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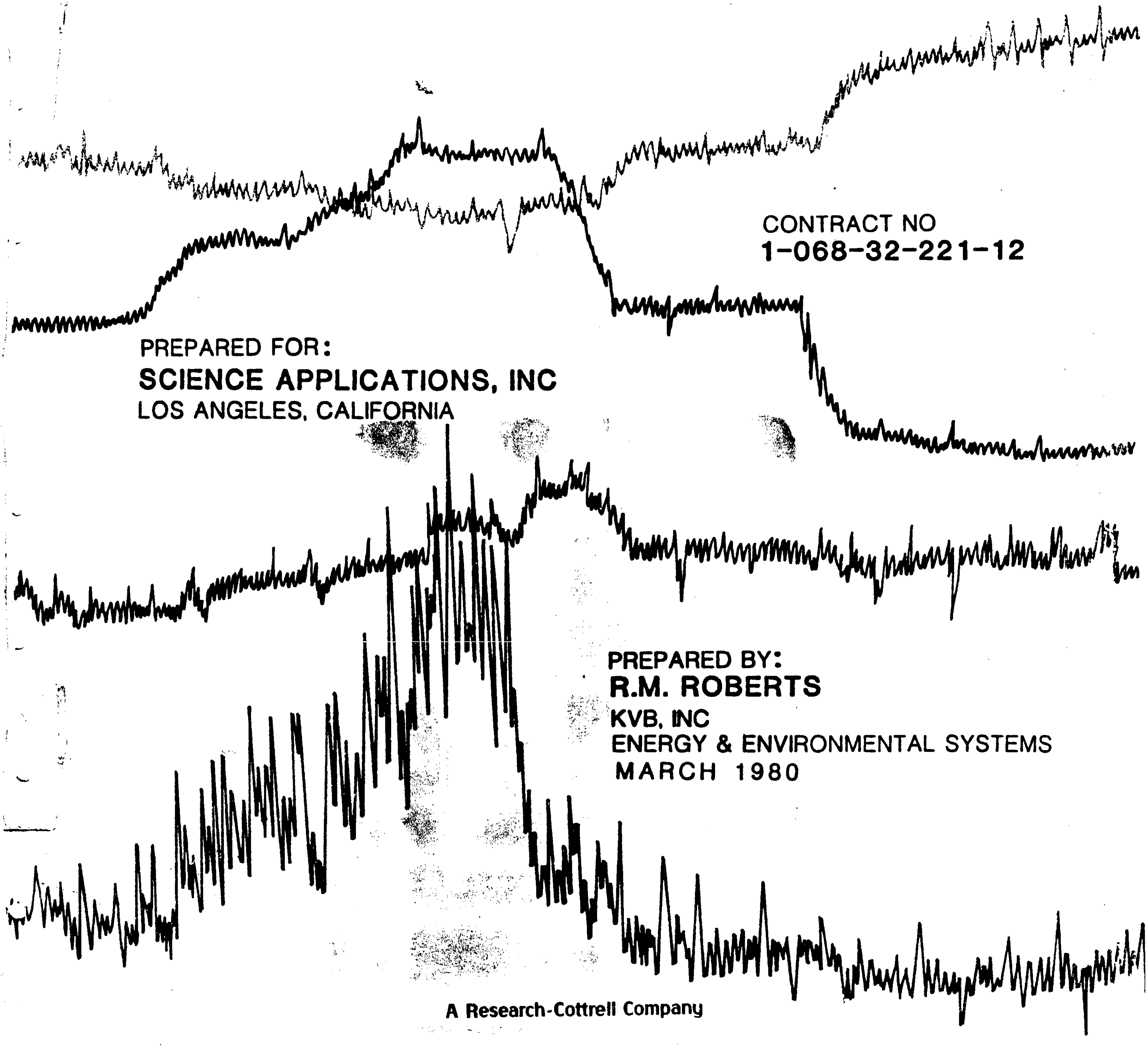
AN INVENTORY OF CARCINOGENIC SUBSTANCES RELEASED INTO THE AMBIENT AIR OF CALIFORNIA

KVB 26900-836

FINAL REPORT - TASK II & IV



CONTRACT NO
1-068-32-221-12

PREPARED FOR:
SCIENCE APPLICATIONS, INC
LOS ANGELES, CALIFORNIA

PREPARED BY:
R.M. ROBERTS
KVB, INC
ENERGY & ENVIRONMENTAL SYSTEMS
MARCH 1980

A Research-Cottrell Company

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AN INVENTORY OF CARCINOGENIC SUBSTANCES RELEASED INTO THE AMBIENT AIR OF CALIFORNIA

TASK II

CONTRACT NO. 1-068-32-221-12

PREPARED FOR
SCIENCE APPLICATIONS, INC.
LOS ANGELES, CALIFORNIA

PREPARED BY
KVB, INC.
A RESEARCH-COTTRELL COMPANY

KVB
A Research-Cottrell Company

MARCH 1980

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SECTION 1.0

INTRODUCTION

The development of an inventory of carcinogenic substances released into the ambient air of California involved a four-element program. Science Applications, Inc. (SAI) performed Task I and III, while KVB, Inc. performed Task II, the results of which are being described in this volume, and Task IV.

The overall objectives of the program have been to:

1) Identify a limited number of carcinogens posing the greatest potential hazard as ambient atmospheric pollutants in California (Task I - SAI);
2) Locate major sources of and estimate emission factors for this list of carcinogens (Task II - KVB);
3) Determine usage patterns, release rates, and population exposures for the sixteen substances regulated by the Occupational Carcinogens Control Act and investigate substances of concern by incorporating into the Task I evaluation (Task III - SAI); and
4) Develop a field test plan to verify the more significant emission factors estimated on Task II (Task IV - KVB).

As discussed in the Task I volume, 114 substances regarded by the EPA as having carcinogenic potential were screened. By rating these under the criteria of: (1) annual U.S. production; (2) fraction lost during production; (3) volatility; and (4) carcinogenicity, the group was reduced to 35 substances (compounds or classes of compounds). Further reduction of the list was done through semi-objective quantitative algorithms based upon adding and multiplying rating factors. These included all of the factors listed above (except applied to the State rather than National level) plus rating factors for: (1) projected growth in usage; (2) stability in ambient air; and (3) potential for dispersion after release.

Application of this refinement resulted in a ranked list of 22 substances.

The final selection process involved a review of an ad hoc panel of experienced scientists convened by SAI. This two-day meeting produced an independent ordering of the 22 substances. From these three final listings the eleven highest scoring substances were then selected for study in Task II. These are listed, alphabetically, in Table 1-1.

TABLE 1-1. ELEVEN SUSPECTED CARCINOGENIC SUBSTANCES SELECTED FOR SPECIFIC STUDY ON TASK II

Arsenic	Ethylene Dibromide
Asbestos	Ethylene Dichloride
Benzene	Nitrosamines
Cadmium	Perchloroethylene
Carbon Tetrachloride	Polycyclic Organic Matter (POM)
Chloroform	

Effort was then initiated on Task II of the study to identify areas where the highest concentrations of emissions might be expected to occur resulting from the use or manufacture of these substances in California. As the materials of greatest concern were identified in Task II, test plan strategies and technical requirements were developed for follow-on field monitoring and detection of actual releases to the environment. Design of the source sampling program comprised Task IV of the overall study and is reported separately.

Emissions resulting from use of the candidate substances listed in Table 1-1 can be expected to be present in the surrounding environment at levels determined by many factors, including release rates from mobile and stationary sources. The approach to Task II, which is summarized in Figure 1-1, was to investigate the suspected areas within the state, verify the releases in these locations whenever possible, and prepare a map showing these "hot spot" areas.

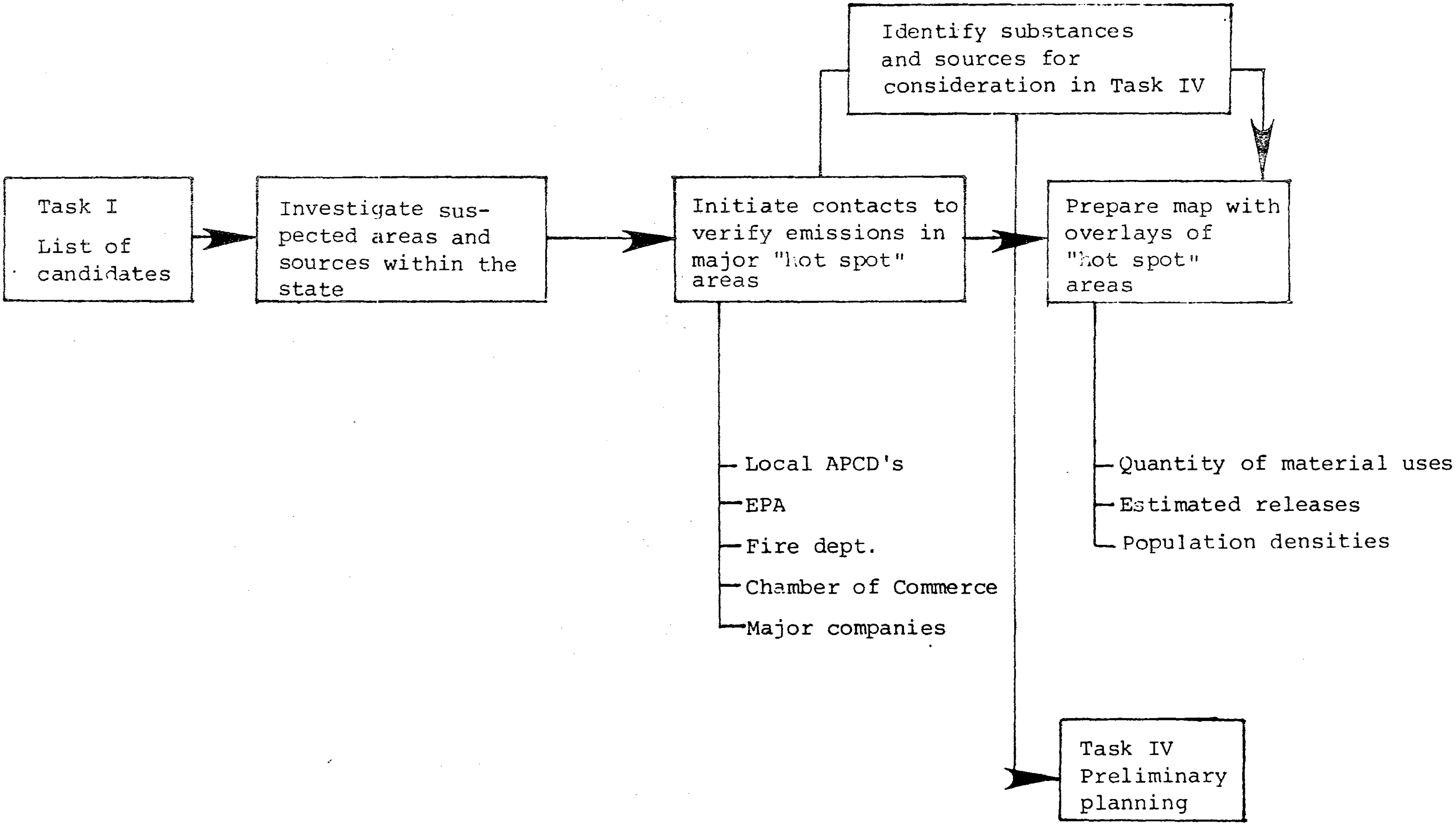


Figure 1-1 ARB Carcinogenic Materials Study; Task II--establish baseline data.

KVB-26900-836

The "hot spot" areas were determined taking the following characteristics into account:

- Number of substances present
- Expected concentrations and flow rates of emissions
- Potential population exposure
- Physical characteristics of the area (topography, meteorology).

Consideration was also given to the monitoring and detection requirements posed by source types, although specific definition of sampling systems were developed during Task IV.

Contacts were made with government agencies and major producers and users of these materials to develop an inventory of emissions. Sources, recognized as "hot spots", were then displayed on maps whenever practical and coded according to ranges of estimated quantities released per unit of time. A pair of composite maps was then prepared to provide quantitative indication of the major "hot spot" areas for these substances in California (see Section 4.0). The mapping was arbitrarily separated into inorganic and organic pollutants.

Wherever sufficient data were available, information was collected regarding quantities of Table 1-1 materials used; process flow, material handling and control systems; and measured or estimated release of emissions.

Where there was a lack of sufficient data, assumptions had to be made concerning process characteristics; these are documented in the report. On completion of Task II, the areas of concern (according to substances and sources) and the quality of the available data had been reasonably identified or the need for more in-depth study specified where sufficient data were lacking.

A number of the pollutants studied were associated with area or dispersed sources. These would not thus emerge as "hot spots" although comparatively large total releases were involved. In many cases, the areas sources are coincident with population density distributions.

This is generally true, for example, with dry cleaning establishments and degreaser works (perchloroethylene emitters) and home fire places (POM emitters). Other distribution patterns are seen where the pollutants are released during vehicular travel (benzene, cadmium, ethylene dibromide and dichloride and POM) and agricultural operation (arsenic, ethylene dibromide and dichloride and, possibly, nitrosamines). Because such emissions cannot be mapped as "hot spots," Figure 1-2 is introduced here for reference when these source types come under consideration under the various carcinogen headings. Figure 1-2 provides population density for the State of California together with overlays showing traffic density (for the State Highway System) and principal agricultural zones of the State.

Occasionally in this report, comparisons are made between ambient levels of the pollutants and OSHA maximum allowable concentrations (MAC'S). These data should be construed in their proper contexts. MAC'S are intended for healthy, adult, usually male workers for 40-hour work-weeks, with 8-hour work days, and with weekends and vacations included as time available for detoxification in the absence of exposure. Furthermore, MAC'S are designed primarily, although certainly not exclusively, to protect the worker from the noncarcinogenic consequences of exposure to substances that may also happen to be carcinogenic, mutagenic or teratogenic.

The present report deals exclusively with Task II results and is organized into four sections. Following this introduction are the summary of findings and conclusions reached (Section 2.0). The main body of the report (Section 3.0) considers, in alphabetic order, each of the eleven suspected carcinogens in separate subsections. The last part of the report (Section 4.0) is addressed to the superpositioning of the "hot spots" on demographic maps of the State. References and appendices follow Section 4.0.

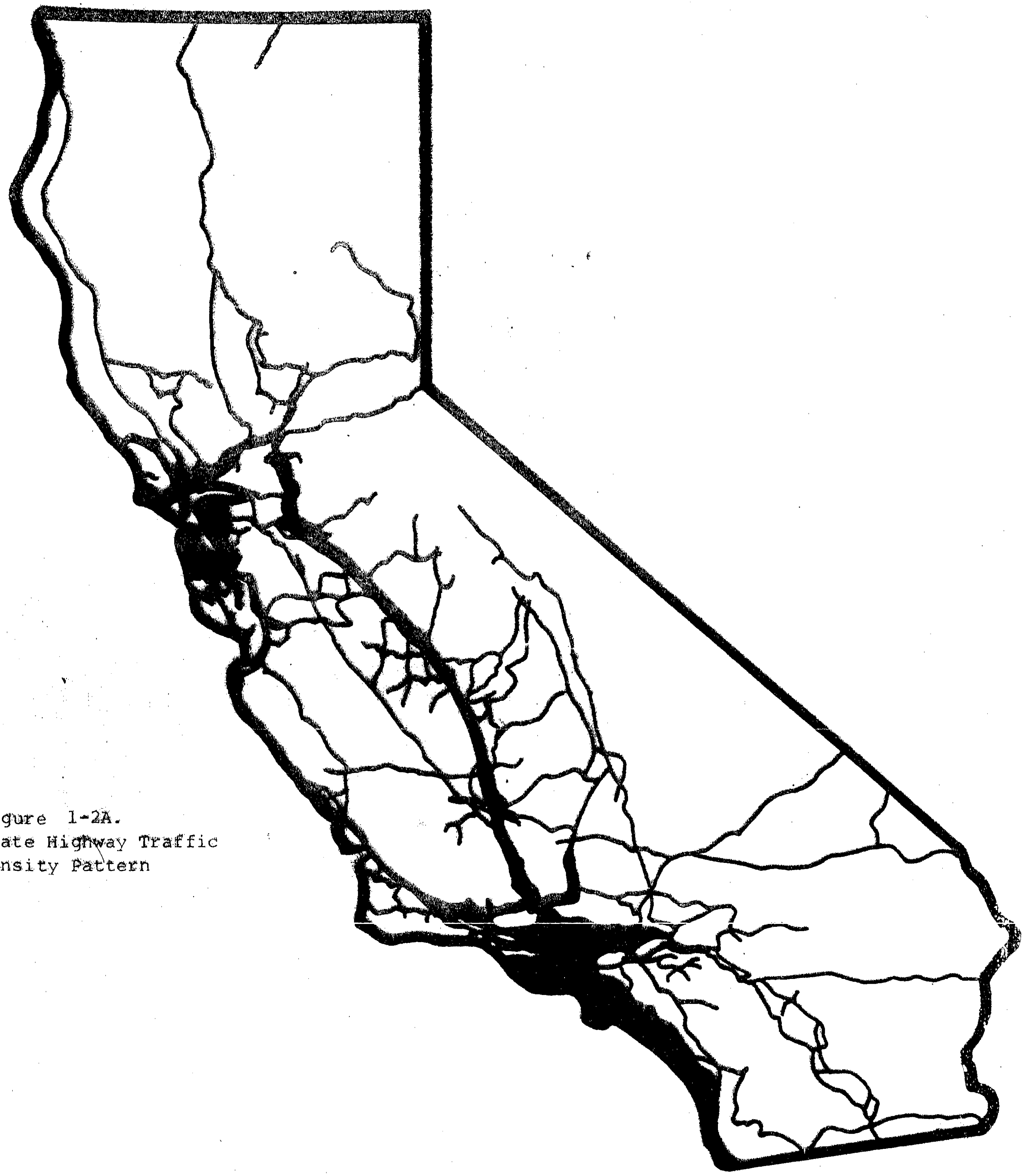


Figure 1-2A.
State Highway Traffic
Density Pattern

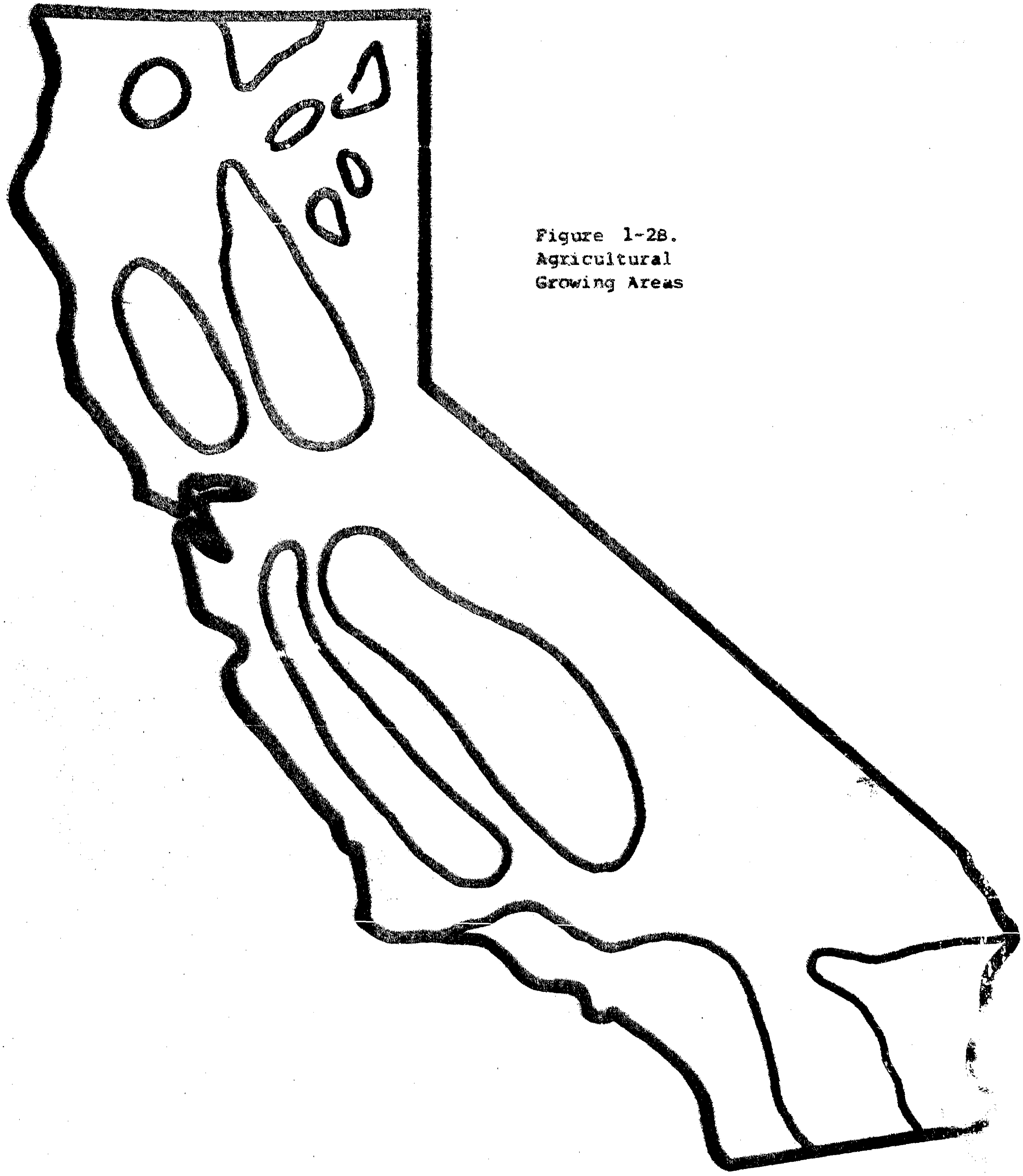


Figure 1-28.
Agricultural
Growing Areas

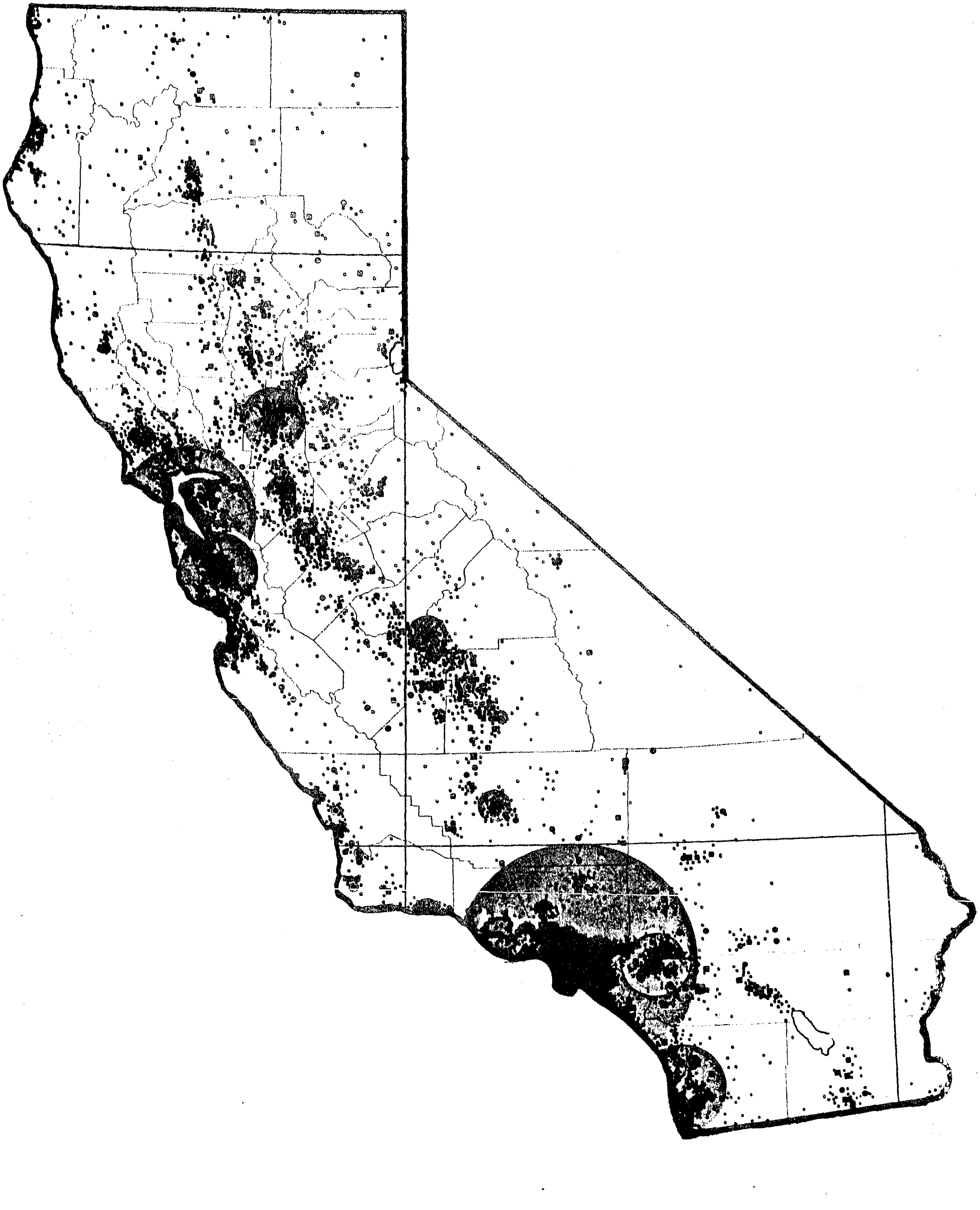
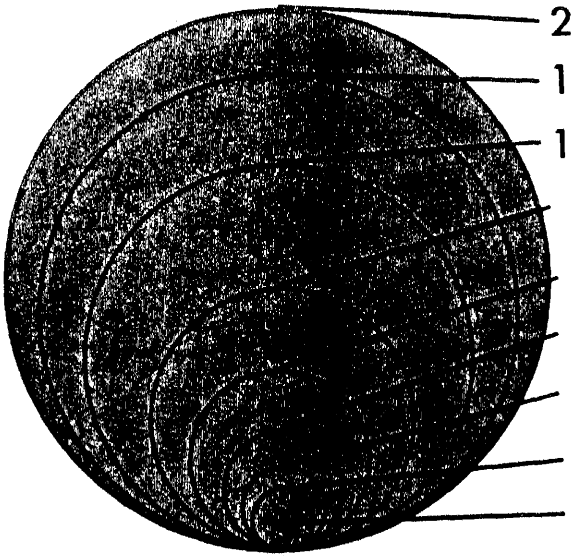
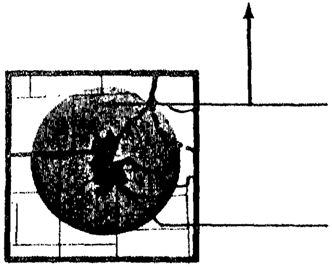


Figure 1-2A. Population Density in California

URBAN POPULATION

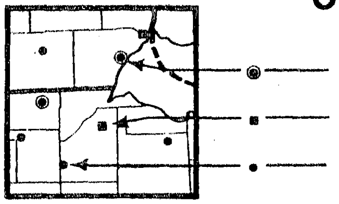
URBANIZED AREAS




Circles proportional to population

Extent of areas

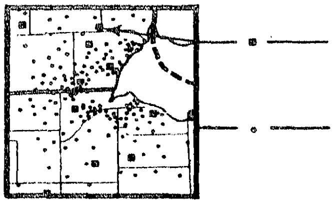
PLACES OUTSIDE URBANIZED AREAS


◉ 25,000 - 50,000

■ 10,000 - 25,000

• 2,500 - 10,000

RURAL POPULATION


▪ Places of 1,000–2,500

· Each dot represents 500 of remaining population

Figure 1-2. Legend (Cont).

SECTION 2.0

SUMMARY OF FINDINGS AND CONCLUSIONS

2.1 ACCURACY OF FINDINGS

The main body of information tapped in this study consisted of four categories. The principal source was EPA-sponsored studies dealing specifically with one or more of the eleven subject carcinogens. Several CARB reports dealing with source or pollutant types, which incidentally included data on some of the carcinogens, was a second useful category accessed. The third category was comprised of government publications furnishing emission or commodity data [e.g., EPA's Compilation of Air Pollutant Emission Factors (AP-42), the Emission Inventory Subsystem (EIS), etc.]. The last category consisted of miscellaneous publications furnishing emission or commodity data developed within the private sector (e.g., API reports, Chemical Marketing Reporter, etc.).

