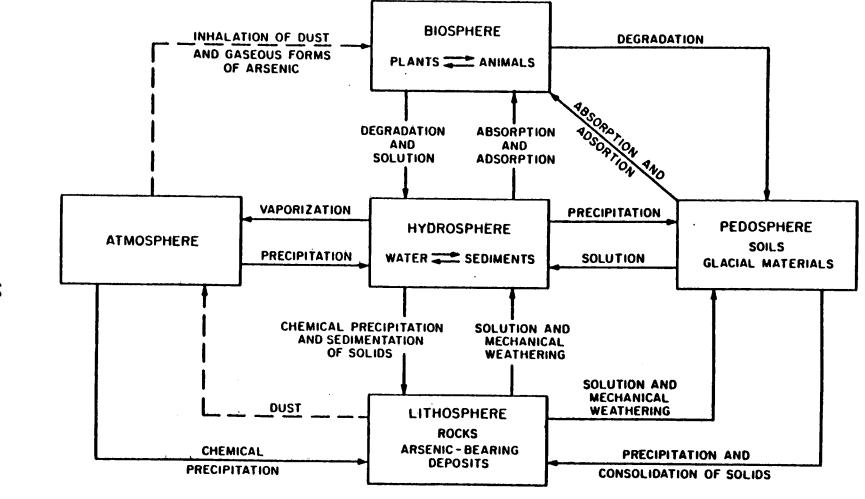
(Metric Tons per Year)

| | Airborne Emissions | Waterborne Effluents | Dissipated to Land |
|--------------------------------|-----------------------|-------------------------|-----------------------|
| Primary zinc | 190 | 0.4 | 120 |
| Primary lead | 240 | | 800 |
| Primary copper | 4,800 (200)* | 32 (1,550)* | 21,800 (7,460)* |
| Other nonferrous metals | 50 | | 50 |
| Lead alloys | 130 | | 300 |
| Phosphates | | 110 | 415 |
| Water and wastewater treatment | .1 | | 67 |
| Boric and boric acid | | 3.9 | |
| Manganese ore | 10 | | 1,080 |
| Iron and steel | 32 | | 37,350 [†] |
| Coal | 650 (170-340)* | | 1,800 (3,000)* |
| Petroleum | 108 | | |
| Pesticide production | 130 | | |
| Pesticide use | 2,300 | | 10,490 |
| Feed additive production | .2 | · | |
| Feed additive use | | | 407 |
| Glass manufacturers | 210 | | |

^{*}These estimates are from Holt and Moberly (1976).

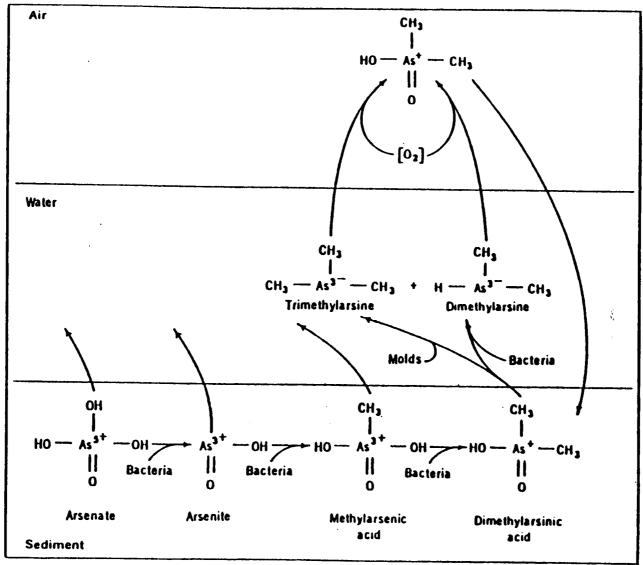
Source: OTS (1976)

The American Iron and Steel Institute (1978) has stated that this estimate is too high by several orders of magnitude.



Source: Union Carbide (1977)

FIGURE 111-1. THE GENERALIZED GEOCHEMICAL CYCLE FOR ARSENIC



Source: Union Carbide (1977)

FIGURE III-2. THE PROPOSED BIOLOGICAL CYCLE FOR ARSENIC

Union Carbide (1976) could not locate residence times for arsenic in the atmosphere in the literature. It is hypothesized that when volatile arsenicals are released to the atmosphere they are oxidized in the presence of light and return to earth by way of dryfall or precipitation (Sullivan, 1969; Woolson and Kearney, 1973).

IV BACKGROUND CONCENTRATIONS OF ARSENIC IN THE ATMOSPHERE

Natural and human activities produce a persistent low-level concentration of arsenic in the atmosphere. However, elevated concentrations are found near certain human activities. To assess the importance of the contributions of some of these activities, it is necessary to estimate the background concentrations for locations in which these activities are not present.

The National Air Sampling Network (NASN) routinely monitors suspended particulate concentration levels in urban and nonurban areas, generally reporting them as quarterly composites for stations in the network. The composite, which pools all samples collected during the quarter, assists in generating sufficient material for laboratory analysis.

The arsenic samples are analyzed by flameless atomic absorption which has a lower detection limit of 0.001 $\mu g/m^3$ and a mean precision, based on duplicates from the same filter, of $\pm 37\%$ (Shearer, 1975).

The quarterly and annual average arsenic concentration data for 1974 for individual NASN locations are given in Table IV-1. For some locations, quarterly data were available from two sources. In the generation of Table IV-1 these two observations were averaged. When 1974 quarterly data were not available for a location, the most recent available quarterly data (from 1973, 1972, or 1971) were used.

Eight of the NASN sites are located in areas that have nonferrous smelters within approximately 50 miles. Another eight of the sites are located in remote national parks or forests.

Table IV-2 lists the 15 NASN locations having average annual arsenic concentrations in excess of 0.010 $\mu g/m^3$. Of these 15 locations, 4 are situated within approximately 10 miles of nonferrous smelters and an additional 4 are situated within 50 miles of nonferrous smelters.

Average annual arsenic concentrations for locations ranged from 0 to 0.083 $\mu g/m^3$. The average annual concentration for all NASN locations was 0.003 $\mu g/m^3$. The average annual concentration for the eight smelter sites was 0.030 $\mu g/m^3$, and the average annual concentration for the eight remote areas was 0.0004 $\mu g/m^3$. Hence, concentrations increase by an order of magnitude for urban over rural and another order of magnitude for smelter cities over urban.

The 1970 populations were obtained for all cities and towns listed in Table IV-1. These populations indicate that the arsenic concentrations

Table IV-1

1974 ATMOSPHERIC ARSENIC CONCENTRATIONS
FOR U.S. LOCATIONS (μg/m³)

| | lst | 2nd | 3rd | 4th | Yrly |
|------------------------|--------|-------------------|--------|------------|-------|
| Location | Qtr. | Qtr. | Qtr. | Qtr. | Avg. |
| ALABAMA | | | | | ٠ |
| Birmingham | 0.022 | 0.015 | 0.000 | 0.000 | 0.009 |
| Gadsen | 0.020 | 0.007 | 0.000 | 0.000 | 0.007 |
| Huntsville | 0.000* | 0.005 | 0.000 | 0.000* | 0.001 |
| Mobile | 0.000* | 0.017 | 0.007 | 0.000* | 0.006 |
| Montgomery | 0.011 | 0.000 | 0.000 | 0.000 | 0.003 |
| ALASKA | | | | | |
| Anchorage | 0.000 | 0.000* | 0.000 | 0.000* | 0.000 |
| Fairbanks | 0.000* | 0.000* | 0.000 | 0.000* | 0.000 |
| ARIZONA | | | | | |
| Apache County | 0.000* | - | - | 0.000* | 0.000 |
| Coconino County | 0.032 | 0.000 | 0.000 | 0.006 | 0.010 |
| Douglas | 0.011 | 0.014 | 0.000 | 0.044* | 0.017 |
| Grand Canyon Nat. Park | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Maricopa County | 0.000 | 0.000 | 0.000* | . - | 0.000 |
| Phoenix ' | 0.013 | 0.000 | 0.000 | 0.009 | 0.006 |
| Superior | 0.000 | 0.000^{\dagger} | 0.000 | 0.000 | 0.000 |
| Tucson . | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |

Note: Readings below the lower detection limit of 0.001 are reported as 0.000.

^{*1973} data.

[†]1972 data.

^{**} 1971 data.

^{- =} No data available.

Table IV-1 (Continued)

| Location | lst Qtr. | 2nd Qtr. | 3rd Qtr. | 4th Qtr. | Yrly Avg. |
|----------------------|--------------------|-------------|-------------|-------------|--------------|
| | | | | | |
| RKANSAS | | 0.006 | 0.007 | 0.000 | 0.005 |
| Little Rock | 0.008 | 0.006 | 0.007 | 0.000 | 0.005 |
| Montgomery County | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Texarkana | - | 0.000 | 0.000 | 0.000 | 0.000 |
| West Memphis | 0.016 | 0.012 | 0.000 | 0.000 | 0.007 |
| ALIFORNIA | | | | | |
| Anaheim | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Berkeley | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Burbank | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Fresno | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Glendale | 0.000 | 0.000 | 0.000* | 0.000* | 0.000 |
| Long Beach | 0.014 | 0.000 | 0.000 | 0.000 | 0.004 |
| Los Angeles | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Oakland | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Ontario | 0.000 | 0.011 | 0.000 | 0.000 | 0.003 |
| Pasadena | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Riverside | 0.000 [†] | 0.000 | 0.000 | - , | 0.000 |
| Sacramento | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| San Bernardino | 0.000 | 0.000 | 0.006 | 0.000 | 0.002 |
| San Diego | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| San Francisco | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| San Jose | 0.000 | 0.000 | 0.000 | 0.000 | ેંગ.000 |
| Santa Ana | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Torrance | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| COLORADO | | | | | |
| Denver | 0.008 | 0.000 | 0.000 | - | 0.003 |
| Mesa Verde Nat. Park | 0.000* | 0.000* | 0.000* | 0.000* | 0.000 |

Table IV-1 (Continued)

| Location | 1st Qtr. | 2nd Qtr. | 3rd Qtr. | 4th Qtr. | Yrly Avg. |
|----------------------|-------------|-------------|--------------------|-------------------|--------------|
| | QLI. | <u> </u> | QCI. | QLI. | Avg. |
| CONNECTICUT | | | | | |
| Bridgeport | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Hartford | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| New Haven | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Waterbury | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| DELAWARE | | | | | |
| Kent County | 0.000 | 0.000 | 0.000* | - | 0.000 |
| Newark | 0.000 | 0.000* | 0.000 | 0.000* | 0.000 |
| Wilmington | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| DISTRICT OF COLUMBIA | | | | | |
| Washington | 0.000 | 0.000 | 0.000 | - | 0.000 |
| PLORIDA | | | | | |
| Hardee County | 0.000 | 0.000 | 0.000 | 0.000* | 0.000 |
| Jacksonville | 0.000* | 0.000* | 0.000 | 0.000 | 0.000 |
| Miami | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| St. Petersburg | .0.000* | 0.000 | 0.000 | 0.000 | 0.000 |
| Татра | 0.000* | 0.000 | 0.000 | 0.000 | 0.000 |
| GEORGIA | | | | | |
| Atlanta | 0.007 | 0.000 | 0.000 | 0.000 | 0.002 |
| Columbus | 0.000* | 0.000 | 0.000 | 0.000 | 0.000 |
| Savannah | 0.000* | 0.000* | 0.000* | 0.000 | 0.000 |
| HAWAII | | | | | |
| Halawa Heights | 0.000 | 0.000 | 0.000 | 0.000^{\dagger} | 0.000 |
| Hawaii County | 0.000 | 0.000 | 0.000 [†] | 0.000 | 0.000 |
| Volcanoes Nat. Park | - | 0.000 | 0.000 | 0.000 | 0.000 |
| Honolulu | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| | | | | | |

Table IV-1 (Continued)

| Location | lst Qtr. | 2nd | 3rd | 4th | Yrly |
|----------------|-------------|---------------------|----------------------|--------------------|-------|
| DOCULION | QLI. | Qtr. | Qtr. | Qtr. | Avg. |
| IDAHO | | | | | |
| Boise City | 0.005 | 0.000 | 0.000 | 0.000 | 0.001 |
| Butte County | 0.006 | 0.000 | 0.000* | 0.000 | 0.002 |
| ILLINOIS | | | | | |
| Chicago | 0.000 | .0.000 [†] | 0.000* | 0.000 | 0.000 |
| East St. Louis | 0.000* | 0.000 | 0.009 | 0.000 | 0.002 |
| Effingham | 0.000* | - | 0.000* | - | 0.000 |
| Joliet | 0.000* | 0.000* | , 0.000 [*] | 0.000 | 0.000 |
| Moline | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| North Chicago | 0.000 | 0.000* | 0.000 | 0.000 | 0.000 |
| Peoria | 0.000* | 0.000* | 0.000* | 0.000 | 0.000 |
| Rockford | 0.000 | 0.000* | 0.000* | 0.000 | 0.000 |
| Rock Island | - | 0.000 | 0.000 | 0.000 | 0.000 |
| Springfield | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| INDIANA | | | | | |
| East Chicago | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Evansville | 0.000* | 0.000 | 0.000 | 0.000 | 0.000 |
| Fort Wayne | 0.000* | 0.000* | 0.000* | 0.000 | 0.000 |
| Gary | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Hammond | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Indianapolis | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Monroe County | 0.000* | 0.000 | 0.000 | 0.000 | 0.000 |
| Muncie | 0.010 | - , | - | - | _ |
| New Albany | 0.000* | 0.000 | 0.000* | 0.000 [†] | 0.000 |
| Parke County | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| South Bend | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Terre Haute | 0.000* | 0.000 | 0.000 | 0.000 | 0.000 |
| | 0.000 | 0.000 | 0.000 | 0.000 | 0.0 |

Table IV-1 (Continued)

| Location | 1st | 2nd Qtr. | 3rd Qtr. | 4th Qtr. | Yrly |
|------------------|--------|-------------|-------------|--------------|-------|
| Dearion | Qtr. | <u> </u> | <u> </u> | <u> </u> | Avg. |
| LOWA | | | | | |
| Cedar Rapids | 0.000* | 0.000 | 0.000 | 0.000 | 0.000 |
| Davenport | 0.005 | 0.005 | 0.012 | 0.000 | 0.006 |
| Des Moines | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Dubuque | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Waterloo | 0.005 | 0.000 | 0.000 | 0.000 | 0.001 |
| KANSAS | | | | | |
| Kansas City | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Topeka | 0.004 | 0.000 | 0.000 | 0.000 | 0.001 |
| Wichita | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| KENTUCKY | | | | | |
| Ashland | 0.014 | 0.000 | 0.000 | 0.000 | 0.004 |
| Bowling Green | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Covington | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Lexington | 0.000 | 0.000* | 0.000 | 0.000 | 0.000 |
| Louisville | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| LOUISIANA | | | | | |
| Baton Rouge | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Iberville Parish | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| New Orleans | 0.000 | 0.000 | 0.000* | 0.000 | 0.000 |
| Shreveport | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| MAINE | | | | | |
| Acadia Nat. Park | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Portland | 0.000 | 0.000 | 0.000 | - | 0.000 |
| MARYLAND | | | | | |
| Baltimore | 0.025 | 0.000 | 0.005 | 0.000 | 0.008 |
| Calvert County | | 0.000 | 0.000 | 0.000* | 0.000 |
| | | | | | |

Table IV-1 (Continued)

| Location | lst | 2nd | 3rd | 4th | Yrly |
|----------------|--------|--------|--------|--------|----------------|
| Location | Qtr. | Qtr. | Qtr. | Qtr. | Avg. |
| MASSACHUSETTS | ± | | | | |
| Boston | 0.000 | 0.000 | 0.000 | 0.000* | 0.000 |
| Cambridge | - | 0.000 | 0.000 | 0.000* | 0.000 |
| Fall River | - | 0.000 | 0.000 | 0.000* | 0.000 |
| New Bedford | - | 0.000 | 0.000 | 0.000* | 0.000 |
| Springfield | 0.000* | 0.000 | 0.000 | 0.000 | 0.000 |
| Worcester | 0.000* | 0.000 | 0.000* | 0.000* | 0.000 |
| MICHIGAN | • | ٠ | .* | | |
| Dearborn | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Detroit | - | • | 0.000 | 0.000 | 5-0.000 |
| Flint | 0.006* | 0.000* | 0.000* | 0.000 | 0.002 |
| Grand Rapids | 0.000* | 0.000* | 0.000* | 0.000 | 0.000 |
| Lansing | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Saginaw | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Trenton | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| INNESOTA | | | | | 5 %, |
| Duluth | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Minneapolis | 0.006* | 0.000 | 0.000 | 0.000 | 0.002 |
| Moorhead | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| St. Paul | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| IISSISSIPPI | | | .• | | |
| Jackson | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Jackson County | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| ISSOURI | ** | | : | | . •. |
| Kansas City | 0.005 | 0.000 | 0.000 | 0.000* | 0.001 |
| St. Louis | 0.009 | 0.007 | 0.000 | 0.000 | 0.004 |
| Shannon County | 0.000 | 0.000 | 0.000* | 0.000 | 0.600 |

Table IV-1 (Continued)

| Location | lst Qtr. | 2nd Qtr. | 3rd Qtr. | 4th Qtr. | Yrly. |
|-------------------|-------------|-------------|-------------|-------------|-------|
| | | | | | |
| MONTANA | * | a aaa* | 0.000* | 0.000* | 0 000 |
| Glacier Nat. Park | 0.000* | 0.000 | | | 0.000 |
| Helena | 0.000 | 0.014 | 0.103** | 0.091** | 0.052 |
| Nebraska | | | | | |
| Lincoln | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Omaha | 0.000 | 0.000 | 0.008 | 0.000 | 0.002 |
| Thomas County | 0.000 | 0.000 | 0.000* | 0.000* | 0.000 |
| NEVADA | | | | | • |
| Las Vegas | 0.000 | 0.000 | - | 0.000 | 0.000 |
| Reno | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| White Pine County | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| NEW HAMPSHIRE | | | | | |
| Belknap County | 0.000* | 0.000* | - | 0.000* | 0.000 |
| Boscawen | - | - | 0.000 | - | |
| Concord | 0.000 | 0.000 | 0.000 | 0.000* | 0.000 |
| Coos County | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| NEW JERSEY | | | | | |
| Bayonne | - | 0.010 | 0.000 | 0.000 | 0.003 |
| Camden | 0.000 | 0.005 | 0.000* | 0.013* | 0.005 |
| Elizabeth | 0.016 | 0.013 | 0.000 | 0.000 | 0.007 |
| Glassboro | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Jersey City | 0.000 | 0.008 | 0.000* | 0.000 | 0.002 |
| Newark | 0.010 | 0.000 | 0.000 | 0.000 | 0.003 |
| Paterson | 0.000 | 0.007 | 0.000* | 0.000 | 0.002 |
| Perth Amboy | 0.019 | 0.010 | 0.007 | 0.022 | 0.015 |
| Trenton | 0.007 | 0.000 | 0.000 | 0.000 | 0.002 |

