3.8 ETHYLENE DICHLORIDE

3.8.1 Production-Usage Summary

In 1977, some 12.5 x 10^9 lbs of ethylene dichloride (EDC) were produced in the United States. About 80% of this product is converted to vinyl chloride monomer (VCM), while an estimated additional 14% is committed to other types of synthetic and chemical processes (Ref. 53). Only one EDC plant operates in California -- the Stauffer Chemical Company plant at Carson. This plant consumes most of its EDC production in the synthesis of VCM. In 1978, Stauffer sold off 9.63 million lbs of EDC to California users. Most (97.6%) of this, they advised KVB, eventually went into gasoline. Other unidentified chemical process uses in California were detected that probably utilized intermediate or solvent EDC. These were small in volume, however.

The EDC production used as gasoline additive and for pesticide applications involves operations quite analogous to those already described for EDB. Notably, however, use of EDC in California pest control activities is quite minor.

3.8.2 EDC Use in Gasoline

A. Gasoline Refineries--

As pointed out in the discussion on EDB, the commonly observed weight ratios for TEL:EDB:EDC solutions are: 1.000:0.294:0.304, respectively. Thus the gasoline usage data developed for EDB can be factored (0.304/0.294=1.034) to furnish equivalent information for EDC. This has been done in Table 3-25 to show the estimated consumption of EDC as gasoline additive for July 1977-June 1978. The assumptions employed are described in the parallel discussions on EDB.

TABLE 3-25. ESTIMATED LEADED GASOLINE PRODUCTION AND ASSOCIATED EDC USAGE IN CALIFORNIA DURING 1977-1978

Area	Number of Refineries	Estimated Leaded Gasoline Production, 10^6 gpd	Estimated EDC Usage 10^6 lbs/yr
Los Angeles Basin	10	10.7	36.5
Carquines Straights	5	5.8	19.7
Bakersfield Area	5	0.93	3.2
Other*	4	3.3	12.0
TOTAL	24	20.7	71.4

*92.4% of the capacity for this category is located at the Chevron-Richmond refinery.

B. Gasoline Marketing and Combustion--

Again the reader is referred to the related discussion on EDB. A significant difference in the possible loss rates of EDC relative to those of gasoline or EDB is the intermediate vapor pressure of EDC. At 77°F, this value is 77 Torr, which is considerably higher than that of EDB (12 Torr @ 77° F) but still well below that of a typical gasoline (∿400 Torr). EDC, however, has not been identified in the off-gases from "soaking" test cars (Ref.54)

3.8.3 EDC Use in Pest Control

Application of EDC as a fumigant is largely done in grain silos, usually in conjunction with carbon tetrachloride (Ref. 53). This practice is not very popular here, since the Pesticide Enforcement Branch of the California State Food and Agriculture Department recorded for 1977 only 26,134 lbs EDC usage within the State. Being a restricted pesticide, this would include operations of both commercial appliers and farmers. The net EDC application is only about 5% that of EDB for the same period.

Of the total recorded usage, over 99% involved three counties. This is tabulated as follows:

TABLE 3-26. EDC USAGE IN CALIFORNIA COUNTIES
IN SIGNIFICANT AMOUNTS FOR PEST CONTROL DURING 1977
SOURCE: California Department of Food and Agriculture Files

County	Type Application	EDC Applied, Lbs	Acreage Treated
Fresno	Other Agencies*	2,419	--
San Francisco	Other Agencies*	5,498	
Yolo	Soil Fumigant	4,050	135
	Tomatoes	14,076	590
	TOTAL (Yolo)	18,126	

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

The data are also mapped on Figure 3-16, a map showing both the county political boundaries and growing areas within the State.

3.8.4 EDC Synthesis

The only facility in California producing EDC is located in Carson. Operated by the Stauffer Chemical Company, plant capacity is rated (Ref.53) at 300 x 10^6 lbs/yr, much of which is converted to VCM at that plant. Actual production data for EDC and VCM were not obtained from Stauffer. In view of the increase in EDC production over the past several years, it is reasonable to assume that the Stauffer/Carson plant is operating at at least 70% of capacity, which was the case for all plants in 1973. For estimation purposes, therefore, a production rate of 210 x 10^6 lbs was assumed* for 1978.

The oxychlorination process, which is used at Stauffer, actually involves three separate processes, these are as follows:

Oxychlorination:

$$\underset{\text{(ethylene)}}{C_2H_4} + 2HCl + 1/2\ O_2 \longrightarrow \underset{\text{(EDC)}}{C_2H_4Cl_2} + H_2O$$

Direct Chlorination:

$$Cl_2 + C_2H_4 \longrightarrow C_2H_4Cl_2$$

EDC Dehydrohalogenation:

$$C_2H_4Cl_2 \xrightarrow{\Delta} \underset{\text{(VCM)}}{C_2H_3Cl} + HCl$$

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*Stauffer later advised that actual 1978 rate was 133 X 10^6 lbs.