The emission data available from this mix of literature were often engineering estimates and not derived from actual source tests. In comparing emission estimates for the same substance and source made by different authors, it is obvious that the values reported can be in error by as much as an order of magnitude. Thus, in a derivative manner, this report furnishes emission data that are highly uncertain in many cases. Where this is not pointed out, the reader is cautioned to remind himself that the data presented are predominately estimates of considerably varying quality.

It is just this condition that lends emphasis to the need of implementing the Task IV source testing plan. Then the emission factors reported here will be verified or displaced with more credible information. The present Task II analysis is nonetheless a big step in moving torwards that achievement. It not only specifies which sources should be tested, but furnishes a first-cut ranking of the identified sources in terms of their potential hazard to receptor populations. Whatever the error band this ranking incorporates, the process will still permit test events in future field efforts to be sequenced or prioritized to accommodate funding and other resource limitations.

In the following two subsections, the findings and conclusions of the study are summarized first in terms of the sources or "hot spots," then, (in alphabetical order) for each of the eleven carcinogens. These comments are presented without literature citations to promote clarity. All statements made in this section are supported by appropriately referenced analyses and discussions that are developed in the pertinent portions of Section 3.0.

2.2 MAGNITUDE OF POLLUTION

All eleven of the studied carcinogens occur as air pollutants in the State of California. Based on the estimates developed or used, two halocarbons constitute the extremes on the scale of pollutant burdens. Perchloroethylene emissions from the principal sources identified are estimated to be 58.2 million lbs/yr. By contrast, chloroform has not been identified with any industrial or commercial processes (outside of test laboratories) for which any quantity of emissions could be assigned.

Perchloroethylene releases occur from hundreds of urban industries (dry cleaners and degreasers), such that the net effect is that of an area source. Benzene, which accounts for the next largest weight of pollutant release (55 million lbs/yr), is also a highly dispersed pollutant. An estimated 98.6% of all the benzene released in the state is from mobile, area (oil fields), and scattered small point sources. Thus, the "hot spots" - the production or conversion plants - associated with these two solvents involve only small fractional amounts of the total material released.

In contrast, the next two largest releases of pollutants predominately are concentrated in only a few point sources. Over 91% of the 0.3 to 3.2 million lbs of ethylene dichloride estimated to be released in the State annually is associated with one vinyl chloride plant in Carson. All of the estimated 677,000 lbs of carbon tetrachloride released per year occurs at two chemical plants within several miles of each other on the San Joaquin River.

The fifth largest quantity of emissions (515,000 lbs/yr) is estimated for ethylene dibromide. Essentially all of this is evaporated from fumigated farm land, losses from gasoline usage being regarded as negligible.

Asbestos is estimated to be discharged into the ambient California air at a rate of about 460,000 lbs/yr. Over 90% of these emissions are associated with our three asbestos mining and milling operations. Asbestos-consuming industries, which must release no visible asbestos from vents, nonetheless do emit some of this mineral but the effect is scattered among hundreds of minor point sources.

Of the other two inorganic carcinogens, some 93,000 lbs of arsenic and 30,000 lbs of cadmium are estimated to be emitted annually. About half the cadmium and over 92% of the arsenic are released from a small number of stationary sources processing molten materials.

Of the eleven materials investigated, the greatest survey uncertainty attaches to the nitrosamines and polycyclic organic matter (POM) findings. Neither of these classes of compounds per se is consumed in California commerce in a manner that would result in their <u>direct</u> release to the atmosphere in significant quantities.

Because nitrosamines are known to form in atmospheric processes from related species, notably secondary amines and amides, sources for the releases of such precursors were identified. This, however, does not constitute an adequate base for estimating nitrosamine formation.

In the case of POM, which arises pyrogenically in inefficient flame processes, releases are poorly quantified because of the complex chemical nature of this very large class of compounds. The single, very carcinogenic member, benzo[a]pyrene (BaP), has been used as an indicator for POM, but the ratios of POM/BaP are apparently variable. Burdens of BaP are estimated at 38,000 lbs/yr, over three quarters of this issuing from area and highly dispersed point(e.g. forest fires and fireplaces) and mobile sources. Some 5,400 lbs/yr are estimated to be emitted from the Kaiser steel mill, Fontana. The amount of total POM which that release of BaP representes could range from 10 to 100 times greater.

2.3 THE PRINCIPAL "HOT SPOTS"

On the program, a number of stationary sources were identified as emitting significant quantities of the materials surveyed. These constituted "hot spots" or releases posing possible health hazards potentially susceptible to improved control. As pointed out in the previous subsection, far greater amounts of some of the materials are emitted by dispersed or area sources.

So that "hot spots" identified can be roughly graded or prioritized for source testing planning, an arbitrary scaling factor was applied. This was arrived at in a manner similar to that (multiplicative approach) used in Task I for the comparison of suspected carcinogens with one another. The formula employed for the present purpose is as follows:

$$\text{Scaling factor} = E \times p \times R_2 \times R_4 \times R_5 \times e^{R_6}$$

Where: E = specific pollutant emissions, tpy

p = population content of 10 km grid with "hot spots" at center, 10^3 people

R_n = rating factors (see definitions in Task I report section); briefly defined, these rank on a scale of 1 to 5 the following parameters:

R_2 - use growth of chemical in CA

R_4 - stability of chemical in ambient air

R_5 - dispersion potential of chemical

R_6 - evidence of carcinogenicity

Exponentiation of the carcinogenicity rating factor was introduced to provide emphasis for this property. It is recognized of course that such exponentiation may have limited value, given the coarseness of the scaling (1 to 5). Populations for the 100 sq km tracts were mostly averaged from CARB data for Universal Tranverse Mercator (UTM) decade coordinates. Some data were developed from Census Bureau maps. This is further explained in Section 4.4.

The results of this "hot spot" or hazard ranking process are shown in Table 2-1. It will be noted that two of the sources are listed as emitting more than one of the eleven carcinogens. What is not obvious is that several of the emission factors for some of the sources involve contributions from different types of processes in which the same pollutant is emitted. An example of this is the Chevron USA plant at El Segundo. Benzene emissions estimated for this plant include those from: (1) normal petroleum operations; (2) benzene manufacturing and marketing; and (3) internal benzene consumption for cumene synthesis.

The formula used in preparing the Table 2-1 ranking is of course quite arbitrary. For this reason, the broad range of scaling factors that resulted was accepted without culling. Some of the sources having small factors could have actual health impacts highly disproportionate to the ranking given. The actual range of the scaling factors is almost 5000. This then was considered to have an adequately broad working base for approaching the Task IV source testing plan development.

TABLE 2-1. SUMMARY OF "HOT SPOTS" IDENTIFIED IN TASK II AND THEIR RELATIVE SCALING USING AN ARBITRARY HAZARD FORMULA

(Scaling Factor = (Emissions, tpy) X (pop. dens. X 10^{-3}) x R_2 x R_4 x R_5 x e^{R_6})

Site	Pollutant	Estimated Annual Emissions, Tons	Pop. density around site * 10^3 People/100 sq. km	Rating Factors † R_2	R_4	R_5	R_6	Scaling Factor x 10^{-6}
Kaiser Steel Corp., Fontana	Benzene	112	43.7	3	5	5	5	54.5
	Cadmium	7.0	"	3	5	5	5	3.4
	Arsenic	1.6	"	3	5	3	5	0.5
	POM	27 §	"	4	5	5	5	17.5
							Total	75.9
Stauffer Chemical, Carson	Ethylene dichloride	150 #	89.9	3	5	5	4	55.2
Dow Chemical USA Pittsburg	Carbon tetrachloride	160 ‡	63.8	3	5	5	4	41.8
	Perchloro-ethylene	22 ‡	63.8	3	5	5	4	5.7
							Total	47.5
DuPont de Nemours & Co, Antioch	Carbon tetrachloride	250 **	63.8	3	5	5	4	41.8
Chevron USA, Richmond	Benzene	50	62.8	3	5	5	5	35.0
ARCO, Carson	Benzene	25	75.9	3	5	5	5	21.1
Allied Chemical, El Segundo	Carbon tetrachloride	133**	32.7	3	5	5	4	17.8
Witco Chemical Co., Carson	Benzene	14	89.9	3	5	5	5	14.0
Chevron USA, El Segundo	Benzene	30	35.9	3	5	5	5	12.0
Gould Inc., Vernon	Arsenic	22	23.6	3	5	3	5	3.5
RSR Corp., Industry	Arsenic	3.3	59.5	3	5	3	5	1.3
ALCO-Pacific, Carson	Arsenic	2.2	88.1	3	5	3	5	1.3
Pacific Gas & Elec, Pitts.	Arsenic	1.0	63.8	3	5	3	5	0.4
Johns-Manville, Stockton	Asbestos	2.9	28.5	1	5	5	5	0.3
Calavaras Asbestos, Copperopolis	Asbestos	148	0.5	1	5	5	5	0.3
So. Cal. Edison, Long Beach	Arsenic	0.8	50.0	3	5	3	5	0.3
Pacific Gas & Elec, Salinas	Arsenic	1.0	0.3	3	5	3	5	0.02

NOTES:

* Point source geographically located in center of 100 sq. km

† Rating factors defined in Task I discussion: R_2 = growth in use of pollutant in California; R_4 = stability of pollutant in air; R_5 = pollutant dispersion potential; R_6 = evidence of pollutant carcinogenicity

§ Assumes POM/benzo(a)pyrene (BaP) = 10; BaP actually measured

\# A minimum estimate

‡ Process factors suggest that the large difference between CT and perc emissions is suspect [See Sec. 3.5.2 (A)]

** May be high by an order of magnitude

2.4 POLLUTION SIGNIFICANCE OF THE INDIVIDUAL MATERIALS

2.4.1 Arsenic

The State's four largest secondary lead smelters appear to be the major emitters of arsenic. All are located in the SCAB and are estimated to release a combined weight of almost 60,000 lbs/yr of this pollutant. The Kaiser coking plant in Fontana is estimated to emit less than one tpy of arsenic while all the secondary steel mills together emit less than one seventh that amount. Although no significant amounts of opal or lead (arsenic recipe) glass is produced in the State, at least one plant adds arsenic to flint glass melts. Emissions of 4,690 lbs/yr were calculated for this plant (identification confidential). The manufacture and application of agricultural arsenicals, including their secondary emission from cotton gins, are not significant sources of ambient air pollution.

Ambient arsenic measurements made during the four quarters of 1974 in 15 California cities included in the National Air Sampling Network (NASN) failed to show any arsenic (detection limit = 1 ng/m^3) in most cases. For just one quarter each, NASN arsenic measurements averaged above detection limits at Long Beach, Ontario, and San Bernardino. The highest such average quarterly concentration was 14 ng/m^3 (Long Beach). As of July 13, 1979, CAL OSHA declared arsenic a regulated carcinogen and set the maximum allowable concentration (MAC) for an eight-hour time weighted average (twa) day at 10 $\mu g/m^3$.

Conclusions: Arsenic emission factors for one or more of the secondary lead smelters in California should be verified by source testing. Because of relative capacity, the Gould plant in Vernon is estimated to be the largest such "hot spot" and should be included in this testing. Sampling of the coking ovens at the Kaiser mill in Fontana should also be undertaken. Although arsenic release during coking may prove minor, three other pollutants (benzene, cadmium, and POM) need to be tested for there, as is explained in those sections, thus justifying the inclusion of arsenic in the survey.

Manufacture of flint glass may involve the deliberate incorporation of arsenic. The practice is shielded by proprietary considerations. Samples of output of flint glassware should be obtained and analyzed for arsenic to determine which plants use the element. Atmospheric release rates can then be estimated using the emission factor already developed from the source testing of one such plant.

2.4.2 Asbestos

Operations at the three California asbestos mines at Copperopolis, Coalinga, and King City probably predominate in terms of emission of this particulate material. At these low population density sites, dust releases are estimated at 148, 56 and 3 tpy, respectively. It is further estimated that an additional 23 tpy of dust are emitted from all California plants manufacturing asbestos-containing products. The actual fractional amounts of these dust releases that comprise asbestos is unknown. Although never measured, outdoor releases from building demolitions and disturbances of asbestos ores by natural and human (e.g., recreationists) forces also contribute to the airborne asbestos burden.

Ambient levels of asbestos have been determined in various California areas. The California Department of Health reported 24-hour asbestos levels for various stations in the Berkeley-San Francisco area that averaged 35 ng/m^3. Applying the Health Department's conversion to give a fiber count (0.4 fibers/cc), this is equivalent to 20% of OSHA maximum allowable concentration (MAC). The accuracy of airborne asbestos counting is highly controversial, a situation that has not yet been resolved.

Conclusions: EIS* dust emissions recorded for plants manufacturing asbestos-containing products are comparatively small and probably conformative with the zero visible asbestos emissions required by regulation. Mass-wise, however, the tonnages involved are large enough in the case of a few of the larger plants to warrant concern if most of the dust released consists of asbestos. Source testing of a large asbestos product plant (e.g., Johns-Manville, Stockton) should thus be undertaken to measure asbestos specifically rather than total dust release.

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* Emission Inventory Subsystem

Further sampling of any of the asbestos mines would probably only confirm previously developed data. A more meaningful approach would be to measure airborne asbestos in one or more of the three individual towns near the mines. Coalinga would be the logical choice because of the scaling factor of the nearby Atlas Asbestos Co. relative to the other two mines.

2.4.3 Benzene

Release of this very common and vital chemical is widespread. Over 27,500 tpy are estimated to be emitted by mobile and point sources in the State. Of this estimate, over 94% is attributed to the automobile (exhaust and tank venting). Gasoline distribution and marketing is identified as the next largest source of benzene release, with some 1,100 tpy estimated for such activities. Thus, the balance or only 1.6% of the total benzene released is identified with stationary sources.

Among the stationary benzene-emitting sources, the greatest output (194 tpy) is estimated for the State's 29 gasoline refineries and asphalt plants which do not produce or consume industrial-grade benzene. About 43% of this is released in the SCAB, 45% in the area of the industrial waterside belt running from Richmond to Martinez, and 10% in the Bakersfield/Oildale area.

Coking at Fontana accounts for the next largest point release (112 tpy) estimated, while benzene conversion (to detergent alkylate and phenol) accounts for an estimated 76 tpy of which 66% is associated with Chevron USA-Richmond and the balance with two SCAB plants. Benzene production is identified with an estimated release of 55 tpy at two SCAB refineries, one of which (Chevron USA-El Segundo) consumes part of its own production. The estimates of the benzene releases for Chevron USA-El Segundo in benzene production and consumption are isolated and therefore additive.

Based on National data, benzene releases from solvent and other minor industrial uses were considered to be too small to warrant investigation.

Ambient levels of benzene measured by the CARB, the EPA, and the API in various urban areas of California are considerably higher than values obtained for other of the studied materials. Los Angeles levels averaged about 140 $\mu g/m^3$ in three measurements, while levels in reasonably ventilated areas (e.g., Palm Springs) were a surprising 30 $\mu g/m^3$.. Although this is 1000 times lower than OSHA MAC, the current direction of this agency is to a MAC of 3000 $\mu g/m^3$.

Conclusions: On the basis of total emissions and resulting ambient levels of the pollutant, benzene emerges as the carcinogen of greatest concern of all the materials studied. This judgment is also supported by the Table 2-1 hazard-ranking of "hot spots." Five of the top nine stationary sources are benzene emitters. At least three of these five should be characterized such that the steel mill, one of the two benzene producers and one of the two benzene converters are included. Further automobile testing for specific determination of benzene emissions is urgently needed.

2.4.4 Cadmium

The principal emitter (estimated at 7.0 tpy) of this metal is found to be the Kaiser steel mill at Fontana. An equivalent amount (7.3 tpy) is estimated to be released by automobile tires most of which (80-90%) precipitates about the roadbeds.

Secondary steel and zinc operations involve negligible cadmium venting. Together, the secondary copper smelters in the State (three in the SCAB, one in San Francisco) are estimated to emit about one tenth the amount of cadmium emissions produced at the Kaiser plant.

Conclusions: The Kaiser mill is probably the principal "hot spot" for cadmium emissions in the State. Sampling at this site has already been indicated for quantitating arsenic and benzene releases. Thus, the inclusion of cadmium analysis in the samples appropriate to this measurement would be a facile additional step. Sampling of secondary steel mills for cadmium should perhaps be deferred until results for scrap-fed furnaces at Fontana have been developed.

2.4.5 Carbon Tetrachloride (CT)

Almost all of the releases of this halocarbon are associated with its production and conversion to fluorocarbons. The Dow plant at Pittsburg, which produces CT, is estimated here to release up to one-third million pounds of this carcinogen annually. The two consuming plants are associated with estimated releases over twice that - the duPont Antioch Works 500,000 lbs/yr and the Allied Chemical plant in El Segundo 175,000 lbs/yr. At least one of the operators place the levels considerably lower. Because the estimates, which are based on National Academy of Sciences' emission factors, may indeed be on the high side, source testing is clearly needed to resolve these differences.

Ambient levels of CT have ranged as high as 38 $\mu g/m^3$, in brief (<1 hour) spotchecks made in industrial Los Angeles. This can be compared with the world background of 0.8 $\mu g/m^3$. Some atmospheric CT probably derives from water bodies where it is known to form through chlorine addition to organic solutes. The OSHA MAC for CT is 65 mg/m^3.

Conclusions: The principal "hot spots" are the one CT production plant and the two CT consuming plants mentioned above. Because of their nearness to one another, the Dow CT plant and the du Pont freon works would be logical sources to sample.

2.4.6 Chloroform

Use of this halocarbon in California commerce was not detected. The Allied Chemical plant in El Segundo did convert large quantities of chloroform to Genetron 22 up until recently. Today, laboratory use of the material is the only known application.

Like CT, chloroform is also released to the atmosphere by aqueous systems. Chlorine in drinking and reclaimed water is associated with this effect. The world background for chloroform is less than 0.2 $\mu g/m^3$, with urban levels averaging about 1.5 $\mu g/m^3$.

Conclusions: No known "hot spots" for chloroform release exist in California. Ambient or source testing for this pollutant is therefore not indicated.

2.4.7 Ethylene Dibromide (EDB)

The principal release paths for EDB are through the automobile and in its application as a pesticide. Air ambient to heavily trafficked (25,000-30,000 vehicles/day) roadways near gasoline stations averaged only 0.08 $\mu g/m^3$ of EDB for measurements taken in three cities. This is considerably lower than the world (troposphere) background for carbon tetrachloride and chloroform (0.8 and 0.2 $\mu g/m^3$, respectively).

In pesticide application, the permitted usage of EDB was recorded at 806,695 lbs for 1978. This is an increase of 57% over the previous year. An unknown but probably large fraction of this fumigant reaches the atmosphere producing acute high local levels in rural areas.

Conclusions: No "hot spots" for EDB were identified, such that point source testing does not appear warranted. Sampling for EDB under controlled or field conditions while and after being applied as a pesticide would be desirable from an industrial hygiene viewpoint.

2.4.8 Ethylene Dichloride (EDC)

The focal point for this suspected carcinogen is the Stauffer Chemical Co. plant in Carson, which synthesizes this material. Annual EDC release to the atmosphere there is estimated to be between 150 and 1600 tpy. Most of the EDC produced is converted internally to vinyl chloride. Because of the wide range in the values (resulting from somewhat disparate emission factors independently developed for the EPA) the need for source testing is emphasized.

Solvent uses of EDC in the State are limited. Total annual EDC consumption is probably around 250 tpy in this application. Only two users could be identified -- Keysor-Century, Saugus (vinyl chloride polymerization tank cleaning) and EMCON, Carmel Valley (vehicle for ceramic paste used in making electronic circuit systems). There are probably fewer than ten plants in the State using EDC in solvent applications.

Emissions of EDC, a lead scavenger, from gasoline handling and consumption processes are considered to be minor. This is also the case for its limited use in agricultural applications as a fumigant. Data for EDC ambient levels in either urban or rural areas, however, could not be found.

Conclusions: EDC emissions from the Stauffer Chemical Co., Carson plant should be monitored to determine actual release rate. A plant using EDC for solvent purposes should also be tested. Although consumption rates for such facilities are comparatively low, fractional loss is probably much higher than for other EDC-use processes.

2.4.9 Nitrosamines

The only industry (Teledyne-McCormick-Selph) associated with the possible release of an in-process, semivolatile nitrosamine (N - nitrosodimethylamine (DMN)) discontinued its use in Summer of 1978. Other sources suspected of releasing nitrosamines as a result of material decomposition (fish meal processing and the thiuram pesticides, ziram, thiram and ferbam) or combustion (tobacco, rocket fuel, boiler and motor fuels) could not be substantiated as ambient air polluters. Despite a fair number of suspected or demonstrated pathways for nitrosamine releases, the level of knowledge extant on the subject does not support the identification of any significant "hot spots" in the State.

Photochemical production of nitrosamines in the atmosphere is a proved process that warrants the investigation of the precursor emissions. These are amines and amides predominately. Feedlots, rendering plants, and various manufacturing processes, can be considered.

Atmospheric surveys for nitrosamines have been limited in number. One extensive study was, however, conducted within the South Coast Air Basin. Most samples showed no detectable ($>0.03 \mu g/m^3$) DMN or its higher homologs. The few stations that did produce measurable catches ranged up to 0.48 $\mu g/m^3$ DMN but retests always gave lower or undetectable yields.

Conclusions: Inclusion of source sampling for nitrosamines does not appear to be warranted at this time. This conclusion derives from: (1) the fact that there are no known "hot spots"; (2) the lack of knowledge as to possible mechanisms promoting secondary formation of nitrosamines from precursor substances, and; (3) the inconclusiveness of atmospheric testing for nitrosamines in California's most prone air pollution area.

2.4.10 Perchloroethylene (Perc)

Large releases of this halocarbon occur in California. Almost 60 million lbs/yr are estimated to be emitted annually by the dry cleaning (∿ 42 million lbs) and the degreaser-using (∿ 17 million lbs) industries. Losses from other sources, including perc manufacture (Dow, Pittsburg), are comparatively small. Most perc emissions occur in high density population areas from over 1300 dry cleaning establishments and 750 degreasers. Essentially all of the perc purchased by these operations is emitted to the atmosphere.

Ambient levels of perc range from about 1 to 4 ppb with a background (San Bernardino mountains) of about 0.1 ppb. Accumulation is supressed by perc's photochemical degradability.

Conclusions: If more accurate determination and mapping of perc releases is necessary, this can best be determined by accessing purchase invoices of perc users and subtracting out any solvent sent out for reclaim. Sampling vents of the Dow, Pittsburg, perc manufacturing operations will be worthwhile, particularly since the same plant also manufactures carbon tetrachloride.

2.4.11 Polycyclic Organic Material (POM)

This class of substances occurs as a pollutant adsorbed on particulate matter released from combustion or related thermal processes. Industrial uses of polycyclic organic chemicals that result in their direct release to the atmosphere in significant quantities are virtually unknown. Measurement of POM releases is frustrated by the incomplete closures of the analytical chemical (chromatographic) routines in use. This situation justifies the practice of measuring only the indicator compound, benzo [a]pyrene (BaP), but hardly solves the problem. of being unable to perform quantitative and complete compositional analysis of the POM system.

Resorting, then, to BaP data, the largest POM-emitting point source identified was the coking plant of the Kaiser steel mill in Fontana. The estimated release is 5,500 lbs/yr (BaP). Larger weights of POM are emitted by home fireplaces (16,000 lbs/yr BaP estimated) and forest fires (∿10,000 lbs/yr BaP). The former source type is, however, highly dispersed while the latter source category is probably susceptible to no more control than is currently available. Tire wear is believed to result in the release of some 3,000 lbs/yr of BaP. Motorcycles, which are predominately powered by two-cycle engines, are estimated to emit some 2,000 lbs/yr BaP. Gasoline engine automobiles emit about half that amount, even though automobiles consume over 150 times the gasoline burned in motorcycles. Diesel engined vehicles, because of their lower populations, are involved in only minor releases of BaP.

Ambient levels of BaP in 7 Southern California stations averaged 1.8 $\mu g/m^3$ with seasonal levels ranging to highs of 7.5 $\mu g/m^3$. The average can be compared with 1.2 $\mu g/m^3$ which is the National average for cities in or near which steel mills operate.

Conclusions: Characterization of POM releases from the Kaiser coking plant should be undertaken. Particulate catches should be analyzed in as much detail as practical. State of the art methodology should also be applied in the continuing efforts to characterize POM releases from Diesel and gasoline engine vehicles.

SECTION 3.0

INVENTORY FINDINGS

3.1 ARSENIC

3.1.1 Occurrence and Release Summary

A considerable number of sources for potential emissions of arsenic compounds exist. These include thermal operations in which the relatively volatile arsenic (sublimes at 615 °C.) would be released as a minor constituent of the bulk material processed, as in metal and glass production, coal and petroleum combustion, and waste incineration. A major source of potential arsenic release is the manufacture and application of arsenic-containing pesticides, both of the inorganic and organometallic types.

The levels of arsenic measured in ambient air by the National Air Sampling Network (NASN) showed an annual National average of 0.020 $\mu g/m^3$ in 1964-1965 and 0.003 $\mu g/m^3$ 10 years later (1974). The difference was probably due more to an improvement in the analytical chemistry applied than to air quality enhancement occurring. Eighteen California cities are covered by the NASN. Arsenic was reported for 1974 at Long Beach (1st Qtr. = 0.014 $\mu g/m^3$), Ontario (2nd Qtr. = 0.011 $\mu g/m^3$) and San Bernardino (3rd Qtr. = 0.006 $\mu g/m^3$). All other quarters, no arsenic was detected (limit = 0.001 $\mu g/m^3$) at these or the other 15 California cities covered by the NASN.

Researchers at Union Carbide (Ref. 1) and Versar (Ref. 2) have published their estimates of atmospheric releases or arsenic. These are compared in Table 3-1. It is interesting to note that the only gross differences occur where one of the survey groups appears to dismiss what the other regards as a fairly significant source. This is the case with petroleum combustion and nonferrous alloy production (secondary smelting).

Of the sources itemized in Table 3-1, several do not exist in the State while others are of limited number. According to the Bureau of Mines (Western Field Operations Center, Spokane), no primary smelters for copper, zinc, lead or manganese operate in California. Mining of arsenic bearing ores (zinc-lead, lead-zinc, and lead ores) is limited, with California ranked 18th out of the 23 zinc-ore producing states in the United States. Secondary lead smelters operate in California, the four major ones all being located in the SCAB.

TABLE 3-1. ESTIMATED 1974 ARSENIC EMISSIONS IN THE U.S. FROM VARIOUS SOURCES

	Arsenic Emissions, 10^3 lbs/yr	
Emission Source	Union Carbide Estimates (Ref. 1)	Versar Corp. Estimates (Ref. 2)
Mining	4	No Estimate
Primary Smelters		
Copper	5,400	10,580
Zinc	2,780	419
Lead	752	529
Iron & Steel	194	71
Nonferrous Alloys (Sec. Smelters)	Negligible	287 (Lead Alloys)
Cotton Ginning & Burning	690	391
Glass Manufacture	1,276	463
Wood Preservatives	Negligible	No Estimate
Nonpesticide Arsenicals	6	No Estimate
Pesticide Production	392	287
Pesticide Application	5,850	5,069
Coal Utilization	1,180	1,433
Incinerators	4	No Estimate
Water & Waste Water Treatment	No Estimate	2.2
Manganese Ore Processing	No Estimate	22
Petroleum Combustion	No Estimate	238
Feed Additive Production	No Estimate	4.4
TOTAL	18,536	19,795.6

Iron-steel production centers in one primary mill - - Kaiser, Fontana - - and five secondary plants all having air pollution control (APC) systems. Coal utilization predominantly involves the Kaiser plant, again, where an estimated 2.0 x 10^6 ton/yr are converted to coke. Only one firm was found that burns coal to produce steam. Two such units are operated by Kerr-McGee in Trona. Portland cement production relies on coal combustion gas to dehydrate lime. Arsenic emissions from Kerr-McGee and the cement plants are doubtless trivial, because the processes themselves preclude such releases.

In the area of glass manufacturers, a local representative of the Glass Packaging Institute advised that the use of arsenic was principally associated with lead and opal glass production. Neither of these specialty glasses is made in the State. On a recent KVB study (Ref. 3), it was found that arsenic was also incorporated into flint glass melts and that emissions of that metal from a major bottle plant were significant.

Arsenic release from water and wastewater treatment (particularly cooling) is estimated at 2200 lbs/yr nationally (Ref. 2). Most of these releases are associated with water streams in contact with the processing, sintering, and smelting of ores high in arsenic. Since these operations are not practiced in the State, the effect can be assumed absent.