Table IV-1 (Continued)

| Location | lst Otr | 2nd | 3rd | 4th | Yrly. |
|-------------------------|------------|---------|--------|-------|-------|
| | Qtr. | Qtr. | Qtr. | Qtr. | Avg. |
| NEW MEXICO | - | | | • | |
| Albuquerque | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Arriba County | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| NEW YORK | | | | | |
| Albany | 0.008 | 0.000 | 0.000 | 0.000 | 0.002 |
| Buffalo | 0.007 | 0.000 | 0.000 | 0.000 | 0.002 |
| Jefferson County | 0.000 | 0.000 | 0.000 | - | 0.000 |
| New York City | 0.000 | 0.008 | 0.000 | 0.000 | 0.002 |
| Niagara Falls | 0.009 | , 0.000 | 0.000 | 0.000 | 0.002 |
| Rochester | 0.015 | 0.000 | 0.000 | 0.000 | 0.004 |
| Syracuse | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Troy | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Utica | · - | 0.000 | - | 0.000 | 0.000 |
| Yonkers | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| NORTH CAROLINA | | .* | | | |
| Cape Hatteras Nat. Park | 0.000 | 0.000 | - | - | 0.000 |
| Charlotte | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Durham | 0.000 | 0.005 | 0.000 | 0.000 | 0.001 |
| Greensboro | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Winston-Salem | 0.007 | 0.007 | 0.000 | 0.013 | 0.007 |
| OHIO | | | | | |
| Akron | 0.019* | 0.007 | 0.008 | | 0.011 |
| Canton | 0.008* | 0.008 | 0.006 | 0.006 | 0.007 |
| Cincinnati | 0.000 | 0.006 | 0.000 | 0.000 | 0.002 |
| Cleveland | 0.005 | 0.006 | - | 0.008 | 0.006 |
| Columbus | 0.000 | 0.000 | 0.000* | 0.000 | 0.000 |
| Dayton | 0.011 | 0.000* | 0.013* | 0.006 | 0.008 |
| Ironton | 0.013* | 0.000 | 0.000* | 0.000 | 0.003 |
| Portsmouth | 0.000* | 0.000 | 0.000* | 0.000 | 0.000 |
| | | | | | |

Table IV-1 (Continued)

| Location | lst Qtr. | 2nd Qtr. | 3rd Qtr. | 4th Qtr. | Yrly. Avg. |
|-------------------|-------------|-------------------|-------------|--------------------|---------------|
| | <u> </u> | <u> </u> | <u> </u> | \ | |
| OHIO (Continued) | • | * . | | + | |
| Steubenville | 0.021 | 0.000 | 0.020 | 0.000 | 0.010 |
| Toledo | 0.014 | 0.000 | 0.000 | 0.000 ^T | 0.004 |
| Youngstown | 0.015 | 0.009 | 0.006 | 0.019 | 0.012 |
| OKLAHOMA | | | | | |
| Cherokee County | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Oklahoma City | 0.012 | 0.000 | 0.006 | 0.000 | 0.005 |
| Tulsa | 0.000 | 0.000* | 0.000 | 0.000 | 0.000 |
| OREGON | | | | | |
| Curry County | 0.000 | 0.000* | 0.000* | 0.000 | 0.000 |
| Portland | 0.000 | 0.000 | 0.000* | 0.000 | 0.000 |
| PENNSYLVANIA | | | | | |
| Allentown | 0.009 | 0.000 | 0.000 | 0.000 | 0.002 |
| Altoona | 0.012* | 0.000 | 0.015 | 0.023 | 0.013 |
| Bethlehem | 0.005 | 0.000 | 0.006 | 0.000 | 0.003 |
| Cambria County | 0.005* | - | - | - | - |
| Clarion County | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Clearfield County | 0.000 | 0.000 | 0.000 | | 0.000 |
| Erie | 0.000* | 0.007 | 0.006 | 0.009 | 0.006 |
| Harrisburg | 0.000* | 0.000 | 0.000 | 0.000* | 0.000 |
| Hazleton | 0.015 | 0.000 | 0.000 | 0.000 | 0.004 |
| Indiana County | 0.000 | 0.000^{\dagger} | 0.000 | 0.000 | 0.000 |
| Lancaster City | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Philadelphia | 0.017 | 0.042 | 0.000 | 0.031 | 0.023 |
| Pittsburgh | 0.017 | 0.009 | 0.000 | 0.000 | 0.007 |
| Reading | 0.000* | 0.000* | 0.000* | 0.000 | 0.000 |
| | | | | | |

Table IV-1 (Continued)

| Location | lst Qtr. | 2nd Qtr. | 3rd Qtr. | 4th Qtr. | Yrly. Avg. |
|--------------------------|-------------|-------------|-------------|-------------|---------------|
| | | | | | |
| PENNSYLVANIA (Continued) | | | | | |
| Scranton | 0.016 | 0.000 | 0.000 | 0.015 | 0.008 |
| Warminster | - | 0.000 | 0.000 | - | 0.000 |
| West Chester | - | 0.000 | 0.000 | 0.000 | 0.000 |
| Wilkes-Barre | 0.014 | 0.000 | 0.000 | 0.000 | 0.004 |
| York | 0.000* | 0.000* | 0.000* | 0.000 | 0.000 |
| PUERTO RICO | | | | | |
| Bayamon | 0.000 | 0.010 | 0.000 | 0.000* | 0.003 |
| Catano | 0.000 | 0.000 | 0.014 | 0.000* | 0.004 |
| Guayanilla | 0.000 | 0.000 | 0.000* | 0.000* | 0.000 |
| Guayanilla County | - | 0.000 | - | - | - |
| Ponce | 0.000 | 0.000 | 0.000* | 0.000 | 0.000 |
| San Juan | 0.010 | 0.000 | 0.000* | 0.000 | 0.003 |
| San Juan County | : - | - | 0.000* | - | - |
| RHODE ISLAND | | | , | | |
| East Providence | 0.000* | 0.000* | 0.000 | 0.000* | 0.000 |
| Providence | 0.000 | 0.000* | 0.000 | 0.000 | 0.000 |
| Washington County | 0.000 | 0.000 | 0.000* | 0.000* | 0.000 |
| SOUTH CAROLINA | | | | | |
| Columbia | 0.000* | 0.000 | 0.000 | 0.000 | 0.000 |
| Greenville | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Richland County | 0.000 | 0.000 | 0.000 | 0.000* | 0.000 |
| SOUTH DAKOTA | - | | | . · | ٠. |
| Black Hills Nat. Forest | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Sioux Falls | 0.000 | 0.000 | 0.000 | - | 0.000 |

Table IV-1 (Continued)

| Location | lst Qtr. | 2nd Qtr. | 3rd Qtr. | 4th Qtr. | Yrly. Avg. |
|------------------|----------------|-------------|-------------|-------------|---------------|
| TENNESSEE | | | | | . = - |
| Chattanooga | 0.000* | 0.000* | 0.000 | 0.000 | 0.000 |
| Knoxville | 0.000 | 0.000 | 0.012 | 0.000 | 0.003 |
| Memphis | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Nashville | 0.014 | 0.000 | 0.000 | 0.000* | 0.004 |
| TEXAS | • | | | | |
| Amarillo | - | 0.000 | - | - | - |
| Austin | 0.000 | 0.000 | - | • | 0.000 |
| Beaumont | - | 0.000 | - | - | - |
| Corpus Christi | _ | 0.000 | 0.000 | - | 0.000 |
| Dallas | 0.010 | 0.006 | 0.000* | 0.000 | 0.004 |
| El Paso | 0.067 | 0.070 | 0.005 | 0.132 | 0.069 |
| Fort Worth | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Houston | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Lubbock | - · | 0.000 | - | - | - |
| Matagorda County | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Pasadena | 0.000 | 0.000* | 0.000* | 0.000 | 0.000 |
| San Antonio | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Tom Green County | 0.000* | 0.000* | 0.000* | 0.000 | 0.000 |
| Wichita Falls | . 0.000 | - | 0.000 | - | 0.000 |
| UTAH | | | | | |
| Ogden | 0.000* | 0.015* | 0.021* | 0.014* | 0.013 |
| Salt Lake City | 0.031 | 0.010 | 0.034 | 0.035 | 0.028 |
| VERMONT | | | | | |
| Burlington | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Orange County | 0.000 | 0.000 | 0.000* | 0.000 | 0.000 |
| | | | | | |

Table IV-1 (Continued)

| * | 1st | 2nd | 3rd | 4th | Yrly. |
|----------------------|------------|----------|--------|--------|-------|
| Location | Qtr. | Qtr. | Qtr. | Qtr. | Avg. |
| VIRGINIA | | • | | | |
| Danville | 0.018 | 0.000 | 0.000 | 0.000 | 0.005 |
| Fairfax County | 0.000* | 0.000* | 0.000 | 0000 | 0.000 |
| Hampton | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Lynchburg | 0.012* | 0.000 | 0.000 | 0.000 | 0.003 |
| New Kent County | - . | - | - | 0.000 | - |
| Newport News | 0.000* | 0.000 | 0.000 | 0.000 | 0.000 |
| Norfolk | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Portsmouth | 0.000* | 0.000 | 0.000 | 0.000 | 0.000 |
| Richmond | 0.016 | 0.011 | 0.000 | 0.000 | 0.007 |
| Roanoke | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Shenandoah Nat. Park | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Wythe County | 0.000 | 0.000* | 0.000* | 0.000 | 0.000 |
| WASHINGTON | | | | | |
| King County | 0.026 | 0.024* | 0.042* | 0.000* | 0.031 |
| Seattle | 0.029 | 0.040 | 0.060* | 0.025 | 0.039 |
| Spokane | 0.000 | 0.000 | 0.000* | 0.000* | 0.000 |
| Tacoma | 0.042 | 0.099* | 0.190* | 0.000* | 0.083 |
| VEST VIRGINIA | | | | | |
| Charleston | 0.058 | 0.054 | 0.075 | 0.037 | 0.056 |
| Huntington | 0.000 | - | 0.006* | 0.309* | 0.005 |
| South Charleston | 0.044 | 0.020 | 0.021* | 0.009 | 0.024 |
| WISCONSIN | | | | | |
| Door County | 0.000* | 0.000 | 0.000* | 0.000 | 0.000 |
| Eau Claire | 0.000 | 0.000* | 0.000* | 0.000 | 0.000 |
| Kenosha | 0.000* | 0.000* | 0.000* | 0.000 | 0.000 |
| Langlade County | - | 0.000* | 0.000* | - | 0.000 |
| Madison | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| | | | | | |

Table IV-1 (Concluded)

| | lst | 2nd | 3rd | 4th | Yrly. |
|-----------------------|--------|--------|--------|--------------------|-------|
| Location | Qtr. | Qtr. | Qtr. | Qtr. | Avg. |
| WISCONSIN (Continued) | | | | | |
| Milwaukee | 0.000* | 0.000 | 0.000 | 0.000 | 0.000 |
| Racine | 0.011 | 0.000 | 0.000 | 0.000 | 0.003 |
| Superior | 0.000 | 0.000 | 0.000 | 0.000* | 0.000 |
| WYOMING | | | | | |
| Casper | 0.000* | 0.000* | 0.000* | 0.000* | 0.000 |
| Cheyenne | 0.000* | 0.000 | 0.000 | 0.000 [†] | 0.000 |
| Grand Teton Nat. Park | 0.000* | 0.000* | 0.000* | 0.000* | 0.000 |
| Yellowstone Nat. Park | 0.000* | 0.011* | 0.000 | 0.000* | 0.003 |

Table IV-2 LOCATIONS HAVING ANNUAL AVERAGE ATMOSPHERIC ARSENIC CONCENTRATIONS IN EXCESS OF 0.01 $\mu g/m^3$

| Location | Average Annual Concentration (µg/m ³) |
|----------------------|--|
| Akron, OH | 0.011 |
| Youngston, OH | 0.012 |
| Ogden, UT | 0.013* |
| Altoona, PA | 0.013 |
| Perth Amboy, NJ | 0.015 |
| Douglas, AZ | 0.017 [†] |
| Philadelphia, PA | 0.023 |
| South Charleston, WV | 0.024 |
| Salt Lake City, UT | 0.028* |
| King County, WA | 0.031* |
| Seattle, WA | 0.039* |
| Helena, MT | 0.052 [†] |
| Charleston, WV | 0.056 |
| El Paso, TX | 0.069 |
| Tacoma, WA | 0.083 |

^{*}Nonferrous smelter within 50 miles.

Nonferrous smelter within 10 miles.

listed in Table IV-1 represent an exposed population of more than 58,000,000. The statistical distribution of people to exposures is given in Figure IV-1. Also shown in Figure IV-1 is the statistical distribution of people to exposures excluding the eight nonferrous smelter locations.

Exposures weighted by city population give an average population exposure of 0.004 $\mu g/m^3$. The population weighted average exposure for the eight nonferrous smelter locations is 0.030 $\mu g/m^3$ (the same as the unweighted average).

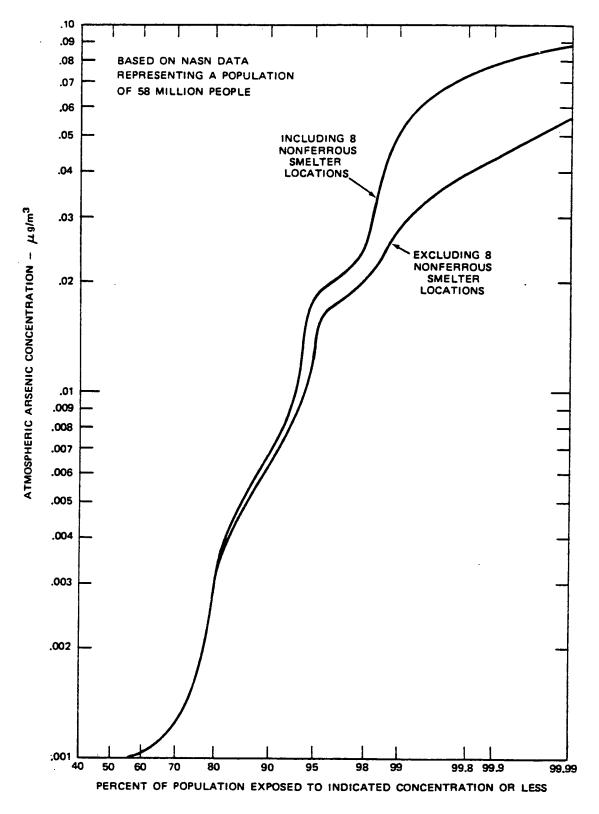


FIGURE IV-1. ATMOSPHERIC ARSENIC CONCENTRATIONS FOR EXPOSED URBAN POPULATIONS

A. General

Arsenic is one of a number of volatile trace elements contained in coal. The average arsenic content of U.S. coals has been reported to be 5.44 ppm, with average estimates of 10 ppm for eastern coal, 5 ppm for coal from interior states, and 1 ppm for coal from western states (Davis, 1971). Ruch et al. (1974) found an average arsenic concentration of 14 ppm for 101 coal samples taken mostly from Illinois. Magee et al. (1973) reported arsenic concentrations of 3-59 ppm for Appalachian coal, 9-45 ppm for interior coal, and 73 ppm for one sample taken from the Four Corners area of Utah, Arizona, New Mexico, and Colorado. Magee et al. did not report average concentrations. The variation in concentrations as reported by different authors is probably indicative of the variation among coal samples and test procedures.

The somewhat higher arsenic content of eastern coals (as reported by Davis, 1971) is partially offset by their higher heating content for the generation of an equivalent unit of power. Appalachian coals give about 12,500 Btu/lb, interior coals about 11,000 Btu/lb, and western coals about 9,500 Btu/lb (Lee et al., 1977).

Table V-1 shows the use of coal by source for 1974. During that year, more than 70% of the coal mined was used for electrical power generation, about 17% was used for coke manufacturing, and 11% was used for other manufacturing and mining. Various authors have estimated the total amount of arsenic released during coal consumption (Table V-2). Estimates of airborne emissions range from 170 to 650 metric tons of arsenic per year.

B. <u>Coal-Fired Power Plants</u>

A computer listing of coal-fired power plant locations, fuel consumptions, and generation capacities was obtained from EPA. These data are too voluminous to include here in their entirety but are summarized by state in Table V-3. Of the 381 coal-fired power plants listed, 368 burn bituminous coal. The remaining 13 plants burn anthracite or lignite coal. The coal capacity of the 381 power plants is 435 million tons/yr.

C. Power Plant Atmospheric Emissions

How arsenic in coal is released during combustion is questionable. The arsenic is probably volatized during combustion and then adsorbs or condenses onto small particles that can most easily pass through

Table V-1
COAL USE BY SOURCE (1974)

| Source | % Use | Millions of Metric Tons per Year |
|--------------------------------|-------|----------------------------------|
| Electric power generation | 71 | 347.9 |
| Coke plants | 17 | 83.3 |
| Other manufacturing and mining | 11 | 53.9 |
| Retail dealers | 1 | 4.9 |
| Total | 100 | 490.0 |

Source: Bureau of Mines (1975).

Table V-2

ARSENIC RELEASED FROM COAL CONSUMPTION--1974
(metric tons)

| Reference | Total | Airborne Emissions | Land Disposal |
|-------------------------|-------|-----------------------|------------------|
| Holt and Moberly (1976) | 3350 | 170-340 | 3000 |
| OTS (1976) | 2450 | 65 0 | 1800 |

Table V-3

STATE TOTALS OF COAL-FIRED POWER PLANTS AND FUEL CAPACITY, BASED ON EPA LISTING

| State | Plants | Total Fuel Capacity (1000 ton/yr) | Fuel Type |
|----------------------|--------|--------------------------------------|--------------|
| Alabama | 10 | 17,849.5 | В |
| Alaska | 2 | 164.1 | В |
| Arizona | 2 | 6,286.5 | В |
| Colorado | 9 | 7,231.2 | В |
| Delaware | 1 | 782.7 | В |
| District of Columbia | 1 | 0.02 | . В |
| Florida | 6 | 6,067.9 | В |
| Georgia | 7 | 8,775.1 | В |
| Illinois | 25 | 31,736.0 | •В |
| Indiana | 25 | 28,207.2 | В |
| Iowa . | 22 | 6,459.8 | В |
| Kansas | 7 | 3,506.8 | . В |
| Kentucky | 16 | 22,955.8 | В |
| Maryland | 6 | 5,083.1 | В |
| Michigan | 27 | 20,250.1 | В |
| Minnesota | 18 | 8,981.6 | - В |
| MINNESOCA | 2 | 671.5 | L |
| Mississippi | 2 | 1,687.0 | В |
| Missouri | 17 | 18,678.6 | В |
| Montana | 2 | 2,060.6 | В |
| Nebraska | 4 | 1,996.4 | В |
| Nevada | 2 | 4,849.9 | В |
| New Hampshire | 1 | 750.9 | В |
| New Jersey | 3 | 2,604.2 | В |
| New Mexico | 2 | 9,667.6 | В |

Table V-3 (concluded)

| State | Plants | Total Fuel Capacity (100 ton/yr) | Fuel Type |
|----------------|--------|----------------------------------|--------------|
| New York | 10 | 6,017.4 | В |
| North Carolina | 13 | 20,961.8 | В |
| North Dakota | 5 | 6,320.4 | L |
| Ohio | 34 | 49,265.4 | В |
| Para - 1 | 26 | 36,088.9 | В |
| Pennsylvania | 3 | 1,349.7 | A |
| South Carolina | 9 | 5,550.7 | В |
| | 2 | 233.5 | В |
| South Dakota | 1 | 2,258.8 | L |
| Tennessee | 8 | 18,558.0 | В |
| — | 1 | 332.7 | В |
| Texas | 2 | 12,018.4 | L |
| Utah | 4 | 1,263.8 | В |
| Vermont | 1 | 8.7 | В |
| Virginia | 6 | 5,666.6 | В |
| Washington | 1 | 4,106.9 | В |
| West Virginia | 12 | 27,433.2 | В |
| Wisconsin | 19 | 10,842.9 | В |
| Wyoming | 5 | 8,982.5 | В |
| Total | 381 | 434,564.4 | |

A - Anthracite coal

B - Bituminous coal

L - Lignite coal

conventional control equipment. Natusch et al. (1974) found the arsenic content of particles emitted by coal-fired ower plants to increase as particle size decreases (Table V-4). Klein et al. (1975) showed that the arsenic concentrations in fly ash from coal-fired power plant outlets are 100 times the concentration in slag.