Feed additive production (from cotton-seed cake) is also a source that is so minor that concern is unwarranted. This is also true, according to SRI (Ref. 4), in the case of the preservation of wood with arsenic compounds.

Because of stringent air pollution regulations, solid waste incineration in California is essentially non-existent.

Opinion on arsenic release associated with petroleum (primarily residual boiler fuels) combustion is divided. In the case of Versar's estimates, this source furnishes 5% of the total arsenic atmospheric burden. This could amount to a much larger fraction for California, since some of the major sources of arsenic emissions tolerated elsewhere do not contribute to the total burden here. Thus, studies are needed to determine what magnitude of arsenic emissions are actually produced by such sources.

Agriculture comprises the major source of potential arsenic emissions in California. In 1978, 101 tons of arsenicals were applied in California. Most of it was applied for the top defoliation of cotton plants. Thus, the emission of arsenic from the State's 233 cotton gins (Ref. 4) comes to question. These devices broadcast considerable particulate matter, which would still retain residues of the arsenical defoliants, if these were previously applied to the cotton plant matter being ginned.

Other published information to the contrary (Ref. 4), manufacturers of agricultural arsenicals is confined to one plant in California -- the Los Angeles Chemical Company of South Gate. This company produces only sodium arsenite, a material in limited usage by California grape growers.

In summary, then, attempts to identify specific arsenic emission sources will therefore focus on the following operations:

- Pesticide application and secondary mobilization (cotton ginning)
- Primary steel mill (coking)
- Secondary steel and lead production
- Oil combustion
- Pesticide manufacture
- Glass Manufacture

3.1.2 Emission Factors

A. Pesticide Application and Secondary Mobilization--

1. Data Source--the pesticide usage data tabulated in this section and the sections dealing with carbon tetrachloride, ethylene dibromide and ethylene dichloride were extracted or derived from:

- 1978 Pesticide Use Report (PUR)
- Pesticide Use Report By Commodity 1978

These publications are prepared and issued annually by the Pest Management, Environmental Protection and Worker Safety Division (Pesticide Registration and

Agricultural Productivity) of the California Department of Food and Agriculture.

County breakdowns of pesticide usage by commodity are not available from the PUR. These were obtained by conducting manual searches of the computer printouts made available at Sacramento by the Pesticide Registration Office.

Data presented in this report that are derived from the PUR or the printouts just mentioned do not furnish total usage. As the PUR itself points out, "uses of restricted materials [all considered in this report are of that category] requiring a permit..., this report reflects approximately 85% of total usage". Other sources have estimated the usages shown in PUR for this category (restricted and requiring permit) to be as low as 52% of actual. This was considered highly unlikely by Pesticide Registration personnel.

In this report, PUR data are used without application of correction factors. The intent was to first dimension releases, then determine what, if any, factors would be appropriate to use.

2. Pesticide application--The amounts of arsenicals applied to California crops during 1978 are shown in Table 3-2. Of the combined amount of all types of arsenicals employed, 64.3% was applied to cotton, 10.4% to grapes, 7.7% to highway weeds, and the balance of 17.6% to a mix of dispersed receptor sites. Use of arsenic acid, arsenic trioxide, calcium arsenate, lead arsenate and sodium arsenate was trivial. No use of arsenic trichloride, calcium or copper arsenite, copper arsenate, Paris green, or zinc arsenate was reported. This is also true of arsine, which erroneously has been called a pesticide by at least one author.

TABLE 3-2. ARSENICALS USED IN CALIFORNIA AGRICULTURAL ACTIVITIES DURING 1978*

	Total Used Lbs	Acres
ARSENICAL		
Arsenic Acid, total	33	-
Arsenic Trioxide, total	0.01	-
Cacodylic Acid		
Cotton	11,558	111,740
State highways	1,465	-
Various small users	2,304	24
Total	15,327	11,764
Calcium Arsenate		
Avocado	44	34
Grapefruit	75	124
Lemon	37	17
Orange	578	597
Strawberries	104	52
Tomato	62	31
Various small users	362	-
Total	1,262	855
Disodium Methanearsonate (DSMA)		
Cotton	40,207	19.248
State highway	1,212	-
Various small users	1,027	150
Total	42,446	19,398
Lead Arsenate (Standard)		
Grapes	15	8
Other	7	-
	22	8
Monosodium Methanearsonate (MSMA)		
Cotton	10,267	5,329
Citrus	1,077	596
State highways	5,460	-
Turf	958	334
Nonagricultural areas	627	242
Irrigation districts	4,386	-
Agr. commissioners	5,611	-
Other agencies	2,137	-
Various small users	3,569	-
	34,092	6,496
Sodium Arsenate		
Grapes	240	20
Sodium Arsenite		
Grapes	20,539	3,743
Small users	195	-
Total	20,734	3,743
Sodium Cacodylate		
Cotton	67,761	111,740
Agr. commissioners	2,996	-
Flood control	2,903	-
City agency	1,023	-
Other agencies	1,962	-
School districts	1,756	-
State highways	7,394	-
Various small users	2,149	24
Total	87,854	111,764

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* Source: "1978 Pesticide Use Report" California Department of Food & Agriculture

Application of arsenicals in quantities over 5,000 lb/yr occurred in only seven of the California counties. These counties and their usage of arsenicals are enumerated in Table 3-3.

The total weight of arsenicals used in these seven counties (158,305 lbs) amount to less than 0.25% of the National consumption, usage being heavily centered in Texas and Oklahoma cotton areas. Emissions from the application of arsenicals are set at about 10% of the amount applied (Ref 2). This figure appears to be high, since none of the compounds in question are appreciably volatile. Cacodylic acid (m. pt - 200 °C) would exhibit the highest vapor pressure of any of the major arsenicals employed in the State. This is in the micrometer range of mercury pressure according to a spokesman of the Vineland Chemical Company, a New Jersey firm making this and other arseno-organics. Arsenic emissions associated with pesticide applications are thus likely to be predominately the aerosol drift occasioned during the actual spraying of the fields. Subsequent releases are probably at such low rates as not to be of concern beyond the immediate perimeters of the receptor crop fields.

Most of the arsenic pesticides are applied to cotton (64.3%) and grapes (10.4%), the balance of spraying being for dispersed targets. Based on the estimates offered by University of California agronomists, a drift loss of 5% of the amount applied was assumed. Spray equipment dealers felt that 2% was a maximum loss value and that very little of this drift could possibly ever survive as an atmospheric hazard.

In any case, factoring the 5% drift loss with application rates given in Table 3-3 for the seven counties of interest, the following acute release data were calculated.

ESTIMATED ACUTE RELEASE FACTORS FOR ARSENICALS, TOTAL GRAMS/ACRE

Cotton				Grapes
Cacodylic Acid	DSMA	MSMA	Sodium Cacodylate	Sodium Arsenite
2.3	44.7	45.8	13.4	130.9

TABLE 3-3. COUNTIES USING OVER 5000 LBS ARSENICALS IN AGRICULTURAL APPLICATIONS DURING 1978*

ARSENICAL Application	lbs - Acres		Totals lbs - Acres	
A. FRESNO COUNTY				
Cacodylic Acid				
Cotton	4,701	40,349	4,701	40,349
DSMA				
Cotton	1,237	776	1,237	776
Lead Arsenate				
Grapes	15.2	8		
Other	14	-		
Total			29	8
MSMA				
Cotton	797	545		
Oranges	182	216		
Other	7	-		
Total			986	761
Sodium Cacodylate				
Cotton	27,562	40,349		
Other	7	-		
Total			27,569	40,349
Sodium Arsenite				
Grapes			8,955	1,834
	County Totals		43,477	84,077
B. IMPERIAL COUNTY				
Cacodylic Acid				
Cotton	572	4,373		
Other	104	-		
Total			676	4,373
DSMA				
Cotton	816	468	816	468
MSMA				
Cotton	1,373	718		
Other	2,174	-		
Total			3,547	718
Sodium Cacodylate				
Cotton	3,354	4,373		
Other	602	-		
Total			3,956	4,373
	County Totals		8,995	9,932
C. KERN COUNTY				
Cacodylic Acid				
Cotton	3,440	36,121		
Other	145	-		
Total			3,585	36,121
DSMA				
Cotton	23,871	10,340	23,871	10,340
MSMA				
Cotton	6,831	3,454		
Other	1,394	-		
Total			8,225	3,454

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* Source: California Department of Food & Agriculture

TABLE 3-3 (Continued)

ARSENICAL

				Totals	
Application	lbs	Acres		lbs	Acres
MSMA					
Cotton	469	121			
Other	340	-			
Total				809	121
Sodium Cacodylate					
Cotton	5,469	9,859			
Other	22	-			
Total				5,491	9,859
Sodium Arsenite					
Grapes	-	-		1,564	189
			County Totals	10,729	21,147
G. TULARE COUNTY					
Cacodylic Acid					
Various agencies	-	-		368	-
Calcium Arsenate					
Oranges	-	-		20	40
DSMA					
Cotton	3,950	1,185			
Other	262	-			
Total				4,212	1,185
MSMA					
Cotton	247	170			
Grapefruit	4	10			
Other	4,698	-			
Total				4,949	180
Sodium Arsenite					
Grapes	-	-		1,460	277
Sodium Cacodylate					
Cotton	1,992	3,604			
Other	165	-			
Total				2,157	3,604
			County Totals	13,166	5,286

TABLE 3-3. (Continued)

ARSENICAL Application	lbs	Acres	Totals lbs	Totals Acres
Sodium Arsenite				
Grapes	-	-	911	175
Sodium Cacodylate				
Cotton	20,171	36,121		
Other	847			
Total			21,018	36,121
County Totals			57,610	86,211
D. KINGS COUNTY				
Cacodylic Acid				
Cotton	583	6,848		
Other	2	-		
Total			585	6,848
DSMA				
Cotton	-	-	4,172	2,767
MSMA				
Cotton	292	226		
Other	15	-		
Total			307	226
Sodium Arsenite				
Grapes	-	-	52	10
Sodium Cacodylate				
Cotton	3,419	6,848		
Other	8	-		
Total			3,427	6,848
County Totals			8,543	16,699
E. MADERA COUNTY				
Cacodylic Acid				
Cotton	857	9,272		
Other	41	-		
Total			898	9,272
DSMA				
Cotton	4,043	2,484		
Other	136	-		
Total			4,179	2,484
MSMA				
Commissioners	-	-	2,580	-
Sodium Cacodylate				
Cotton	5,023	9,272		
Other	105	-		
Total			5,128	9,272
County Totals			12,785	21,028
F. MERCED COUNTY				
Cacodylic Acid				
Cotton	933	9,859		
Other	4	-		
Total			937	9,859
DSMA				
Cotton	-	-	1,928	1,119

Applying the actual usage values to the total acreage involved, the distributions of material released can be geographically organized as shown in Figure 3-1. Because of the size distribution of the aerosol involved, durations of airborne pesticide releases are probably very brief. Also, application to produce defoliation is undertaken in any given area no more than once a year.

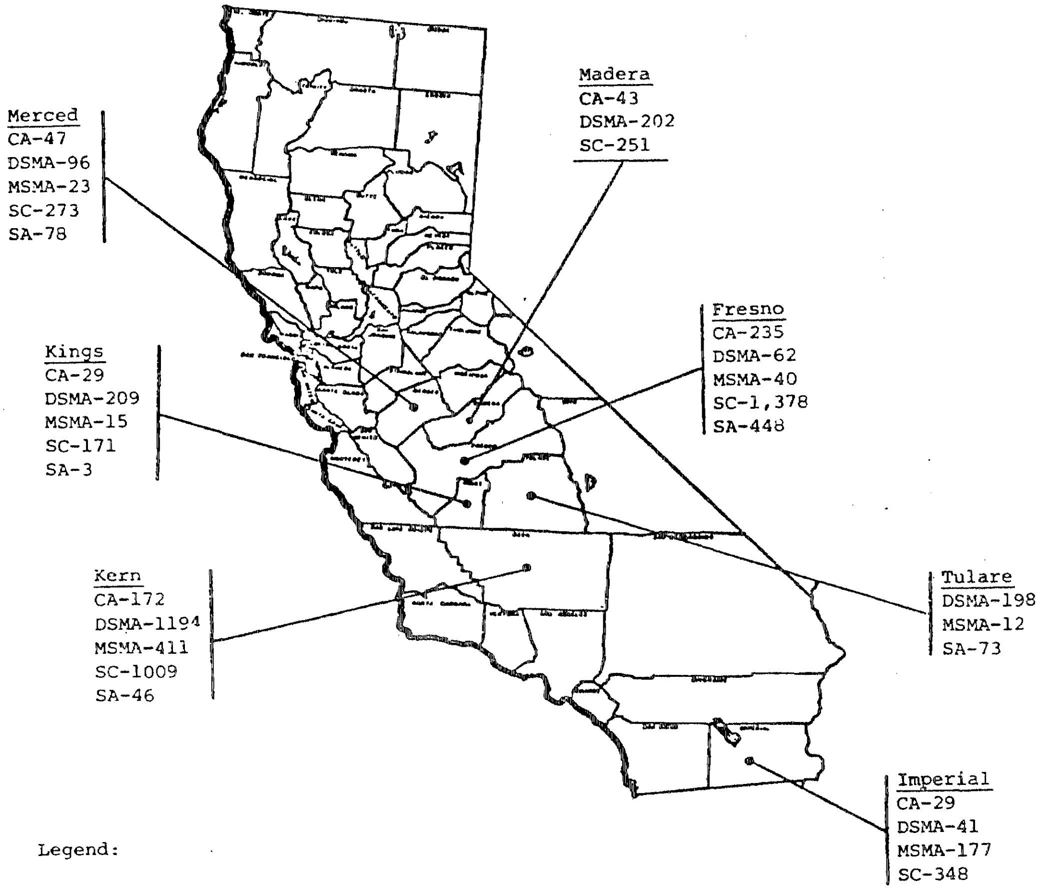
3. Secondary Mobilization of Arsenical Spray Residues--Cotton ginning and the inceration of gin trash become sources for arsenic release if the gin input material had been contacted with arsenicals while in the field. In California, gin-trash burning occasionally occurs illicitly, but most trash is returned to the fields and plowed under. There are 233 operating gins in California according to listings obtained from the three Cotton Division offices of the USDA Agricultural Marketing Service.

Particulate emissions from well-controlled gins have been estimated at 2.6 lbs/bale by EPA's Youngblood (Ref. 5). A Texas Air Control Board spokesman advised that arsenic levels as high as 0.7% have been measured in gin dust in that State. This would suggest an arsenic release as high as 0.02 lb/bale.

Youngblood's particulate emission factor was checked to determine its appropriateness with State gins. Using Imperial County as the site having the most normal weather in 1978, production of individual gins were obtained and compared with the particulate release rates on file with the local APCD. With seasonal throughputs for 10 of the 13 gins operating there, it was calculated that the average emission of particulate was 2.7 lbs/bale. This value, which agrees very well with Youngblood's, included extremes of 1.3 and 4.5 lbs/bale.

Excepting the Texas value, data on the arsenic content of gin feed or emissions were not found. It was apparent from the usage rate of arsenicals that the value would have to be quite low. According to the USDA Agricultural Marketing Seravice (Cotton Division), cotton defoliation in California is predominately done using nonarsenicals, notably Paraquat and DEF.

A preliminary scenario was therefore tested. Data for Fresno



Legend:

Cotton Defoliants

CA - Cacodylic Acid
DSMA - Disodium Methanearsonate
MSMA - Monosodium Methanearsonate
SC - Sodium Cacodylate

Grape Crops

SA - Sodium Arsenite

Figure 3-1. Estimated release by drift of arsenicals (in pounds) applied to agricultural areas in seven California counties in 1978.

County, the largest cotton producer (252 million lbs) and largest applier of arsenicals on cotton (34,297 lbs), were used. It was assumed that all the arsenicals applied eventually went into the gin. The elemental arsenic content (47.7%) was derived from the usage data for the four arsenicals used in Fresno County (predominately sodium cacodylate). The calculated arsenic input was then distributed over the mass of input material, of which about 30% typically results as the baled lint. The balance is seed, trash, and moisture. An arsenic content of only 6.5×10^{-3} wt % is calculated.

Further, it was assumed that the dust emitted to the atmosphere from the gin's cyclone had the same composition as the feed material. Then, given the particulate emission factor of 2.7 lbs dust/bale produced (from 504,000 bales) the total arsenic release for all the Fresno County gins in 1978 was found to be 88 lbs. Thus, gins may be dismissed as arsenic sources here.

B. Primary Steel Production--

According to the Versar report (ref. 2), arsenic is emitted during the basic ore reduction process (13.2 tons/yr) and later (22.0 tons/yr) during casting operations. In the case of the ore reduction, an APC* efficiency of 99% was assumed. These data are for the National steel industry.

The only integrated steel plant in California is the mill at Fontana operated by Kaiser Steel, Inc. According to a company spokesman, Kaiser's output of steel and iron products was just under two million tons in 1978. This represents about 2.1% of the national production, so the arsenic emission factor for ore working (555 lbs) and iron casting (925 lbs) would be 1,480 lbs/yr, based on the Versar release data cited above.

Arsenic emission from coal coking are dismissed by the Versar authors because low-sulfur coal is used for this process. It was assumed that the arsenic content was more or less at a constant ratio with respect to sulfur level. Western coals contain only about 18% of the arsenic considered average (5.44 ppm) for all American coal (Ref. 2). Yet, 1.0 ppm is sufficiently high in terms of masses involved to warrant consideration. Using the arsenic

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* Air Pollution Control

release rate associated with coal combustion (Ref 2), an additional 1,635 lbs of arsenic are calculated. This is based on Kaiser's coal capacity 2,336,000 tons/yr containing 1 ppm arsenic, 35% of which is released to the atmosphere.

The overall emission factor for the Kaiser Fontana plant is thus estimated as follows:

ESTIMATED ARSENIC EMISSIONS FROM THE KAISER STEEL MILL, FONTANA

	Iron Ore Reduction	Foundry Operations	Coking	Total
Total Arsenic Emitted, lbs/yr	555	925	1635	3115

C. Secondary Metal Processing--

1. Steel Mills--Besides the Kaiser plant, five other mills are operated in the State that work scrap and pig iron. These secondary mills together with their estimated outputs (furnished by an industry representative) are itemized as follows:

Company	Location	Estimated 1978 Output, 10^3 tons
Bethlehem Steel	Vernon	400
U.S. Steel	Torrance	100
Soule Steel	Carson	110
Ameron	Etiwanda	300
Judson Steel	Emeryville	90

Because these mills do not process coke or iron ore, arsenic release would be associated only with pig iron usage. This burden was estimated at 26,500 lbs for the nation in the Versar report. Considering the production fraction of the National total represented by the five secondary plants, an annual release of only 279 lbs arsenic total is calculated for all five mills.

2. Secondary Lead Smelters--With the exception of scattered, much smaller smelters, four secondary lead plants essentially represent that industry in California. These are listed together with production figures which represent rough estimates furnished by the technical manager of one of the smelters.

SECONDARY LEAD SMELTERS IN CALIFORNIA

Company	Location	Estimated Annual Lead Production, 10^3 Tons
Gould Inc.	Vernon	50
RSR Corporation	City of Industry	7.5
Southwest Smelting	San Bernardino	5
ALCO-Pacific	Carson	5
	Total	67.5

Much of the lead scrap processed by these smelters, all of which operate blast and/or rotary furnaces, is antimonial lead. This alloy contains up to 0.5% arsenic. For such feed, SRI (Ref. 4) speculates that arsenic emissions may be about the same as for primary lead smelters. The emission factor imputed to the latter, is 0.88 lb/ton including fugitive emissions at 10% of the amount released from the stack (Ref. 6). From this, one could infer that the above four smelters are responsible for a combined arsenic release of 59,400 lbs arsenic per year. This, however, is based on uncertain technical information since there is relatively little arsenic data for secondary lead smelters. Clearly, source testing will clarify this situation.

Considering the above emission factor as an estimated maximum, the calculated releases for the four plants are geographically located on Figure 3.2.

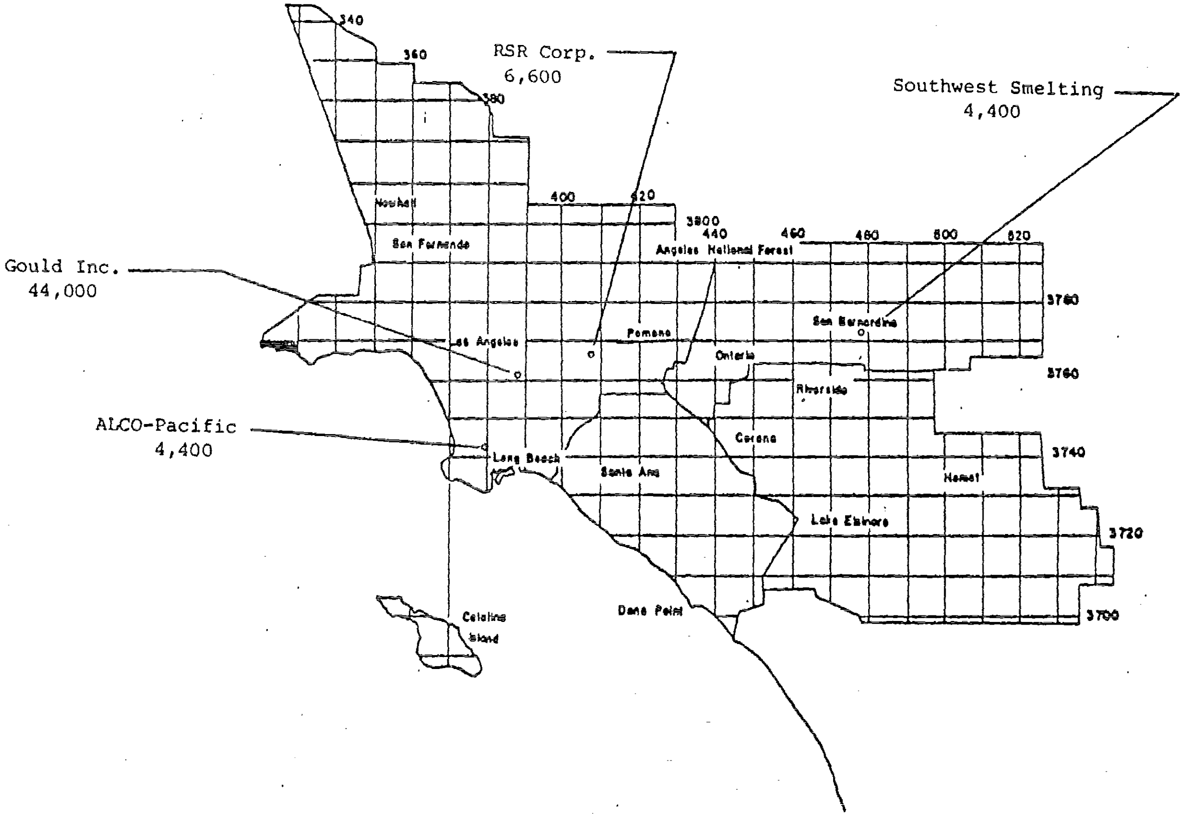


Figure 3-2. Estimated maximum arsenic releases (lbs/yr) from California secondary lead smelters.

D. Oil Combustion--

Consideration of naturally occurring arsenic in combusted fuel oils led the Union Carbide and Versar analysts to disparate conclusions (Ref. 1,2). The former regarded the arsenic emissions associated with this process as insignificant. The Versar associated an annual National release of 2.36 x 10^5 lbs/yr from fuel oil combustion.

The Versar estimate was based on an average arsenic level of 0.14 ppm in crude oil processed in this country. That arsenic concentration fortuitously happened to be based on analytical data obtained for California crude. They then pointed out that of the 1.85 x 10^{12} lbs of crude processed in 1974, 90.1% was combusted as fuel. They further assumed that all the arsenic present in the oil was emitted in some form or other to the atmosphere.

Updating the Versar data from 1974 to 1978 at an assumed increase in oil consumption rate of 6%, current national demand would be about 2.33 x 10^{12} lbs/yr in 1978. Burning 90.1% of this would release some 0.3 x 10^6 lbs of arsenic, according to Versar.

Because of the comparative volatilities of petroleum hydrocarbons and the arsenic compounds present, processing of crude should tend to concentrate most, if not all, of the arsenic into the residual oil, asphalt, and coke produced. Thus arsenic emissions would have to be associated with only those of these products (as well as any unprocessed crude) that are combusted. It can be assumed that asphalt and coke are accounted for in the unburned or 9.9% fraction of the petroleum product pool. Thus, if California's share of the national arsenic burden is 10%, some 30,000 lbs would be involved in the combustion of nondistillate fuel oils.

The consumption of residual fuel oils in California during 1977 was dominated (73%) by the utility companies. Data on sales of this commodity obtained from a DOE spokesman are tabulated as follows:

TABLE 3-4. RESIDUAL FUEL OIL SALES IN CALIFORNIA DURING 1977
(Source: Dept. of Energy, Washington, D.C.)

User Category	Fuel Purchased, 10^3 Bbls.	Vol % of Total
Space Heating	2,540	1.4
Industry	3,941	2.2
Oil Companies	5,349	2.9
Railroads	9	-
Vessel Bunkering	35,893	19.9
Military	343	0.2
Electricity	132,555	73.4
Miscellaneous	54	-
Total	180,684	100

Actually, the utilities purchased 4.2% more fuel than they burned in 1977, but that difference has been absorbed since then by increased power demand.

The electrical utilities and maritime trade consume over 93% of the residual fuel oil purchased in the State. Focus therefore rests on the power plants, since most of the maritime fuel use occurs on the high seas. Thus, 73.4% of the arsenic imputed to California oil (30,000 lbs), or some 22,020 lbs, would be going into utility-class boilers. It is moot whether all of this is emitted as Versar (Ref. 2) estimates, however. Estimates for arsenic emissions from coal are about 27% of the arsenic input (Ref. 4). This would average out somewhere around 80% if the bottom ash were hypothetically mobilized. The arsenic retained apparently condenses on surfaces in the flue path and could be assumed to do this regardless of the fuel used. The value of 80% was therefore applied to oil combustion, where the soot is effectively all mobilized. This would suggest a release of 17,600 lbs arsenic per year or an emission factor of 0.13 lb arsenic per 1000 bbl residual fuel fired.

This emission factor clearly implies an arsenic content that is higher than 0.14 ppm typical of California crudes. As pointed out earlier, however, it is assumed that in the production of a residual oil from a crude, arsenic does not volatilize and, thus, tends to remain in the process bottoms. This would then raise the arsenic level in the residual oil and exclude it from the distillates produced.

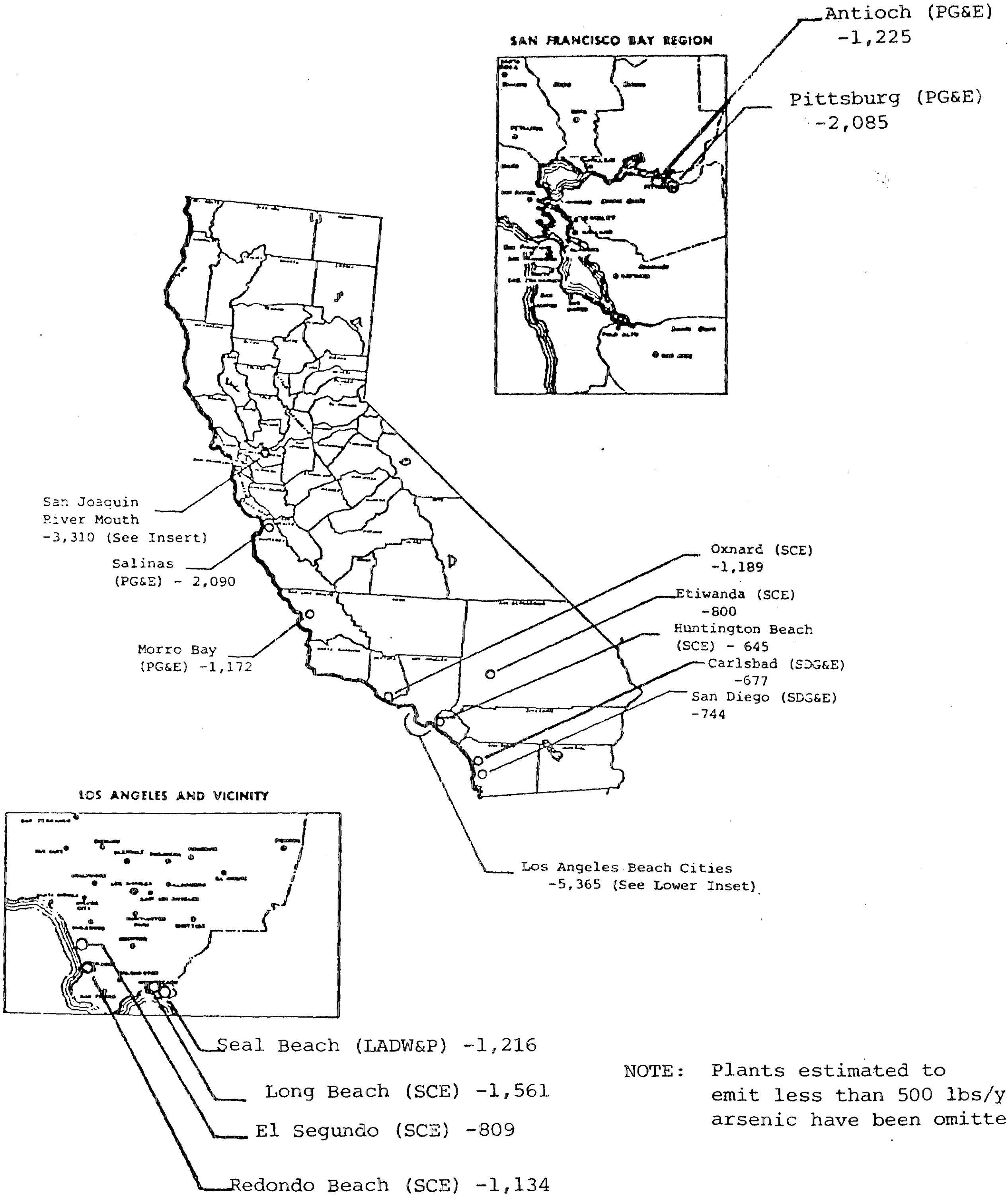
Distribution of the estimated 17,600 lbs arsenic released by power plants is shown in Figure 3-3. This distribution is prorated on the basis of electricity production for 1977 (according to "Electrical World"). Contributions to the total power produced, 88.1 x 10^9 kw-hr, by natural gas and jet fuel were assumed to be evenly distributed. Plants estimated to be emitting less than 500 lbs/yr of arsenic are not shown.

E. Pesticide Manufacture--

According to SRI's Suta (Ref. 4), there are three manufacturers of arsenical pesticides in California. Two manufacture arsine at three plants (Airco, Santa Clara,and Matheson Gas Products, Cucamonga and Newark), while the third, Los Angeles Chemical Co., South Gate, produces seven different arsenicals.

It was found that Airco and Matheson purchase arsine from East Coast sources and dilute the gas for resale to electronics manufacturers who use the material in the production of light-emitting diodes and other arsenide-doped solid state devices. The amounts of arsine used in this application are minor but, more importantly, releases must be negligible. Waste gas is passed through chemical scrubbers where the labile hydride is destroyed under very high reaction velocities. The same practice is observed at Airco and Matheson with returning arsine cylinders from which the residual gas must be removed. It is thus believed that this use of an arsenic compound, however volatile, does not entail significant emissions.

In the case of the Los Angeles Chemical Co., only one of the seven arsenicals associated with their product line is still produced there. This is sodium arsenite. Most of the other compounds, calcium arsenate and arsenite, lead arsenate and Paris green have not been produced there in five or more years. Production of arsenic acid was halted recently while cacodylic



NOTE: Plants estimated to emit less than 500 lbs/yr arsenic have been omitted.

Figure 3-3. Estimated arsenic emissions associated with utility-class steam generators (lbs/yr).

acid was never made there, only jobbed. The production of sodium arsenite may also be discontinued in the near future. Although the Los Angeles Chemical Company spokesman who provided the information given here declined to offer production data, the use of sodium arsenite in the State (20,539 lbs in 1978) would not suggest a major market. Since most (99.0%) was applied to grape vineyards for an agricultural industry in which California is nationally dominant, company out-of-state sales of the arsenite were probably minor.

Assuming that Los Angeles Chemical's sodium arsenite production amounted to half of what was consumed in the State, and 1% of that were emitted, the annual release (59 lbs as arsenic) would still be equivalent to that estimated for a small power plant. Suta (Ref. 4) estimates the releases for this firm at 50 to 2000 lbs/yr depending on the (undetermined) degree of APC being practiced. This estimate, however, is based on an erroneous product line of seven arsenicals, as discussed above.

F. Glass Manufacture--

On a recently completed CARB-sponsored program (Ref. 3), KVB sampled two glass plants. The names of the owners are confidential. Plant A (test 20J) operated side-port continuous, regenerative furnaces and incorporated APC equipment on the units tested. Arsenic release was insignificant from the ESP[*] controlled units. At that plant, uncontrolled units were also operated and produced flint glass. These were not tested.

Plant B (tests 28S, 35S, and 35J) employed end-port fired units that were not controlled. The plant output is over 110 tons/day of glass products. Arsenic was added to the flint glass melts. Plant B operated four units, one of which was tested by KVB three times. This unit was melting for flint production. The particulates emitted averaged 10.3±0.4 lbs/hr. The arsenic content of the particulate catches averaged 2.6%.

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[*] Two sampling trains were used simultaneously to sample the inlet and exit of the ESP. A trace of arsenic was found but only in the 1μm cyclone and filter of the inlet sampler.

In Plant B, two of the four units were running flint melts. Although the fraction of flint glass produced was not specified, it was probably greater than 50%. Using that fraction nonetheless, the annual arsenic output from Plant B would then be calculated to be 4,690 lbs/yr.

Because of the confidentiality of these data, a mapping of glass plants will not be attempted. The CARB is, of course, aware of the identities of these plants and their locations.

G. Coal-Fired Facilities--

1. Kerr-McKee Trona Works--This facility operates two boilers (each rated at 600,000 lbs/hr steam) for the production of plant electricity, process steam and high-SOx flue gas that is also needed for the process. The units are fired with a mixture of coal and high sulfur petroleum coke. The SOx and CO_2 in the flue gas is removed by contacting it with Trona brine to induce the preciptation of sodium carbonate. SOx removal is better than 98%. It is thus highly unlikely that any arsenic could penetrate this effect.

2. Cement plants--Combustion gas from coal-fired furnaces are used to decarbonate limestone in countercurrent kiln flow. Thus all the volatiles and particulate matter in this gas stream is heavily contacted by this assorptive counterflowing process. Then, at the cooler sections of the kiln, the moist combustion gas, laden with elutriating lime fines, is passed through a bag house to remove the latter. It is thus again quite unlikely that arsenic released by the fired coal could survive to vent.

In any case, what are believed to be the seven largest cement plants in California were identified. These are:

Company	Location
Riverside Cement Company	Riverside
Monolith Portland Cement Company	Tehachapi
Southwestern Cement Company	Victorville
General Portland Cement Company	Mojave
General Portland Cement Company	Colton
Calaveras Cement Division, Flintkote	San Andreas
Kaiser Portland Cement Company	San Jose

3.2 ASBESTOS

3.2.1 Production-Usage Summary

California has some of the richest deposits of asbestos in the Nation (see Figure 3-4). These are occluded principally in serpentine rock strata, which yield the commonest form of commercially usable asbestos, chrysotile. Production of asbestos in the State reached 78,390 tons in 1978, which is a major fraction of the National output. This represents a drop of about 40% from the 1966 annual production. This reduced demand reflects an on-going trend to replace asbestos with safer materials. The dynamics of the situation can be seen in the marked changes in the distribution of asbestos within the various product areas (see Table 3-5).

Five asbestos mines have operated in California, of which two now have been closed down. The remaining three mines and the estimated annual production furnished by mine executives are tabulated as follows:

Company	Mine Location	Approx. Annual Asbestos Output, 10^3 Tons
Atlas Asbestos Co.	Coalinga	15-20
Calaveras Asbestos Co.	Copperopolis	32-36
Union Carbide Corp.	King City	22-31

The Copperopolis mine is the largest asbestos producer in the U.S. All three facilities have extensive APC systems that have been tested by EPA teams. All three facilities are regularly visited by APCD inspectors (as well as OSHA and Bureau of Mines representatives).

Asbestos is used in over 4000 different applications. Plants handling and producing such materials must protect workers by reducing air levels below two fibers of asbestos per cc of air breathed. The National Emissions

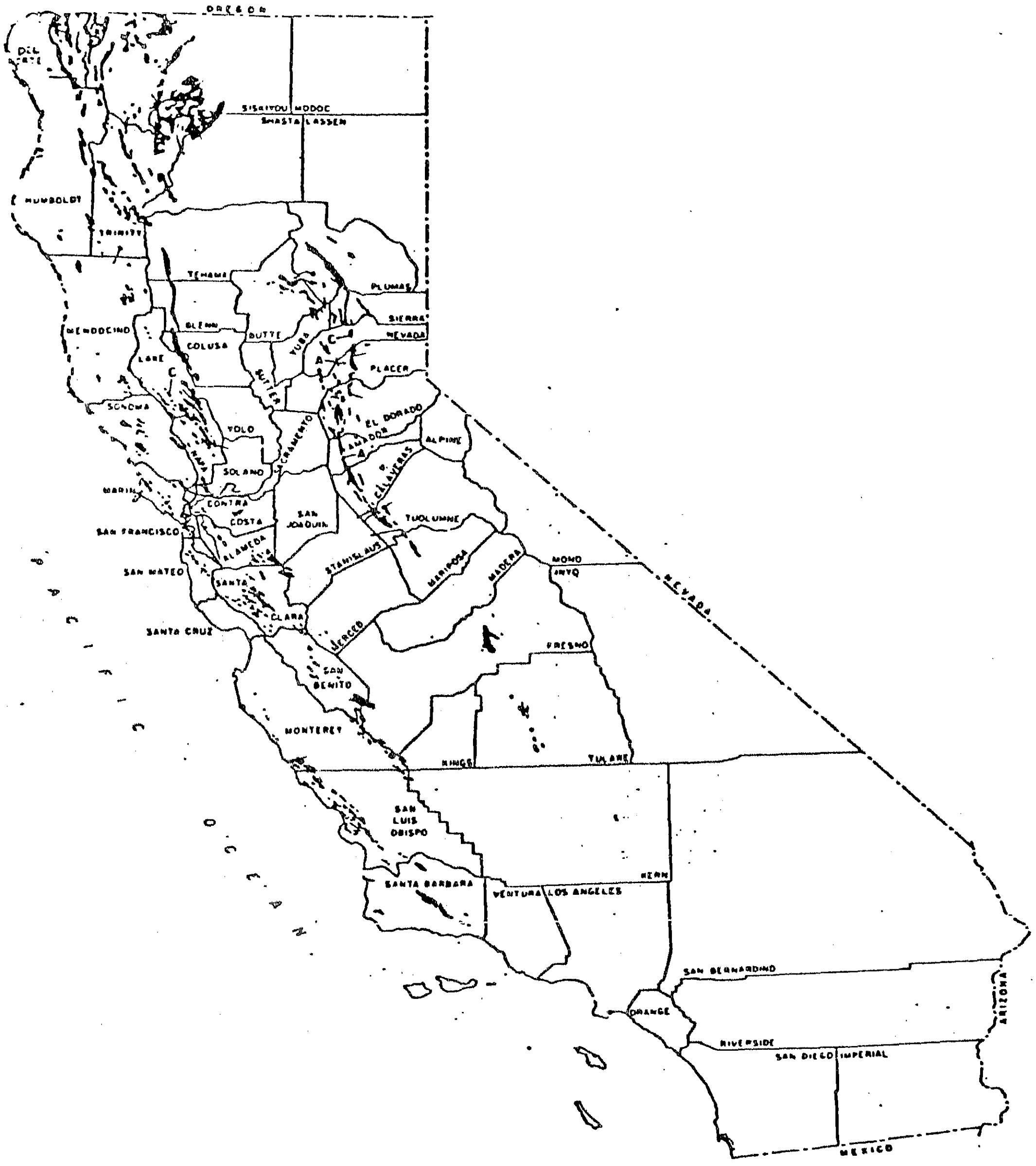


Figure 3-4. Map of California showing principal asbestos deposits (source: U.S. Bureau of Mines)

TABLE 3-5. NATIONAL MARKET AREAS FOR ASBESTOS: DEMAND CHANGES OVER TWO YEAR PERIOD

Product(s)	Asbestos Use, Percent of Total	
	1976	1977
Asbestos Cement Pipe	25	19
Flooring Products	22	16
Friction Products	11	9
Paper	11	4
Roofing Products	8	35
Asbestos Cement Sheet	7	3
Packing & Gaskets	35	3
Insulation	1	1
Textiles	1	1
Other	11	8

Source: U.S. Bureau of Mines, "Mineral Commodity Summaries 1977 and 1978"

Standards for Hazardous Air Pollutants, (NESHAP - Code of Federal Regulation Part 40, Sec. 6122) requires that any vents from such works exhibit no visible emissions. Thus, industrial operations involving the conversion of asbestos into marketable products is under the control of specific State and Federal regulations, unlike other of the hazardous substances considered here.

Activities involving asbestos released that are not controlled or may not be amenable to complete control (in accordance with NESHAP) are limited. In the latter category are mining (but not the associated milling) operations. In the former are: (1) demolition of buildings containing fire proofing or acoustic and/or thermal insulation; (2) the periodic maintenance of industrial facilities incorporating such materials; (3) activities promoting erosion (natural or man-made) of asbestos-bearing open land structures; and (4) the disposal of asbestos-containing solid wastes at land fill sites. These categories were developed as a consensus of the views expressed by the following individuals contacted by the project:

- Dr. W. M. Nicholson, Director
  Environmental Health Laboratory
  Mt. Sinai Hospital, N.Y.

- Robert Fowler, Associate Director
  Western Institute of Occupational and Environmental Sciences, Inc.

- R. W. Mason, Chief
  Research & Quality Assurance Branch
  USEPA Region II, Edison, N.J.

3.2.2 Emission Factors

A. Mining and Milling Operations--

Release of asbestos dust in mining and milling was largely associated with the latter activity. Figure 3-5 shows the typical elements of the milling process. Under uncontrolled conditions, milling is estimated to release 100 lb asbestos for every ton of asbestos output. All other uncontrolled operations (mining, loading, hauling, unloading - or collectively, "mining") amounts to less than 10% of that release (Ref. 7). In reaction to economic incentives to reduce such losses and with the later institution of NESHAP, milling operations have come under more effective control, which is achievable considering the configuration and confinability of the process.

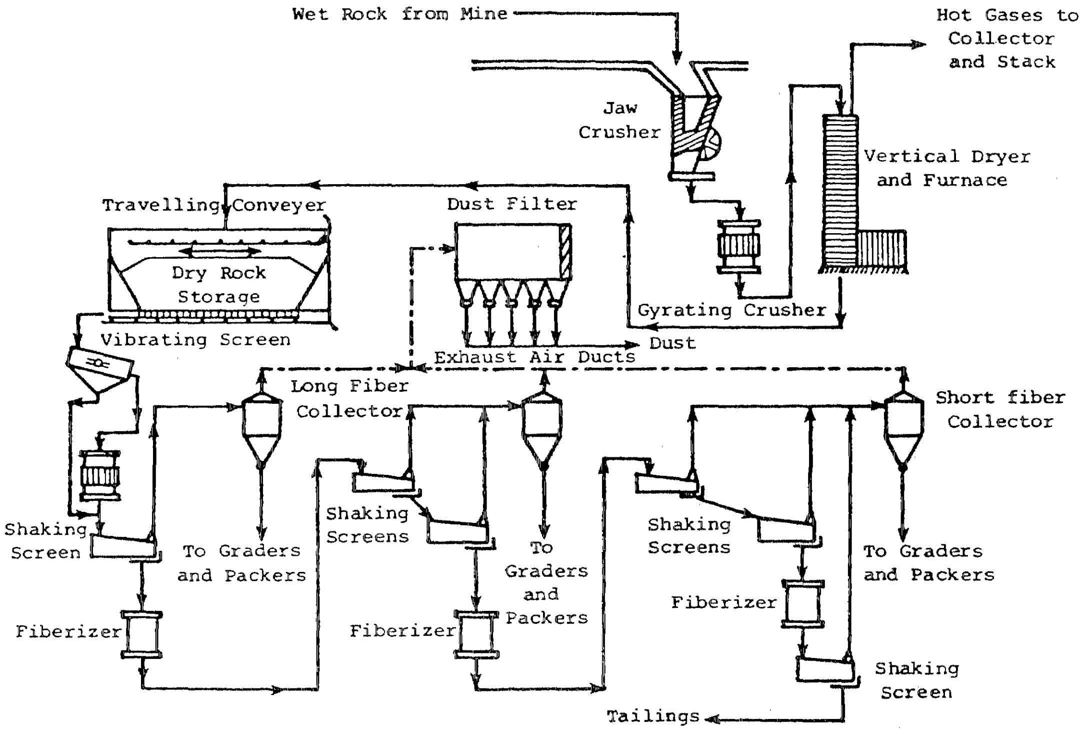


Figure 3-5. Flow diagram for typical asbestos mill.

The mining phases of asbestos production are not similarly amenable to control since many stages are carried out in the open. The EPA report cited above estimates emissions under 50% control conditions for all mining operations to be 5 lbs per ton of product. This would be equivalent to emissions in the amount of 196 tons per year based on the 1978 output from the three asbestos production facilities in the State. It would probably be much closer to the truth, however, to reckon that control is nearer 90%. This estimate would still imply asbestos emissions of 39 tons/year.

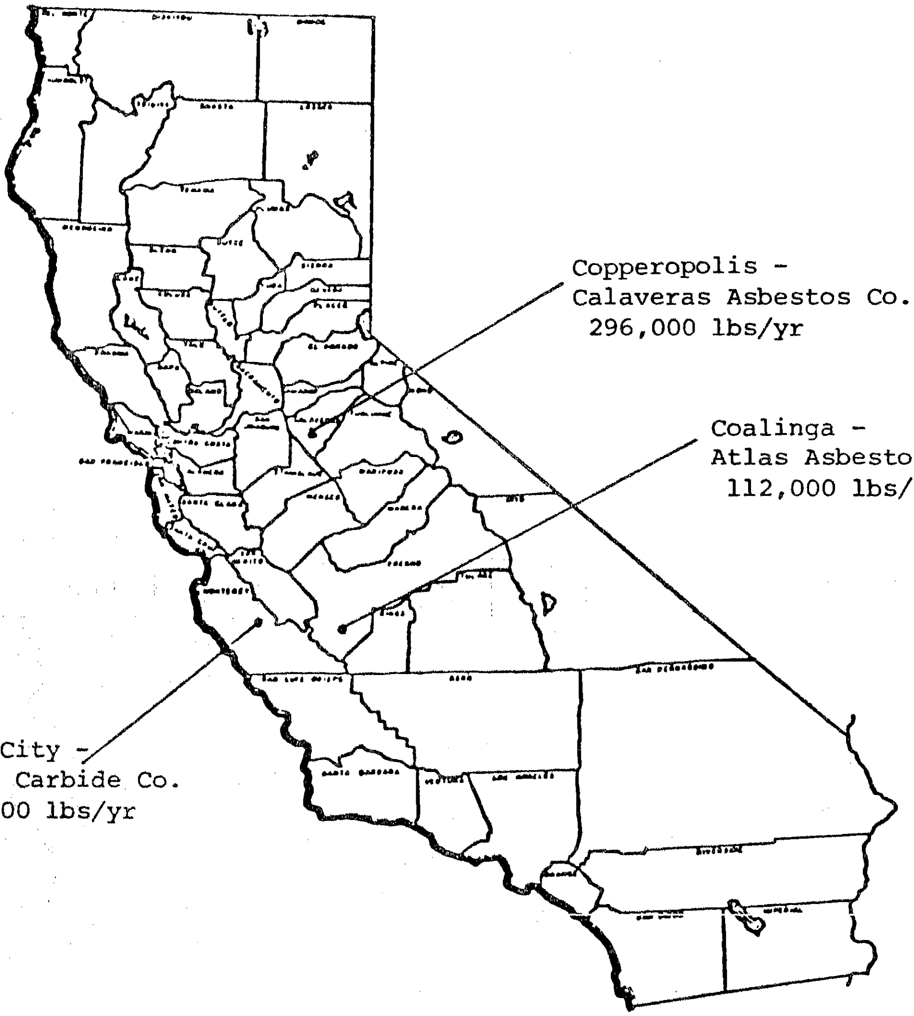
Monitoring efforts in the vicinities of the asbestos mining and milling operations unfortunately tend to predate the upgrading of APC capabilities of the California asbestos mines. John (Ref. 8), however, has published fairly recent data for atmospheric levels near the Union Carbide asbestos mine/mill at King City. Asbestos concentrations ranging from 6,000 to 1,600,000 fibers/m^3 downwind and 200 to 1,000 fibers/m^3 upwind were measured. The maximum downwind value, which is equivalent to 1.6 fibers/cc, approaches the OSHA MAC to 2.0 fibers/cc/. The latter, however, is a time-weighted-average (twa) for an 8-hour work shift. The twa equivalent for the ambient release downwind of Union Carbide may have been considerably lower than 1.6 fibers/cc but then the duration of the release is typically over three shifts, 5 days per week. Additional testing at these sites is clearly suggested.

The emission factors obtained from the EIS are shown in Table 3-6. It can be seen that if the ratio (49.3) of emissions for the King City/Copperopolis operations proves valid, asbestos levels in the latter town could be quite high. It should be pointed out, however, that the data are expressed as particulate rather than asbestos release rates, the fractional amount of the latter in the former not being known. In the case of the Copperopolis situation, emissions are predominately from hard rock blasting. There the serpentine contains only a few percent asbestos such that the particulates could be predominately dusts from the host mineral. Geographic locations of the three asbestos mining and milling sites are shown in Figure 3-6 together with the associated emission factors from the EIS.

TABLE 3-6. DUST EMISSIONS FROM THE ENVIRONMENTAL INFORMATION SUBSYSTEM FOR THREE ASBESTOS MINING AND MILLING FACILITIES

Point Source	Particulate Emissions, tons/yr
Atlas Asbestos Co.	
Asbestos drier	20
Conveying & tailings handling	24
Milling & crushing	12
Calaveras Asbestos Co.	
Pit blasting	126
Ore crushing	19
Milling and grinding	1
Storage	2
Union Carbide Corp.	
Asbestos drying	3

KVB 26900-842



Copperopolis -
Calaveras Asbestos Co.
296,000 lbs/yr

Coalinga -
Atlas Asbestos Co.
112,000 lbs/yr

King City -
Union Carbide Co.
6,000 lbs/yr

Figure 3-6 Location of asbestos mining and milling facilities in the state and emission factors.

B. Random Uncontrolled Releases--

1. Demolition of buildings--The release of asbestos from industrial and commercial buildings (family houses typically contain little asbestos) being razed depends on a number of factors, including of course the amount of asbestos containing materials used in the original construction. Since the machine-induced collapse of a structure is hardly a reproducible process, and other variables such as site, condition of insulation and weather conditions will also have an effect on the amount of asbestos released, emission factors would be difficult to estimate. It is doubtful, in fact, whether there would be any point in attempting it. It would probably be far more cost-effective to sample airborne asbestos from two or more demolitions, then design suitable control strategies if the magnitude of asbestos release does prove dangerous. Techniques that could control asbestos releases from collapsing structures would include external water sprays, draping outside walls with plastic sheeting, and selectively saturating insulated areas with dilute wetting agents.

2. Maintenance and installation of insulated materials--Refineries, natural gas compression stations, chemical process plants, centralized energy plants, shipyards, and many other facilities are continuously maintaining or installing fireproofing materials or thermal and even acoustical insulations. This entails handling of asbestos-containing materials through cutting, sawing, spraying (wet or dry) and various other mechanical operations. Based on comments offered by CALOSHA inspectors, such practices are now highly controlled. It is therefore unlikely that significant atmospheric releases can initiate from areas that are acceptable in terms of occupational hazards.

3. Erosion of serpentine deposits--There can be no question that very large quantities of asbestos become airborne due to wind erosion of the bearing serpentine deposits. Studies have been conducted to determine the compositions of windborne dusts impacting various type areas. An example of this is the work of Murchio, et al, (Ref. 9), of the University of California, Berkeley. They studied asbestos levels in the Clear Creek area, where extensive serpentine deposits occur.

It is obvious that any sampling effort directed towards establishing emission factors for naturally occurring asbestos releases would leave no practical corollary in terms of fashioning a source control mechanism. If, however, dangerous levels of asbestos are transported into urban or even rural populated areas by prevailing winds, the people affected should be warned. The opportunity would at least then exist for some kind of self-protection against such insalubrious conditions. This could range from staying indoors during dust storms to leaving the area permanently.

Another phenomenon closely related to wind erosion is the release of asbestos dusts by recreational vehicles and even hikers traversing remote serpentine areas. Although such activities probably do not impact populated areas, the levels of asbestos inhaled by the recreationists themselves could be extremely high.

4. Solid waste disposal--The solid wastes produced during the manufacture and use of asbestos-containing products and the demolition of structures are typically buried at dumps. In California, these disposal sites are predominately land-filled so that emissions are much lower than for open (particularly burning) dumps. Emissions would expectedly occur during actual dumping and waste burial.

Regulation of land-fill operations is handled by the Solid Waste Management Board, the county solid waste enforcement agency, the State Water Resources Department, the Health Department (Hazardous Materials Section), and CALOSHA. The net effect has been that asbestos-containing wastes must be wetted down and drummed before dumping is allowed. The drums are then immediately covered with earth. Class 2 sites may be used, although most asbestos wastes are going into Class 1 dumps. Asbestos releases from such operations are probably now quite minor.

C. Utilization of Asbestos in Manufactured Products--

A number of use points exist where asbestos in refined or formed condition is used in the manufacture of asbestos-bearing products. A breakdown of the principal consumption areas is as follows:

- Floor coverings
- Ready-mix insulation
- Fire-resistant cloth tape, rope and miscellaneous
- Asbestos cement piping
- Roofing products
- Filters, fibers, felt, and paper
- Filled rubbers, coatings, plastic resins
- Gaskets, packings, frictional shapes

A list of the major users of asbestos in the State was prepared for the U.S. EPA in 1973. This list, although in obvious need of correction and updating, is included as Appendix A. All of these businesses would be expected to evince no visible asbestos emissions if compliant with regulations. The question then is what release rate of asbestos from an industrial complex would still furnish Ringelmann measurements of zero.

In addition to the data shown in Table 3-6, the EIS provides emission factors for two of the largest asbestos processing plants in the State. These are both Johns Manville operations; one is at Long Beach (asbestos-cement pipe) and the other at Stockton (transite and plastic pipe). The former is listed to have an annual particulate release of 1 ton/yr while the latter is rated at 19 tons/yr. As in the case of mining operations, the fractional amount of this dust that is asbestos is uncertain. In any case, a range of dust releases from 0.2 to 4 lbs/hr from plants equipped with multiple exhaust ducts would seem consistent with an invisible atmospheric release. Dust release points are in the blending rooms where asbestos is mixed with lime, sand and other ingredients. The dry-basis asbestos content of this mix is about 15%. If the dust released contained this amount of asbestos, then the release would be 300 and 5700 lbs/yr for the Long Beach and Stockton plants respectively.

In investigating the Johns-Manville releases, the South Coast AQMD and the San Joaquin County APCD were consulted. In the latter case, it was stated that no attempt had been made to determine what fraction of the dust released from the Stockton plant (bag house) was actually asbestos. The SCAQMD had attempted to do this in the case of the Long Beach plant but the results provided by the laboratory retained were questionable (very few laboratories are capable of quantifying this substance reliably).

Johns-Manville reported to the project sampling of the six vents of the Stockton plant specifically for asbestos over a four year period. These data, based on optical microscopy showed an annual plant release of only 38 lbs total of that mineral. As is pointed out in the Task IV volume, optical microscopy furnishes unacceptably low results.

If an average release rate of 200 lbs/yr dust from major asbestos-handling plants is assumed, a quantity for the total release from the asbestos-user category can be roughly estimated. Appendix A is comprised of 117 listings which is probably an adequate count of the major asbestos users even if compositional errors are recognized. The major users would then emit an estimated 23,500 lbs/yr of dust. It can further be assumed that there are also at least five times the number of major users that are minor consumers of asbestos. If we assume that emissions from all the minor users are equal to the total from all the major users, an annual dust release of 47,000 lbs is seen. Distribution of this burden would be predominately in heavily populated areas of the State. The fractional amount of these dust releases that is asbestos is highly uncertain but would probably vary widely with the processes involved.