Table V-4

ARSENIC CONCENTRATION OF AIRBORNE
FLY ASH PARTICLES EMITTED BY
COAL-FIRED POWER PLANTS

| • | • |
|------------------------------|------------------|
| Particle Diameter (µm) | Arsenic (ppm) |
| > 11.3 | 680 |
| 7.3-11.3 | . 800 |
| 4.7- 7.3 | 1,000 |
| 3.3- 4.7 | 900 |
| 2.1- 3.3 | 1,200 |
| 1.1- 2.1 | 1,700 |

Source: Natusch et al. (1974).

It has been estimated that 73% of the arsenic is captured either in bottom fly ash or collected fly ash and that 27% is released in uncontrolled stack emissions (Davis, 1971). Based on a mass balance of trace impurities, Bolton et al. (1975) concluded that electrostatic precipitators were 95% to 98% efficient in the recovery of arsenic. A well-controlled power plant was found to discharge 0.2 g/min of arsenic to the atmosphere (Klein et al., 1975). The power plant consumed 110 ton/hr of coal at peak; because the arsenic flow into the plant with the coal was estimated as 6 g/min, 3.3% of the arsenic input was released as stack emissions. Ferguson and Gravis (1972) have calculated that 2.5 g of arsenic are released into the atmosphere for every ton of coal consumed.

Youngblood (1978) used dispersion modeling to estimate the atmospheric arsenic concentrations in the vicinity of power plants. Three cases were modeled corresponding to the stack characteristics of 25-, 250-, and 1000-MW power plants. All three plants were assumed to have abnormally high arsenic emissions of 100 g/s to enable the model's detection of significant atmospheric arsenic concentrations. The results of the modeling of the three cases are given in Table V-5.

Table V-5

ESTIMATED ANNUAL AVERAGE ATMOSPHERIC ARSENIC CONCENTRATIONS FOR COAL-FIRED POWER PLANTS BASED ON DISPERSION MODELING

Atmospheric Arsenic Concentration

| Distance From | | (µg/m ³) | |
|---------------|----------|----------------------|----------|
| Plant (km) | Plant A* | Plant B* | Plant C* |
| 0.3 | 0.096 | ** | ** |
| 0.8 | 2.784 | 0.480 | 0.016 |
| 1.3 | 2.928 | 0.526 | 0.196 |
| 2.0 | 2.296 | 0.438 | 0.260 |
| 3.0 | 1.680 | 0.395 | 0.198 |
| 5.0 | 1.240 | 0.326 | 0.140 |
| 8.0 | 0.920 | 0.222 | 0.108 |
| 12.0 | 0.656 | 0.156 | 0.080 |
| 16.0 | 0.496 | 0.135 | 0.066 |
| 20.0 | 0.392 | 0.122 | 0.054 |
| | | | |

^{*}All three plant types were assumed to have an arsenic emission rate of 100 g/s. Plant type A corresponds physically to a 25-MW power plant; plant type B to a 250-MW power plant; and plant type C to a 1000-MW power plant.

Source: Modified from Youngblood (1978)

D. Population Exposures

In estimating population exposures, it is assumed that the average arsenic content of coal is 5.44 ppm, with a worst case of 14 ppm. Because a listing of the type of emission controls at each power plant is unavailable, two cases are evaluated: Case 1 assumes that all power plants are well-controlled, with 3.3% of the coal's arsenic emitted

^{**} Negligible.

(arsenic emissions of 0.16 g/ton for 5.44 ppm coal); Case 2 assumes that all power plants are poorly controlled, with 27% of the coal's arsenic emitted (arsenic emissions of 1.3 g/ton for 5.44 ppm coal).

The power plant coal capacity from the EPA plant listing is used to estimate arsenic emissions. This assumption should lead to an overestimate of exposures because power plants infrequently operate at capacity, and some plants are operated intermittently for standby reserve or for peak demand.

The dispersion modeling results for the three cases given in Table V-5 are applied by first estimating the atmospheric arsenic emissions for each power plant in terms of grams per second. The ratios of these estimated emissions to 100 g/s (the emission on which the modeling results are based) are calculated and used to proportionately scale the atmospheric arsenic concentrations from modeling given in Table V-5. The 25-MW power plant characteristic dispersion curve was used to scale concentrations for all power plants smaller than 100 MW; the 250-MW dispersion curve was used to scale concentrations for all plants of 100 to 500 MW; and the 1000-MW dispersion curve was used to scale concentrations for all power plants larger than 500 MW.

When this procedure was applied, it became apparent that no environmental arsenic exposure for 5.44 ppm coal would exceed 0.001 µg/m³. Consequently, a number of worst-case exposures were estimated, leading to the conclusion that the very worst-case annual average exposure does not exceed 0.003 ug/m^3 (the national average urban exposure). These worstcase analyses are given in Table V-6. The largest coal consuming power plants were selected from the EPA listing for each of the three plant types defined in Table V-5. These largest plants consumed 380,000, 3,200,000, and 7,500,000 tons of coal per year, respectively, for the 25-, 250-, and 1000-MW dispersion curve classifications. Well controlled and poorly controlled cases were evaluated by assuming average arsenic in coal (5.44 ppm) and high arsenic in coal (14 ppm). The results given in Table V-6 indicate that most maximum annual exposures are less than $0.001 \,\mu\text{g/m}^3$ and the very worst exposure is $0.0021 \,\mu\text{g/m}^3$. Additional calculations assuming that all the arsenic in the coal is released to the atmosphere lead to estimated very worst case maximum annual-average environmental arsenic concentrations of 0.003 $\mu g/m^3$ for 5.44 ppm coal and $0.008 \, \mu g/m^3$ for 14 ppm coal.

E. Summary

Because the realistic worst-case annual average environmental arsenic exposures for coal-fired power plants are less than 0.003 $\mu g/m^3$ for all power plants and less than 0.001 $\mu g/m^3$ for most power plants, it must be concluded that power plant emissions do not add appreciably to nominal urban background concentrations.

Table V-6

MAXIMUM AVERAGE ANNUAL ATMOSPHERIC ARSENIC CONCENTRATIONS IN THE VICINITY OF LARGE POWER PLANTS

| Condition | Plant Type ^b and Consumption (ton/yr) | Arsenic Concentration ^c (µg/m ³) |
|--|--|---|
| Average coal arsenic-poorly controlled | A - 380,000 | 0.000 5 |
| | B - 3,200,000 | 0.000 7 |
| | C - 7,500,000 | 0.000 8 |
| Average coal arsenic-well controlled | A - 380,000 | 0.000 0 |
| | B - 3,200,000 | 0.000 1 |
| | C - 7,500,000 | 0.000 1 |
| High coal arsenic-poorly controlled | A - 380,000 | 0.001 2 |
| | B - 3,200,000 | 0.001 8 |
| | C - 7,500,000 | 0.002 1 |
| High coal arsenic-well controlled | A - 380,000 | 0.000 1 |
| | B - 3,200,000 | 0.000 2 |
| | C - 7,500,000 | 0.000 3 |
| | | |

^aAverage coal arsenic is 5.44 ppm, high coal arsenic is 14 ppm, poorly controlled allows 27% arsenic emissions, and well controlled allows 3.3% arsenic emissions.

Plant types A, B, and C correspond to the dispersion curves given in Table V-5.

^CFrom distance of highest concentration given in Table V-5.

VI ARSENIC EXPOSURES FROM NONFERROUS SMELTERS

A. General

Ores of two types have elevated arsenic concentration: sulfide deposits, associated with copper, lead, zinc, and other ores; and sedimentary deposits such as iron ore, phosphate rock, borax ore, manganese ore, and fossil fuels. The very high temperatures required to smelt metallic ores generally result in the release of a large portion of the naturally occurring arsenic to the atmosphere. Both elemental arsenic and its common oxide, $\mathrm{As}_2\mathrm{O}_3$, are extremely volatile at typical smelting temperatures (OTS, 1976).

Three factors, aside from the inherent volatility of ${\rm As}_2{\rm O}_3$, contribute to the generally high losses of this material to the atmosphere during smelting:

- (1) As203 is slow to condense as higher temperature flue gases cool. Hence, it may pass through baghouses or electrostatic precipitators as a supersaturated vapor even if their temperatures are below the equilibrium sublimation temperatures (OTS, 1976).
- (2) Because dust collection devices such as electrostatic precipitators and baghouses are routinely operated at elevated temperatures, they remain well above the dew point of the flue gas (OTS, 1976).
- (3) The nonferrous metals industry generally recycles collected flue dusts until concentrations of valuable metals build up sufficiently for economical processing. At each stage of recycle, the volatile As₂O₃ has another opportunity to escape collection (OTS, 1976).

B. Primary Nonferrous Smelter Locations

Currently 16 copper, 6 lead, and 7 zinc primary nonferrous smelters are in operation in the United States. The location of these smelters is shown on Figure VI-1.

1. Copper Smelters

The 16 primary copper smelters and their annual production figures are listed in Table VI-1. Seven of the smelters are located in Arizona, two in New Mexico, with one each in Washington, Utah, Texas, Tennessee, Nevada, Montana, and Michigan. Secondary copper smelters account for

Source: NIOSH, 1976.

FIGURE VI-1. DOMESTIC PRIMARY NONFERROUS SMELTERS

Table VI-1
PRIMARY U.S. COPPER SMELTERS

| Company/Location | Annual Production (metric tons per year) |
|-----------------------------------|--|
| Phelps-Dodge Morenci, AZ | 160,000 |
| Kennecott Hayden, AZ | 73,000 |
| Cities Services Copperhill, TN | 17,000 |
| Anaconda Anaconda, MT | 170,000 |
| Kennecott Hurley, NM | 77,000 |
| Kennecott McGill, NV | 61,000 |
| Kennecott Garfield, UT | 250,000 |
| Nagma San Manuel, AZ | 100,000 |
| White Pine White Pine, MI | 73,000 |
| Inspiration Miami, AZ | 99,000 |
| Phelps-Dodge Ajo, AZ | 65,000 |
| ASARCO El Paso, TX | 66,000 |
| ASARCO Hayden, AZ | 120,000 |
| ASARCO Tacoma, WA | 99,000 |
| Phelps-Dodge Douglas, AZ | 120,000 |
| Phelps-Dodge Hidalgo, NM | 91,000 |

Source: OAQPS (1974)

about 30% of the U.S. copper demand (Environmental Sciences and Engineering, 1976) and are situated close to a source of scrap or near inexpensive transportation. They are believed to produce much less arsenic pollutant than the primary smelters.

The primary copper industry employs a pyrometallurgical process. Primary copper smelters conventionally produce blister copper after roasting, smelting, and converting. In some cases, the blister copper is purified by fire refining. If further purification is desired, an electrolytic process is used to produce cathode copper. Copper production in 1974 is estimated as 1,470,000 metric tons with 1,440,000 metric tons from domestic sources and 30,000 metric tons from foreign sources (OTS, 1976).

2. Lead Smelters

The domestic lead industry is comprised of six smelters. Their locations are described in Table VI-2. Three plants are located in Missouri, with one each in Montana, Idaho, and Texas. The smelter in El Paso, Texas produces both copper and lead, and the smelter in Idaho produces both lead and zinc. A lead refinery owned by ASARCO is located in Omaha, Nebraska.

Table VI-2
PRIMARY U.S. LEAD SMELTERS

| Company/Location | Annual Production (metric tons per year) |
|-------------------------------------|--|
| ASARCO Glover, MO | 74,000 |
| ASARCO East Helena, MT | 35,000 |
| ASARCO El Paso, TX | 50,000* |
| Bunker Hill Kellogg, ID | 120,000 |
| St. Joe Minerals Herculaneum, MO | 180,000 |
| Missouri Lead Operating Boss, MO | 130,000 |

^{*}The Bureau of Mines (1978) lists the ASARCO-El Paso capacity as 80,000 metric tons per year.

Source: OAQPS (1974)

The six lead smelters employ pyrometallurgical smelting and use domestic or foreign sulfide ores. Lead production in 1974 is estimated to be 608,000 metric tons, of which 526,000 metric tons was from domestic concentrates and 82,000 metric tons was from imported concentrates (OTS, 1976).

Zinc Smelters

The domestic primary zinc industry is comprised of seven smelters that produce zinc. Their locations and production capacities are described in Table VI-3. Two plants are located in Texas, two in Pennsylvania, and one each in Idaho, Illinois, and Oklahoma. An eighth smelter owned by ASARCO and located in Columbus, Ohio roasts concentrates to make calcine.

Table VI-3
PRIMARY U.S. ZINC SMELTERS

| Company/Location | Annual Production (metric tons per year) |
|-----------------------------------|--|
| ASARCO Amarillo, TX | 45,000* |
| ASARCO Corpus Christi, TX | 99,000 |
| AMAX Sauget, IL | 64,000 [†] |
| Bunker Hill Kellogg, ID | 99,000 |
| New Jersey Zinc Palmerton, PA | 100,000 |
| St. Joe Minerals Monaca, PA | 210,000 |
| National Zinc Bartelsville, OK | 46,000 |

^{*}Production for the old Amarillo smelter.

Source: OAQPS (1974)

Estimate from Environmental Sciences and Engineering (1976).

Plans to expand production include one new smelter in Tennessee scheduled to come on line in 1979. In addition, the old horizontal retort smelter of National Zinc at Bartlesville, Oklahoma was replaced with a new electrolytic plant. ASARCO may expand its Corpus Christi plant (Environmental Sciences and Engineering, 1976).

Primary zinc production in 1977 was estimated at 411,114 metric tons, of which 299,825 metric tons were from domestic concentrates and 11,289 metric tons were from imported concentrates. It is further estimated that 194,500 metric tons were produced pyrometallurgically and 216,614 metric tons were produced electrolytically (Bureau of Mines, 1978).

C. <u>Sampling of Atmospheric Arsenic Concentrations Near Nonferrous</u> <u>Smelters</u>

From 1973 to 1975, EPA analyzed the atmospheric arsenic concentrations near a number of the nonferrous smelters. Most locations had one monitoring site; however, there were 10 monitoring sites in El Paso, Texas. Concentration data were analyzed by neutron activation analysis and atomic absorption. The neutron activation analysis has a lower detection limit of 0.003 $\mu g/m^3$ and the atomic absorption has a lower detection limit of 0.001 $\mu g/m^3$ (Shearer, 1975). Data for the individual locations are summarized in Table VI-4. El Paso concentration data are summarized in Table VI-5. In addition, the concentrations as a function of distance from the El Paso smelter are given in Figure VI-2.

Roberts et al. (1976) collected atmospheric arsenic concentrations for four monitoring points in Tacoma during November and December 1975 (Table VI-6). These data are also plotted on Figure VI-3 as a function of distance from the smelter.

As part of the Helena Valley, Montana, air pollution study (U.S. EPA, 1972), atmospheric arsenic concentrations were recorded for five monitoring sites near the East Helena smelter. Data from this program are summarized in Table VI-7 and plotted as a function of distance from the smelter on Figure VI-4. The plot on Figure VI-4 also shows the one NASN site from Table VI-4.

D. Atmospheric Emissions

Although some atmospheric monitoring data for the vicinity of non-ferrous smelters are available, these data are insufficient to characterize population exposures for all nonferrous smelters. It is therefore necessary to use atmospheric dispersion modeling to estimate exposures in the vicinity of those smelters for which few or no monitoring data exist. Youngblood (1978) performed dispersion modeling to

Table VI-4

EPA ATMOSPHERIC ARSENIC SAMPLES TAKEN NEAR NONFERROUS SMELTERS*

| | Sampling Site Location in Test | | | цg/m ³ As | | |
|-----------------|--------------------------------|---------------------------|------|----------------------|-------------|--|
| | Relation to Stack | <u>Method[†]</u> | Days | Average | Range | |
| Hurley, NM | 2.0 km ESE | NAA | | NA | | |
| | | AA | | NA | | |
| Anaconda, MT | 5.9 km NE | NAA | 28 | 0.269 | 0.006-0.854 | |
| • | | · AA | 7 | 0.269 | 0.073-0.719 | |
| East Helena, MT | 2.6 km S | NAA | 52 | 0.043 | 0.000-0.185 | |
| | | AA | 11 | 0.047 | 0.002-0.159 | |
| Carfield, UT | 6.4 km ESE | NAA | 42 | 0.347 | 0.002-1.355 | |
| • | | AA | 10 | 0.380 | 0.093-0.883 | |
| Ajo, AZ | 0.2 km W | NAA | 32 | 0.009 | 0.000-0.053 | |
| • | | AA | 11 | 0.014 | 0.001-0.044 | |
| Douglas, AZ | 0.5 km. NE | NAA | 44 | 0.022 | 0.000-0.102 | |
| • | • | NA | 11 | 0.030 | 0.011-0.075 | |
| Hayden, AZ | 0.9 km SSE | NAA | | NA | • | |
| • | | AA | , | NA | | |
| Miami, AZ | 3.8 km NNE | NAA | 39 | 0.050 | 0.003-0.192 | |
| • | | AA | 8 | 0.044 | 0.000-0.114 | |
| Morenci, AZ | O.2 km NW | NAA | | NA | | |
| • | | , AA | | NA | | |
| San Manuel, AZ | 1.5 km N | NAA | 39 | 0.020 | 0.000-0.073 | |
| | | AA | 9 | 0.035 | 0.004-0.075 | |
| McGill, NV | 3.3 km SSW | NAA | 48 | 0.090 | 0.004-0.315 | |
| • | | AA | 11 | 0.065 | 0.004-0.176 | |
| Kellogg, ID | 0.8 km W | NAA | 50 | 0.299 | 0.024-0.848 | |
| | | AA | 11 | 0.220 | 0.024-0.546 | |
| | | | | | | |

^{*24-}hr samples recorded during 1973 and 1974.

Source: Based on data given by Shearer (1975)

Table VI-5

AVERAGE ATMOSPHERIC ARSENIC CONCENTRATIONS
FOR EL PASO, TEXAS

| Sampling Site | | Annual Av | verage* | (µg/m ³) |
|-------------------|-------------|-------------|--------------|----------------------|
| Location in | | | | Most Recent |
| Relation to Stack | <u>1973</u> | <u>1974</u> | <u> 1975</u> | 12 Months |
| 0.27 km W | 0.666 | 0.293 | | 0.300 |
| 0.46 km NW | 0.902 | 0.568 | 0.556 | 0.582 |
| 1.75 km ESE | 0.098 | 0.074 | | 0.062 |
| 1.84 km NE | 0.037 | 0.037 | | 0.037 |
| 2.30 km SE | 0.103 | 0.072 | 0.055 | 0.056 |
| 3.14 km N | 0.098 | 0.096 | | 0.095 |
| 3.35 kom SSE | 0.150 | 0.115 | | 0.112 |
| 5.34 km ESE | 0.023 | 0.032 | 0.029 | 0.026 |
| 6.70 km SSE | 0.073 | 0.089 | 0.059 | 0.060 |
| 6.81 km NNE | 0.076 | 0.081 | | 0.076 |

^{*}There were generally four to eight 24-hr samples available per month; however, 12 months of data were not available for every year.

Source: Cooper (1978A)

TNAA - Neutron activation analysis, AA - atomic absorption.

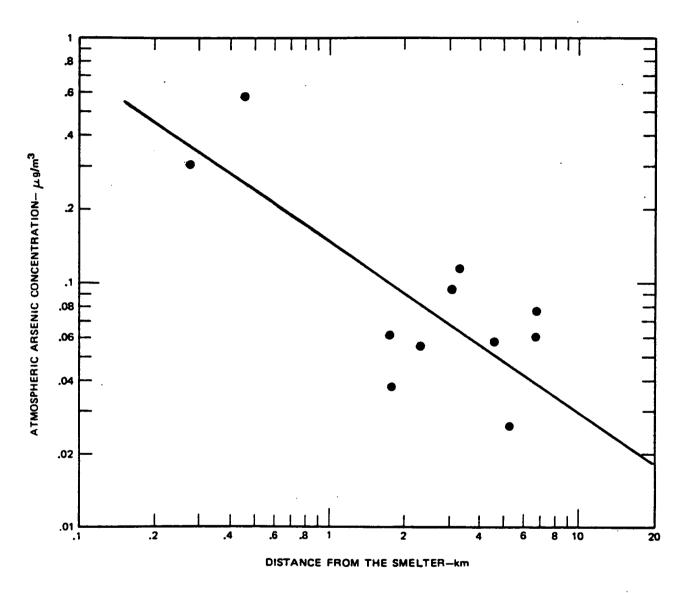


FIGURE VI-2. ATMOSPHERIC ARSENIC CONCENTRATIONS AS A FUNCTION OF DISTANCE FROM THE EL ASARCO SMELTER

Table VI-6
ATMOSPHERIC ARSENIC CONCENTRATIONS
FOR TACOMA, WASHINGTON

| Sample Site Location | Number of | μ | g/m^3 |
|----------------------|-----------|---------|-------------|
| Relative to Smelter | Samples* | Average | Range |
| 0.28 km W | 8 | 3.004 | 0.318-9.353 |
| 0.40 km SSW | 9 | 1.426 | 0.025-2.843 |
| 0.49 km SW | . 8 | 0.515 | 0.188-0.985 |
| 0.94 km S | 7 | 0.314 | 0.190-0.379 |

^{*24-}hr samples collected during November and December 1975.

Source: Roberts et al. (1976)

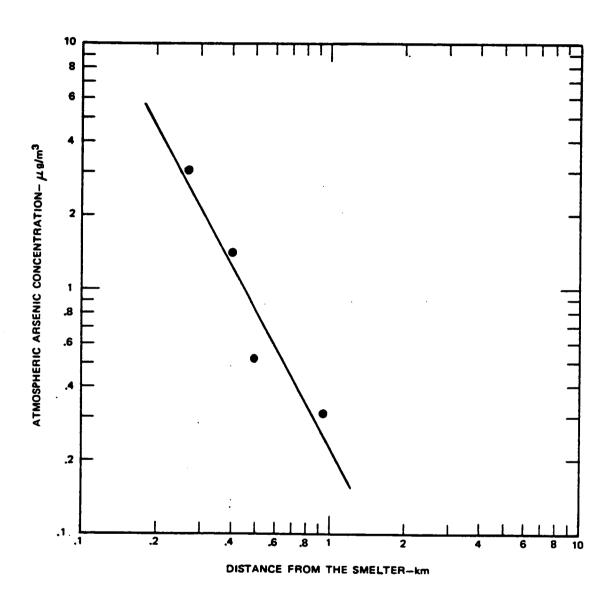


FIGURE VI-3. ATMOSPHERIC ARSENIC CONCENTRATIONS AS A FUNCTION OF DISTANCE FROM THE TACOMA SMELTER

Table VI-7

ATMOSPHERIC ARSENIC CONCENTRATIONS RECORDED FOR THE HELENA VALLEY ENVIRONMENTAL POLLUTION STUDY

| Sampling Site Location | Test | Sample Size | As Concentra | ation (µg/m³) |
|---------------------------|-------------------|----------------|--------------|---------------|
| Relative to Smelter | Method* | (days) | Average | Range |
| 1.29 km, 34° | GF | 76 | 0.006 | 0.000-0.070 |
| | MF | 28 | 0.007 | 0.000-0.020 |
| 4.02 km, 105 ⁰ | $\mathbf{GF}^{'}$ | 87 | 0.011 | 0.000-0.090 |
| • | MF | 25 | U.006 | 0.000-0.020 |
| 0.64 km, 112 ⁰ | GF | 85 | 0.060 | 0.000-0.260 |
| ••••, ==== | MF | 23 | 0.082 | 0.000-0.400 |
| 7.24 km, 274 ⁰ | GF | 82 | 0.005 | 0.000-0.070 |
| | MF | 8 | 0.009 | 0.000 - 0.010 |
| 0.80 km, 2° | GF | 34 | 0.084 | 0.000-0.260 |
| 0.00, | MF | | . | |

^{*}GF - glass fiber, MF - membrane filter.

Source: U.S. EPA (1972)

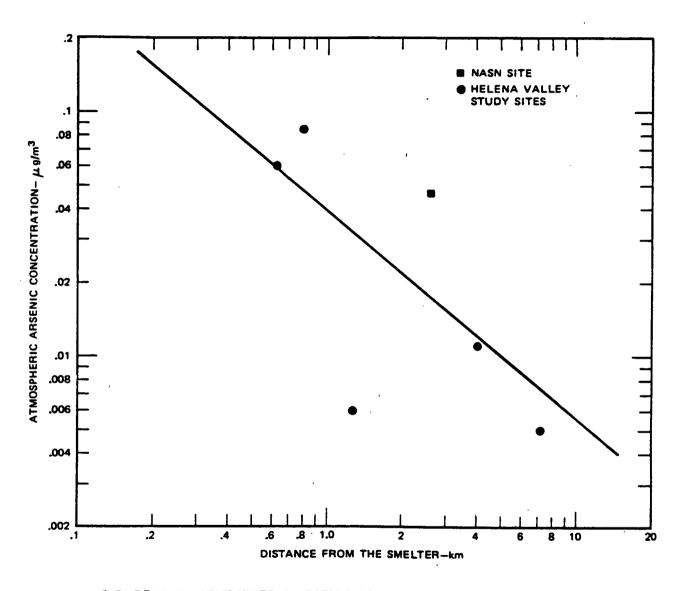


FIGURE VI-4. ATMOSPHERIC ARSENIC CONCENTRATIONS AS A FUNCTION OF DISTANCE FROM THE EAST HELENA SMELTER

assist in estimating atmospheric arsenic concentrations near nonferrous smelters. Both stack and low-level fugitive emissions must be considered. Table VI-8 shows results of the dispersion modeling for hypothetical conditions for four copper smelter stacks. Table VI-9 shows estimated atmospheric concentrations for three levels of fugitive emissions at copper smelters. Tables VI-10 and VI-11 show estimated atmospheric concentrations for stack and fugitive emissions for hypothetical lead and zinc smelters.

Table VI-8

ATMOSPHERIC DISPERSION MODELING FOR ARSENIC CONCENTRATIONS
IN THE VICINITY OF COPPER SMELTERS DUE TO STACK EMISSIONS ALONE^a

Annual Average Atmospheric Arsenic Concentration $(\mu g/m^3)^b$ Magma Acid Magma Main Ajo Main Tacoma Main Distance from $(E=222.9)^{c}$ $(E=385.7)^{C}$ $(E=1.63)^{c}$ $(E=102.9)^{c}$ Smelter (km) - Negligible -.0.30.092 0.008 0.190 0.210 0.8 0.007 0.180 0.220 0.205 1.3 0.005 0.160 0.150 0.200 2.0 0.004 0.130 0.130 0.120 3.0 0.003 0.100 0.110 0.086 5.0 0.002 0.071 0.096 8.0 0.073 0.001 0.053 0.071 12.0 0.058 0.001 0.055 0.043 0.047 16.0 0.001 0.045 0.040 0.039 20.0

Source: Based on Youngblood (1978)

^aStack characteristics correspond to the stacks at Ajo, Tacoma, and Magma; however, arsenic emissions were arbitrarily selected for dispersion modeling.

^bOmnidirectional average obtained by dividing 24-hr downwind concentration dispersion modeling results by 12.5.

CArsenic emission rate in 1b/hr.

Table VI-9

ATMOSPHERIC DISPERSION MODELING FOR ARSENIC CONCENTRATIONS DUE SOLELY
TO FUGITIVE EMISSIONS IN THE VICINITY OF COPPER SMELTERS

| | Annual Average | Atmospheric Arsenic Con | centrations a (µg/m³) |
|---------------|-----------------------|-------------------------|------------------------|
| Distance from | . Case 1 | Case 2 | Case 3 |
| Smelter (km) | (E=20.6) ^b | (E=89.2) b | (E=115.7) ^b |
| 0.3 | 5.200 | 22.500 | 29.200 |
| 0.8 | 2.100 | 8.800 | 12.000 |
| 1.3 | 1.040 | 4.500 | 6.000 |
| 2.0 | 0.570 | 2.400 | 3.200 |
| 3.0 | 0.320 | 1.400 | 1.800 |
| 5.0 | 0.160 | 0.680 | 0.880 |
| 8.0 | 0.080 | 0.340 | 0.430 |
| 12.0 | 0.044 | 0.190 | 0.240 |
| 16.0 | 0.030 | 0.120 | 0.160 |
| 20.0 | 0.021 | 0.088 | 0.110 |
| | | | |

^aOmnidirectional average obtained by dividing 24-hr downwind concentration dispersion modeling results by 12.5.

Source: Based on Youngblood (1978)

b Arsenic emission rate in lb/hr.

Table VI-10

ATMOSPHERIC DISPERSION MODELING FOR ARSENIC CONCENTRATIONS IN THE VICINITY OF A LEAD SMELTER^a

| • | Atmospheric Arsenic Concentration (µg/m ³) | | | |
|----------------------------|--|----------------------------------|--|--|
| | Stack (E=18.3) b | Fugitive (E=5.5) ^b | | |
| Distance from Smelter (km) | Annual Average ^C | Annual Average ^C | | |
| 0.3 | Negligible | 1.380 | | |
| 0.8 | 0.014 | 0.540 | | |
| 1.3 | 0.014 | 0.260 | | |
| 2.0 | 0.015 | 0.150 | | |
| 3.0 | 0.014 | 0.083 | | |
| 5.0 | 0.007 | 0.040 | | |
| 8.0 | 0.006 | 0.020 | | |
| 12.0 | 0.005 | 0.011 | | |
| 16.0 | 0.004 | 0.008 | | |
| 20.0 | 0.004 | 0.005 | | |

^aStack characteristics correspond to those of St. Joe in Herculaneum.

Source: Based on Youngblood (1978)

Table VI-11

ATMOSPHERIC DISPERSION MODELING FOR ARSENIC CONCENTRATIONS IN THE VICINITY OF A ZINC SMELTER^a

| | Atmospheric Arsenic Concentration $(\mu g/m^3)$ | | | |
|----------------------------|---|-----------------------------|--|--|
| | Stack (E=34.7) ^b | Fugitive (E=6.9) b | | |
| Distance from Smelter (km) | Annual Average ^C | Annual Average ^C | | |
| 0.3 | Negligible | 1.700 | | |
| 0.8 | 0.070 | 0.680 | | |
| 1.3 | 0.048 | 0.350 | | |
| 2.0 | 0.041 | 0.180 | | |
| 3.0 | 0.035 | 0.100 | | |
| 5.0 | 0.022 | 0.052 | | |
| 8.0 | 0.018 | 0.026 | | |
| 12.0 | 0.014 | 0.014 | | |
| 16.0 | 0.011 | 0.010 | | |
| 20.0 | 0.009 | 0.007 | | |

^aStack characteristics correspond to those of New Jersey Zinc.

Source: Based on Youngblood (1978)

 $^{^{\}mbox{\scriptsize b}}\mbox{\sc Assumed}$ arsenic emission rate in 1b/hr.

 $^{^{\}mbox{\scriptsize c}}\mbox{Omnidirectional}$ average obtained by dividing the 24-hr downwind concentration by 12.5.

Assumed arsenic emission rate in lb/hr.

^COmnidirectional average obtained by dividing the 24-hr downwind concentration by 12.5.

The difficulty in applying the atmospheric modeling results to specific smelters is in estimating their stack and fugitive emissions. Ore arsenic and nonferrous metal contents, smelting processes, and emission controls vary considerably for each smelter.

The arsenic content of copper concentrates varies widely for copper ores, depending on the area in which they are mined. For this study it is assumed that material processed by smelters in Arizona, New Mexico, Tennessee, and Nevada contains 0.015% arsenic, material smelted in Montana contains 0.96% arsenic, whereas material processed in Texas, Michigan, and Washington contains 0.80%, 0.4%, and 5.2% arsenic, respectively (Holt and Moberly, 1976 and OTS, 1976).

Generally, it is expected that smelters that process ore concentrates with high arsenic content will have high arsenic emission. However, because of emission controls and smelting processes this is not always the case. These differences are evaluated in more detail later in this chapter.

Missouri lead concentrates are assumed to contain 0.05% arsenic, and lead concentrates from other states are assumed to contain 0.1% arsenic. All zinc concentrates are assumed to contain 0.05% arsenic (Holt and Moberly, 1976; and OTS, 1976).

Davis and Associates (1971) list average atmospheric arsenic emission factors to be 4.9 lb/ton of copper, 0.8 lb/ton of lead, and 1.3 lb/ton of zinc. NAS (1977) states that in 1974 the average emission factor for copper smelters was 2.1 lb/ton. Using the Davis emission factors, OTS (1976) estimates that 15% of the arsenic in copper concentrates, 25% in lead concentrates, and 35% in zinc concentrates is emitted to the atmosphere during smelting.

OAQPS (1974) lists stack particulate emissions for all primary non-ferrous smelters. They do not, however, estimate the arsenic content on the particulates. Davis (1971) presents data from a copper smelter in Northern Chile showing the arsenic concentration on dust from the stack to be 10 times higher than in the ore concentrate; Davis (1971) also reports on another South American copper smelter in which the arsenic concentration on the flue dust was more than 9 times that of the ore concentrate. Weisenberg and Serne (1976A) present data showing the arsenic concentration of the particulates at Tacoma to be 10 times higher than that of the ore concentrate. For four other U.S. copper smelters, Weisenberg and Serne (1976B, C, D, E) show arsenic concentration on the particulates to be 5 to 25 times that of the ore concentrate.

Recently, the EPA made rough estimates of current and "best possible" arsenic emissions for copper smelter stacks (EPA, 1978). However, no estimates were made of fugitive emissions. These emission estimates were updated in September 1978 (Verveart, 1978). Preliminary sampling results by EPA of the El Paso smelter indicates that fugitive emissions may be on the order of 5% of arsenic input. This may, however, be an overestimate for the Tacoma smelter which processes arsenic trioxide. EPA

currently plans to test the Tacoma smelter for fugitive arsenic emissions (Verveart, 1978).

The copper smelter industry has recently estimated the arsenic emissions for the ASARCO-Tacoma, ASARCO-Hayden, and Phelps Dodge-Ajo copper smelters as 21, 6, and 24 lb/hr, respectively (Pendleton, 1978). These emissions estimates are about five times smaller than the EPA estimates used in this report.

In estimating atmospheric arsenic concentrations near nonferrous smelters it is difficult to determine the relationship between fugitive and stack emissions. Weisenberg and Serne (1976A) report 80 ton/yr stack and 90 ton/yr low level arsenic trioxide emissions for the Tacoma smelter in 1975. The Tacoma smelter is probably an unusual case because of the high arsenic content of the ore and because of the additional arsenic trioxide processing facilities. Cooper (1978B) suggests using a range of 10%-20% of stack emissions to represent fugitive emissions.

E. Human Exposures

Because of the many unresolved uncertainties in arsenic emissions for nonferrous smelters, population exposures are estimated by using several assumptions. These assumptions have been selected to be broad enough to attempt to span the actual exposures. In addition, the recorded ambient concentration data are used to help select the "best estimate" of exposures.

Populations residing near nonferrous smelters and subject to arsenic exposures are estimated by two methods, depending on population distribution near the smelter. For rural locations, the populations residing at various distances from the smelter were estimated by consulting maps and measuring distances between the smelter and towns. For urban locations, the populations residing at various distances from the smelter were estimated by using maps in which the population has been allocated to 1-km and 5-km grids. Resident populations were assumed to be uniformly distributed within each grid. The 1970 census population was used for urban and rural locations. Because of the uncertainties in the dispersion modeling, exposures were estimated only for populations residing within 20 km of each smelter.

1. Copper Smelters

Population exposures to arsenic emissions from copper smelters were made by using six cases:

Case A An arsenic emission of 4.9 lb/ton of copper, as reported by Davis (1971), for all smelters. Fugitive emissions were estimated to be 10% of stack emissions.

- Case B 15% of the arsenic in the copper concentrate is emitted to the atmosphere (OTS, 1976). The assumed arsenic concentrations of the ores, as previously reported for each smelter, were used. The ore concentrate feed rates reported by OAQPS (1974) were used. Fugitive emissions were estimated as 10% of stack emissions. The Tacoma smelter was treated differently by assuming 80 ton/yr stack emissions and 90 ton/yr low-level arsenic trioxide emissions.
- Case C An arsenic concentration of the particulates 10 times the concentration of the ore concentrate. The assumed arsenic concentrations of the ores, as previously reported for each smelter, were used. Particulate emission rates as reported by OAQPS (1974) were used. Fugitive emissions were estimated as 10% of stack emissions. The Tacoma smelter was treated in the same manner as in Case B.
- Case D Uses the recent EPA estimate of current stack emissions and assumes that fugitive emissions are 5% of arsenic input.
- Case E Uses the recent EPA estimate of current stack emissions and assumes that fugitive emissions are 5% of arsenic input for all smelters but Tacoma. The fugitive arsenic emissions for the Tacoma smelter are taken as 90 T/yr.
- Case F Uses the recent EPA estimates of current stack emissions and assumes that fugitive emissions are 10% of stack emissions.
- Case G Uses industry estimated emissions for the ASARCO-Tacoma, ASARCO-Hayden, and Phelps Dodge-Ajo smelters. EPA estimates of current stack emissions were used for all other smelters. Fugitive emissions are assumed to be 5% of arsenic input.

Each set of assumptions leads to the generation of a set of emission factors for the copper smelters. These emission factors are used to scale the dispersion estimates to make population and sure estimates. The estimated population exposures for copper smelters are given in Table VI-12.

2. Lead Smelters

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Three sets of assumptions were used in estimating population exposures to arsenic emissions from lead smelters:

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Case A The arsenic emission factor of 0.8 lb/ton as reported by Davis (1971) for all smelters. Fugutive emissions were estimated to be 10% of stack emissions.