Ambient levels of asbestos have been measured, although the process is compromised by reliability problems in the quantitation of catches obtained. That issue notwithstanding, data were selected by Wesolowski (Ref. 10) to illustrate levels in the Berkeley-San Francisco area. Values ranging from 1.5 to 72 ng/m^3 were cited, with a range average of about 35 ng/m^3 being estimated. This is equivalent to about 0.4 fibers/cc of air. This is 20% of the OSHA MAC, a surprisingly high ratio for open urban air. Source testing at selected plants would be useful in determining to what degree such releases can be associated with ambient urban asbestos levels.

3.3 BENZENE

3.3.1 Summary of Utilization and Releases

California is a minor producer and user of benzene. Of the 11.4 billion lbs consumed in the U.S. in 1977, only 1.5% of this was produced in California. The consumption of benzene in the state about equalled production. Two refineries were responsible for this output, while three plants constituted the major consumption points. A large amount of the benzene produced was converted to cumene (a phenol intermediate) and detergent alkylate (dodecylbenzene). Some 22 million lbs were estimated to be exported. Solvent uses for benzene have diminished greatly because of hygienic concern.

Apart from the benzene market itself, the chemical also occurs in gasoline, which poses the greatest emission problem. Another source of benzene emission is the coking oven, which points to the Kaiser steel mill in Fontana. Benzene releases from all sources are shown in Table 3-7.

TABLE 3-7. ESTIMATED BENZENE EMISSIONS IN THE U.S. FROM VARIOUS SOURCES

	Benzene Emissions, 10^6 lbs/yr	
Emission Source	PEDCO Estimate (Ref. 11)	GCA Estimate (Ref. 12)
Gasoline Engines	443.6	909
Petroleum Refineries	4.1	58
Coke-Oven Operations	7.8	No Estimate
Benzene-Based Syntheses	60.0	58
Storage and Distribution of Gasoline & Benzene	24.8	69
Solvent Operations	Unknown	55
Other Miscellaneous	4.0	No Estimate
TOTAL EMISSIONS	544.3	1,149

Inventories of emission from these and other sources have been estimated in two recent EPA reports. The data posited by PEDCO (Ref. 11) and GCA Corporation (Ref. 12) in their independent studies are compared in Table 3-7. While these data reflect obvious differences, the authors agree only too well that above 80% of the total benzene emissions derive from the automobile.

3.3.2 Benzene Production and Major Uses

A. Producers--

According to the Benzene Annual, the only producers of benzene in California are the ARCO refinery, Wilmington, and the Chevron U.S.A. refinery, El Segundo. Production for 1977 was listed at 87.5 million lbs at each, which is well below capacity, particularly for Chevron (160 x 10^6 lbs/yr). With the exception of some 22 million lbs exported by ARCO, all of this production is consumed in California. No industrial benzene was produced in California from coal or coke retorts.

Both the Chevron U.S.A., El Segundo, and ARCO, Carson, refineries produce benzene by the catalytic dehydrogenation of naphthenic stocks, followed by the refining of the aromatic product. A simplified schematic of one version of this process is shown in Figure 3-7.

By definition, naphthene is cycloparaffinic and because of comparative ease of formation, predominates in five-and-six-carbon rings. Dehydrogenation of cyclohexane produces benzene and three mols of hydrogen or the alkylbenzene corresponding to any alkylated cyclohexane starting form. The catalyst promoting this effect is platinum or an alloy thereof. At Chevron, platinum-rhenium catalyst (Rheniforming process) is used while at the ARCO plant, a straight platinum catalyst is employed.

In the Rheniforming process used at Chevron, El Segundo, the reformate is distilled. Following the dehydration or reforming process the benzene-rich cut is then extracted to feed back undesired naphthenic and paraffinic material acquired in the same boiling cut. Benzene is then stripped from the extraction solvent, the latter being recycled in the process. At Chevron, solvent refining involves the use of phenol, while at ARCO, the solvent is a mixture of glycols and water (Udex process).

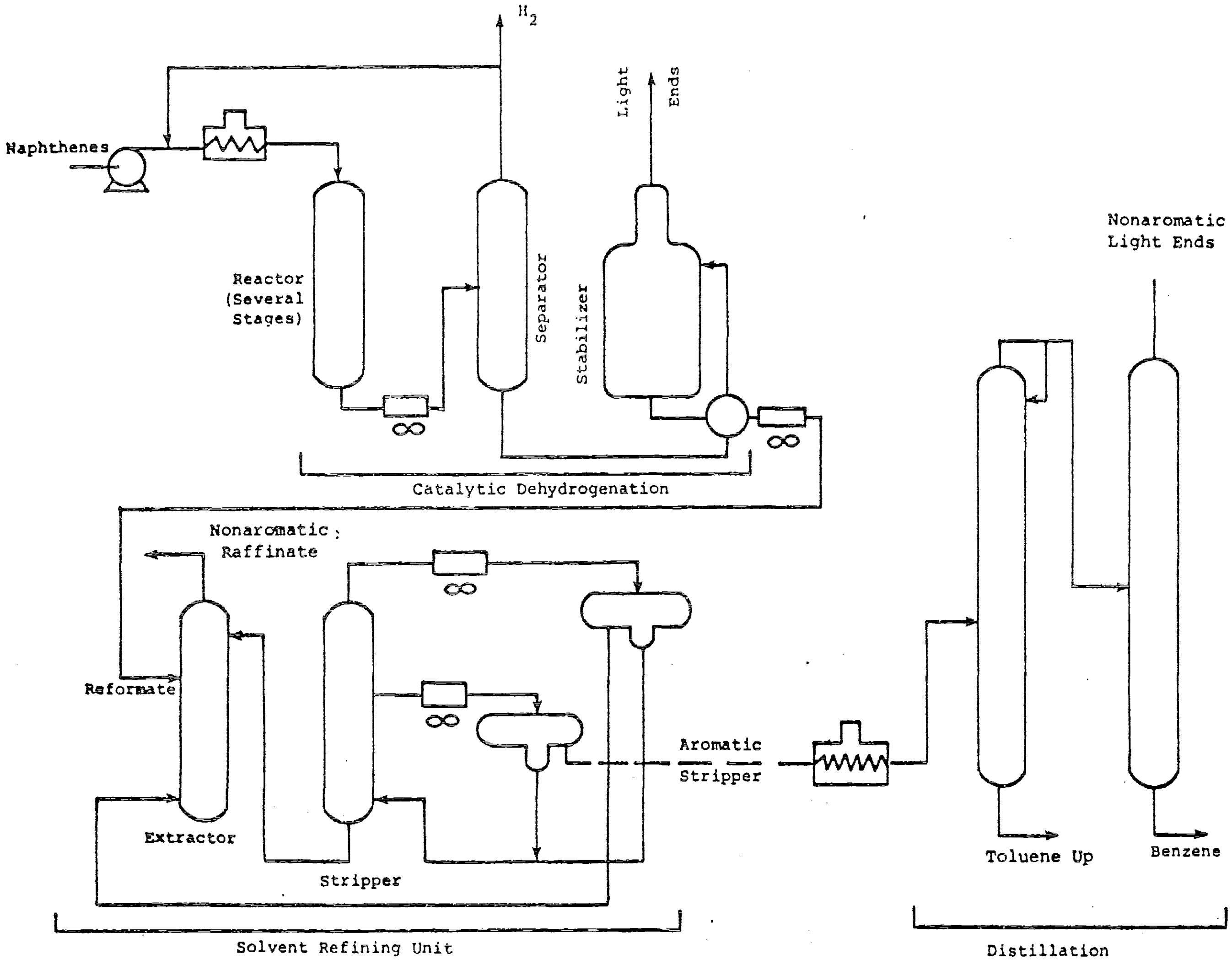


Figure 3-7. Overall benzene production process.

With the exception of benzene storage, which is done in floating roof tanks, emissions from the enclosed, benzene processes must occur through fugitive sources, such as valves, flanges, pump and compressor seals and related devices.

B. Major Users--

The principal users of benzene in California are listed in Table 3-8. The benzene inputs are about stoichiometric with respect to the rated output capacities of the Chevron (El Segundo) and WITCO plants but well below capacity in the case of the Chevron-Richmond phenol/detergent alkylate operation. Chevron, Richmond, was contacted about this who pointed out that their benzene feedrate for 1977 was 36,000 gals per day. This is equivalent to a usage rate of 96.3×10^6 lbs/yr. Chevron, Richmond, also pointed out that all of its benzene feed is converted to detergent alkylates, none being used for phenol synthesis as stated in <u>Benzene Annual</u>.

Other consumers have been listed (Ref. 13) in the literature (together with benzene emission factors, in one case) that do not input benzene at all. Ferro Corporation, Santa Fe Springs, produces phenol but from crude phenolic wastes, not benzene. Specialty Organics Co., Irwindale, separates dichlorobenzene into its isomers but does not synthesize the mixture from benzene. Montrose Chemical Co., Torrance, purchases over 50×10^6 lbs of benzene per year but converts it to chlorobenzene in Henderson, NV. This material is then shipped to Los Angeles where it is converted to DDT (for export). The above information was obtained by telephoning various executives of the companies concerned.

TABLE 3-8. PRINCIPAL BENZENE CONSUMERS
IN STATE OF CALIFORNIA - 1977 DATA
SOURCE: Benzene Annual

Company and Location	Benzene Consumed 10^6 lbs/yr	Supplier	End Product (s)	End Product Plant Capacity 10^6 lbs/yr
Chevron U.S.A., El Segundo	65.6	Internally Made	Cumene	100
Chevron U.S.A., Richmond *	21.9	Chevron, El Segundo	Phenol	55
	36.5	ARCO, Wilmington	Detergent	200
Witco, Carson	29.2	ARCO, Wilmington	Detergent	55

* According to Chevron, these data are incorrect; see Section 3.3.2.

3.3.3 Coking Operations

The thermal conversion of coal to coke expectedly releases large quantities of hydrocarbons. With appropriate equipment and process conditions, yields of light oils and tar (the "benzol condensate") can be recovered in commercial quantities. In steel production, the coking oven design provides poor vapor containment. Emissions occur from various points during charging, pushing and quenching operations; from doors during the coking cycle; and from the waste-gas stack. The Kaiser Steel Company mill at Fontana is the only coal-coking operation in the State. This plant operates 7 coking batteries incorporating a total of 315 ovens having a coke production capacity of 1,547,000 tpy. The benzol condensate amounted to some 57×10^3 lbs in 1977. The tar fraction is sold to Koppers Co., Fontana. The secondary light oil, rich in benzene, goes to Western Fuel Oil, San Pedro, where it is blended with fuel stocks. This information was supplied by a company executive at Kaiser.

3.3.4 Petroleum Production, Storage & Marketing

Two refineries were discussed earlier in the context of industrial benzene production. While benzene emissions must be associated with such operations, other refineries (including ones that do not produce gasoline) need also be considered. Benzene is a natural constituent of crude oil and persists in the refining processes. For example, Runion (Ref. 14)reports an average of 1.25 Vol. % benzene in three grades of Gulf Corporation gasolines obtained from six different refineries. Similarly, NIOSH (Ref. 15) tested several different brand gasolines of different grades and reported a range of benzene contents from 0.88 to 1.49 Vol. %. At the present time, CARB estimates that the average benzene level in all gasolines is between 1.24 and 2.5 Vol. %. This higher value is believed to reflect the current trend to increased aromaticity in gasoline production. This is required to compensate for government-directed decreased usage levels of tetraethyllead (TEL).

Benzene emissions from a refinery include both process and non-process emissions. The former include those emanating from: (1) light and heavy naptha streams from the crude unit; (2) fluid catalytic cracking units; (3) hydro-cracking units; (4) gasoline mixing tanks; and (5) fugitive sources. Non-process emissions originate from wastewater treatment systems, heaters, boilers, and product storage tanks. In the case of refineries that produce benzene as well as gasoline, emissions of the former are bound to increase as a result of storing the refined benzene itself. Finally, emissions of benzene are associated with the in-and-out flow of crude and product to and from the refineries. Radian estimated a total U.S. evaporative hydrocarbon emission rate of 1.77×10^9 lbs/yr from crude oil (oil field) production and transportation (Ref. 16).

Transportation of gasoline (and industrial benzene) is also an obvious source for additional emissions. A complex system of pipelines, tank trucks, rail tankers, barges, and ocean tankers connects bulk terminals, bulk plants, service stations, commercial yards, and transshipment points. It is estimated (Ref. 11) that 3.75 X 10^6 lbs/yr benzene are emitted in the U.S. from gasoline transportation operations, and an additional 6.6 X 10^6 lbs/yr from the operation of service stations.

3.3.5 Automobile and Other Vehicular Traffic

Hydrocarbon, including benzene, emission from gasoline engines (and even Diesel engines, but at lower levels) is a well studied and published subject and need not be reviewed here. In cars with and without catalytic converters, benzene appears to enrich in the exhausted hydrocarbons. Unfortunately, only one set of data is available (Ref. 17) in which the benzene contents of both the fuel and the exhaust hydrocarbons were determined. In this case, only one car not equipped with a catalytic converter was tested (with nine newer models). The benzene content of the unleaded fuel used in all was only 0.03 wt %. In any case, the results of the standard dynamometer testing showed that the average benzene/THC ratio for the fuel Vs. that of the exhaust gas increased 84 times for the older car (1972 Chevrolet) and an average of 70 times for the catalyst-equipped cars. The latter group emitted about 40% on the average of the THC exhausted by the older car. This benzene enrichment effect is consistent with the refractory nature of benzene, but obviously cannot be extrapolated to fuels containing "normal" levels of benzene (∿2 Vol.%).

Data obtained by Olson Laboratories (Ref. 18) for three gasolines of graded aromaticity burned in six variously APC-equipped automobiles are itemized in Table 3-9. Although only a PONA* analysis was available for the gasolines used, it can be seen that the benzene content of the THC's emitted by cars burning a typically aromatic rich fuel averages about 5%.

3.3.6 Solvent Operations and Other Miscellaneous Sources of Benzene Emissions

A. Solvent Uses--

SRI's Mara and Lee (Ref. 13) identified 13 types of operations which consumed benzene as a solvent. This list was reduced to five, based on

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* Class analysis for: paraffins, olefins, naphthenes, and aromatics.

TABLE 3-9. EXHAUST EMISSIONS OF BENZENE FROM AUTOMOBILES BURNING THREE UNLEADED GASOLINES OF VARYING AROMATICITY

Source: Olson Laboratories (Ref. 18)

	Benzene Emissions, g/mile (wt.% of THC)		
Automobiles	Typical Clear I, 35% Aromatic	Indolene Clear, 22% Aromatic	High Alkylate, 10% Aromatic
1972 Olds Delta 88 with Base-Metal oxidation catalyst & EGR*	0.025 (7.7)	0.026 (6.0)	0.015 (2.9)
1971 Ford LTD with ESSO Ram Reactors & EGR	0.008 (4.5)	0.005 (4.3)	0.002 (1.8)
1971 Plymouth Fury III with platinum oxidation catalysts & EGR	0.023 (5.8)	0.015 (3.9)	0.008 (1.5)
1972 Ford Torino with platinum oxidiation catalyst & EGR	0.030 (4.2)	0.025 (3.2)	0.011 (1.3)
1971 Plymouth Fury III with Ethyl Lean reactors & EGR	0.022 (5.0)	0.015 (3.5)	0.006 (1.7)
1970 Chevrolet Impala with GEM Monel NOx reduction catalyst & platinum oxidation catalyst	0.011 (3.7)	0.009 (2.5)	0.004 (1.1)

*Exhaust Gas Recirculation

employee count, as representing the solvent sector of benzene users. These industries (the number of plants in California are shown in parentheses) are involved in the manufacture of the following items:

- Tires and Innertubes (22)
- Rubber & Plastic Footware (3)
- Plastic Materials & Synthetics (51)
- Floor Coverings (62)

The authors state that 32% of such operations, based on employee counts, are located in California and Georgia (146 and 270 plants total, respectively). Because of the declining usage of benzene in such applications, the SRI authors declined to estimate emission factors.

B. Miscellaneous Other Sources--

Other sources of benzene emissions have been identified (Ref. 11). These include coal gasification, refuse incineration, forest and structural fires, and agricultural burning. The first two operations are not practiced in the State. Benzene emissions from uncontrolled fires have yet to be measured. Emissions from the burn-off of agricultural wastes have only been perfunctorily considered. The practice, however, is considerably restricted in the State. Burning of ligneous substances can be expected to produce benzene. In studies sponsored by the CARB and conducted at UC Riverside (Ref. 19), emissions were analyzed from the burning of the following eight crop wastes: barley, wheat, sorghum, almond, grape, corn, rice, and peach. The benzene content in the volatile hydrocarbons speciated in the flue of the portable incinerator ranged from 19 to 51% and averaged 33% for the eight types of crop-wastes. Because of the difference in the combustion effects involved, development of emission factors from these data that would be applicable to open-field burns would not be acceptable.

3.3.7 Emission Factors

A. Benzene Production and Major Uses--

1. Benzene production--In the PEDCO study (Ref. 11), benzene emissions were derived from AP-42 data and estimated compositions of emitted vapors. Based on the degree of APC practiced, a weighted estimate of 0.759 lb/1000 bbl crude fed was derived. Fully controlled refineries were assigned a factor of 0.415 lb/1000 bbl crude. This factor, however, is basically a gasoline refinery factor and does not take into account benzene production. It was, therefore, considered appropriate to add to the PEDCO estimate by assuming an additional benzene loss of 0.5 lb/10^3 gals benzene produced in the manufacture of that chemical.

Benzene losses occurring during storage and handling of crude oil were excluded from refinery emissions and were treated as an isolated topic by the PEDCO authors. They used factors developed at Radian (Ref. 16) for total hydrocarbon releases involved in crude oil storage and working, proportioning these to benzene factors. These estimates in lbs of benzene emitted per 1000 bbls of crude input were 0.125 for storage and 0.071 for working losses. These factors were included in the estimates for total refinery benzene emissions given here.

Emission factors for gasoline storage and withdrawal are also applied. Based on PEDCO's estimates these were found to be 1.66 X 10^{-4} and 1.95 X 10^{-6} lb benzene per thousand gallons of gasoline, respectively.

Standing and withdrawal losses of benzene from fixed-roof storage tankage were also derived. Based on the National usage of tanks and assuming 30 days product residence time in tanks normally 75% full, an emission factor of 0.01 lb/day per 1000 gals of product was estimated. Withdrawal losses were estimated at 0.0074 lb/day per 1000 gals of benzene.

The above sets of factors were then applied to furnish the estimated emissions shown in Table 3-10 for the two Los Angeles refineries producing benzene (12 X 10^6 gals/yr each). These mass values are considerably lower than those that were calculated from the benzene emission factors that were

TABLE 3-10. ESTIMATED BENZENE EMISSIONS FROM TWO BENZENE PRODUCING GASOLINE REFINERIES

Emission Source	Benzene Emitted, lbs/yr Chevron El Segundo	 ARCO Carson
Crude Storage & Handling	16,454	13,235
Gasoline Production	34,839	28,023
Benzene Production	6,000	6,000
Benzene Storage & Withdrawal	2,239	2,239
Gasoline Storage & Withdrawal	346	222
TOTAL	59,878	49,719

Emission factor source: PEDCO (Ref. 11)

developed by Patterson (Ref. 12) or Mara and Lee (Ref. 13). The latter authors assumed that benzene emissions at benzene-producing refineries would be just twice that of the conventional refinery and perhaps did not consider the impact of APC equipment.

2. Major benzene users--About 80% of the benzene produced in the State is consumed in three facilities synthesizing cumene (Chevron-El Segundo) and detergent alkylate (Chevron-Richmond and Witco-Carson). The annual benzene consumption for these three plants is estimated at 65.6, 96.3 and 29.2 million lbs, respectively. Union Carbide (Ref. 20) has developed benzene emission factors for both types of processes and for phenol. The benzene releases derived from these factors and assuming full capacity production are as follows:

TABLE 3-11. ESTIMATED BENZENE EMISSIONS FROM THREE CONVERSION PLANTS

Company and Location	Material Produced	Annual Product Capacity, 10^6 lbs	Emission Factor, lb Benzene/lb Prod.*	Annual Benzene Release, lbs
Chevron, El Segundo	Cumene	100	2.45×10^{-4}	24,500
Chevron, Richmond	Detergent	200	5×10^{-4}	100,000
Witco, Carson	Detergent	55	5×10^{-4}	27,500

* Source: Union Carbide (Ref. 20)

The Union Carbide benzene emission factors are based on actual test data. These data, however, range widely and possibly reflect regulatory inconsistencies from state to state. Union Carbide did, however, tend to use benzene release data for facilities that obviously were regarded as not under the best possible APC management.

In the case of Witco, AQMD measurements resulted in an assignment of 15.6 tpy THC emissions. Witco estimates that 85% of that would be benzene, or 26,520 lbs/yr. This agrees well with Table 3-11.

Considering their benzene consumption data, it appeared reasonable to assume full-capacity operation for Chevron, El Segundo, and Witco In the case of Chevron, Richmond, it is possible that the plant is operating at well above (50-60% KVB estimate) its rated capacity.

Not included in the Table 3-11 emission estimates were values for the loading, transit and off-loading for benzene. Benzene flow between Witco and ARCO is by pipeline. Chevron, El Segundo produces its own benzene used in cumene production and the benzene losses calculated (PEDCO emission factors) for the suppliers of and the Chevron plant at Richmond were too small to be noted.

Comparing the Table 3-11 values with those reported by SRI (Ref. 13) very close agreement is noted for the Chevron, El Segundo plant (24,255 vs. 24,500 lbs/yr). In the case of the other Chevron plant, SRI's estimates are about five times higher. Siting of benzene production and consuming plants is shown in Figure 3-8 together with estimated benzene emissions.

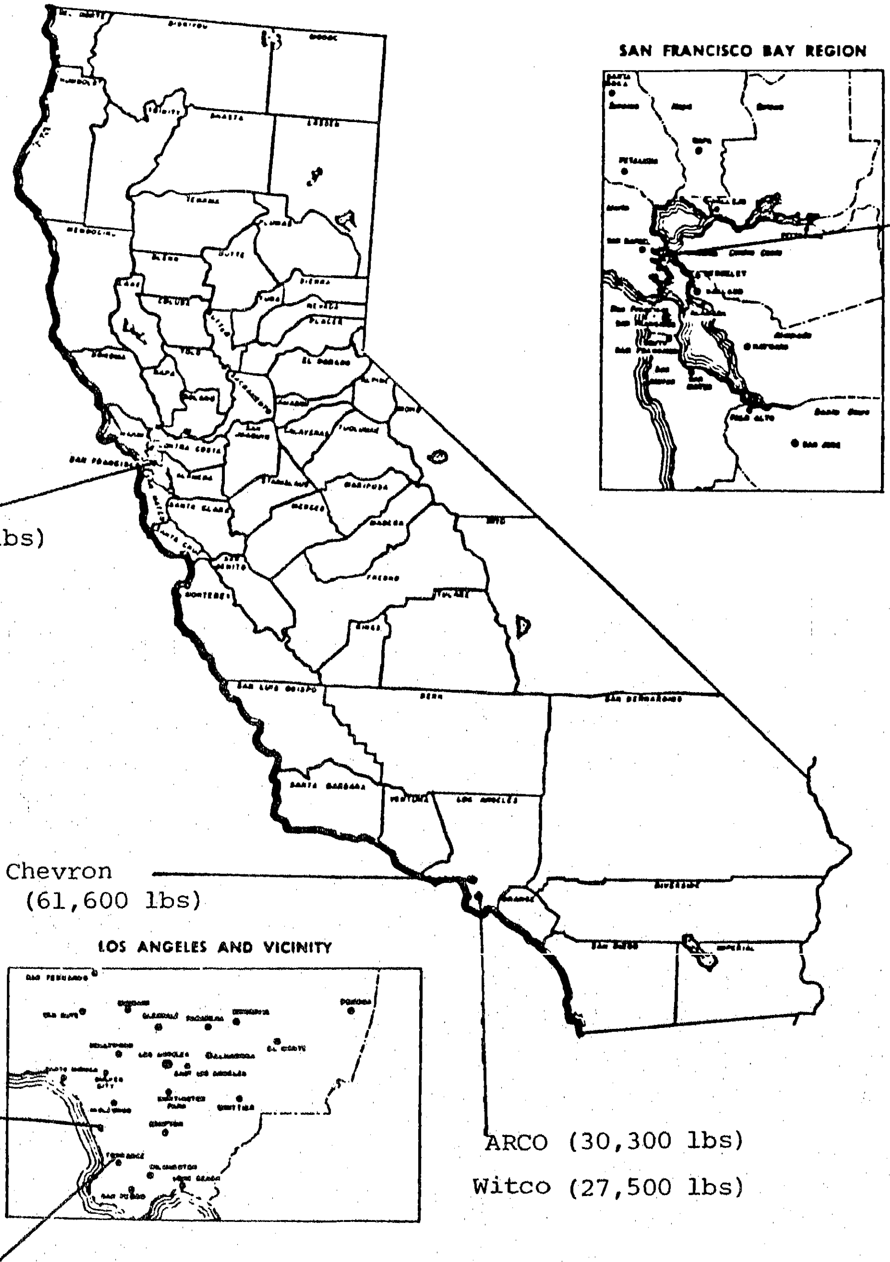
B. Coking Operations--

Emission factors for benzene released during steel mill coking are hardly reliable. Based on European (USSR and Czechoslovakia) experience, the values clearly demand validation by domestic source testing. This need is particularly emphasized in considering the higher benzene release rates calculated for the Kaiser Steel mill at Fontana:

ESTIMATED BENZENE EMISSION FROM
KAISER STEEL MILL, FONTANA

Reference	Plant Emission Factor, g/sec	Benzene Emitted lbs/year	Average
PEDCO (Ref. 11)	4.4	307,740	223,400
SRI (Ref. 13)	2.0	139,048	

The differences in the two emission factors largely result from the benzene content in the hydrocarbon effluents assigned by each group. SRI estimated 1.32% and PEDCO 2.23% as the benzene content for the hydrocarbons released.



Chevron USA
Richmond

Chevron
(141,250 lbs)

Chevron
(61,600 lbs)

Chevron USA
El Segundo

ARCO (30,300 lbs)
Witco (27,500 lbs)

ARCO & Witco, Carson

Figure 3-8. Benzene production and major user sites and estimated annual emissions.

C. Petroleum Production, Storage and Marketing--

1. Crude oil operations--Excluding offshore production on Federal lease sites, 1978 production of crude in California is estimated by the California Division of Oil and Gas at 334 million bbls. This is based on a linear extrapolation of data for nine months of production. The total yield includes about 45 million bbls of off-shore production from state leased plots. This fraction was retained for emission calculations while production of the Federal lease-holders (13.3×10^6 bbls) was excluded. This arbitrary distinction was based on the relative distances of the two types of operations with respect to shore line.

Data obtained in oil fields in Monterey and Santa Cruz Counties (Ref. 21) indicated a net emission rate for crude production operations of 107 lbs hydrocarbons for every 1000 bbl of crude produced. Assuming, as PEDCO did, that these emissions contain 0.06 wt. % benzene (probably overly conservative), the emission rate for benzene would be 0.064 lb/1000 bbl crude. This would be increased to 0.164 when evaporation losses associated with crude transportation are factored in (Ref. 16). Based on the State's oil production for 1978, this would imply a release of only 54,776 lbs of benzene from the entire population of oil producing facilities in the State. Because of the dispersion factor, impact on adjacent urban areas would probably not be warranted. It would be well, however, to check the estimated factors by conducting specific benzene measurements in selected fields.

2. Refinery operations--The inventory of gasoline refineries in the State includes the two refineries (Chevron, El Segundo and ARCO, Carson) considered earlier which also produce industrial benzene, six petroleum plants that produce asphalt but not gasoline and 24 gasoline refineries. The asphalt plants are identified in Table 3-12.