Table VI-12

ESTIMATED HUMAN POPULATION EXPOSURES TO ATMOSPHERIC ARSENIC EMITTED BY COPPER SMELTERS

| | • | | | Assumed Ententions | | | |
|---|---|--|--|--|---|--|---|
| Annual Average Atmospheric Arsenic Concentration ^a (µg/m ³) | Case A 4.9 lb/ton 10% Fugitive ^b | Case B 15% Arsenic Emitted, 10% Fugitive ^c | Case C Particulate Concentration 10x, ' 19% Fugitive ^d | Case D EPA Current Stack Emissions, 5% of Input ^e | Case E EPA Current Stack Emissions, 5% and Tacoma ^f | Case F EPA Current Stack Emissions, 10% Fugitive ^B | Case G EPA and Industry 5% of Inputh |
| 6.0-9.9 | | | | 4,350 | | | |
| 3.0-5.9 | | | | 7,220 | | : | • |
| 1.0-2.9 | | 14,000 | | 111,200 | | | • |
| 0.60-0.99 | 3,500 | 4,000 | ` | 7,900 | 24,420 | •• | 12,260 |
| 0.30-0.59 | 5,900 | 144,000 | 11,600 | 293,180 | 19,380 | 18,960 | 19,380 |
| 0, 10-0, 29 | 38,000 | 255,000 | 33,800 | 26,250 | 137,450 | 21,370 | 137,450 |
| 0.060-0.099 | 50,000 | 166,000 | 95,000 | 119,860 | 119,860 | 90,980 | 119,410 |
| 0.030-0.059 | 317,000 | 300,000 | 281,000 | 5,550 | 286,560 | 286,560 | 282,400 |
| 0.010-0.029 | 536,000 | 28,000 | 135,000 | 313,380 | 313,380 | 46,186 | 318,000 |
| 0.005-0.009 | | | 239,000 | 8,810 | 8,810 | 129,950 | 8,810 |
| 0.003-0.004 | | | ** | 12,960 | 12,960 | 226,470 | 12,960 |

Annual omnidirectional average.

bassumes 4.9 lb of arsenic emitted to the atmosphere for each ton of copper produced. Fugitive emissions are assumed to be 10% of stack

CASSUMES 15% of arsenic in concentrates emitted to the atmosphere. Fugitive emissions assumed to be 10% of stack emissions.

dassumes the arsenic concentration of particulate emissions is 10 times the concentration of copper ore concentrate. Fugitive emissions are assumed to be 10% of stack emissions.

ellacs EPA estimate of current stack emissions. Fugitive emissions are assumed to be 5% of input arsenic.

 f_{Uses} EPA estimate of current stack emissions. Fugitive emissions are assumed to be 5% of input for all smelters but Tacoma for which a 90 T/yr estimate was used.

^gUses EPA estimate of current stack emissions. Fugitive emissions are assumed to be 10% of stack emissions.

liuses industry estimated stack emissions for the ASARCO-Tacoma, ASARCO-Hayden, and Phelips Dodge-Ajo smelters. EPA estimates of current stack emissions were used for all other smelters. Fugitive emissions are assumed to be 5% of input arsenic.

- Case B 25% of the arsenic in the lead concentrate emitted to the atmosphere (OTS, 1976). Lead concentrates from Missouri were assumed to contain 0.05% arsenic, and concentrates from other states were assumed to contain 0.1% arsenic. Fugitive emissions were estimated to be 10% of stack emissions.
- Case C An arsenic concentration of the particulates 10 times the arsenic concentration of the ore concentrate. The arsenic content of the ores are assumed to be the same as in Case B. The particulate emission rates reported by OAQPS (1974) were used. Fugitive emissions were estimated as 10% of stack emissions.

The exposure estimates are given in Table VI-13.

3. Zinc Smelters

Five sets of assumptions were used in estimating population exposures to arsenic for zinc smelters:

- Case A An arsenic emission of 1.3 lb/ton of zinc for each smelter (Davis, 1971). Fugitive emissions are estimated to be 10% of stack emissions.
- Case B Same as Case A, except only the pyrometallurgical smelters have arsenic in their stack emissions (OTS, 1976). Fugitive emissions are assumed to be 10% of the Davis emission factor (1.3 lb/ton) for stack emissions.
- Case C 36% of the arsenic in the zinc concentrates is emitted to the atmosphere (OTS, 1976). All zinc concentrates are assumed to contain 0.05% arsenic. Fugitive emissions are estimated to be 10% of stack emissions.
- Case D Same as Case C, except only the pyrometallurgical smelters have arsenic in their stack emissions (OTS, 1976). Fugitive emissions are assumed to be 10% of the stack emissions.
- Case E Arsenic concentrations of the particulates 10 times the arsenic concentration of the ore concentrate. Fugitive emissions are estimated to be 10% of stack emissions.

The exposure estimates are given in Table VI-14.

4. Comparison of Dispersion Modeling to Ambient Data

Some inferences can be drawn about which of the dispersion modeling cases to use by comparing the estimated concentrations for these cases with the ambient data recorded in Tables VI-4, -5, and -6. Table VI-15 compares measured and predicted atmospheric arsenic concentrations near copper smelters.

Table VI-13

ESTIMATED HUMAN POPULATION EXPOSURES TO ATMOSPHERIC ARSENIC EMITTED BY LEAD SMELTERS

| | | Assumed Emissions | | |
|---|---|---|---|--|
| Annual Average Atmospheric Arsenic Concentration ^a (µg/m ³) | Case A 0.8 lb/ton 10% Fugitive ^b | Case B 25% Arsenic Emitted, 10% Fugitive ^C | Case C Particulate Concentration 10x 10% Fugitive ^d | |
| 0.10-0.29 0.060-0.099 0.030-0.059 0.010-0.029 0.005-0.009 | 800 2,600 5,100 38,000 46,000 | 2,300 7,200 26,000 57,000 | 550 1,100 | |
| 0.003-0.004 | 67,000 | 70,000 | 800 | |

^aAnnual omnidirectional average.

bAssumes 0.8 lb of arsenic emitted to the atmosphere for each ton of lead produced. Fugitive emissions were assumed to be 10% of stack emissions.

^cAssumes 25% of arsenic in concentrates emitted in the atmosphere. Fugitive emissions were assumed to be 10% of stack emissions.

dAssumes arsenic concentration of particulate emissions is 10 times the concentration of the lead ore concentrates. Fugitive emissions were assumed to be 10% of stack emissions.

Table VI-14

ESTIMATED HUMAN POPULATION EXPOSURES TO ATMOSPHERIC ARSENIC

EMITTED BY ZINC SMELTERS

| | | Assumed Emissions | | | | | | |
|--|---------------------------------|---|---|--|--|--|--|--|
| Annual Average Atmospheric Arsenic Concentration ^a (µg/m ³) | Case A 1.3 lb/ton 10% Fugitiveb | Case B 1.3 lb/ton at Pyrometallurgical, 10% Fugitive ^c | Case C 36% Arsenic Emitted 10% Fugitive ^d | Case D 36% Arsenic Emitted by Pyrometallurgical, 10% Fugitive ^e | Case E Particulate Concentrate 10x, 10% Fugitive | | | |
| 0.10-0.29 0.060-0.099 | 52,000 | 9,000 | 3,000 | 3,000 | | | | |
| 0.030-0.059 | 22,000 155,000 | 18,000 101,000 | 6,000 | 6,000 | | | | |
| 0.010-0.029 | 1,182,000 | 170,000 | 47,000 189,000 | 119,000 | 2,700 | | | |
| 0.005-0.009 | 1,811,000 | 110,000 | 344,000 | 144,000 | 33,000 | | | |
| 0.003-0.004 | 800,000 | 13,500 | 1,176,000 | 137,000 | 10,000 | | | |

Annual omnidirectional average.

Assumes 1.3 lb of arsenic emitted to the atmosphere for each ton of zinc produced. Fugitive emissions were assumed to be 10% of stack emissions.

^CAssumes 1.3 lb of arsenic emitted to the atmosphere for each ton of zinc produced by pyrometallurgical smelters and no stack emissions at electrolytic smelters. Fugitive emissions were assumed to be 10% of stack emissions.

Assumes 36% of arsenic in concentrates emitted to the atmosphere. Fugitive emissions were assumed to be 10% of stack emissions.

^eAssumes 36% of arsenic in concentrates emitted to the atmosphere by pyrometallurgical smelters and no stack emissions at electrolytic smelters. Fugitive emissions were assumed to be 10% of stack emissions.

Assumes arsenic concentration of particulate emissions is 10 times the concentration of the zinc ore concentrates. Fugitive emissions assumed to be 10% of stack emissions.

Table VI-15 COMPARISON OF MEASURED AND PREDICTED ATMOSPHERIC ARSENIC CONCENTRATIONS NEAR COPPER SMELTERS a (µg/m 3)

| | Measured Arsenic | | Predict | ed Arseni | c Concent | ration | |
|------------------------------------|------------------|---|---------|-----------|-----------|--------|-----------|
| Place | Concentration | Case A | Case B | Case C | Case D | Case E | Case F |
| Anaconda, MT | 0.27 | 0.25 | 1.85 | 0.24 | 0.68 | 0.68 | 0.02 |
| Garfield, UT | 0.35 | 0.14 | 0.24 | 0.00 | 0.00 | 0.00 | 0.00 |
| Douglas, AZ | 0.02 | 10.80 | 4.57 | 0.97 | 0.11 | 0.11 | 0.09 |
| Miami, AZ | 0.05 | 0.12 | 0.02 | 0.00 | 0.01 | 0.01 | 0.00 |
| San Manuel, AZ | 0.02 | 0.24 | 0.09 | 0.00 | 0.04 | 0.04 | 0.01 |
| McGill, NV | 0.09 | 0.06 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 |
| Tacoma, WA (1 km) | 0.24 | 0.49 | 46.37 | 0.79 | 17.45 | 1.91 | 0.87 |
| El Paso, TX ^C (1 km) | 0.15 | 0.32 | 4.05 | 0.22 | 1.05 | 1.05 | 0.07 |
| El Paso, TX ^c (7 km) | 0.04 | 0.08 | 1.01 | 0.05 | 0.06 | 0.06 | 0.01 |
| · | | + · · · · · · · · · · · · · · · · · · · | | | | | 1 m in 11 |

^aAnnual average concentrations. Both measured and predicted concentrations are estimated at the same distance from the smelter.

^bSee Table VI-12 for a description of the various cases.

c In addition, arsenic from lead smelting is also emitted to the environment in El Paso.

These comparisons are not expected to be precise because the ambient data are usually recorded for one monitoring point for a relatively few days and because the predicted dispersion values are only rough approximations. Based on these comparisons it appears that Cases A, C, and E give predictions nearer the actual concentrations than do any of the other cases. Generally, a comparison of the measured and predicted values by both Cases A and C agree within a factor of 4. Case A used the Davis emission factor of 4.9 lb/ton, and for Case C the particulate arsenic concentrations are 10 times that of the ore concentrate.

Few ambient monitoring data are available for comparison with dispersion modeling estimates for lead and zinc smelters. Table VI-16 shows the comparisons for locations in East Helena and Kellogg. Based on these comparisons, it is difficult to distinguish between the case that uses the Davis emission factor and the case that uses a percent of the arsenic in the ore concentrates. It is fairly clear that the estimates are too low for the case that uses an arsenic concentration on the particulates of 10 times that of the ore concentrate.

Table VI-16

COMPARISON OF MEASURED AND PREDICTED ATMOSPHERIC ARSENIC CONCENTRATIONS NEAR LEAD AND ZINC SMELTERS (µg/m³)

| | Measured Arsenic | * Predicted Arsenic Concentration | | | | | |
|-------------------------------|------------------|-----------------------------------|--------|--------|--------|--------|--|
| Place | Concentration | Case A | Case B | Case C | Case D | Case E | |
| East Helena, MT (lead) | 0.03 | 0.12 | 0.01 | 0.01 | | | |
| Kellogg, ID (lead) | 0.30 | 0.33 | 0.09 | 0.00 | | | |
| <pre>Kellogg, ID (zinc)</pre> | 0.30 | 0.09 | 0.00 | 0.18 | 0.00 | 0.00 | |

^{*}See Tables VI-13 and VI-14 for a description of the cases.

F. Summary

When compared, concentrations predicted by dispersion modeling (based on selected assumptions) and of concentrations recorded by monitoring are shown to generally agree within a factor of approximately 4. When all the factors involved are considered, this is considered fairly close agreement.

Population exposures were not estimated for concentrations less than 0.10 $\mu g/m^3$ for copper smelter emissions for some of the cases because

this would have entailed extrapolating the dispersion modeling results beyond 20 km from the smelters. At distances beyond 20 km from the source, the dispersion estimates are considered to be unreliable.

With Case A assumptions (Davis emission factors), it is estimated that 950,000 people are exposed to emissions from copper smelters, resulting in annual average concentrations of 0.01 to 1.0 $\mu g/m^3$. The EPA estimate of current stack emissions resulted in an estimated 923,000 exposed to annual average concentrations of 0.003 to 1.0 $\mu g/m^3$.

It is estimated that 160,000 people are exposed to annual average concentrations of 0.003 to $0.3~\mu g/m^3$ due to lead smelter emissions. This estimate assumes that the arsenic emission factor is 0.8~lb/ton of concentrate and that fugitive emissions are 10% of stack emissions. An alternative estimate assumed that 25% of the arsenic in the ore concentrate is emitted to the atmosphere as stack emissions, with 10% additional fugitive emissions. This assumption resulted in an estimated 163,000 people exposed to annual average concentrations of 0.003 to $0.1~\mu g/m^3$.

. .

4 - 21 - 31 - 4

It is estimated that 442,000 people are exposed to annual average concentrations of 0.003 to 0.3 $\mu g/m^3$ of emissions from zinc smelters. This estimate assumes an arsenic emission factor of 1.3 $1h/\tan$ of concentrate for pyrometallurgical zinc smelter stacks and no emissions from electrolytic smelter stacks.

G. Secondary Nonferrous Smelters

1. General

Small quantities of arsenic are retained in copper, lead, and zinc after the refining process. In addition, arsenic is added to these metals in the manufacture of some products. When copper, lead, and zinc scrap metals are salvaged and reprocessed, arsenic may be released during the secondary smelting.

Table VI-17 contains estimates of the amount of arsenic retained in or added to copper, lead, and zinc. Arsenic is added to copper for the manufacture of admiralty brass and auto radiators, and it is added to lead for the manufacture of lead shot, bearing metals, and batteries and battery cables. A total of 755 kkg of arsenic is estimated to be retained in or added to these metals each year.

2. <u>Secondary Smelter Locations</u>

Total annual production figures for the secondary copper, lead, and zinc industry are given as 513,308, 698,698, and 182,665 tons per year (1974) by the American Metal Market (1977). Environmental Sciences and Engineering (1976) list locations of secondary smelters. However, no

Table VI-17

ESTIMATED ARSENIC RETAINED IN OR ADDED TO COPPER, LEAD, AND ZINC METALS

| Source | Arsenic (kkg/year) |
|-------------------------------------|-----------------------|
| Retained in primary copper | 43 |
| Added to copper for admiralty brass | 7 |
| Added to copper for auto radiators | 100 |
| Retained in primary lead | 20 |
| Added to lead for lead shot | 60 |
| Added to lead for bearing metals | 25 |
| Added to lead for batteries, cables | 495 |
| Retained in primary zinc | 5 |
| Total | 755 |
| | |

Source: OTS (1976)

figures on individual plant capacity or production are available. The Environmental Sciences and Engineering lists include 50 secondary copper smelters. 40 secondary lead smelters, and 6 secondary zinc smelters.

3. Secondary Smelter Emissions

Because arsenic is added during the manufacture of certain products from nonferrous metals, arsenic emissions during secondary smelting will depend, in part, on the material being refined. The arsenic content of copper, lead, and zinc products in which arsenic has not been added is estimated as 9, 33, and 10 ppm, respectively. These concentrations are on the order of 30 to 1,000 times lower than the arsenic concentrations in the original ore concentrates. Assuming that arsenic emission factors for secondary smelting are 100 times less than those for primary smelting, secondary smelting emissions would result in insignificant environmental atmospheric arsenic concentrations (average annual exposures of less than 0.003 $\mu g/m^3$).

^{*}This assumption probably leads to an overestimate of emissions because the temperatures used for refining processes will rarely release the arsenic.

Because of the value of copper scrap, almost all auto radiators are recycled. Auto radiator copper contains about 0.3% arsenic and is normally fire refined. Fire refining removes little if any arsenic from elemental copper because arsenic in elemental copper is very difficult either to oxidize or to volatize. Some of this secondary refined product is later electrolytically refined (to remove arsenic and other impurities), and some is used directly in products that require arsenic (OTS, 1975). Hence, atmospheric emissions of arsenic from secondary copper refining of auto radiators are estimated to be near zero.

Lead from bearing materials and batteries is extensively recycled. Lead tin bearings contain about 0.6% arsenic. The arsenic content of the battery alloys ranges from 0.15% for arsenical lead to 0.5% for antimonial lead. These concentrations are approximately the same as the arsenic content of the original lead concentrates. Bearing material is kettle refined and should produce insignificant atmospheric emissions because the melting points of lead (327°C) and babbitt materials (260-270°C) are low compared to the vaporization temperature of arsenic (613°C) (OTS, 1976). Antimonial lead is recovered in lead blast furnaces; thus, the atmospheric arsenic emission factors of secondary smelting of this type of lead may be similar to those for primary lead smelting. The American Bureau of Metal Statistics (1978) estimates that, in 1977, 324,000 metric tons of lead were recovered from old antimonial lead scrap and old cable covering scrap. About 3,000 metric tons were recovered of primary smelters and the remainder was recovered at secondary smelters.

4. Potential Human Exposures from Secondary Smelters

Humans are expected to be exposed to atmospheric arsenic from secondary smelting of lead from battery materials. Arsenic exposures from other nonferrous secondary metal smelting are estimated to be insignificant by comparison with normal urban background concentrations.

Production data for secondary smelters of battery lead are not available in the literature. It is therefore not possible to estimate accurately the number of people exposed to arsenic from this source. It is estimated that a smelter producing 6.5 kkg/year of lead from batteries could produce annual average atmospheric concentrations of 0.003 $\mu g/m^3$ at distances of 3.5 km from the smelter and concentrations of 0.020 $\mu g/m^3$ near the smelter boundry. Most secondary lead smelters are located in fairly densely populated areas (average population density of 1,100 people/km²). It is therefore likely that an average of several thousand people could be exposed to arsenic emissions from each such secondary smelter. These estimates are spectulative and require further data for verification.

A. General

Arsenical pesticides are used mainly as insecticides and herbicides. Other uses include fungicides, rodenticides, acaricides, and nematocides. Table VII-1 lists 25 of the main arsenical pesticides and their uses.

Bornstein (1975) estimates that 70% of the domestic arsenic consumption (25.5 million 1b) is used annually for pesticide manufacturing. It is estimated that well over 95% of this arsenic is used in the manufacture of six pesticides: lead arsenate, arsenic acid, copper arsenate, MSMA, DSMA, and cacodylic acid. The remaining 1.5 million 1b of arsenic is used by the industry for the manufacture of other pesticides. Table VII-2 gives an estimate of arsenic used by major arsenical pesticides. (Because of some differences in production years, the total arsenic given in Table VII-2 slightly exceeds the total estimated by Bornstein.)

B. Pesticide Manufacturers

Producers capable of manufacturing of arsenical pesticides include 20 companies at 27 plants. These plants are listed in Table VII-3, along with the arsenical pesticides that each produces. This list of producers differs slightly from a similar list prepared by the EPA Office of Toxic Substances that includes 32 manufacturing plants. However, most of the production is attributable to only a few firms included in both lists. Data on the production of these pesticides by manufacturer are difficult to obtain because such information is proprietary. Most of the arsenic acid is manufactured by the Pennwalt Corporation, which was expected to have a production capacity of 12.5 million 1b for 1977. MSMA is produced primarily by two firms: The Ansul Corporation, with an annual capacity of 25 million 1b; and Diamond Shamrock, with an annual capacity of 9 million lb. Two basic manufacturers produce cacodylic acid: The Ansul Corporation and Vineland Chemical (OPP, 1975A). In 1973, three companies produced DSMA: Ansul, W. A. Cleary, and Vineland (OPP, 1975B). City Chemical is the major producer of copper arsenate. L. A. Chemical and Woolfolk are the major producers of calcium arsenate, and lead arsenate is primarily produced by Woolfolk, L. A. Chemical, and Dimension Pigments.

C. Pesticide Plant Emissions

Bornstein (1975) estimated atmospheric emissions for arsenical pesticide manufacturing. These emissions are given in Table VII-4. They indicated that the total arsenic emissions from these activities range

Table VII-1

ARSENICAL COMPOUNDS AND THEIR USE

| Compound | Use |
|--|--|
| O - Arsanilic acid (sodium arsanilate) | Feed additive |
| I - Arsenic acid (arsenic pentoxide, arsenic oxide) | Cotton defoliant |
| I - Arsenic disulfide (tri and penta) | Textile printing, tanners paint pigment, medicinals |
| I - Arsenic iodide (arsenous iodide) | Antiseptic |
| I - Arsenic pentafluoride | Laboratory research |
| I - Arsenic thioarsenate | Scavenger |
| I - Arsenic tribromide (arsenous bromide) | Medicinals |
| <pre>I ~ Arsenic trichloride (arsenous chloride, arsenic butter)</pre> | Herbicide |
| I - Arsenic trifluoride (arsenous fluoride) | Laboratory research |
| I - Arsenic trioxide (arsenous oxide, arsenous acid) | Precursor in production of other arsenical compounds |
| I - Arsine (arsenous hydride) | Semiconductor industry |
| O - Cacodylic acid (dimethylarsinic acid) | Herbicide |
| I - Calcium arsenate | Insecticide |
| I - Calcium arsenite | Insecticide |
| I - Copper arsenate | Insecticide - wood preservative |
| I - Copper arsenite | Insecticide |
| O - Fluor chrome arsenate phenol | Wood preservative |
| I - Lead arsenate | Insecticide |
| O - Methanearsonic acid (mono- and disodium salts) (MSMA and DSMA) | Herbicide |
| 0 - Methinearsonic acid (calcium salt) | Herbicide |
| O - Methanearsonic acid (ammonium salts) | Herbicide |
| O - Par_s green (copper acetoarsenite) | Insecticide |
| I - Sodium arsenate | Wood preservative Herbicide |
| I - Sodium arsenite (arsenous acid, sodium salt) | Tree depar ing Herbicide |
| I - Zinc arsenate | Insecticide |

Notes: O - Organic I - Inorganic

Source: Bornstein (1975)

Table VII-2

ANNUAL USE OF ARSENIC IN MAJOR ARSENICAL PESTICIDES

| Product | 1974 Production (1b active ingredient) | Arsenic in Product (1b) |
|------------------------------|--|-------------------------|
| Arsenic trifluoride | <100 | • • |
| Arsine | <10,000 | <9,500 |
| Cacodylic acid | 1,500,000 ^a | 800,000 ^a |
| Calcium arsenate | <1,000 | <400 |
| Copper arsenate ^b | 11,700,000 ^a | 2,900,000 ^a |
| Lead arsenate | 3,000,000 | 500,000 |
| MSMA | 36,000,000 | 16,700,000 |
| DSMA | 9,000,000 | 3,600,000 |
| Arsenic acid | 6,000,000 ^c | 3,200,000 ^c |
| Arsenic pentafluoride | 10 | • |
| Total | | 27,700,000 |

^a1973 production.

Source: Modified from Bornstein (1975), OPP (1975A), and OPP (1975B)

between 4 and 151 ton/yr, depending on assumptions about the degree of controls used by the industry. Many of the large producers of pesticides have already installed control equipment so that emissions are in fact much lower than the 151 ton/yr. These data indicate emission factors of 0.63 lb/ton for controlled manufacturers and 24 lb/ton for uncontrolled manufacturers. W. E. Davis and Associates (1971) estimated atmospheric arsenic emissions at 20 lb/ton of arsenic processed for pesticide manufacturing.

The most common means of controlling emissions from the pesticide manufacturing industry are baghouses employing cotton sateen bags. In some applications, water scrubbers are used to control dust emissions. Inertial separators such as cyclones and mechanical centrifugal separators are not recommended because collection efficiencies are too low for smaller particles. In the manufacture of liquid pesticides, air pollution control problems usually entail collection of dust in a wet airstream. For these cases, wet scrubbers are employed (Bornstein, 1975).

bChromated copper arsenate.

^c1971 production. Current arsenic acid production is probably much larger.

Table VII-3

MANUFACTURERS OF ARSENICAL PESTICIDES

| Manufacturer | Compound |
|---|---|
| Abbott Labs North Chicago, IL | Arsanilic acid |
| Ansul Chemical Marinett, WI | Carodylic acid, MSMA, and DSMA |
| Arico Inc. Santa Clara, CA | Arsine |
| Blue Spruce Co. Bound Brook, NJ | Sodium arsenite |
| City Chemical Jersey City, NJ | Arsenic iodide, copper arsenate, copper arsenite, zinc arsenate |
| Diamond Shamrock Green Bayou, TX | MSMA and DSMA |
| Dimensional Pigments Bayonne, NJ | Lead Arsenate |
| Fleming Labs Inc. Charlotte, NC | Arsanilic acid, arsine |
| G. D. Searle Co. Cucamonga, CA East Rutherford, NJ Gloucester, MA Joliet, IL La Porte, TX Morrow, GA Newark, CA | Arsine Arsine Arsine Arsine Arsine Arsine Arsine Arsine |
| Los Angeles Chemical South Gate, CA | Arsenic acid, cacodylic acid, calcium arsenate, calcium arsenite, lead arsenate, paris green, sodium arsenite |
| Osmoro Wood Preserving Memphis, TN | Arsenic acid |
| Pennwalt Bryan, TX Tulsa, OK Tacoma, WA | Arsenic acid Arsenic pentafluoride, arsenic trifluoride Sodium arsenite |
| Rohm and Haas Myertown, PA | Arsanilic acid |
| Vineland Chemical Vineland, NJ | Cacodylic acid, MSMA and DSMA, MSMA calcium |
| W. A. Cleary Somerset, NJ | MSMA and DSMA |
| Woolfolk Fort Valley, GA | Arsenic acid, calcium arsenate, lead arsenate, sodium arsenite |

Source: SRI estimate

Table VII-4

ANNUAL ATMOSPHERIC ARSENIC EMISSIONS FOR PESTICIDE MANUFACTURERS

| Operation | Controlled Emissions (ton/yr) | Uncontrolled Emissions (ton/yr) |
|-------------------------------------|-------------------------------------|---------------------------------|
| Raw material handling and equipment | · 1 | . 7 |
| Reactor | <1 | 1 |
| Product purification equipment | 1 | 136 |
| Final product packaging equipment | 1 | 7 |
| Total | <4 | 151 |
| | | |

Source: Estimates based on Bornstein (1975)

A rough estimate was made of the amount of arsenic used in the manufacture of arsenical pesticides for the assumed nine largest producers (Table VII-5). Because no published data are available on the amount manufactured by producers, these estimates were based on information relating to which company produces the material, production capabilities, and other qualitative information relating to producer size. Although an effort was made to estimate capacities of actual manufacturers, these estimates must be regarded as hypothetical until better data are available. Atmospheric arsenic emissions were estimated by using controlled and uncontrolled emission factors of 0.63 and 24 lb/ton.

The total annual arsenical pesticide production assigned to the nine plants listed in Table VII-5 accounts for most of total annual production for all plants in the United States. As the analysis later indicates, environmental emissions for producers smaller than those listed in Table VII-5, are estimated not to add significantly to the ambient background arsenic concentrations. For these reasons the information listed in Table VII-5 should be sufficient for parametrically assessing whether emissions from arsenical pesticide producers constitute a health hazard. Evaluation of exposures for specific producers will require more detailed information.

D. Population Exposures

Because atmospheric arsenic concentration data were unavailable for the vicinity of the pesticide manufacturing plants, it was necessary to estimate atmospheric concentrations by using atmospheric dispersion modeling. Youngblood (1978) used dispersion modeling to estimate the atmospheric arsenic concentrations for two manufacturers with emissions of 2 x 10^{-5} lb/yr and 207 lb/yr of arsenic. The lower emission rate

Table VII-5

ESTIMATED ARSENIC USE AND ATMOSPHERIC EMISSIONS FOR MAJOR HYPOTHETICAL ARSENICAL PESTICIDE MANUFACTURERS*

| Manufacturer | Arsenic Processed (1b/yr) | | c Emissions lb/yr) Uncontrolled |
|----------------------------|---------------------------|-------|---------------------------------------|
| Plant A Byran, TX | 3,200,000 | 1,010 | 38,400 |
| Plant B Marinette, WI | 14,200,000 | 4,470 | 170,000 |
| Plant C Green Bayou, TX | 4,200,000 | 1,320 | 50,000 |
| Plant D Vineland, NJ | 1,400,000 | 440 | 16,800 |
| Plant E Somerset, NJ | 1,200,000 | 370 | 14,400 |
| Plant F Jersey City, NJ | 2,900,000 | 910 | 34,800 |
| Plant G Fort Valley, GA | 167,000 | 50 | 2,000 |
| Plant H South Gate, CA | 167,000 | 50 | 2,000 |
| Plant I Bayonne, NJ | 167,000 | 50 . | 2,000 |

^{*} These are crude estimates, subject to refinement as better data become available.

resulted in negligible atmospheric arsenic concentrations for all distances from the plant. The results for the plant with emissions of 207 lb/yr of arsenic are given in Table VII-6. The concentrations given in Table VII-6 were scaled proportionately to estimate concentrations for manufacturers having the emission rates listed in Table VII-5. This procedure indicates that pesticide manufacturers whose emissions are well controlled and whose production rates are less than those for the manufacturers listed in Table VII-5 would produce maximum annual average

Table VII-6

ESTIMATED ARSENIC CONCENTRATIONS FOR VARIOUS DISTANCES
FOR A MANUFACTURER HAVING EMISSIONS OF 207 LB/YR ARSENIC

| Distance from Plant (km) | 24-hr Maximum Downwind Concentration $(\mu g/m^3)$ | Annual Omidirectional Average (ng/m ³) |
|--------------------------|--|--|
| 0.20 | 0.0110 | 0.880 |
| 0.30 | 0.0110 | Α |
| 0.45 | 0.0130 | 1.040 |
| 0.60 | 0.0120 | 0.960 |
| 0.75 | 0.0100 | 0.800 |
| 1.00 | 0.0076 | 0.608 |
| 1.25 | 0.0058 | 0.464 |
| 1.60 | 0.0042 | 0.336 |
| 2.50 | 0.0023 | 0.184 |
| 4.00 | 0.0012 | 0.096 |
| 6.00 | 0.0007 | 0.056 |
| | _ | |

Source: Modified from Youngblood (1978)

environmental concentrations of less than 0.001 $\mu g/m^3$. Because these concentrations are below average urban background concentrations, the exclusion from this analysis of the smaller pesticide manufacturers is justified.

A series of 14 concentric geographic rings was drawn around each of the 9 major manufacturing plants listed in Table VII-5. The radii of the rings ranged from 0.4 to 20 km. It was assumed that no residential population occurred within 0.4 km of each plant. Residential population was estimated for each of the geographic rings by using the 1970 county population density. The average annual atmospheric arsenic concentration was estimated for the midpoint of each geographic ring through use of the dispersion modeling technique previously described. Two bounding cases were evaluated: (1) all plants with well controlled emissions and (2) all plants with uncontrolled emissions. Exposures were not estimated for concentrations less than 0.003 $\mu \rm g/m^3$. The atmospheric concentrations

and estimated exposed populations are given in Table VII-7 for the controlled and uncontrolled cases.

Table VII-7

ESTIMATED POPULATION EXPOSED TO ATMOSPHERIC ARSENIC EMITTED FROM PESTICIDE MANUFACTURING

Number of People Exposed

| Assessed Amounto | | | |
|---|------------------------------------|------------------------------------|--|
| Average Arsenic Concentration* (µg/m ³) | Assuming Emissions Well Controlled | Assuming Emissions Uncontrolled | |
| 0.600-0.999 | | 20 | |
| 0.300-0.599 | | 35 | |
| 0.100-0.299 | | 20,800 | |
| 0.060-0.099 | | 13,800 | |
| 0.030-0.059 | | 119,000 | |
| 0.010-0.029 | 60 | 296,000 | |
| 0.005-0.009 | 800 | 413,000 | |
| 0.003-0.004 | 11,900 | 74,000 | |
| | | | |

^{*}Annual omnidirectional average.

Assuming that the emissions from all major arsenical pesticide manufacturing plants are well controlled results in an estimated 12,760 people exposed to average arsenic concentrations that range from 0.003 to 0.020 $\mu g/m^3$. Assuming that the emissions from all major arsenical pesticide manufacturing plants are uncontrolled results in an estimated 936,000 people exposed to average arsenic concentrations from 0.003 to 0.80 $\mu g/m^3$. Actual exposures should fall somewhere between the uncontrolled and well controlled bounds. Bornstein (1975) has indicated that many of the large pesticide manufacturers have already installed control equipment. The estimated population exposures given here are for the larger manufacturers; hence, the actual exposures are probably close to the estimates for well controlled plants.

E. Summary

It is estimated that approximately 13,000 people are exposed to arsenic concentrations that range from 0.003 to 0.020 $\mu g/m^3$. Because

the general urban population exposures average about $0.003~\mu g/m^3$, it appears that emissions from arsenical pestified manufacturers do not present a significant increased environmental health risk. A possible exception would occur if one of the larger manufacturers (processing more than 200,000 lb/yr arsenic) has poor emission controls.

VIII ARSENIC EXPOSURES FROM COTTON GINS

A. General

Arsenic acid is used as a desiccant to aid in cotton harvesting. During ginning, arsenic from the cotton is released to the atmosphere and thus constitutes potential occupational and environmental exposures.

Cotton production in Texas and Oklahoma is of two basic types, distinguished by the cotton planted and the manner of harvesting. In the irrigated regions of Texas and Oklahoma, farmers successfully grow high quality cotton that can be harvested with a spindle picker. Chemical defoliants, such as chlorate and phosphorus materials, are frequently used to remove the top leaves in preparation for spindle harvesting (USEPA, 1976).

In the dryland areas of these two states, the High Plains, Rolling Plains, and Black Frairie areas, the spindle-picked cotton varieties cannot be grown because of lack of moisture. Production in the dryland areas depends on harvesting only once a year with a stripper harvesting machine. Stripper harvesting consists of taking up the cotton boll and burr and frequently the leaves and stems, in a rake-like action. This harvesting requires that the moisture of the cotton be very low, lest the cotton be stained thereby bringing a lower price. To ensure low moisture content, the cotton plants are dried out before stripping (USEPA, 1976).

The cotton matures late in the season in much of the dryland area of Oklahoma and the High Plains and Rolling Plains of Texas. In these areas the growers can frequently wait for the first frosts to dry the cotton plants before harvest. Because cotton degrades in quality if harvest is delayed after it reaches maturity, late frosts necessitate the use of a chemical desiccant. Furthermore, in areas south of Dallas where the cotton matures in late August or September, a chemical desiccant must be used practically every year. In regard to both cost and effectiveness, arsenic acid is the preferred chemical desiccant (USEPA, 1976). During 1973, approximately 85% of the Texas cotton was machine stripped and 15% was spindle picked (USEPA, 1976).

Part of the desiccant adheres to the parts of the cotton plant that are taken during harvesting. Because this desiccant can then be released to the atmosphere during ginning, it presents a potential health hazard to cotton gin employees and to the surrounding residential population.

B. Cotton Gins

Table VIII-1 estimates the cotton gins active in the United States during 1972 and their employees; 3517 gins were active, with an estimated 35,000 workers. Of these gins, 1040 are in Texas and 118 in Oklahoma.

Cotton ginning is not a year-around operation. Bureau of the Census Bulletin 202 (1965) states that ginning of each crop begins in mid-July, continues through the autumn and winter, and is substantially completed by the following February. In most locations the ginning season lasts 2-4 months. Many of the gins are operated 24 hours a day during ginning season.

C. Cotton Gin Emissions

Durrenberger (1974 and 1975) monitored particulates around 16 Texas cotton gins that processed machine-stripped cotton. The purposes of his study were twofold: (1) to determine emission levels of suspended particulates, arsenic, and cellulose and (2) to develop a method of predicting cotton gin emissions as a function of control equipment. Three classes of control equipment were defined: uncontrolled, controlled, and well controlled.

Atmospheric particulates were monitored around each gin. Durrenberger found that, if particulate concentrations were expressed as the ratio of atmospheric concentration to the amount of trash processed per hour, gins processing similar cotton and with similar controls could be grouped to give average atmospheric particulate concentration as a function of distance from the gin. These functions were derived for distances as far as 300 m from the gin. To obtain atmospheric arsenic concentrations it is necessary to multiply the particulate concentrations by their arsenic content. Durrenberger (1974) found that the arsenic content of trash from arsenic desiccated cotton was 0.2%. This is in agreement with the concentrations found by Aboul-Ela and Miller (1965). Hence, the atmospheric arsenic concentrations can be estimated by multiplying the particulate concentrations by 0.002.

Because the validity of Durrenberger's methods does not extend beyond 300 m from the gins, a method to estimate concentrations for greater distances is required. Youngblood (1978) mathematically modeled the expected concentrations for distances of 300 m to 20 km from two types of gins: well controlled and poorly controlled. The poorly controlled gins were assumed to have particulate emissions of 490 lb/hr for a 10 bale/hr gin; the well-controlled gins were assumed to have particulate emissions of 26 lb/hr for a 10 bale/hr gin as noted by Herring (1973). These modeling data were for 24-hr downwind concentrations, which were converted to annual downwind concentrations by dividing by 5.0; the annual downwind were converted to average omnidirectional concentrations by further dividing by 2.5. Youngblood's estimates were

Table VIII-1

COTTON GINS IN THE UNITED STATES, 1972

| Location | Number of Cotton Gins | Estimated Workers* |
|----------------|-----------------------|--------------------|
| Alabama | 226 | 1,582 |
| Arizona | . 115 | 1,725 |
| Arkansas | 397 | 4,367 |
| California | 234 | 3,510 |
| Florida | 4 | 28 |
| Georgia | 153 | 1,071 |
| Illinois | | |
| Kentucky | 1 | 11 |
| Louisiana | 148 | 1,628 |
| Mississippi | 458 | 4,122 |
| Missouri | 114 | 1,254 |
| Nevada | 1 | 15 |
| New Mexico | 53 . | 742 |
| North Carolina | 91 | 637 |
| Oklahoma | 118 | 826 |
| South Carolina | 165 | 1,155 |
| Tennessee | 196 | 1,372 |
| Texas | 1040 | 11,440 |
| Virginia | 3 | 21 |
| United States | 3517 | 35,480 |

^{*} Estimates based on number of workers by state given in Wellford (1963).

Source: Active gins from Bureau of the Census (1972)

further modified by assuming that the arsenic concentration of the particulates is 2000 ppm, rather than the 300 ppm he used. The results of the modified modeling procedure and the results of Durrenberger's method, which is based on ambient data, are compared on Table VIII-2. The results for the two methods are almost identical for uncontrolled gins and within a factor of 3 for controlled gins.

Table VIII-2

COMPARISON OF ATMOSPHERIC ARSENIC CONCENTRATIONS NEAR COTTON GINS BASED ON MODELED AND MEASURED METHODS* (µg/m³)

| Environmental | Concentration Estimation | | roduction |
|-----------------|-----------------------------|------------|-------------|
| <u>Controls</u> | <u>Method</u> | 5 bale/day | 20 bale/day |
| Uncontrolled | Measured | 0.250 | 1.000 |
| | Modeled | 0.256 | 1.024 |
| Well-controlled | Measured | 0.037 | 0.148 |
| | Modeled | 0.014 | 0.054 |

Modeled results are based on Youngblood (1978), and measured results are based on Durrenberger (1974); both are for concentrations 300 m from the gins.