TABLE 3-12. PETROLEUM PLANTS PRODUCING ASPHALT*
(But Not Gasoline)

Firm	Location		Crude Oil Input Capacity 10^3 bbls/day
Road Oil Sales	Bakersfield		1.6
Edgington Oil Co.	Long Beach		29.0
Newhall Refining Co.	Newhall		7.5
Golden Bear Division, WITCO Chemical Corp.	Oildale		10.5
San Joaquin Refining Co.	Oildale		17.0
Lunday-Thagard Oil Co.	South Gate		5.0
		TOTAL	70.6 X 10^3 bbls/day

Source: Oil & Gas Journal

Added to the input capacities of the gasoline-refining plants, asphalt producers represent an additional 3.6% to the State's crude oil consumption. Although operations at asphalt plants are considerably different than at gasoline refineries, the small population of these plants did not warrant the development of type-specific emission factors. They are, therefore, treated as gasoline refineries.

The benzene emission factors for refineries have actually been introduced previously under the section dealing with benzene producers. Benzene emission rates were based on both gasoline operations and benzene production.* Releases associated uniquely with the latter were isolated so that the balance of the emissions would be identified with normal gasoline refining. These emission rates are tabulated below again for convenience (Table 3-13).

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*See Table 3-10

TABLE 3-13. ESTIMATED BENZENE EMISSION RATES FOR OIL REFINERIES

Source		Emission Rates, lbs. Benzene
Crude Oil		
Storage		3×10^{-3}
Working Loss		1.7×10^{-3}
	Combined	$4.7 \times 10^{-3}/10^{3}$ gals crude
Refinery Operations		$1 \times 10^{-2}/10^{3}$ gals crude
Gasoline		
Storage		1.66×10^{-4}
Withdrawal		1.95×10^{-6}
	Combined	$1.68 \times 10^{-4}/10^{3}$ gals gasoline

* Source: PEDCO (Ref. 11)

The emission assignments for the California refineries are itemized on Table 3-14 and these data are mapped sectionally on Figure 3-9.

Again, these values are considerably lower than the estimates offered by other workers (Refs. 13 & 16) who acknowledged a lack of test information on refinery emissions. Fortunately, on its survey of hydrocarbons in the South Coat Air Basin (Ref. 22), KVB was able to conduct an extensive hydrocarbon survey at one gasoline refinery. This was the Douglas Oil Company facility in Paramount. Testing there was not entirely comprehensive but extensive enough to permit fairly reliable extrapolations. Results of the sampling program are tabulated in Appendix B. Points sampled included hydrocarbon measurements of the following:

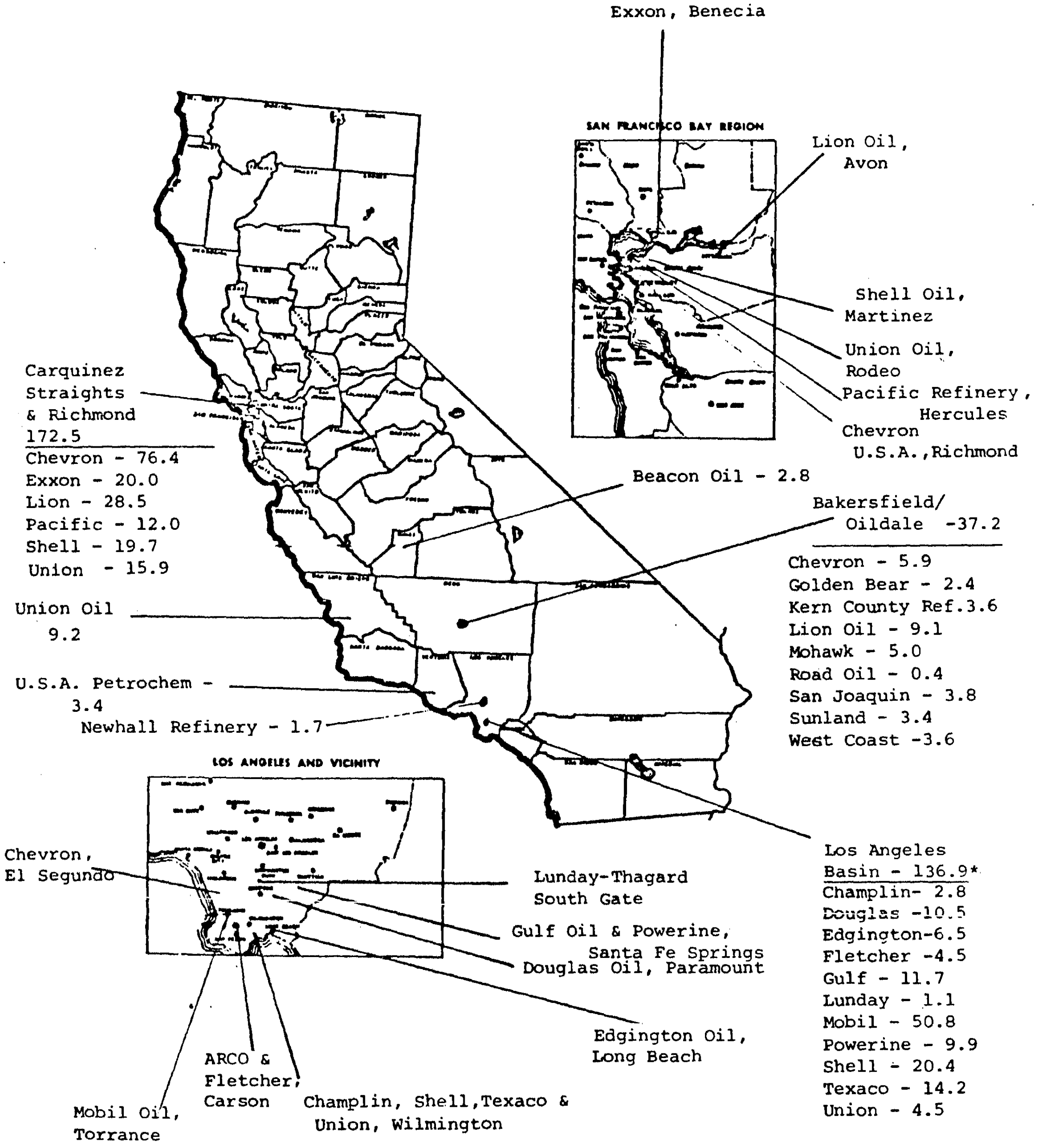
- Stack Emissions
    - Heaters
    - Boilers
    - Flaring
    - Asphalt Blowing
    - SCOT Incinerator

TABLE 3-14. ESTIMATED BENZENE EMISSIONS FROM GASOLINE REFINERIES AND ASPHALT PLANTS OPERATING IN THE STATE OF CALIFORNIA

Company	Location	Crude Oil Operating Capacity, 10^3 bbl/day	Gasoline Prod. Capacity, 10^3 bbl/day	Benzene Emissions, 10^3 lbs/yr
ARCO	Carson	185	87.4	See Fig. 3-8
Beacon Oil Co.	Hanford	12.4	2.6	2.8
Champlin Petroleum Co.	Wilmington	30.7	3.0	6.9
Chevron U.S.A.	Bakersfield	26.0	2.6	5.9
Chevron U.S.A.	El Segundo	230	125.4	See Fig. 3-8
Chevron U.S.A.	Richmond	338	145.8	76.4
Douglas Oil Co.	Paramount	46.5	8.5	10.5
Edgington Oil Co.	Long Beach	29.0	0	6.5
Exxon Co., U.S.A.	Benicia	88.0	73.8	20.0
Fletcher Oil & Ref.Co.	Carson	20.0	4.2	4.5
Golden Bear Div,WITCO	Oildale	10.5	0	2.4
Gulf Oil Corp.	Santa Fe Springs	51.5	28.5	11.7
Kern County Refinery	Bakersfield	15.9	2.6	3.6
Lion Oil Co.	Avon	126	74.3	28.5
Lion Oil Co.	Bakersfield	40.0	33.2	9.1
Lunday-Thagard Oil Co.	South Gate	5.0	0	1.1
Mobil Oil Co.	Torrance	123	88.4	50.8
Mohawk Petroleum Corp.	Bakersfield	22.1	2.2	5.0
Newhall Refining Co.	Newhall	7.5	0	1.7

TABLE 3-14 (Continued)

Company	Location	Crude Oil Operating Capacity, 10^3 bbl/day	Gasoline Prod. Capacity, 10^3 bbl/day	Benzene Emissions, 10^3 lbs/yr
Pacific Refining Co.	Hercules	53.3	17.7	12.0
Powerine Oil Co.	Santa Fe Springs	44.1	13.4	9.9
Road Oil Sales	Bakersfield	1.6	0	0.4
San Joaquin Refining Co.	Oildale	17.0	0	3.8
Shell Oil Co.	Martinez	87.4	43.3	19.7
Shell Oil Co.	Wilmington	90.0	45.0	20.4
Sunland Refining	Bakersfield	15.0	1.0	3.4
Texaco, Inc.	Wilmington	62.5	74.4	14.2
USA Petrochem Corp.	Ventura	15.0	5.0	3.4
Union Oil Co. of Calif.	Arroyo Grande	41.0	4.2	9.2
Union Oil Co. of Calif.	Rodeo	70.0	51.0	15.9
Union Oil Co. of Calif.	Wilmington	108	79.5	24.5
West Coast Oil Co.	Bakersfield	16.0	2.0	3.6
	TOTAL	1957.4	1019.0	387.8



* Excludes ARCO & Chevron

Figure 3-9. Estimated benzene emissions associated with oil refinery operations (10^3 lbs/yr).

- Valves, Flange & Pump Inventory
  - Reformer Unit
  - Naptha Unit
  - Crude Unit
- Other Fugitive Emissions
  - Reformer Unit
  - Naphtha Unit
  - Crude Units
  - Asphalt Plant
  - Oil-Water Separators
  - Cooling Towers
- Tank Storage & Transfer
  - Crude Storage
  - Gasoline Storage
  - Other Petroleum Storage
  - Gasoline Transfer
  - Other Petroleum Transfer

Based on the mass of data obtained, an emission factor (24 hr average) of 162 lb/hr or 1.4 X 10^6 lb/yr was derived. Applying the benzene concentration factor used by PEDCO (0.6 wt %*), which is slightly higher than SRI's (0.5 wt.%), benzene emission of 8,514 lbs/yr is obtained. The value shown in Table 3-14 for Douglas is 10,500 lbs/yr. Thus, the use of the PEDCO emission factor estimates, as amended here, appears to be justified.

3. Gasoline distribution and marketing--The process of moving gasoline and other petroleum products to user networks, including the extensive system of State service stations, occasions hydrocarbon and thus, benzene, emissions. Nationally, the benzene emissions from distributional operations (including marinas) is estimated at 3.8 million lbs annually. Losses at service stations and commercial fleet fueling facilities is estimated at an additional 14.6 million lbs. The much larger loss at service stations includes not only loading and refueling but tank vent losses and spillage.

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* Not to be confused with value (0.06 wt %) given on Page 3-50, which is for oil field emissions.

Thus, an estimated 18.4 X 10^6 lbs benzene is dispersed to the atmosphere in what are largely urban areas. Based on 1977-1978 FY gasoline consumption in California (11.7 of the 100 billion gals consumed nationally), 2.2 X 10^6 lbs of this benzene was vented in the State. This, however, does not include losses occurring after vehicles are filled and back on the street.

The distribution of these vapor releases follow trucking lines, but are predominately patterned by the 16,135 (as of January 1979) service stations in the State. This pattern can be assumed to fit reasonably well with the human population distribution within the State. This is shown in Figure 1-2.

D. Automobile and Other Vehicular Traffic--

Estimates derived for benzene emissions from vehicular operations (Refs. 11 & 13) show this to be the greatest source of all those existing. The assumed average release rates for benzene varied considerably, SRI using a release rate about 10 times higher than the composited value adopted by PEDCO. The latter authors used test-stand measurements (Ref. 18) that included the specific determination of benzene in the exhaust stream. Thus, their estimates appear better supported and were therefore used.

Based on a 1976 automobile population, PEDCO calculated total benzene emissions from gasoline engine exhaust (373.5 x 10^6 lbs/yr) and car-tank evaporation (70.1 x 10^6 lbs/yr) at 443.6 x 10^6 lbs/yr. An additional 3.7 x 10^6 lbs were imputed to Diesel-engine traffic. This emission burden would be expected to decline over the past few years with the enrichment of the vehicular population with more catalyst-cars. Yet PEDCO did not take into account the present trend to use leaded gas in catalyst cars. This is now variously estimated by the media to have rendered from 15 to 35% of such rolling stock worse emitters than the precatalyst vehicles. In view of this, the estimated National vehicular benzene emission burden for 1976 was assumed to have remained unchanged for this study.

Using California's fraction (11.7%) of the National gasoline consumption rate, gasoline and Diesel engine vehicular emissions of benzene were thus estimated at 52 X 10^6 lbs/yr or about 2.9 lbs/yr per vehicle.

Dissemination of this released benzene is a complex traffic function which involves standing (tank evaporation) as well as movement. For 1978, the DMV reports (Ref. 23) 80.7 X 10^9 vehicle miles driven on the State highway system and 69.6 X 10^9 miles on road beds administered by local State jurisdictions. The traffic intensity for the State system (for 1977) is shown on Figure 1-2. This mapping includes only 54% of traffic flow and must be further increased by the other 46% of the traffic miles travelled on municipal and county road beds and parking areas. The city and county roads are of course predominately in urban locations.

E. Solvent Operations and Other Miscellaneous Sources of Benzene Emissions--

In a recent EPA report (Ref. 24), the minor uses of benzene were considered. The estimated amounts of benzene consumed and released in the U.S. for such applications are shown in Table 3-15. The dramatic drop in consumption between 1976 and 1978 is attributed to the imposition of the OSHA Emergency Benzene Standard of May 1977. The trend is continuing towards elimination of benzene in those applications that are known to still involve its use.

Of the remaining minor users of benzene, only 2% of this consumption is reported to occur in the Pacific, Mountain, South Atlantic and New England States. This corresponds to 418,362 lbs annually consumed and an associable emission of benzene of 17,840 lbs/yr for this large area (Ref. 24).

Because of this comparatively small and widely distributed release, a survey was considered unwarranted. Nonetheless, one of the authors of the EPA report cited above was contacted. Mr. Marcus Sittenfield acknowledged that any benzene still used in California for solvent and other minor applications would have to be minuscule.

TABLE 3-15. CONSUMPTION VERSUS ENVIRONMENTAL LOSS
IN THE U.S. FOR BENZENE IN SOLVENT AND OTHER MINOR USES (1,000 GAL)
SOURCE: REF. 24

Consumption Area	Estimated Consumption		Estimated Environmental Loss	
	1976	1978	1976	1978
A. Chemicals Production				
General Organic Synthesis	2,962	2,213	691	309
Pharmaceutical Synthesis	650	220	200	66
Small Volume Chemicals				
Aluminum Alkyls	312	312	312	312
Alcohols	465	100	225	55
Bisphenol-A*	0	0		
Ethyl Cellulose	0	0		
B. Formulated Industrial & Consumer Products				
1. Adhesives				
Rubber Based Adhesives	0	0		
Tire Manufacture	0	0		
Tire Retreading	0	0		
Industrial Rubber Products	0	0		
Tire Patch Repair Kits	100	0	100	0
2. Miscellaneous				
Automotive	0	0		
Shoe	0	0		
3. Paints and Allied Products				
Paints & Coating	0	0		
Removers	300 to 500	0	300 to 500	150**
TOTAL	4,789 To 4,989	2,845	1,828 To 2,029	898

*Use in 1976 was 2,990,000 gallons

**Estimated amount in product made prior to May 1977 and sold in 1978

3.3.8 Ambient Benzene Levels

Benzene has been measured in the ambient air of California, all in the southern portion of the State, on a number of studies (Refs. 25-29). The results obtained are shown in Table 3-16. After comparison with ambient data obtained for other volatile organics studied on this program, it will be seen that benzene is present at considerably higher levels. This is particularly true of the stations in the highly urbanized areas of the SCAB.

TABLE 3-16. BENZENE IN THE AMBIENT AIR OF SOUTHERN CALIFORNIA

	Benzene Level, ppb		
Location	Average	Maximum	Reference
Azusa	10	18	25
Azusa	3.3	11	29
Banning	2.3	11	25
Camarillo	0.6	1.9	29
Death Valley	< 0.5	< 0.5	29
Downey	2.6	4.8	29
El Monte	11	19	25
Long Beach	7.3	13	25
Los Angeles	10	21	25
Los Angeles	15	57	26
Los Angeles	40	60	27
Palm Springs	2.1	10	25
Redlands	3.5	12	25
San Luis Obispo	< 0.5	< 0.5	29
San Nicholas IS.	< 0.5	< 0.5	29
Torrance	4.1	(One Sample)	28
Upland	7.5	18	25

Source: Refs. 25-29.

3.4 CADMIUM

3.4.1 Summary of Utilization and Releases

In 1970, according to the Bureau of Mines, California ranked 18th of the 23 zinc-ore producing states in the United States. Lead-zinc, zinc-lead, and lead ores occur in the Eastern border of California, ranging south from Mono County through the Eureka and Death Valleys into northeast Mojave. Such ores are the major source of cadmium, most of which is recovered from dusts or precipitates collected at zinc production plants. Some cadmium is also recovered from lead smelters and waste recovery operations (e.g., involving spent nickel cadmium batteries).

Primary zinc smelting, which is not practiced within the State, accounts for the greatest airborne cadmium releases. Goldberg (Ref. 30) also noted that mining operations do not involve airborne cadmium releases. He did suspect secondary zinc and copper smelters of emitting cadmium fumes. Such operations are basically recycling processes, working scrap of the metal or alloy of interest. Because of the nature of the feedstock (clean scrap), cadmium emission factors (particularly in the case of copper smelters) should be low. Goldberg, however, rates the cadmium releases from secondary zinc and copper smelters at about one-tenth that of the primary zinc smelter.

Utilization of cadmium in the State is fairly prevalent and involves electroplating, cadmium-pigmented paint manufacture and use, cadmium stabilized plastics production, Ni-Cd battery assembly, and such miscellaneous uses as in alloying, nuclear engineering applications, and in various electronic devices (e.g., solar cells). Air release from all of these cadmium-consuming activities is considered to be negligible (Ref. 31 and 32).

Significant cadmium emission sources are actually not involved with the cadmium market. Refuse and sludge incineration, neither of which is practiced to any extent in California, is the second largest source of cadmium release according to Yost (Ref. 31). He estimates that primary smelters and refuse incinerators account for over 96% of the airborne cadmium released in the United States.

Thus, California's principal concern is with the minor (in the National context) remaining cadmium source-types, two of which are industrial in nature: steelmaking and coal-based processes. Another area is the emission of cadmium from automobiles. This particular emission effect results from the wear of automobile tires and the exhaust of lube oil residues. Cadmium occurs in the former as a rubber additive and in the latter as a natural constituent.

3.4.2 Steel Production*

The production of steel is associated with cadmium releases through two pathways: (1) coke production; and (2) use of scrap containing pieces that are cadmium-plated. Thus, in considering steel manufacture, cold rolling operations (U. S. Steel, Pittsburg) and certain types of specialty steel production that do not utilize scrap or coke are not of concern.

In California, only one integrated steel mill (ore to finished steel products) exists: the Kaiser Steel facility at Fontana. This plant is responsible for about two-thirds of the steel made in the State, producing just under two million tons last year. This facility produces its own coke on-site, operating 315 ovens in seven batteries.

Five other mills are operated in the State that input scrap and pig iron. These secondary steel mills are itemized as follows:

Company	Location	Approximate Output (1978) 10^3 Tons
Bethlehem Steel	Vernon	400
U. S. Steel	Torrance	100
Soule Steel	Carson	110
Ameron	Etiwanda	300
Judson Steel	Emeryville	90

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*Much of the information in this subsection was introduced in Section 3.1, q.v. for references, etc.

One mill, the Pacific States Steel Company's Union City Plant, was shut down last November. Reactivation is not anticipated.

3.4.3 Coal Consumption*

The three identified types of coal-consuming processes operating within the State are: (1) coke-forming; (2) Portland Cement production; and (3) steam generation.

A. Coke-forming--

The Kaiser Steel plant in Fontana is the only known coal-coking operation within the State. Annual coal consumption, based on coke feed rate, should be in excess of two million tons. The rated coal capacity is 2,336,000 tons. Because of the relatively low boiling point of cadmium, most of this metal in the feed coal is volatilized off during coking, such that the steel furnaces themselves do not emit much of the metal unless scrap containing cadmium plate is used. Steelmakers try to avoid the inclusion of cadmium plate in feed scrap since it deteriorates the quality of the melts produced.

B. Portland Cement Production--

Coal and coke are used to produce the hot gas feed for the production of lime in counter-current rotary kilns. A number of such facilities were identified, including the following larger ones:

- Riverside Cement Company, Riverside
- Monolith Portland Cement Company, Tehachapi
- Southwestern Cement Company, Victorville
- General Portland Cement Company, Mojave and Colton
- Calaveras Cement Division, Flintkote, San Andreas
- Kaiser Portland Cement Company, San Jose

Coal/coke consumption data were not available, although the use of 100,000 tpy total was specified in one case as being typical. In all of the works contacted, efficient air cleaning systems were described. These typically involved bag-houses for the last-stage of exhaust cleaning, although an electrostatic precipitator was employed in at least one kiln.

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* See previous footnote

C. Steam Generation--

The only coal-fired steam generators operating within the State of California are in Trona. These two boilers are rated at 600,000 lbs/hr steam production each and are at the Kerr-McGee Chemical Company facility. Feed is New Mexican coal and petroleum-derived coke produced in California. The generators are equipped with an electrostatic precipitator (98.5% efficient). The cleaned E.P. output, however, is sent through liquid scrubbers to extract CO_2 which is used to carbonate brine and thus promote yields of the end product, soda ash. The CO_2 removal also results in an SO_x removal that is 98% efficient.

3.4.4 Automobile Emissions

According to the Department of Motor Vehicles, the 1978 population of vehicles utilizing the roads in California was:

Vehicle Type	Quantity
Passenger Cars	12,219,230
Trucks	3,012,150
Motorcycles	672,162
Trailers	2,080,746
	17,984,288

This rolling stock consumed over 11 billion gallons of gasoline in 1978 and in the neighborhood of 400 million quarts of lube oil. The estimated tire rubber abraded away by this California vehicle inventory is 54,000 tons per year (based on Ref. 33). While gasoline contains only traces of cadmium, it is present in various natural amounts in petroleum-derived lube oils. Cadmium soaps (usually stearates) are often used in tire rubber recipes. Cadmium release mechanism has been speculated (Ref. 33). Lube oil cadmium emission probably occurs in the combustion chamber of the engine. The formed oxidation products of organic cadmium then exit through the exhaust system. Tire rubber attrition is probably a more complicated process but apparently involves the generation of fine particulate matter and some vapor. Williams and Cadle (Ref. 33) found that between 1 to 20% of the wear-loss dispersed in the atmosphere, while the balance largely settled near the roadbed. Harrison and Winchester (Ref. 34) implicate the automobile (including its gasoline combustion products) for some contribution to the airborne cadmium found in urban areas.

3.4.5 Secondary Zinc Smelters

Aside from zinc slab melters/casters, which are not considered to be cadmium emitters (Ref. 26), only three secondary zinc smelters operate in the State. These were identified by the Bureau of Mines as:

- Aetna Metals Company, City of Industry
- Pacific Smelting & Refining Company, Torrance
- ASARCO* Federated Metals Division, San Francisco

Such facilities rework zinc scrap in sweat furnaces to produce ingot metal (sows). After chemical analysis, the sows are remelted and realloyed to specifications. Unlike primary zinc smelters which work ore, no cadmium dust is produced and collected. Because of the prior removal of cadmium from marketed zinc, rework of scrap in secondary zinc smelters is not likely to occasion air releases of cadmium that approach those produced in zinc ore roasting, sintering and smelting (Ref. 31).

3.4.6 Secondary Copper and Copper Alloy Smelters

There are no primary copper (ore) smelters located in the State of California, according to the Bureau of Mines. Facilities that melt scrap or prepare alloys from scrap and/or pure ingot metals are few in number. The possibility of cadmium releases from these plants would have to be considered on a case by case basis.

3.4.7 Cadmium Emission Factors

A. Steel Production--

1. Integrated steel plant--The cadmium emission factor for the Kaiser integrated steel mill at Fontana is estimated at 0.2 g/sec or 7.0 metric tons cadmium/yr. This is derived from Yost's estimate (Ref. 35) for all steel mills of 266 metric tons cadmium/yr. Kaiser's contribution was factored from this on the

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* American Smelting and Refining Co.

basis of rated coal capacity (2.336×10^6 tons/yr vs. 97.298×10^6 tons/yr for all U.S. Steel plants). It should be recognized that variations of considerable degree exist in the coal ash and iron ore cadmium content, the manufacturing processes and feed compositions employed, and in the type of APC equipment typically in place throughout our Nation's steel mills. These factors will significantly influence cadmium emissions.

The cadmium release estimated for Kaiser, Fontana, represents the potentially highest rate identified for that metal on this study. It should be noted also that the atmospheric cadmium concentrations for the nearby City of San Bernardino were the highest of any recorded in California by the National Air Sampling Network (NASN). The data cited are for 1973 in which year average cadmium levels of 0.013 $\mu g/m^3$ were measured. This is over twice the average (0.006 $\mu g/m^3$) for the 15 other California cities monitored.

2. <u>Secondary steel mills</u>--Data on the release of cadmium from mills working scrap with pig iron are limited. Yost's (Ref. 35) values estimated for controlled and uncontrolled furnaces are 0.05 and 2.62 g, respectively, per ton of steel produced. This assumes an APC efficiency of 98%. The five mills in California are all equipped with APC systems, bag houses in most cases (U.S. Steel, Torrance, employs an E.P.). It can be assumed that cleaning efficiency is 98% or better. Thus, using Yost's release factors for controlled mills and factoring in production data, the following releases (Table 3-17) are estimated:

TABLE 3-17. ESTIMATED CADMIUM RELEASE RATES FOR SECONDARY STEEL MILLS IN CALIFORNIA

Company/Location	Estimated Cadmium Release Rate, lbs/yr
Bethlehem Steel, Vernon	45
U.S. Steel, Torrance	11
Soule Steel, Carson	12
Ameron, Etiwanda	33
Judson Steel, Emeryville	10

3. Geographic distribution of California steel mills and associated cadmium release estimates--Figure 3-10 sites the steel mills in California and the estimated emission rates calculated for each.

B. Coal Consumption--

1. Coke forming--See integrated steel plant.

2. Portland cement production--Cadmium (and arsenic) release in calcining is not only controlled by the APC equipment installed but by the nature of the process itself. Countercurrent flow of the dehydrating cement powder and coal/coke combustion gases promotes the capture of cadmium-containing particulates and condensation of cadmium vapor on elutriated fines in the colder (cement input) sections of the kiln.

For the above reasons, an insignificant emission of cadmium from cement kilns is probably the case.

3. Steam generation--The two Kerr-McGee coal/coke-fired boilers at Trona are rated at 98% efficient for SO_2 removal. This stage, which is actually a critical step in the soda ash production scheme and is not intended for APC per se, follows an E.P. rated at 98.5% efficiency. As in the case of arsenic, it is therefore believed that cadmium release is insignificant (see Section 3.1).

C. Automobile Emissions--

Subramani (Ref. 31) estimates that the loss of particulate tire matter from the average automobile is 0.918 lb/1000 miles of travel. Assuming a conservative mileage of 10 miles/gal, tire-wear loss would be 54,000 tons in 1978, based on the 11.8 x 10^9 gals consumed in the State from July 1977 to June 1978. Goeller et al (Ref. 37) estimated the national emissions of cadmium from tire-wear and lube oil to be 12.8 x 10^3 lbs/yr. Assuming (conservatively) that California contributed 10% of this, and correcting for the ensuing increase in gasoline consumption (13.5%), roadbed cadmium emissions would now be about 1.5 x 10^3 lbs/yr.

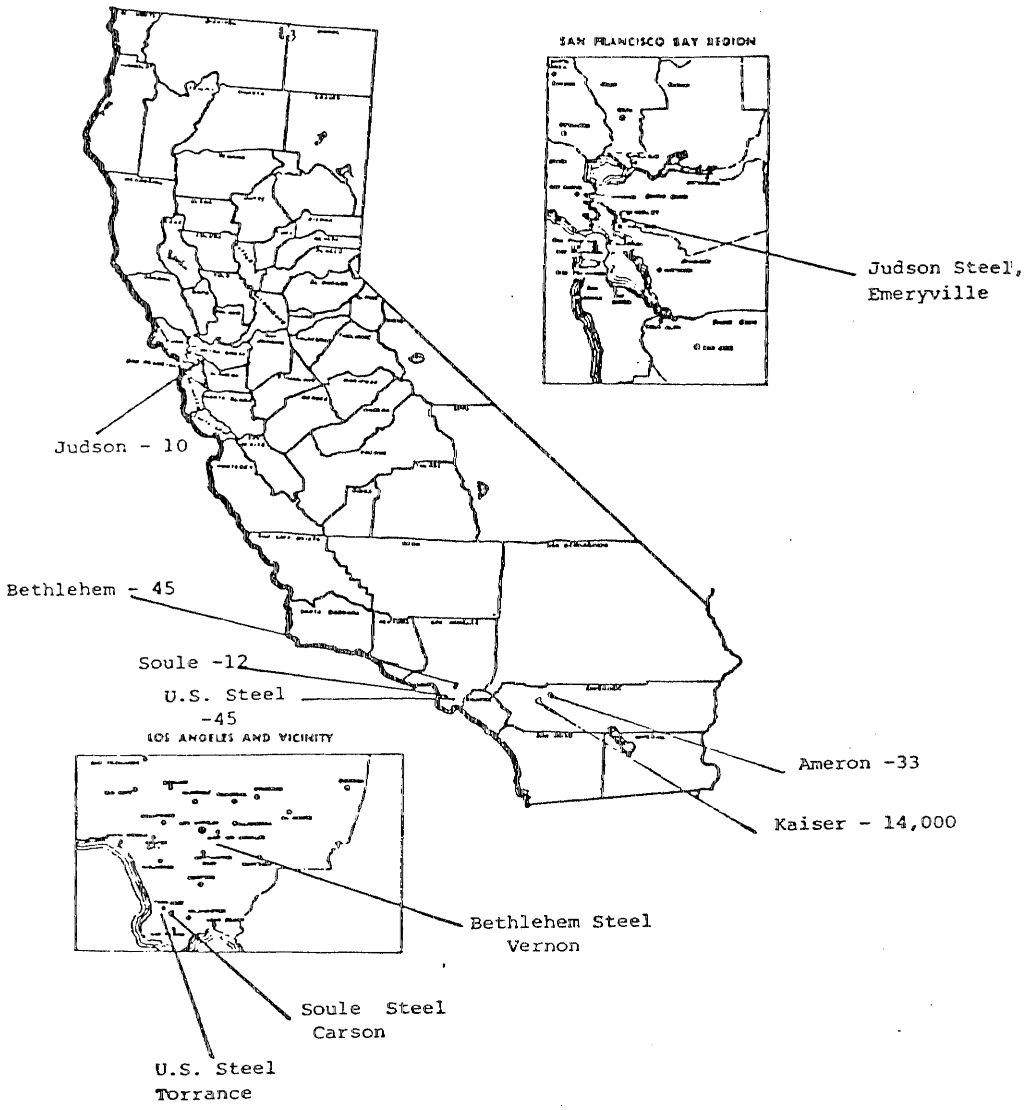

Figure 3-10. Estimated cadmium emissions (lbs/yr) from steel production plants.

Distribution of this cadmium tends to concentrate about the roadbed itself. Somewhere between 80 to 99% of it is particulate and this fraction probably incorporates all or most of the released cadmium (Ref. 33).

D. Secondary Smelters--

1. Secondary Smelters--Unlike primary zinc smelters and secondary copper smelters, the secondary zinc smelter has apparently not been characterized for cadmium emissions. Because of the primary process from which it was formed, zinc scrap, the feed for the secondary smelter should be low in cadmium content. Furthermore, the nature of the primary process is far more conducive to cadmium release than is the secondary process.

Thus, lacking any survey data or related estimates, the cadmium emission factor* for the scrap steel/pig iron mill was assumed to apply. This was arbitrarily increased by a factor of twenty and was multiplied by production figures. The latter were rough approximations furnished by a technical manager of one of the smelters. The resulting releases computed, which proved quite small, are shown in Table 3-18.

TABLE 3-18. ESTIMATED CADMIUM EMISSION RATES FOR SECONDARY ZINC SMELTERS

Mill/Location	Estimated Cadmium Emission Rate, Lbs/yr
Aetna Metals, City of Industry	200
Pacific Smelting & Refining Co., Torrance	300
ASARCO Federated Metals Division, San Francisco	60

2. Secondary copper smelters--The Bureau of Mines identifies four secondary smelters that process scrap copper and copper alloys in the State. They are:

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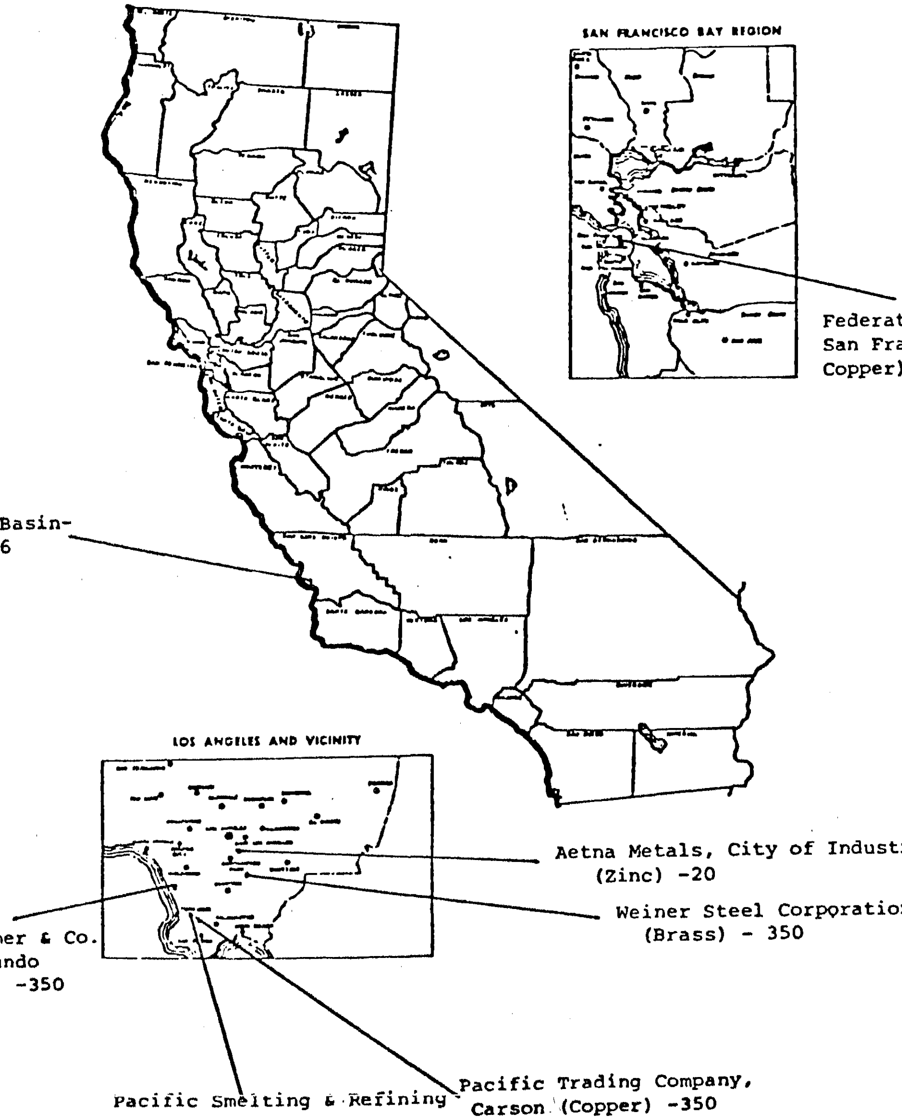
* 0.05 lb per ton of metal produced (See Sec. 3.4.7.A.2)

- Federated Metals Division, ASARCO, Inc., San Francisco
- H. Kramer & Company, El Segundo
- Pacific Trading Corporation, Carson
- Weiner Metals Division, Weiner Steel Corporation, Paramount

Factors have not been derived for cadmium emissions, although Goldberg (Ref. 30) estimates that, nationally, such installations release as much as 70 tons per year of cadmium. This would suggest fairly large releases for the four smelters itemized. All, however, operate APC systems and it is doubtful that releases exceeding 10% of what would be estimated from Goldberg's data for secondary smelters would be likely. This should be verified, of course, by actual testing on-site. For the purposes of this report, it was assumed that the output of California's secondary copper metal/alloy smelters would be 10% of the National product, which is undoubtedly an overcredit. Then, using Goldberg's factor and applying a 90% reduction for APC benefits, an emission of 1,400 lbs cadmium per year was estimated. Since the specific production figures for the four smelters could not be obtained, the release was equally divided. From the comments offered by their representatives, it is believed that ASARCO and Kramer merit larger fractions.

E. <u>Geographic distribution of cadmium emissions from nonferrous secondary smelters</u>--The potential release points of cadmium from secondary zinc and copper metal/alloy smelters is shown on Figure 3-11.



ASARCO,
Federated Metals Div.,
San Francisco (Zinc &
Copper) -370

L.A. Basin-
1086

Aetna Metals, City of Industry
(Zinc) -20

Weiner Steel Corporation, Paramount
(Brass) - 350

H. Kramer & Co.
El Segundo
(Brass) -350

Pacific Smelting & Refining
Company, Torrance
(Zinc). -30

Pacific Trading Company,
Carson (Copper) -350

Figure 3-11. Estimated cadmium emissions (lbs/yr) for secondary non-ferrous smelters.

3.5 CARBON TETRACHLORIDE

3.5.1 Summary of Production and Usage

A. Production--

The role of carbon tetrachloride (CT) as an industrial chemical has been diminishing. Following the announcement of its suspected carcinogenicity in 1974, use of the material in solvent and related applications particularly declined. The surviving and principal use of CT is for conversion to trichlorofluoromethane and dichlorodifluoromethane (fluorocarbon -11 and -12, respectively). These materials have been used primarily as aersol propellants, which usage now has given way to LPG mixtures that are deemed environmentally more acceptable.

National CT production was 770 million lbs in 1978, a drop of 34% from the 1974 peak. Annual CT production is expected to drop further to 500 million lbs by 1982, according to the Chemical Marketing Reporter (April 10, 1978). Du Pont has closed its Freon plant in East Chicago; Union Carbide stopped all fluorocarbon production by shutting down its plant at Institute, West Virginia; Stauffer ceased CT production at its Niagara Falls facility; and FMC expects to discontinue CT manufacture at its Charleston, West Virginia plant by the end of this year.

The only CT made in California is by Dow Chemical Co. at its Pittsburg plant on the San Joaquin River. Capacity is 80 million lbs/yr. Production varies considerably, however, since Dow depends on sales to the nearby Du Pont freon plant at Antioch, which also receives CT from du Pont, Corpus Christie, TX. Fluctuations in CT demand are compensated for by Dow by varying the output of perchloroethylene, which is a coproduct in the synthesis, the comparative yield of which can be varied by altering the feed stock composition. All of Dow's CT output is used as intermediate in fluorocarbon syntheses. The above information was furnished by Dow's Mr. Bryant Fischback who was a member of the Panel of Experts convened for this program by SAI.

According to Dow's Daniel (Ref. 38), CT and perc are produced in equimolar amounts by the chlorination of methane at 550 to 650 °C without need of a catalyst:

$$\underset{\text{(Methane)}}{CH_4} + \underset{\text{(Chlorine}}{Cl_2} \longrightarrow \underset{\text{(CT)}}{CCl_4} + \underset{\text{(Perc)}}{C_2Cl_4} + HCl$$

$$+ \text{ excess } Cl_2$$

Ethylene can be substituted for methane or combined with it to increase the yield of perc with respect to CT or, by eliminating methane produce no CT at all.

The process flow described by DeShon of Dow (Ref. 39) is shown in Figure 3-12. The reaction is exothermic and so rapid that undesired products will form unless heat is absorbed in the reactors. This is done by feeding back through the evaporator cooler vapors of the halocarbon products along with recycled (excess) chlorine and unreacted hydrocarbon feed.

Hot gases leaving the reactor are similarly cooled by contacting them with liquid product in the quench column. The condensate from the quench tower is sent on to the fractionation column while the vapors are passed through the condenser system to furnish the recycle liquid for the quench tower and the evaporator supplying cooling vapor to the reactor.

Distillation cuts of CT and perc are further purified to remove traces of chlorine and acid. The products are then held in check tanks until passed by QC for removal to regular storage.

Being an entirely closed system, volatile losses are likely to occur at pump seals, valves, flanges, and the vents of the check tanks and distillation column. External to the process, additional losses can be expected at the storage tank and in handling the materials for shipment.

B. Usage--

1. Fluorocarbon synthesis--The du Pont Antioch Works was consulted as to CT usage and emissions in the production of Freons 11 and 12. They advised by letter that the CT consumption at Antioch was 50.2 million lbs during 1978. This value proved to be a fair validation of the KVB estimate of 60 million lb which was developed from an assumptive scenario for use had not du Pont been so cooperative.

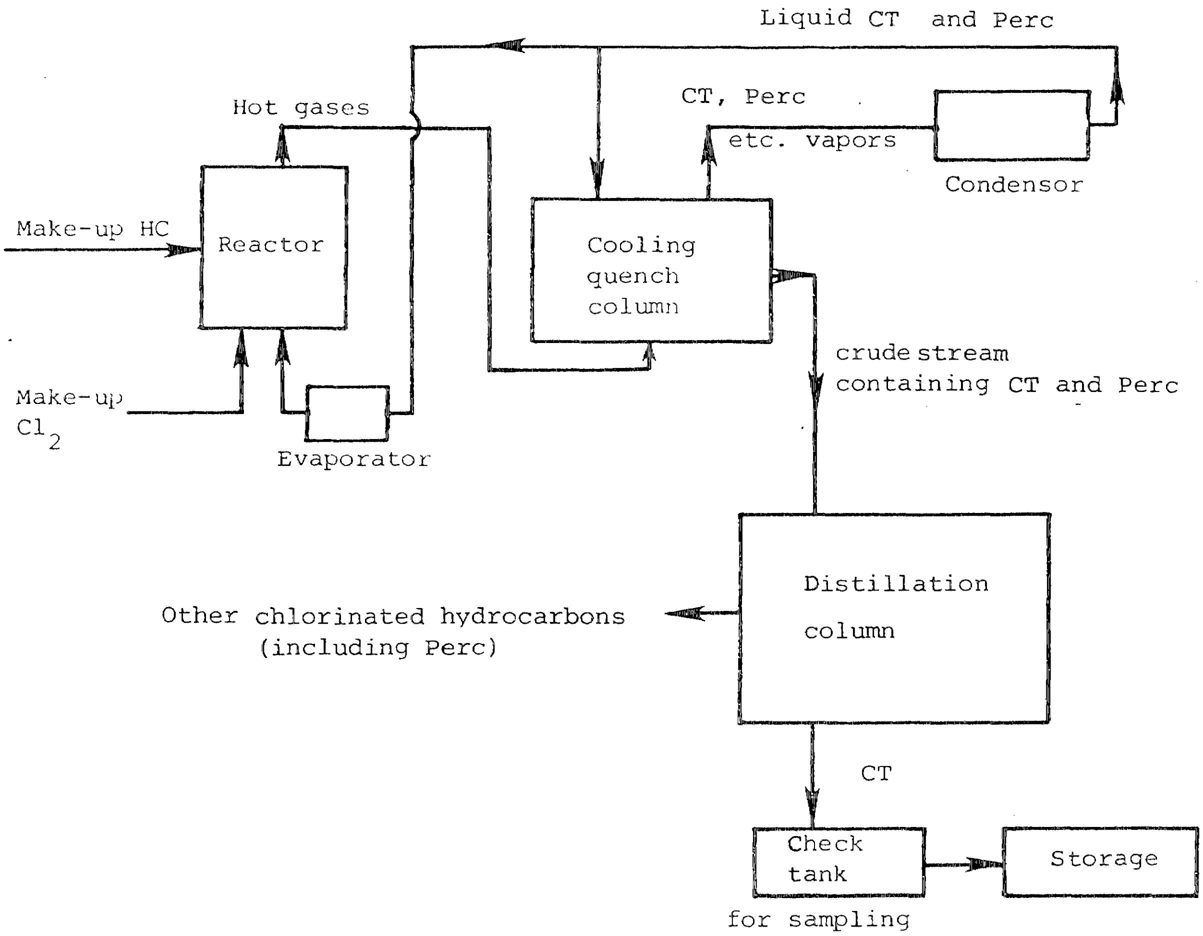


Figure 3-12. Process flow diagram for the production of carbon tetrachloride (and perchloroethylene) (Source: Ref. 39)

Allied Chemical Corp. as late as 1977 produced Genetron 11 and 12* from CT at its El Segundo Plant. Production was then shifted over to Genetron 22, using chloroform as the hydrofluorination intermediate. Then, in March, 1979, Allied returned to G-11 and -12 production, in reaction to market fluctuations, according to a company spokesman.

CT consumption at the Allied El Segundo plant in 1977 was reported to KVB by that company as 26.6 million lbs/yr. Because CT consumption in 1978 (6.8 million lbs) was interrupted with the substitution of chloroform and 1979 CT input data would be for too short a period, the current rate was assumed to be the same as for 1977.

The generally used process (Ref. 40) for synthesizing F-11 and F-12 fluorocarbons is shown in Figure 3-13. The reaction involves the anhydrous reaction of CT with hydrogen fluoride (HF) in the presence of a catalyst, typically antimony pentachloride ($SbCl_5$):

$$\underset{\text{(CT)}}{CCl_4} + HF \longrightarrow \underset{\text{(F-11)}}{CCl_3F} + HCl$$

$$CCl_4 + 2HF \longrightarrow \underset{\text{(F-12)}}{CCl_2F_2} + 2HCl$$

If chloroform is substituted for CT, as was done for a time at Allied Chemical, El Segundo, F-22 results.

$$\underset{\text{(Chloroform)}}{CHCl_3} + 2HF \longrightarrow \underset{\text{(F-22)}}{CHClF_2} + 2HCl$$

In the process, CT and HF are bubbled through molten $SbCl_5$ (m.p.t. = 2.9 °C). Because the reaction is weakly endothermic the reactor is steam jacketed and maintained at between 66 and 94 °C. The product vapor is passed through a fractionation tower, the CT condensate is recycled to the reactor, while the flurocarbon and HF vapors are passed through a water scrubber to remove most of the HF. The last traces of HF and any chlorine produced in the synthesis are removed in a caustic scrubbing tower. The wet fluorocarbon vapor is then passed through a concentrated sulfuric acid scrubber to dry the gas.

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* Genetron and freon (G & F) are trade names denoting the same chemicals by numerical suffixes.

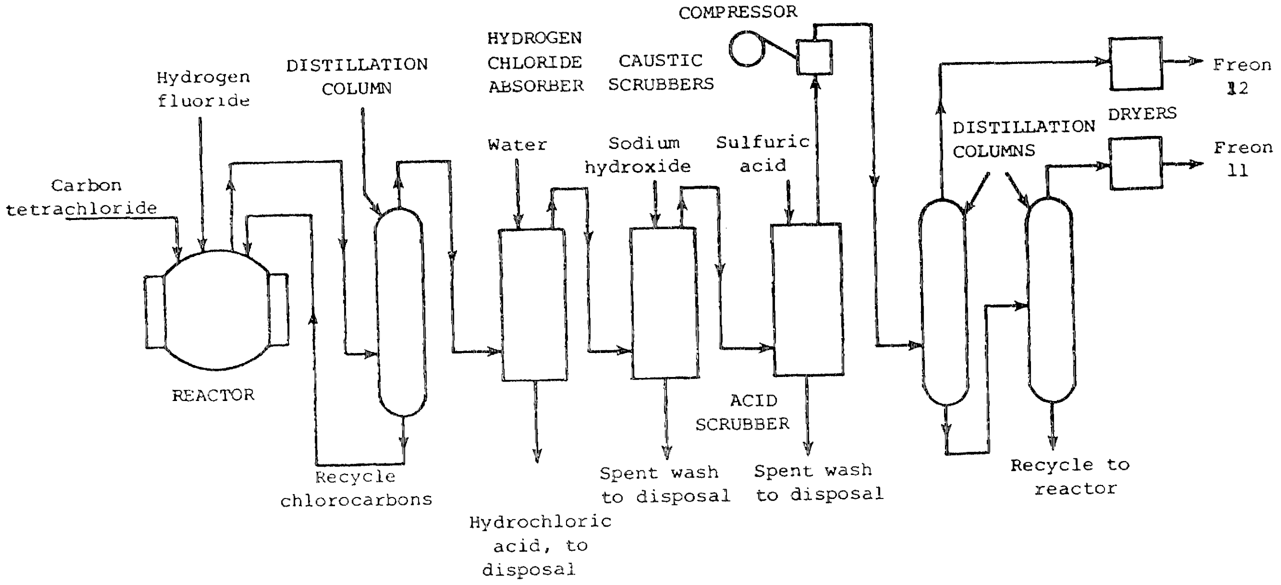

Figure 3-13. Flow diagram of process for conversion of carbon tetrachloride to flurocarbons (Source: Ref. 40)

The mixture of F-11 and F-12 is then compressed and passed through two condensation stages. The first removes liquid F-11, passing off F-12 vapor for final drying and condensation. The F-11 is vaporized in the last distillation stage, any condensate (predominately CT) being recycled back to the reactor.

Because the process largely converts a bulk of the feed CT in the first stage of this closed process, release of CT from the system will be restricted to the input piping. External to the process, storage and handling of CT would represent the most likely points for atmospheric release of CT.

2. Other uses of CT--In other uses of CT, agricultural fumigation operations consumed 6,802 lbs in 1977 according to the Pesticide Usage Reports. Most (68%) of that amount was reported by the Food and Agriculture Division as controlled by "other agencies". These were primarily in San Francisco and Alameda Counties. This indicates probable use in grain ships and elevators, the principal use-points for CT in agricultural operations. In any case, the total amount was quite small and does not warrant further attention.

Other CT uses in California could not be identified. With one exception, none of the manufacturers of CT acknowledged sales of the chemical in California for other than use as a flurocarbon synthetic-intermediate. The one exception was Vulcan Materials Co. who declined to divulge any CT marketing information that "would be available to public scrutiny". This also applied to the three other halocarbons (chloroform, ethylene dichloride, and perchloroehylene) Vulcan manufactures that were also studied on this program.

C. Ambient CT Levels--

The many atmospheric values obtained for this pollutant (predominately in the Los Angeles Basin) show rather low levels. Pellizzari (Ref. 28) found a "hot spot" concentration of 38 $\mu g/m^3$ CT at ground level in the city of Torrance. The sampling point was in the vicinity of the Montrose Chemical Co. pesticide plant and within a two mile radius of the Mobil Oil Refinery, a PPG Industries paint factory, and a Dow Chemical Co. plant. The CT level at this "hot spot" can be compared with the National Academy of Sciences value ($0.82 \mu g/m^3$) for world background, which was derived from tropospheric CT data reported by various scientists (Ref. 34). The Torrance level can also be compared with the OSHA MAC (65 mg/m^3, 8 hr twa), three orders of magnitude higher.

3.5.2 Emission Factors

A. Production Losses--

The amount of carbon tetrachloride lost to the atmosphere during synthesis is estimated at 1.6 wt % by the National Academy of Sciences (Ref. 41). Thus, using that fractional loss and assuming production at 25% of capacity, the Dow plant could be responsible for a release of 0.32×10^6 lbs/yr (4.75 g/sec). These losses would occur during production itself, storage of the output, and shipping of material.

This same plant also manufacturers perchloroethylene (see Section 3.10). Production of this solvent ($22\text{x}10^6$ lbs/yr) is estimated to be about the same as has been assumed here for CT ($20\text{x}10^6$ lbs/yr). Using the release factor (Ref. 67) estimated by a different source, the total plant emissions of perchloroethylene turn out to be about one seventh those of CT. The latter has a considerably lower boiling point (75 °C vs. 121 °C) than perchloroethylene, but it is doubtful that this property would account for such a large difference in the losses of the two compounds. This matter will best be clarified through source testing.

Because Dow did not wish to comment on perchloroethylene release estimates (see Section 3.10.5.A) made by others, they were not consulted in the CT emission matter.

B. Conversion Losses--

Carbon tetrachloride loss during conversion to fluorocarbons is estimated estimated at 3 wt % by A. D. Little, Inc. (Ref. 42). Monsanto put the factor at 1.7 wt % (Ref. 41). On the basis of other estimates (Ref. 44-46), the NAS estimated (Ref. 41) atmospheric losses at 1.0 wt % of CT input. This would impute an annual CT release at du Pont, Antioch, of 502,000 lbs/yr and at Allied, El Segundo, of 265,000 lbs/yr, based on the CT consumption data cited earlier. Du Pont stated that their CT atmospheric releases were in the range of 20,000 to 40,000 lbs/yr, arising almost entirely from CT off-loading and storage (20,000 to 30,000 lbs/yr) with smaller losses (∿3200 lbs/yr) occuring at the reactor vent, a device that is utilized only about six times a year to accommodate maintenance. Allied stated that no chloroform could be detected at the Genetron tails tower (the principal process emission source) when working that halocarbon. They further stated that the same result would occur when CT was the processed chemical. KVB's sampling results (Ref. 22) at the Genetron plant in 1977 confirm this assessment. In terms of storage and offloading, however, the more diffused nature of any emissions occurring at these points may have escaped detection. The instruments used were not highly sensitive in CT measurement. Based on du Pont's emission estimate and factoring for comsumption rate, the CT release at El Segundo would be less than 7,000 lbs/yr. This is equivalent to a release of 0.1 g/sec.

Although KVB is inclined to agree with du Pont that the NAS emission factor is far too high, a range (with the NAS and du Pont estimates as the extremes) is tabulated as follows:

ESTIMATED CT LOSSES FROM TWO FLUOROCABRON PLANTS

Plant	Annual CT Consumption, 10^6 lbs	Estimated Range of CT Emissions, lbs/yr
Du Pont, Antioch	50.2	20,000-502,000
Allied, El Segundo	26.5	10,000-265,000

C. Natural CT Formation--

Trace amounts of CT are known to form in water bodies where organic solutes are broken down to halomethanes. As explained in Reference 47, these progressively add chlorine, producing CT, chloroform and other halocarbon species.

D. Geographic Distribution--

Because only three point sources are identified, two of which are in adjacent towns, a map is not shown here. The demographic CT impact is, however, mapped in Section 4.0.

3.6 CHLOROFORM

3.6.1 Summary of Distribution and Usage

As with CT, the usage of chloroform has become considerably restricted because of health considerations, including carcinogenicity factors. The single major end-use of chloroform is in the production of chlorodifluoromethane (Fluorocarbon-22). This refrigerant/propellant has recently absorbed some of the diminishing markets for F-11 and F-12, such that chloroform production has increased in the past few years. According to the Chemical Marketing Reporter (September 25, 1978), the six month periods ending June 1977 and 1978 saw National chloroform production at 130 and 172 million lbs, respectively. The same report shows F-22 production during the latter six month period at 99 million lbs. This would require 80% of the chloroform produced during that same period, assuming stoichiometry and no process losses.

No chloroform is produced in the State but one F-22 plant was operated at El Segundo. This is owned by Allied Chemical Corp. and was on F-22 stream a relatively short time. The plant formerly produced F-11 and F-12. As of March, 1979, Allied switched back to F-11 and F-12 production and now no longer consumes chloroform (see Section 3.5.1. B-1).

Solvent and other minor uses of chloroform in the State were quite limited. According to CALOSHA officers, the only known users of chloroform in the State are laboratories. The Rancho Los Amigos, for example, uses hundreds of gallons each year in testing inmate urine specimens for narcotics. Significant industrial uses, other than at El Segundo, are virtually unknown. The principal minor use of chloroform is in pharmaceuticals synthesis, little of which is done in this State according to trade contacts.

Chloroform is produced in natural and in sanitary water systems where the effect is certainly not sought. Chlorine in drinking water, for example, can produce up to 90% conversions of trace carboxylic acids to chloroform (Ref. 47). Sources of this type, the oceans, and other natural processes account for a world chloroform background (tropospheric) of about 32 ppt according to the NAS (Ref. 41). This same source estimates a typical urban level of chloroform at about ten times that concentration. The CALOSHA MAC (8 hr twa) is 25 ppb, which is about 75,000 higher than the urban average.

Further consideration of this compound is felt not to be warranted for the following reasons:

- No "hot spots" could be associated with its very small usage.
- Usage is not likely to increase.
- Present ambient levels of chloroform are relatively low.