Production data for cotton gins were analyzed to determine the frequency distribution of gins as a function of bales of cotton produced per hour. This analysis is summarized in Table VIII-3 and indicates that four representative production rates should be used: 5, 7, 14, and 20 bale/hr. In addition, the frequency distribution of types of emission controls at gins was evaluated (Table VIII-4). Based on this evaluation, it was assumed that 50% of the gins are well controlled, 20% are uncontrolled, and that 30% have some type of controls. For these estimates we have used the definition of "controlled" and "well-controlled" given by Durrenberger (1974): Controlled means controlled with cyclones and bur hoppers. Well controlled means having controls in addition to cyclones and bur hoppers.

To determine the number of gins processing desiccated cotton at the various production rates and with different controls, it was assumed:

- That there are 1040 gins in Texas and 118 gins in Oklahoma.
- That 85% of the gins in Texas and Oklahoma process desiccated cotton.
- The type of control at a gin is independent of the production rate.

The estimated number of gins in each production rate-control class is shown in Table VIII-5.

Table VIII-3

ASSUMED DISTRIBUTION OF PRODUCTION RATES FOR COTTON GINS*

| •• | • | , . |
|---------------|---------------|------------|
| Production Ra | te (bales/hr) | Percent of |
| Average | Range | Gins |
| 5 | 4-7 | 50 |
| 7 | 8-11 | 30 |
| 14 | 12-15 | 10 |
| 20 | >15 | 10 |
| | | • |

^{*}Based on an analysis of data for 17 cotton gins.

Table VIII-4

DISTRIBUTION OF EMISSION CONTROLS
FOR COTTON GINS*

| Control | Percent of Gins |
|-------------------------|--------------------|
| High-efficiency cyclone | 50 |
| Inline filter | 4 |
| Other controls | 28 |
| No controls | 18 |

^{*}Based on a 1972 EPA survey.

Table VIII-5

ESTIMATED NUMBER OF GINS PROCESSING MACHINE STRIPPED COTTON IN TEXAS AND OKLAHOMA

| Production | Emission Controls | | | | |
|------------|-------------------|------------|-----------------|--|--|
| (bales/hr) | Uncontrolled | Controlled | Well Controlled | | |
| 5 | 98 | 148 | 246 | | |
| 7 | 55 | 89 | 148 | | |
| 14 | 20 | 30 | 50 | | |
| 20 | 20 | 30 | 50 | | |

Atmospheric arsenic concentrations as a function of distance from the gin were calculated for well controlled, controlled, and uncontrolled gins and for production rates of 5, 7, 14, and 20 bales of cotton per day for each class of control. These are given in Table VIII-6. The methods given by Durrenberger were used to estimate the concentrations for distances as far as 300 m and Youngblood's methods modified as previously described, were used for distances greater than 300 m. These concentrations were not extended to distances beyond which the concentration would be less than 0.003 $\mu g/m^3$.

Data on particle sizes of particulate emissions--composed of plant foliage, lint, motes, and dirt--from cotton gins are not well documented. Particulate size analysis of gin trash data extracted from the USDA by Herring (1973) indicate that 99% of the particulates was 25 μm or larger; and EPA tests indicate that particulates in controlled emissions are preponderantly composed of particle sizes greater than 3 μm . It is expected that the larger particles settle out near the cotton gin. A 1965 study by the Texas State Department of Health shows that at a distance of 200 ft downwind from the gin, 50% of the particles are larger than 5 μm ; whereas, at 1000 ft, this fraction drops to 20%.

D. Population Exposures

This study did not attempt to locate and count the resident population within the vicinity of all gins processing arsenic desiccated cotton as these data are not readily available. It is known that most of the gins are located in rural areas. Maps given by Durrenberger (1974), the Texas Department of Health (1965), and others indicate that residential housing exists within 300 m of some of the gins. In this exposure study, it is assumed that residential populations are uniformly distributed around the gins with a density of 40 people per square mile. This density is consistent with the average statewide population densities of Texas and Oklahoma. It is further assumed that there are no residences within 50 m of any of the gins.

The resident population was estimated for 19 concentric rings about each gin, for radii up to 20 km. These populations were multiplied by the number of gins in each of the nine production rate-emission control groups given in Table VIII-5. It is assumed that none of the gins are colocated. Arsenic concentrations from Table VIII-6 were assigned to the estimated exposed populations. These were then used to derive the exposure estimates shown in Tables VIII-7 and VIII-8. Table VIII-7 gives average population exposures during the ginning season. Table VIII-8 gives annual average population estimates, based on the assumption that the ginning season lasts approximately 8 weeks per year.

Table VIII-6

ESTIMATED ATMOSPHERIC ARSENIC CONCENTRATIONS* (μg/m³)

FOR VARIOUS DISTANCES FROM GINS

PROCESSING ARSENIC DESICCATED COTTON

| | Distance from Gin (meters) | | controll Emission | | | | Contr Emiss | olled ions | | W | ell Con Emiss | | |
|----|-------------------------------|----------------|----------------------|-----------------|-----------------|----------------|----------------|-----------------|-----------------|------------|------------------|-----------------|-----------------|
| | | 5 [†] | 7 [†] | 14 [†] | 20 [†] | 5 [†] | 7 [†] | 14 [†] | 20 [†] | <u>5</u> † | 7 [†] | 14 [†] | 20 [†] |
| | 50 | 7.249 | 10.148 | 20.297 | 28.995 | 4.789 | 6.704 | 13.409 | 19.155 | 1.804 | 2.526 | 5.051 | 7.216 |
| | 75 | 5.498 | 7.697 | 15.395 | 21.992 | 3.600 | 5.040 | 10.079 | 14.399 | 1.312 | 1.837 | 3.674 | 5.248 |
| | 100 | 4.211 | 5.895 | 11.790 | 16.843 | 2.550 | 3.570 | 7.141 | 10.201 | 0.861 | 1.205 | 2.411 | 3.444 |
| | 150 | 1.898 | 2.658 | 5.315 | 7.593 | 1.349 | 1.888 | 3.777 | 5.396 | 0.312 | 0.436 | 0.872 | 1.246 |
| | 200 | 0.951 | 1.332 | 2.663 | 3.805 | 0.763 | 1.068 | 2.135 | 3.050 | 0.152 | 0.212 | 0.425 | 0.607 |
| | 250 | 0.500 | 0.700 | 1.401 | 2.001 | 0.349 | 0.488 | 0.976 | 1.394 | 0.062 | 0.086 | 0.172 | 0.246 |
| 85 | 300 | 0.250 | 0.350 | 0.700 | 1.000 | 0.201 | 0.281 | 0.563 | 0.804 | 0.037 | 0.052 | 0.103 | 0.148 |
| ٥. | 450 | 0.147 | 0.205 | 0.411 | 0.587 | 0.076 | 0.107 | 0.213 | 0.304 | 0.008 | 0.011 | 0.021 | 0.031 |
| | 600 | 0.096 | 0.134 | 0.269 | 0.384 | 0.050 | 0.069 | 0.139 | 0.198 | 0.005 | 0.007 | 0.014 | 0.020 |
| | 750 | 0.067 | 0.093 | 0.187 | 0.267 | 0.033 | 0.046 | 0.093 | 0.132 | 0.003 | 0.005 | 0.009 | 0.013 |
| | 1000 | 0.043 | 0.060 | 0.119 | 0.171 | 0.023 | 0.032 | 0.065 | 0.093 | · - | 0.003 | 0.007 | 0.009 |
| | 1250 | 0.032 | 0.045 | 0.090 | 0.128 | 0.017 | 0.023 | 0.046 | 0.066 | - | - | 0.005 | 0.007 |
| | 1600 | 0.021 | 0.029 | 0.058 | 0.083 | 0.010 | 0.014 | 0.028 | 0.040 | - | - | 0.003 | 0.004 |
| | 2500 | 0.010 | 0.015 | 0.029 | 0.042 | 0.007 | 0.009 | 0.019 | 0.026 | - | - | - | 0.003 |
| | 4000 | 0.005 | 0.007 | 0.014 | 0.020 | 0.003 | 0.004 | 0.007 | 0.011 | - | | _ | 0.001 |
| | 6000 | 0.003 | 0.004 | 0.008 | 0.012 | - | - | 0.005 | 0.007 | - | _ | - | - |
| | 9000 | - | | 0.004 | 0.006 | - | - | - | 0.003 | - | ~ | - | · <u>-</u> |
| | 14000 | ~ | | - | 0.003 | - | - | - | - | _ | . - | - | - |
| | 20000 | - | | | - | - | _ | - | _ | _ | · - | | · – |

^{*}Based on annual average meterological conditions.

[†]Bales per hour production.

Indicates a concentration less than 0.003 $\mu g/m^3$.

Table VIII-7

ESTIMATED HUMAN POPULATION EXPOSURES TO ARSENIC EMITTED FROM COTTON GINS DURING GINNING SEASON

| Assumed Concentration* (µg/m ³) | 50% well controlled, 30% controlled, 20% uncontrolled | 100% well Controlled | 100% Uncontrolled |
|---|---|-------------------------|----------------------|
| 20-24 | 5 | | 10 |
| 15-19 | 15 | | 20 |
| 10-14 | . 40 | | 30 |
| 6-9 | 60 | 10 | 70 |
| 3-5 | 310 | 80 | 540 |
| 1-2 | 1,050 | 430 | 2,160 |
| 0.6-0.9 | 620 | 300 | 860 |
| 0.3-0.6 | 1,700 | 670 | 3,800 |
| 0.1-0.2 | 8,800 | 2,040 | 25,000 |
| 0.06-0.09 | 11,500 | 990 | 32,000 |
| 0.03-0.05 | 30,000 | 4,500 | 82,000 |
| 0.01-0.02 | 208,000 | 5,100 | 645,000 |
| 0.005-0.009 | 410,000 | 27,000 | 1,057,000 |
| 0.003-0.004 | 747,000 | 66,500 | 2,290,000 |

^{*}These are average exposures during the ginning season. Annual averages would be approximately 10% to 25% of these values and are estimated in Table VIII-8.

Table VIII-8

ESTIMATED ANNUAL AVERAGE * HUMAN POPULATION EXPOSURES TO ARSENIC FROM COTTON GINS

| Annual Average Concentration* (µg/m ³) | No. of People Exposed [†] |
|--|--|
| 3.0-5.9 | 5 |
| 1.0-2.9 | 100 |
| 0.60-0.99 | 200 |
| 0.30-0.69 | 700 |
| 0.10-0.29 | 2,000 |
| 0.06-0.99 | 3,000 |
| 0.030-0.059 | 5,900 |
| 0.010-0.029 | 20,000 |
| 0.005-0.009 | 56,000 |
| 0.003-0.004 | 135,000 |

These annual average concentrations are based on the assumption that the ginning season occurs during 15% of the year.

E. Summary

It is estimated that approximately 1.4 million people are exposed to atmospheric arsenic concentrations of 0.003 to 29 $\mu g/m^3$ during the ginning season. Annual average population exposures are much smaller because the ginning season occurs for a few weeks out of a year. Based on annual average exposures, it is estimated that approximately 223,000 people are exposed to atmospheric arsenic concentrations of 0.003 to 6 $\mu g/m^3$. These exposure estimates assume that all Texas and Oklahoma machine-stripped cotton is desiccated with arsenic acid. During some years, however, it is not necessary to desiccate all machine-stripped cotton. For those years, the number of exposed people on Tables VIII-7 and -8 should be reduced proportionately.

Exposures are based on the assumption that 50% of the gins are well controlled, 30% are moderately controlled, and 20% are uncontrolled.

IX ARSENIC EXPOSURES FROM GLASS MANUFACTURERS

A. General

Arsenic is added to the glass batch during manufacturing for three purposes: (1) to assist in freeing the glass from small bubbles or "seeds," (2) to diminish the perceived color of the glass by oxidizing Fe (II) (green) to Fe (III) (light orange brown), and (3) to stabilize the selenium added to the glass batch for color balancing (Maasland, 1975).

The use of arsenic in the manufacture of glass has been decreasing in recent years, particularly because of the increased use of cerium oxide as a decolorizing agent. Cerium oxide cannot be used if arsenic trioxide is present in quantities greater than 8 oz/ton of sand because solarization will very rapidly occur (Shult et al., 1970).

The ingredients used in glass manufacturing are batch weighed and mixed before they are charged into the furnace. In the furnace, the mixture of materials is held in a molten state at about 2800°F until it acquires the homogeneous character of glass. It is then gradually cooled in other sections of the furnace to about 2200°F to make it viscous enough to form. In a matter of seconds, while at a yellow hot temperature, the glass is drawn from the furnace and worked on forming machines by a variety of methods, including pressing, blowing in molds, drawing, rolling, and casting (Research Triangle Institute, 1972).

Most U.S. furnaces use the regenerative system for heat recovery. Regenerative firing systems consist of dual chambers filled with brick checkerwork. While the products of combustion from the melter pass through and heat one chamber, combustion air is preheated in the opposite chamber. The functions of each chamber are interchanged by reversing the flow of air and combustion products. Reversals occur every 15 to 20 minutes as required for maximum conservation of heat (Research Triangle Institute, 1972). The use of regenerative furnaces for the production of glass is slowly declining because of the increased use of recuperative and electric furnaces.

Apparently all of the arsenic mixed in the batch does not remain in the finished glass. Ideally, the arsenic dissolves in the melt and is the last volatile compound to distill out. The arsenic vapor condenses to a submicron fume as it cools. Some vapor may condense on the brick checkerwork in the chamber, and some fumes may be caught by impingement. If a baghouse is in use, still more may be caught (Maasland, 1975). Owens Corning data suggests that 70% to 99% of the arsenic remains in the glass (Mosely, 1978).

B. Glass Manufacturers

The glass industry is divided into three four-digit SIC categories:

SIC 3211 Flat Glass

SIC 3221 Glass Containers

SIC 3229 Pressed and Blown Glass.

Flat glass manufacturers produce sheet (window) glass, plate glass, laminated glass, and other flat glass. Flat glass production is approximately 3.2 million ton/yr of finished products. Total production is approximately 4.4 million tons, the difference being that off-quality glass is recycled. During 1975, arsenic was estimated to be used in less than 10% of the flat glass made (Reznik, 1975). The use of arsenic in the manufacture of flat glass has continued to decline. As a consequence, arsenic exposures from flat glass manufacturing have been excluded from this study.

Glass container manufacturers produce glass containers for commercial packing and pottling, and for home canning. Glass container production is approximately 13 million tons annually, with an additional 10% to 20% recycled. Reznick (1975) estimated that in 1975 less than 15% of this industry used arsenic. As with flat glass manufacturing, the use of arsenic for container manufacturing has continued to decline. As a consequence, arsenic exposures from container glass manufacturing have been excluded from this study.

Pressed and blown glass manufacturers produce glasses and glassware by pressing and blowing or shaping glass produced in the same establishment. Textile glass manufacturing is included in this industry, but glass wool insulation is not. Production of pressed vehicular lighting, beacons, and lanterns is also included. Other manufactured items include table, kitchen, art, and novelty glassware; tumblers; stemware; lighting and electronic envelopes and blankets; and electric light bulb blanks. Reznik (1975) estimated production at 4.5 million tons annually. Excluding textile fibers, Schorr et al. (1977) estimated finished products at 1.6 million tons for 1974. Total production is approximately 3.3 million tons, with about 52% of production used as recycled cullet or ending as waste. An additional 0.3 million tons of glass are produced in this industry for textile fibers. Excluding textile fibers, production of glass by type for the industry is 77% soda/lime, 11% borosilicate, 5% lead silicate, and 7% opal (Schorr et al., 1977). Reznik (1975) states that arsenic is still used in the specialty glasses, but probably less than 10% is used in the soda/lime glasses. On the basis of recent responses to Section 114 letters, Cuffe (1978) estimates that arsenic is mainly used in lead and opal glass and that a very small amount is used in a few types of borosilicate glass and none is used in soda/lime glass. Using Cuffe's estimates and assuming that 25% of borosilicate production uses arsenic suggests that about 15% of pressed and blown glass uses Therefore, approximately 0.7 million tons of pressed and blown glass containing arsenic are produced annually.

Research Triangle Institute (1972) listed glass manufacturers by SIC and state. They attempted to include complete mailing addresses, sales, and a percentage share of the industry, but not all of the information was available for every plant. They list 219 plants for SIC 3219. Schorr et al. (1977) provide a more recent listing of manufacturing plant addresses for SIC 3219 excluding the glass textile manufacturers. Their list of 176 plants includes names and locations; however, no information is given about manufacturing volume. Annual glass production rates for the 176 plants listed by Schorr et al. (1977) were estimated by using a combination of (1) the information presented by Research Triangle Institute (1972), (2) production sales, employment, and location data given by Standard and Poor's Register (1977) and Dun & Bradstreet (1977), and (3) the statistical distribution of number of firms vs. value of shipments as reported by the Bureau of the Census (1975). The estimated distribution of plants by production volume is given in Table IX-1.

Table IX-1
ESTIMATED PRODUCTION OF PRESSED AND BLOWN GLASS BY NUMBER OF PLANTS*

| Number of | Plant Produc | tion (Annual) [†] |
|-----------|--------------------|----------------------------|
| Plants | 10 ³ kg | Tons |
| 71 | 145 | 160 |
| 17 | 500 | 550 |
| 11 | 890 | 990 |
| 9 | 2,080 | 2,290 |
| 11 | 4,950 | 5,450 |
| 22 | 11,280 | 12,430 |
| 12 | 37,760 | 41,620 |
| 16 | 76,230 | 84,030 |
| 7 | 139,000 | 153,000 |
| | • | |

Excludes textile fiber manufacturers.

No data were located to indicate which of the plants still use arsenic in their manufacturing process because such data could only be obtained through a survey of the manufacturing plants, an activity beyond the scope of this study. Potential population exposures to arsenic from glass manufacturing will be explored through a series of parametric analyses in which assumptions concerning arsenic use are varied.

This is the total annual production, of which approximately 48% is converted to finished products.

C. Glass Manufacturing Emissions

Potential significant sources of atmospheric emissions are the raw materials handling operations, the glass furnace, and the forming operations. Of these, the glass furnace is usually the major source (RTI, 1972). The rate of emissions from the glass melting furnace usually varies considerably, depending on the composition of the glass produced, the design and operating characteristics of the furnace, and the emission controls installed. The arsenic volatizes during glass melting and is thought to condense on the particulates and thus be released to the atmosphere on the particulates. As with coal emissions, the arsenic concentration on smaller particulates probably exceeds that on larger particulates. RTI (1972) states that the particulate emission rates for container glass furnaces is usually between 0.8 and 3.0 g/kg (1.5 and 6.0 lb/ton). Table IX-2 shows particulate and arsenic emission rates for the manufacture of lead and opal glass reported by Reznik (1975). These particulate emission rates varied between 2.1 and 4.3 g/kg (4.1 and 8.6 lb/ton). The arsenic concentration of the particulates ranged from 6% to 9% and averaged 7%. Particulate emissions for pressed and blown glass manufacturing have been analyzed by Schorr et al. (1977). They found particulate emission factors for 19 soda/lime glass manufacturers to vary from 0.49 to 12.57 g/kg (0.97 to 25.14 lb/ton). The average emission factor was 5.22 g/kg (10.44 lb/ton). The particulate emission factor for a lead glass manufacturer was 4.52 g/kg (9.04 lb/ton). Another manufacturer reported uncontrolled emissions for lead glasses to be about 15 g/kg (30 1b/ton) and about 25 g/kg (50 1b/ton) for borosilicate glasses (Schorr et al., 1977).