3.7 ETHYLENE DIBROMIDE

3.7.1 Production-Usage Summary

Ethylene dibromide (EDB) is produced by some 23 firms, although some 59 firms have registered as manufacturers of the material in the U.S. None are located in California. Most EDB production goes into leaded gasoline. In this role, its use is declining in proportion to the diminishing use of tetraethyllead. This market nonetheless constitutes about 80% of the national demand for EDB.

In agriculture, EDB is used for the control of fruit fly larvae, wire worms, and nematodes. The first mentioned application comprises the largest pesticide use of EDB but is only practiced in Florida and Texas. The principal agricultural use of EDB in California has been on fields on which beans, watermelon and carrots have been grown. Because of its demonstrated toxicity, EDB is not allowed in home-used pesticide formulations.

Other markets for EDB include its use as an organic synthetic intermediate and as a specialty solvent for certain resins, gums and waxes. No significant comsumption of EDB in California for either of these applications could be identified on this study.

3.7.2 EDB Use in Gasoline

A. Gasoline Refineries--

Antiknock solutions that are added to gasoline typically contain tetraethyllead (TEL), EDB, and ethylene dichloride (EDC), the last item being subject to separate consideration in this report. The weight ratios reported to KVB by the Ethyl Corporation for these mixtures are 1.000: 0.294:0.304, respectively. On an elemental basis, this is equivalent to an atom ratio of 1:1:2 for Pb:BR:Cl. The function of the two haloethanes is to provide available halogen with which combustion-formed lead oxide may react and thus produce volatile lead halides that will then pass through the exhaust system. In preventing lead build-up in the engine, the additives are thus called lead scavengers.

The consumption of EDB in gasoline production is fixed to the amount of TEL that is incorporated. Thus EDB purchases by refiners have dropped as the permissable levels of TEL have been set lower by regulation. In the summer of 1978, the following average TEL contents were reported by DOE (Ref.48) for gasolines sampled at refineries and service stations.

	TEL Content (As Pb) in Gasoline, g/gal	
	Regular	Premium
Northern California	1.13	1.63
Southern California	1.10	2.03

Present usage, according to the CARB, is 1.00 g Pb/gal. This is based, however, on total gasoline production. If the unleaded gasoline volume (about 34% of the total according to the Franchise Tax Board) is omitted, the average lead content would be 1.52 g.gal for the leaded types of gasoline.

According to the California Energy Commission, total gasoline production in California for July 77 - June 78 was 12.7 X 10^9 gals. This includes imports and exports, which amounted to a net export of about 8%. This called for the use of 12.7 X 10^9 g of Pb in that portion of that gallonage that was leaded. This is equivalent to 19.8 X 10^9 g as TEL or 5.8 X 10^9 g EDB or an annual demand of 12.8 X 10^6 lbs of EDB for gasoline doping in the state.

Distribution of this demand is among some 26 refineries in the state. A listing of these facilities and their capacities are shown in Table 3-19. The total capacity reflects an annual gasoline output of 15.6 x 10^9 gals. Since the annual (July 77 - 78) recorded production was 12.7 X 10^9 gals, operations were 81% of capacity.

The relative amount of leaded gasoline that is produced at each of the refineries listed in Table 3-19 of course varies. Most refineries produce

TABLE 3-19 GASOLINE REFINERIES OPERATING IN THE STATE OF CALIFORNIA

Company	Location	Crude Oil Operating Capacity, 10^3 bbl/day	Gasoline Prod. Capacity, 10^3 bbl/day
ARCO	Carson	185	87.4
Beacon Oil Co.	Hanford	12.4	2.6
Champlin Petroleum Co.	Wilmington	30.7	3.0
Chevron USA	Bakersfield	26.0	2.6
Chevron USA	El Segundo	230	125.4
Chevron USA	Richmond	338	145.8
Douglas Oil Co.	Paramount	46.5	8.5
Exxon Co., USA	Benicia	88.0	73.8
Fletcher Oil & Ref. Co.	Carson	20.0	4.2
Gulf Oil Corporation	Santa Fe Springs	51.5	28.5
Kern County Refinery	Bakersfield	15.9	2.6
Lion Oil Co.	Avon	126	74.3
Lion Oil Co.	Bakersfield	40.0	33.2
Mobile Oil Co.	Torrance	123	88.4
Mohawk Petroleum Corp.	Bakersfield	22.1	2.2
Pacific Refining Co.	Hercules	53.3	17.7
Powerine Oil Co.	Santa Fe Springs	44.1	13.4
Shell Oil Co.	Martinez	87.4	43.3
Shell Oil Co.	Wilmington	90.0	45.0
Sunland Refining	Bakersfield	15.0	1.0
Texaco, Inc.	Wilmington	62.5	74.4
USA Petrochem Corp.	Ventura	15.0	5.0
Union Oil Co. of Calif.	Arroyo Grande	41.0	4.2
Union Oil Co. of Calif.	Rodeo	70.0	51.0
Union Oil Co. of Calif.	Wilmington	108	79.5
West Coast Oil Co.	Bakersfield	16.0	2.0
	TOTAL	1957.4	1019.0

Source: Oil & Gas Journal

KVB 26900-836

two grades of leaded gasoline, the premium grade typically containing higher concentrations of TEL, EDB, and EDC than the regular grade. In contrast Union Oil offers only one grade, their premium. Not all of the refineries operating within the state produce unleaded gasoline. Thus the amount of TEL added per output gallon of gasoline varies somewhat from refinery to refinery and within the same refinery as demand and reserves fluctuate.

Determining by canvass the actual amount of TEL and, thus, EDB and EDC blended into production by each refinery was not practical. The adopted simplification was to apply the statewide TEL doping level (1.00 g Pb/gal) for all gasoline (including lead-free) to each of the individual producers. In terms of the end consideration (EDB emissions in populated areas), this approach does not pose serious inaccuracies. Most of the California refineries are grouped in three discrete geographical areas: (1) the Los Angeles basin; (2) Carquinez Straights; and (3) the Bakersfield area. With the exception of the Chevron-Richmond refinery, which is only about 12 miles from the Carquinez refineries centerpoint, all of the other refineries in the state account for less than 2% of the total gasoline production in the state. Because of this grouping, any variations in TEL usage-ratios from plant to plant within each area should only be discernible in the associated emissions on a very localized basis.

Variations in TEL doping levels between the three State refining areas was also assumed to be minor. This is supported by the DOE lead data tabulated earlier.

Observing these assumptions, Table 3-20 lists the State refineries in the geographic grouping cited. The estimated leaded gasoline production is derived from total production data that was shown earlier in Table 3-19, the assumption that the average refinery production was 81% of capacity, and that 34% of the resultant gallonage is unleaded. The TEL doping level is assumed to be 1.52 g Pb/gal of leaded gasoline produced, and that 0.445 g of EDB is added to the composite gallon of leaded gasoline.

TABLE 3-20. ESTIMATED LEADED GASOLINE PRODUCTION AND ASSOCIATED EDB USAGE IN CALIFORNIA DURING 1977/1978

AREA	Number of Refineries	Estimated Leaded Gasoline Production, 10^6 gal/day	Estimated EDB Usage, 10^6 lbs/yr
Los Angeles Basin	10	10.7	3.8
Carquines Straights	5	5.8	2.1
Bakersfield Area	5	0.93	0.3
Other*	4	3.3	1.2
Total	24	20.7	7.4

* 92.4% of the production for this category is located at the Chevron-Richmond Refinery.

TABLE 3-21. EDB USAGE IN CALIFORNIA FOR VARIOUS TYPES OF PEST CONTROL DURING 1977

Source: Pesticide Usage Report 1977

TYPE APPLICATION	EDB APPLIED, LBS	ACRES TREATED
Crop Applications		
Barley	91	40
Beans	170,460	8,746
Broccoli	144	4
Carrots	78,603	2,032
Cauliflower	114	2
Lettuce	10,577	135
Melons	1,037	30
Parsnips	3,408	100
Bell Peppers	11,357	502
Potatoes	13,873	230
Tomatoes	133,125	3,015
Watermelons	55,676	465
Land Applications		
Fallow Land	8,640	48
Open Land	4,320	200
Non-Agricultural Areas	6,920	267
Soil Fumigation	13,069	314
Other Applications		
Structural Control	1,158	
Residential Pest Control	4.6	
Other Agencies*	2,801	
TOTAL	515,378	

*Material use controlled by other agencies, exact use not known.

B. Gasoline Marketing and Combustion

Although the largest potential point-source releases of EDB would be expected to be the refinery (during mixing), the marketing paths for gasoline and the roadbeds over which gasoline is carried and its combustion by the vehicular traffic must also be considered. Gasoline vapor emissions associated with transport, transfer, vehicle fitting and operation of the latter have been reasonably well estimated. Because EDB has a much lower vapor pressure than gasoline, (12 vs ∿ 400 Torr at 25° C), only slight losses can be expected. With the increasing population dominance of the newer production, controlled-vent automobile and the introduction of vapor recovery systems at gasoline and other pumping stations, this source of EDB emissions may not be significant. (See Section 3.7.5.B)

3.7.3 EDB Use in Pest Control

The data examined on the consumption of EDB for pest control were for the calendar year 1977. In that year, the Pesticide Enforcement Branch of the California State Food and Agriculture Department recorded applications totalling 515,378 lbs. This includes the use of EDB in both the neat form and as constituent in compounded products. The breakdown of this usage by types of applications are shown in Table 3- 21.

The usage of EDB is restricted by law and it is not permitted in products used in households. No exemptions are allowed in use, as is common with other pesticides, so that applications made either by commercial operators or by the farmers themselves must be reported to the State. Despite this requirement, the usage reports are probably on the low side since some illicit usage probably occurs.

The quantity recorded for pest control is 0.75% of the amount consumed in doping gasoline in 1977. This agrees with the 0.5% fraction estimated by Johns for 1975 (Ref. 49). In view of the directed reduction of TEL concentration in gasoline, one would expect a higher relative farm usage of EDB after the two intervening years.

California is not a heavy user of EDB. Texas and Florida use considerably more of the chemical because of their problems in the control of fruit flies. These are exterminated in the larval stage by fumigating citrus fruit. This is done in confined structures, including transport trailers, sometimes near populated areas. California has yet to employ this technique, according to information reported to the State. If present trends in fruit fly populations within the State should worsen, EDB usage in California could greatly increase. Because of the way the chemical is handled for this particular application, special consideration of the associated emission factors would then have to be given.

Of the 58 counties in California, only 6 reported EDB usage to the Food and Agriculture Department in amounts that exceeded 1,000 lbs for the year 1977. Data for these counties and the type of application reported are given in Table 3-22. Usage data for all counties reporting EDB applications are mapped on Figure 3-14, which also outlines the major growing areas within the State. Most of the material applied involved one-time disinfection.

It would be noted from these data that almost 70% of the EDB reported for 1977 in pest control applications was used in two counties: Stanislaus and Imperial. Over 10% of the EDB used in pest control was applied to only 465 acres of watermelon fields in Imperial County. The Agricultural Commission of that county pointed out, however, that this small acreage was probably scattered in 40 to 80 acre plots throughout the county. The application rate of 120 lbs/acre involved there was exceeded in Fresno and Merced Counties, where 190 lbs/acre was applied to fallow farm land.

TABLE 3-22. EDB USAGE FOR PEST CONTROL IN CALIFORNIA COUNTIES IN AMOUNTS EXCEEDING 1000 LB/YEAR DURING 1977

SOURCE: California Department of Food and Agriculture Files

County	Application	EDB Applied, Lbs.	Acreage Treated
Fresno	Fallow Farm Land	5,400	30
Imperial	Carrots	66,354	1,773
	Lettuce	10,577	135
	Parsnips	3,408	100
	Watermelon	55,676	465
	TOTAL	136,015	
Merced	Fallow Farm Land	3,240	18
Solano	Other Agencies*	2,457	--
Stanislaus	Beans	147,821	7,644
	Tomatoes	71,027	1,354
	TOTAL	218,848	
Ventura	Beans	4,729	82
	Tomatoes	1,584	115
	TOTAL	6.313	

*Material use controlled by other agencies, exact use not known.

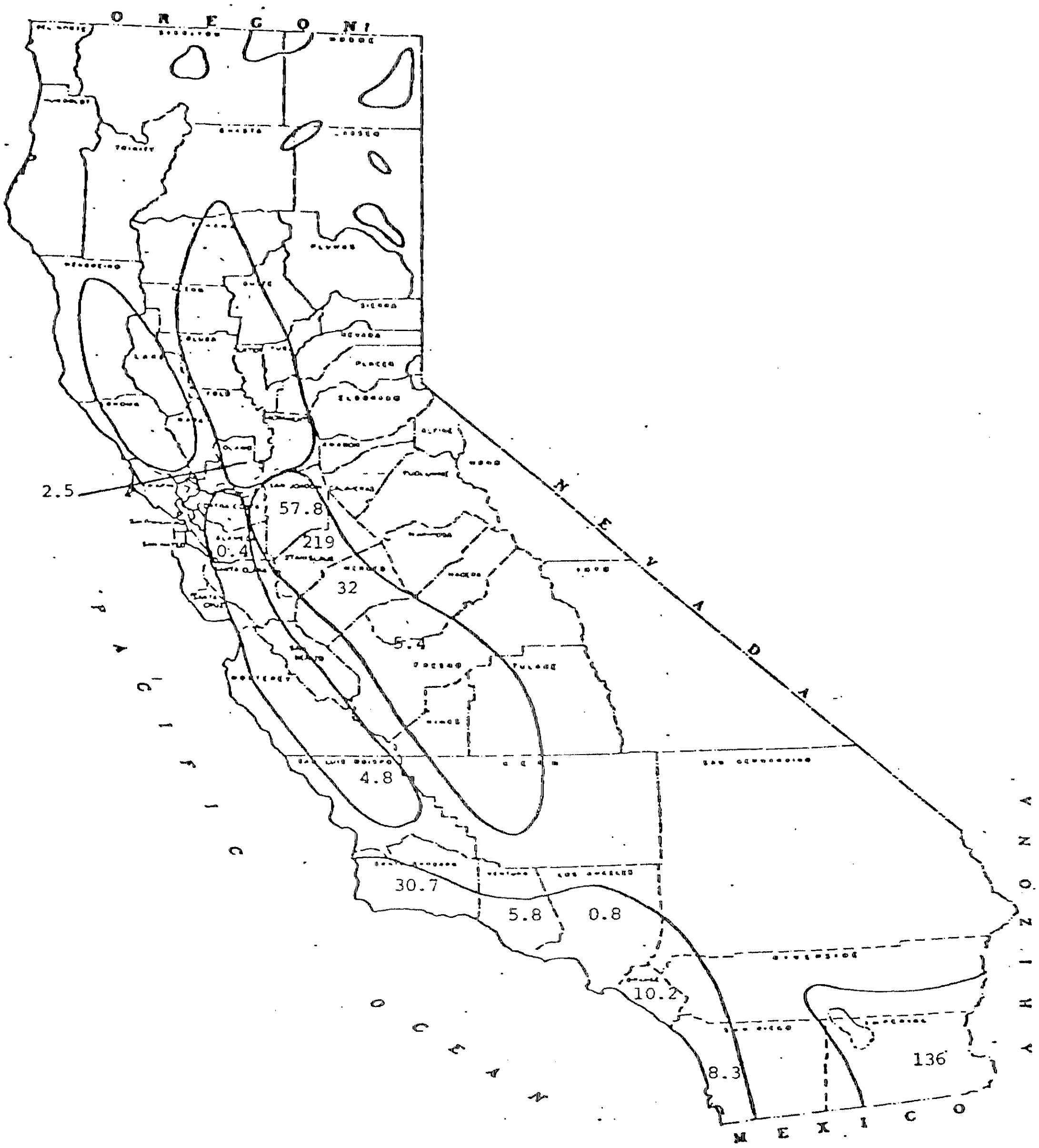

Figure 3-14. Ethylene dibromide agricultural applications for 1977 by county (10^3 lbs).

In considering these data, it should be borne in mind that the use of soil fumigants is much less regular than for other types of pesticides. The areas infected that must be treated vary considerably in both time and space. Thus the usage data for EDB maintained by the state can be expected to change considerably from year to year.

3.7.4 EDB Use in Other Applications

According to Johns (Ref. 49), some 14% of the National EDB production in 1975 was used as intermediate in production synthesis (5%) and in miscellaneous applications (9%), including that of specialty solvent. Processes in which EDB has been or may be utilized as a solvent or intermediate include the following:

- Manufacture of some drugs
- Fat processing
- Fire extinguisher manufacture
- Processing of certain gums and resins
- Wool reclamation
- Specialty-wax production
- Synthesis of some chemicals

Attempts to locate any of these EDB use-points in the State were not rewarded. CALOSHA knew of no users for EDB aside from the gasoline producers and pesticide appliers. Representatives of the major EDB producers listed by Johns (Ref. 49) were also contacted with the following results:

MANUFACTURER	COMMENT
Ethyl Corporation	Manufacturing point - Magnolia, AR; all used in gasoline additive product
PPG Industries	Manufacturing point - Beaumont, TX; all used in gasoline
Northwest Industries (Velsecol Division)	Discontinued production
Dow Chemical	Manufacturing points - Magnolia, AR and Midland, MI; no solvent sales for EDB, no EDB shipped into California for intermediate synthetic use.
Great Lakes Chemical Corporation	Manufacturing point - El Dorado, AR; product used in pest control; little if any used in solvent or intermediate applications

3.7.5 Emission Factors

A. Gasoline Production--

On an EPA-sponsored study (Ref.50), the atmospheric concentration of EDB was measured at 50 and 400 ft downwind of bulk transfer and tank trunk loading operations at an oil refinery of unspecified capacity. Levels of 1.65 and 0.23 ug/m^3 EDB were determined, respectively. Based on the diffusion equation and using reasonable estimates for wind speed and vector coefficients, emission rates were calculated. These came to 65 mg/sec at 50 ft. and 1.7 mg/sec at 400 ft. or 4520 and 118 lb/yr, respectively. The calculations are shown in Appendix C.

On the KVB hydrocarbon survey of the South Coast Air Basin (Ref. 22), it was calculated from actual measurements at the Douglas refinery that the THC release from gasoline mixing, transfer, and storage operations was 38 lb/hr (24 hr-average).

Assuming from the statistics already discussed [an average EDB content of 0.46 g/composite gal (regular, premium and unleaded)], one calculates a mol-fraction for EDB in gasoline of 8.4 X 10^{-5}. An average mol wt of 114 (octane) is applied to the gasoline itself. For an ideal solution, the partial pressure of the EDB over the liquid would then be 9.3 X 10^{-4} Torr, according to Henry's law. This corresponds to 3.8 x 10^{-4} wt % of the organic vapor phase, if one assumes a partial pressure of 400 Torr for the gasoline. Then, if a homogenous evaporation process operates (zero plate effect) in the ducts, vents and other loss-paths, the fraction of EDB in the THC releases can be calculated. In the case of the Douglas refinery, the EDB emission factor would be 1.3 lbs/yr, assuming no downtime. Factoring on the basis of relative gasoline capacities, the release rate for the State's largest refinery (Chevron U.S.A.-Richmond) would be 22 lbs/ yr. The Douglas estimate agrees poorly with those derived by reverse diffusion calculations (118 to 4520 lbs/yr). In either case, the release rates may be too small to be of concern.

Because of the limited work that has been done in monitoring EDB anywhere, further air sampling should probably be conducted around refineries. It does not appear, however, that the levels will be found to be high. The ambient levels cited above, 0.23 - 1.65 μg/m^3, are about a thousand-fold lower than the new stringent MAC (0.13 ppm or 1.0 mg/m^3) proposed by OSHA.

B. Gasoline Marketing and Consumption--

The only work done in this area that pertains to EDB was on the same EPA effort cited above (Ref. 50). Atmospheric concentrations of EDB were determined at urban roadway sites in three cities: Phoenix, Los Angeles, and Seattle. Each roadbed selected handled 25,000 to 30,000 vehicles per day and each site was situated within 200-300 ft downwind of two or more gasoline service stations. The results reported were:

TABLE 3-23. ATMOSPHERIC CONCENTRATION OF EDB AT URBAN ROADWAY SITES

City	Measured EDB $\mu g/m^3$
Phoenix, Arizona	0.07
Los Angeles, California	0.11
Seattle, Washington	0.08

Source: Ref. 50

These levels ranged to about one-tenth of the highest value reported for the refinery survey. Agreement between the urban sites was quite good and probably do not need to be validated with additional tests unless it is desired to quantitate traffic and gasoline station effects separately.

C. Pest Control--

EDB application rates of 100 lb/acre are reasonable (see Table 3-22). This is equivalent to a loading of about 2 mg/cm^2, or maximum (ideal flat surface) film thickness of only 10µm. Saturation volume would be about 16 cc/cm^2.

Typically, application is subsurface using hollow-shank fumigant applicators. After introduction into the infected fields, the furrows may be soil-filled to retard loss of the EDB. In terms of air pollution, the characterization of agricultural plots treated with EDB has not been undertaken.

A number of models have been developed for the estimation of pesticide release rates from various agricultural media. Those involving fumigants, include hydrological parameters as well as soil diffusion coefficients. Eureka Laboratores (Ref. 51) have reviewed these and, while acknowledging the difficulty of calculating pesticide evaporation from a hydrolytically active soil process, have recommended Hartley's equation (Ref. 52). This states that the pesticide release rate, dm_i/dt, is as follows:

$$\frac{dm_i}{dt} = (Q_w)_v \cdot \frac{p_i \, (M_i)^{\frac{1}{2}}}{p_w \, (M_w)^{\frac{1}{2}}} + (Q_w)_L \cdot C_i$$

Where:

$(Q_w)_v$ = water loss rate, vapor

$(Q_w)_L$ = water loss rate, liquid

p_i = vapor pressure, pesticide

p_w = vapor pressure, water

M_i = molecular weight, pesticide

M_w = molecular weight, water

C_i = concentration of pesticide in soil water

The equation states, in effect, that release rate of pesticide is controlled by the rate of loss of water (liquid and vapor) from the soil in which the pesticide is incorporated. This implies that pesticide fugacity over a dry soil is zero, which is hardly likely.

In the Hartley equation, the final terms $(Q_w)_L \cdot C_i$, can be ignored. EDB has a very low solubility in water and liquid water movement in a fumigated field should be nil. Thus the equation reduces to the statement essentially that EDB evaporation will be 1.6 times the loss of water from the plot until all undegraded material is released. The hydrolytic decomposition and/or biodegradation of EDB would of course subtract from the evaporative loss.

Eureka Labs (Ref. 52) estimated that water evaporation rate (E_A) from soil moist enough to promote seedling growth is about 40% that of standard pan evaporation (E_{pan}) at the same temperature. Atmospheric humidity, which is an important parameter in this estimation, was based on Fresno County averages. Under conditions for soil fumigation, the soil may be drier and E_A would be quite low with respect to E_{pan}.

In any case, KVB plotted in Figure 3-15 the relationship of Hartley's pesticide release rates against E_{pan}. Potential E_A values are assigned for fumigation with and without soil covering the furrows in the treated fields.* For reference purposes, the E_{pan} values for Fresno County for 1976 are listed in Table 3-24 together with the monthly average climatic conditions (Ref. 52).

It can be seen from Figure 3-15 that EDB release rates are greatly influenced by E_{pan} and the corresponding E_A, which is determined to a large degree by soil moisture (covering being absent). If all assumptions (particularly for E_A) are correct, for a covered field, all of the EDB would evaporate from the average Fresno field in less than two hours during the coldest month of the year. The loss would occur in a few minutes in July if the field were uncovered and wet enough to germinate seeds. An application rate of 100 lbs EDB/acre is still assumed.

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*According to U. of Calif., Div. of Ag. Sciences leaflet 2903, less volatile fumigants should be chiseled in 12 to 14-inch in moist soil. Immediately after treating, the furrowed area should be cultipacked twice to retard fumigant loss.

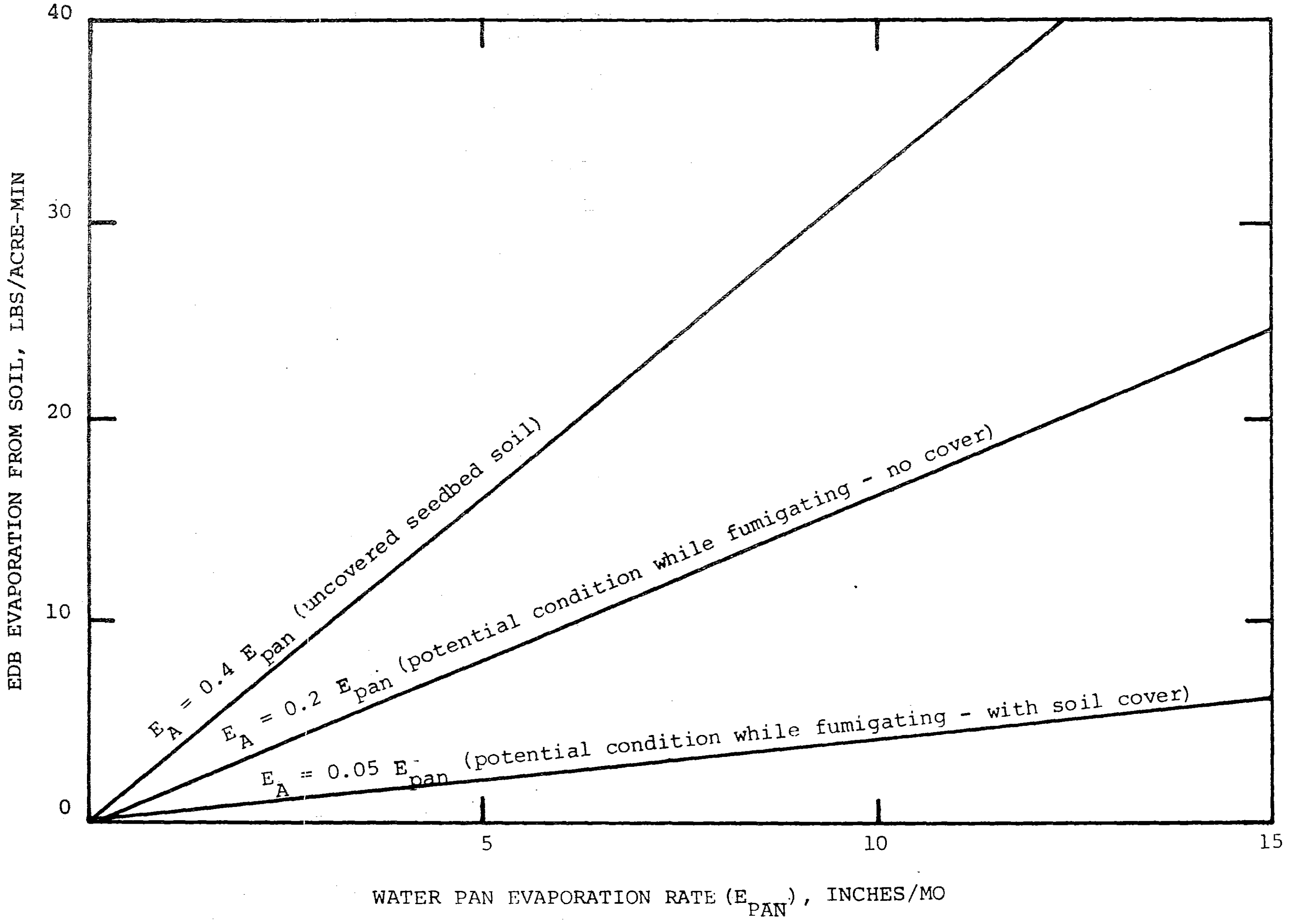

Figure 3-15. Estimated EDB evaporation rates from fumigated soil under different moisture conditions.

TABLE 3-24. GENERAL CLIMATOLOGICAL DATA FOR FRESNO COUNTY IN 1976

Month	Wind Speed (mph)	R.H. (%)	Pan Evaporation (inches)	Temperature (°F)	(°C)
January	3.4	75	1.76	44.3	6.8
February	5.1	80	2.39	49.6	9.8
March	6.7	65	4.13	52.4	11.3
April	6.2	60	5.49	57.2	14.0
May	6.9	44	10.81	69.7	20.9
June	8.4	41	12.48	73.0	22.8
July	9.0	44	14.71	79.4	26.3
August	8.1	58	10.07	72.7	22.6
September	6.4	62	7.96	72.2	22.3
October	4.3	65	4.98	65.1	18.4
November	4.1	80	2.33	53.4	11.9
December	4.0	69	1.72	46.5	8.1

Source: Eureka Laboratories (Ref. 52)