Table IX-2
STACK EMISSIONS FOR GLASS MANUFACTURING

| Product Case | Feed Rate (lb/hr) | Particulates (lb/ton) | Arsenic (lb/ton) | % As in Particulate |
|---------------|-------------------|--------------------------|------------------|---------------------|
| 2% lead glass | 175 | 4.1 | 0.27 | 6.6 |
| Opal glass | 85 | 6.8 | 0.40 | 5.9 |
| Opal glass | 100 | 8.6 | 0.74 | 8.6 |

Emissions are based on feed rates rather than glass manufactured. There is a 10%-15% loss of feed due to volatilization.

Source: Reznik (1975).

On the basis of a worst case engineering analysis, Schorr et al. (1977) estimated the highest particulate emission factor for borosilicate glass to be 25 g/kg (50 lb/ton), for opal glass to be 5 g/kg (10 lb/ton), and for lead glass to be 15 g/kg (30 lb/ton). The accuracy of these estimated emissions was reported as $\pm 100\%$. Schorr et al. (1977) then used a weighted average particulate emission factor of 8.7 g/kg (17.4 lb/ton) for all pressed and blow glass. This results in a worse case arsenic emission factor of 0.6 g/kg (1.2 lb/ton) assuming that the particulates contain 7% arsenic.

Cuffe (1978) analyzed recent particulate emission data on controlled glass furnaces. Particulate emissions for 10 furnaces equipped with electrostatic precipitators (ESPs) ranged from 0.03 to 4.79 g/kg (0.06-9.58 lb/ton) and averaged 0.16 g/kg (0.31 lb/ton). No data were available for particulate emissions for all-electric melting furnaces or for furnaces equipped with baghouse controls. Preliminary test results, however, showed that arsenic is removed by ESPs and baghouses in the same proportion as total particulates are removed. Particulate emissions from one furnace using electric boosting were 1 g/kg (2 lb/ton), but the amount of arsenic used in this process is very small.

The arsenic emission factor for well controlled pressed and blown glass manufacturers who use arsenic in their process is estimated at 0.015 g/kg (0.03 lb/ton) (Cuffe, 1978). This estimate assumes that all furnaces are equipped with emission controls equivalent to ESPs and that the particulates contain 7% arsenic. It also includes an allowance for possible emissions of arsenic as vapor. This estimated emission factor is significantly lower than the one presented in the Davis report (Davis, 1971), which gives a particulate emission factor of 1.0 g/kg (2.0 lb/ton) of glass and estimates the arsenic trioxide concentration of the particulates to be 7.7% (6.7% arsenic). Maasland (1975) implies that the Davis estimate is unreliable because in its development, arsenic was reported in the particulate catch of only five melters, one of which was melting amber glass at an unspecified rate.

Particle size distributions for particulates emitted from a flint and from an amber glass furnace are shown on Figure IX-1. The geometric median particle diameter of the flint glass particles was 0.13 μm , and the geometric standard deviation was 1.5 μm . Corresponding values for the amber glass furnace effluent particles were 0.11 and 1.7 μm .

Youngblood (1978) used atmospheric dispersion modeling to estimate the 24-hr downwind arsenic concentrations for two sizes of glass manufacturers that had arsenic emissions of 0.016 and 0.047 g/s, respectively. These 24-hr concentrations were converted to annual worst case by dividing by 5. They were then converted to omnidirectional by dividing the result by an additional 2.5. These estimated 24-hr downwind and annual concentrations are given in Table IX-3. Concentrations for manufacturers of other sizes were estimated by proportionately scaling the values given in Table IX-3 on the basis of the ratio of arsenic emissions.

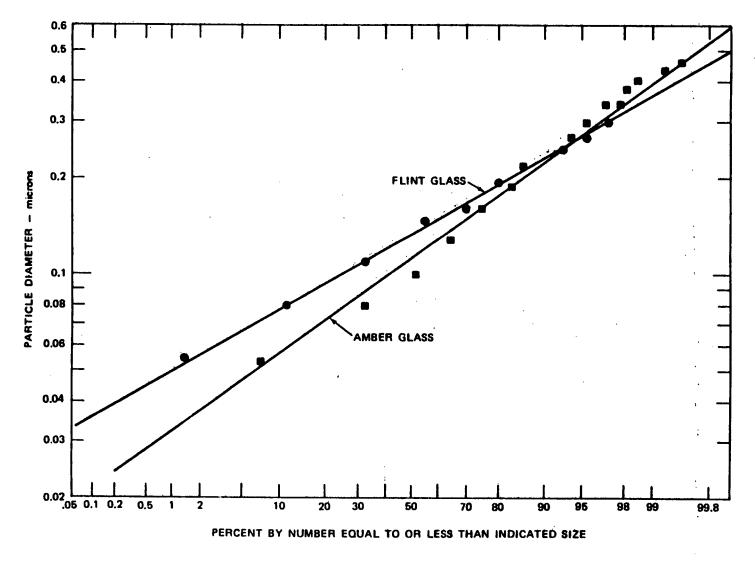


FIGURE IX-1. PROBABILITY DISTRIBUTION OF PARTICLE SIZES PRESENT IN GLASS FURNACE EFFLUENTS

Table IX-3

ATMOSPHERIC ARSENIC CONCENTRATIONS FOR GLASS MANUFACTURERS
BASED ON DISPERSION MODELING

| Distance from | 0.016.9/s | Emission | 0.047 g/s | Emission |
|------------------|--------------------------|-----------------------|-----------------------|-----------------------|
| Plant (km) | 24-hr Downwind (μg/m) | Annual Average (µg/m) | 24-hr Downwind (µg/m) | Annual Average (µg/m) |
| 0.3 | 0.069 | 0.0056 | 0.120 | 0.0096 |
| 0.8 | 0.036 | 0.0029 | 0.046 | 0.0036 |
| 1.3 | 0.026 | 0.0020 | 0.038 | 0.0031 |
| 2.0 | 0.019 | o. 0016 | 0.029 | 0.0024 |
| 3.0 | 0.015 | 0.0011 | 0.024 | 0.0020 |
| 5.0 | 0.011 | 0.0009 | 0.020 | 0.0015 |
| 8.0 | 0.009 | 0.0007 | 0.015 | 0.0013 |
| 12.0 | 0.007 | 0.0006 | 0.013 | 0.0011 |
| 16.0 | 0.005 | 0.0004 | 0.012 | 0.0010 |
| 20.0 | 0.004 | 0.0003 | 0.009 | 0.0007 |

Source: Modified from Youngblood (1978)

D. Population Exposures

Population exposures were estimated for atmospheric arsenic emissions from glass manufacturing. These exposure estimates were made by using the plant sizes summarized in Table IX-l and by assuming an arsenic emission factor of 0.015 g/kg of glass produced for well controlled manufacturers and 0.6 g/kg for poorly controlled manufacturers. The estimated arsenic emissions for each plant were used to proportionately scale the concentrations for the dispersions modeling results given in Table IX-3. Because it is not known which plants use arsenic or which plants are controlled, several alternative situations are evaluated.

At-risk populations were estimated for a number of concentric geographic rings about each manufacturing plant by using the 1970 county population density for each plant. It was assumed that no population resides within 0.4 km of a plant.

The estimated population exposures are listed in Table IX-4. Because of the uncertainties concerning the use of arsenic, four cases are evaluated using different assumptions. These cases are:

- (1) A random use estimate. This case assumes that 15% of the pressed and blown glass is manufactured with arsenic and that all plants are well controlled. It is further assumed that all glass produced at certain plants is made with arsenic. Fifteen percent of the plants were randomly selected from each of the Categories in Table IX-1. For this case it is estimated that approximately 19,000 people are exposed to concentrations ranging from 0.003 to 0.009 µg/m³.
- (2) A largest plant estimate. This case assumes that 15% of the pressed and blown glass is manufactured with arsenic and that all plants are well controlled. It is further assumed that this production is made by the largest manufacturing plants. For this case, it is estimated that approximately 65,000 people are exposed to concentrations ranging from 0.003 to 0.009 ug/m³.
- (3) A uniform use estimate. This case assumes that 15% of the pressed and blown glass is manufactured with arsenic. It is assumed that all manufacturing plants are well controlled and use arsenic for 15% of their production. For this case, it is estimated that no exposures exceed 0.003 μ g/m³.
- (4) A mixed controls estimate. This case assumes that 15% of the pressed and blown glass is manufactured with arsenic and that 90% of the plants are well controlled and that 10% are poorly controlled. It is further assumed that all glass produced at certain plants is made with arsenic. For this case it is estimated that approximately 1.2 million are exposed to concentrations ranging from 0.003 to 0.29 µg/m³.

No attempt was made in these exposure estimates to assess the effect of several plants located in close proximity. In effect, it was assumed that all plants are not collocated. This assumption has little effect on the estimated exposures because significant exposures were not found more than a few kilometers away from even the largest plants for the well controlled cases.

E. Summary

Population exposures to arsenic from glass manufacturing are estimated to involve a few thousand people and fairly low concentrations when it is assumed that all plants are well controlled. The mixed controls case shows these estimates are very much dependent on the emission factors that are assumed.

Table IX-4

ESTIMATED HUMAN POPULATION EXPOSURES TO ATMOSPHERIC ARSENIC CONCENTRATIONS FROM GLASS MANUFACTURING

| | | People Ex | ple Exposed, Assuming | | | |
|---|--|---|--|--|--|--|
| Arsenic Concentration ^a (µg/m ³) | 15% of Plants Use Arsenic ^b | Largest Plants Use Arsenic ^c | All Plants Use Arsenic 15% of Timed | Mixed Controls 15% of Plants Use Arsenic ^e | | |
| 0.100-0.299 | | | | 1,400 | | |
| 0.060-0.099 | | | | 10,140 | | |
| 0.030-0.059 | | | | 75,180 | | |
| 0.010-0.029 | | | | 212,040 | | |
| 0.005-0.009 | 370 | 1,770 | | 363,870 | | |
| 0.003-0.004 | 15,510 | 63,060 | | 583,360 | | |
| | | | | | | |

^aAverage annual concentration.

Assumes that 15% of pressed and blown glass is manufactured with arsenic, that only certain manufacturers use arsenic, and that the size distribution of manufacturers who use arsenic is proportionate to the size output given in Table IX-1. All plants are assumed to be well controlled.

^CAssumes that 15% of pressed and blown glass is manufactured with arsenic and that only the largest plants use arsenic. All plants are assumed to be well controlled.

dAssumes that 15% of pressed and blown glass is manufactured with arsenic and that all manufacturers use arsenic 15% of the time. All plants are assumed to be well controlled.

Assumes that 15% of pressed and blown glass is manufactured with arsenic, that only certain manufacturers use arsenic, and that the size distribution of manufacturers who use arsenic is proportionate to the size output given in Table IX-1. It is assumed that 90% of the manufacturers are well controlled and that 10% are poorly controlled.

X SECONDARY HUMAN EXPOSURES RESULTING FROM ATMOSPHERIC ARSENIC EMISSIONS

A. General

Atmospheric arsenic emissions eventually are deposited on the earth or on bodies of water. Plants may absorb arsenic, and they may in turn be consumed by humans or by animals that are eaten by humans. Humans may drink the contaminated waters or consume aquatic organisms with increased arsenic concentrations caused by residing in contaminated waters. Humans are not only exposed by inhalation to atmospheric arsenic emissions but may also be subjected to secondary exposures by ingestion of these emissions.

The primary purpose of this report was to evaluate human inhalation exposures to selected atmospheric emissions. This discussion of secondary exposure routes is intended to suggest the relative magnitude of exposures from various sources.

B. Exposures

To view these secondary exposures in their proper perspective, it is necessary to point out that arsenic is ubiquitous in the environment. Arsenic ranks twentieth among the elements in abundance in the earth's crust, and arsenic at low concentrations is distributed throughout the natural world. The earth's crust contains arsenic at about 5 ppm, with a range of 0.1 to 50 ppm. Untreated soils usually have arsenic levels of 5 to 10 ppm, whereas soils to which arsenical pesticides have been applied contain as much as 165 ppm arsenic. At that concentration, arsenic may reduce growth rates and inhibit generation of many plant species if it is present in available form. The arsenic content of uncontaminated water is low, averaging from 0.002 to 0.003 ppm in seawater and about 0.0004 ppm in rivers (Union Carbide, 1976).

Arsenic concentrations in plants vary from less than 0.01 to about 5 ppm (dry-weight). Differences in arsenic content reflect differences in plants and in environmental and edaphic factors in particular geographic regions. Plants growing in arsenic-contaminated soils generally have higher residues than plants grown in normal soils. However, concentrations in some nontreated plants are as high or higher as those found in plants treated with arsenic or grown in arsenic-contaminated soils. Natural variations in plants, plant species, available soil arsenic, and growing conditions are all partly responsible for these discrepancies. There appears to be little chance that animals would be poisoned by consuming plants that contain arsenic residues from contaminated soils, because less than toxic concentrations cause plant injury (NAS, 1977).

Arsenic is present in all living organisms. Marine fish may contain up to 10 ppm; coelenterates, some mollusks, and crustaceans may contain even higher arsenic concentrations. Freshwater fish may contain up to 3 ppm, although most values are less than 1 ppm. Domestic animals and man generally contain less than 0.3 ppm on a wet-weight basis (NAS, 1977).

The contribution of atmospheric fallout to soils of arsenic from the sources considered in this report seems insignificant because 32% of the arsenic released into the environment comes from pesticides and herbicides (Table III-1). These products are applied to croplands and have more chance to affect food crops than do emissions from power plants, glass plants, and smelters.

Ecological damage directly associated with the arsenic emitted from nonferrous smelters other than the Tacoma copper smelter is poorly documented. Both acceptable and unacceptable levels of arsenic (based on Food and Drug Administrations standards) have been found in foods and forage grown near nonferrous smelters (Environmental Science and Engineering, 1976). The Tacoma smelter has undoubtedly produced high past atmospheric arsenic emissions. Soil arsenic concentrations of more than 300 ppm have been found near the smelter, with concentrations generally decreasing to 10-30 ppm 5 miles away. This is primarily an urban area; however, vegetation from the area near the smelter (within a 1-mile radius) has had arsenic concentrations of up to 30 ppm, and vegetation from the remainder of the city has had concentrations of 1-9 ppm (Ratsch, 1974).

The Helena Valley Study (EPA, 1972) points out that the average arsenic content of soil is normally about 5 ppm, and the upper 4-inch layer of soil outside the Helena Valley has a geometric mean arsenic content of 6 ppm. Yet the concentration in the upper 4-inch layer within a mile of the Helena Valley smelter complex averages 50 ppm and is sometimes as high as 150 ppm.

The annual arsenic deposition within 56 km² (34.80 mi²) of a coal-fired power plant (amount of coal processed annually is not given) has been estimated at 2.8 mg/mi², assuming 99% efficiency in electrostatic precipitators (Rancitelli et al., 1974). This would result in an annual increase in arsenic concentration in the soil of 0.2 ppm, assuming that the arsenic has no mobility and that the top 3 inches of the soil are uniformly contaminated.

What people eat greatly affects the amount of arsenic they will consume per day. For most people, ingestion of arsenic in food varies from 10 to 100 μg per day, with an estimated average of about 60 μg per day (Suta, 1977). The commodity of greatest concern is fish; purchased and nonpurchased fish account for about 50% of the average daily consumption of arsenic in food. An estimated average of another 7 μg per day is consumed in drinking water (Suta, 1977).

The potential for arsenic toxicity in drinking water is limited because arsenic forms insoluble sediment complexes, becomes less toxic when it is oxidized, and is removed by municipal water treatment (Environmental Sciences and Engineering, 1976). Furthermore, many communities get their drinking water from sources that are unaffected by major airborne arsenic emissions. Arsenic concentrations in drinking waters of six cities near nonferrous smelters are given in Table X-1. Most of these arsenic concentrations are below the test detection level and all are near the U.S. median arsenic concentrations in drinking water of < 0.005 ppm (Suta, 1977).

Table X-1

ARSENIC CONCENTRATIONS IN DRINKING WATER
OF CITIES NEAR NONFERROUS SMELTERS
(ppm)

| City | Sample Size | Range |
|----------------------|-------------|----------------|
| Salt Lake City, Utah | 4 | <0.005 < 0.010 |
| El Paso, Texas | 4 | <0.005-0.012 |
| Anaconda, Montana | 1 | <0.005 |
| East Helena, Montana | 14 | 0.000<0.030 |
| Butte, Montana | 2 | <0.005<0.010 |
| White Pine, Michigan | 1 | <0.005 |
| | • | |

Source: Kent (1976)

Arsenic bioaccumulates in various organisms in the environment, but it is not biomagnified. Macroinvertebrates and fishes high in the food chain contain low concentrations of arsenic even when they feed on lower level organisms with high concentrations (Union Carbide, 1976).

The most likely route of secondary human exposure to atmospheric emissions of arsenic is eating vegetables grown in contaminated soils. An average person in the United States consumes about 200 grams of vegetables per day, although the amount varies with dietary preferences. If these vegetables were contaminated with arsenic at average U.S. concentrations, the average person would consume about 1.5 μg of arsenic per day from vegetables. The arsenic concentrations in vegetables grown in the Tacoma area could lead to daily consumption of 200 to 2,000 μg of arsenic by persons who eat only locally grown produce.

Appendix

DISPERSION ESTIMATES OF ATMOSPHERIC ARSENIC CONCENTRATIONS FOR SELECTED SOURCES

The arsenic exposure concentrations given in this report are based on rough dispersion modeling estimates supplied by EPA (Youngblood, 1978). These dispersion calculations assumed source emission rates that are rough estimates of actual emissions. The sources of arsenic that were considered are power plants, pesticide plants, cotton gins, glass plants, and nonferrous smelters (copper, lead, and zinc). Although the calculations were made under well-defined assumptions about source characteristics and meteorological data, they are intended to be applicable to a wide range of sources and geographical/climatological situations. they are to be used as rough approximations. The effects of complex terrain were not considered in the calculations. In specific cases, the source characteristics, local meteorological conditions, and the presence of complex terrain may make the estimates inapplicable. This is particularly true with regard to smelters in complex terrain, for which estimated concentrations will be very much higher in situations of plume impaction.

The dispersion modeling provided estimates of maximum 24-hour average concentrations for various distances out to 20 km from each source. These 24-hour maximum estimates were converted to maximum annual values by dividing by 5. These values were then further divided by 2.5 to smooth the maximum annual values with respect to direction. This procedure leads to upper-limit estimates for elevated point sources such as smelter stacks.

The 24-hour maximum concentration estimates were derived by two techniques. For the elevated point sources (power plants, smelter stacks, and glass plants), the Single Source (CRSTER) Model was used. In the case of the glass plants, a version of CRSTER was used that allows the consideration of building wake effects. For the low-level sources (pesticide plant, cotton gin, and the fugitive emissions from the smelter), the PAL dispersion model was used.

For the CRSTER executions, meteorological data for a 1-year period from Phoenix, Arizona (surface), and Tuscon, Arizona (upper air), were used because Arizona meteorological conditions roughly typify those at many smelter sites. However, the choice was also a matter of convenience because the intended application of the results does not call for site-specific considerations. Within the range of uncertainty inherent in the exposure study, the 24-hour maximum concentration estimates from CRSTER would not differ significantly over a variety of choices for the

meteorological data base. The CRSTER output was screened to eliminate spurious concentration estimates stemming from anomalous meteorological events.

In regard to the PAL executions, 1-hour estimates were made for various distances along the downwind plume centerline under the assumed meteorological conditions of neutral stability (Pasquill-Gifford "D") and a wind speed of 4 m/s (9 mph). These 1-hour estimates were multiplied by 0.25 to convert them to maximum 24-hour estimates.

The emission rates used in the dispersion modeling were largely contrived. This, however, does not affect the utility of the results because, for a given source, the results are directly proportioned to the emission rate. Thus, the estimates can be scaled up or down according to the actual emission rate in any given situation.

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