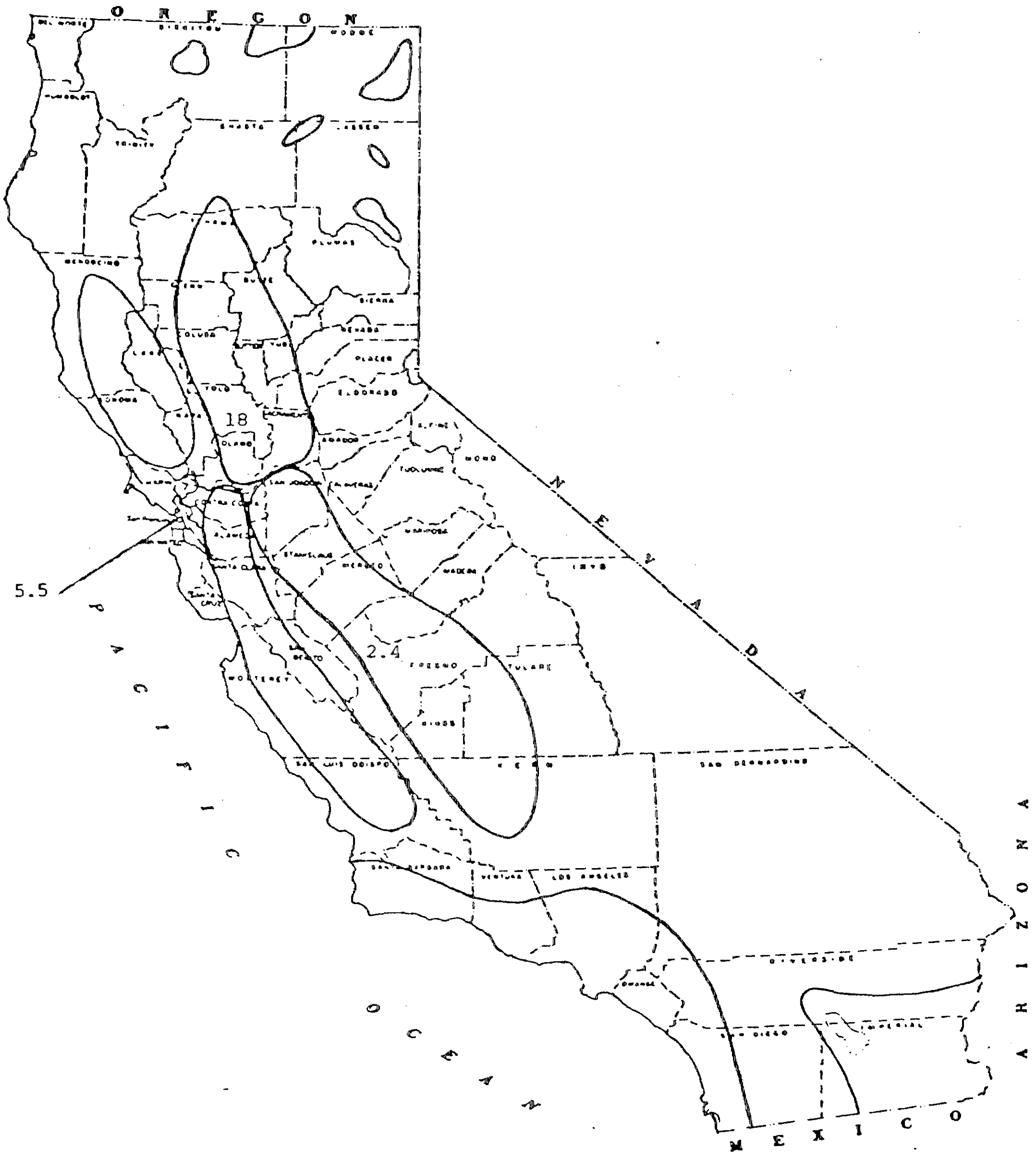

Figure 3-16. Ethylene dichloride agricultural applications in 1977 by county (10^3 lbs/yr)

The combined process is arranged so that all of the HCl produced in the VCM step is fed back to the oxychlorination process. The latter, however, consumes twice as much HCl than is produced from its output EDC when converted to VCM. Thus,the direct chlorination process is also used to furnish the additional EDC needed to balance the overall process. Thus, if all the EDC produced were converted to VCM, just one-half of the feed ethylene would go to the oxychlorinator and one-half to the direct chlorinator. To compensate for any EDC withdrawn for sale in that form, the oxychlorination process rate is turned down correspondingly.

The typical overall process (Ref. 56) is shown in Figure 3-17. The oxychlorination reaction is carried out in a catalyst bed incorporating cupric chloride. A catalyst is also used in the direct chlorination side of the system, where the reaction is carried out at 50 °C and 20 psig with excess EDC serving as solvent. Purified EDC from both reactions is dehydrohalogenated or cracked at about 400 °C and elevated pressure. The formed products are partially condensed, the HCl and VCM being fractionally distilled. Uncracked EDC is returned to the purification stage.

Being a closed process, EDC release is through valving, pump shaft packings, pipe connections, and the storage and handling of the EDC that is tapped off for sale in that form.

3.8.5 Other Industrial EDC Uses

Some EDC is used in the State for applications other than those itemized above. These other uses may vary widely, including specialty solvent, extraction, chemical intermediate, and stripping. EDC is not used in degreasers in California according to the spokepersons of manufacturers of such equipment (Baron-Blakeslee and Delta Industries).

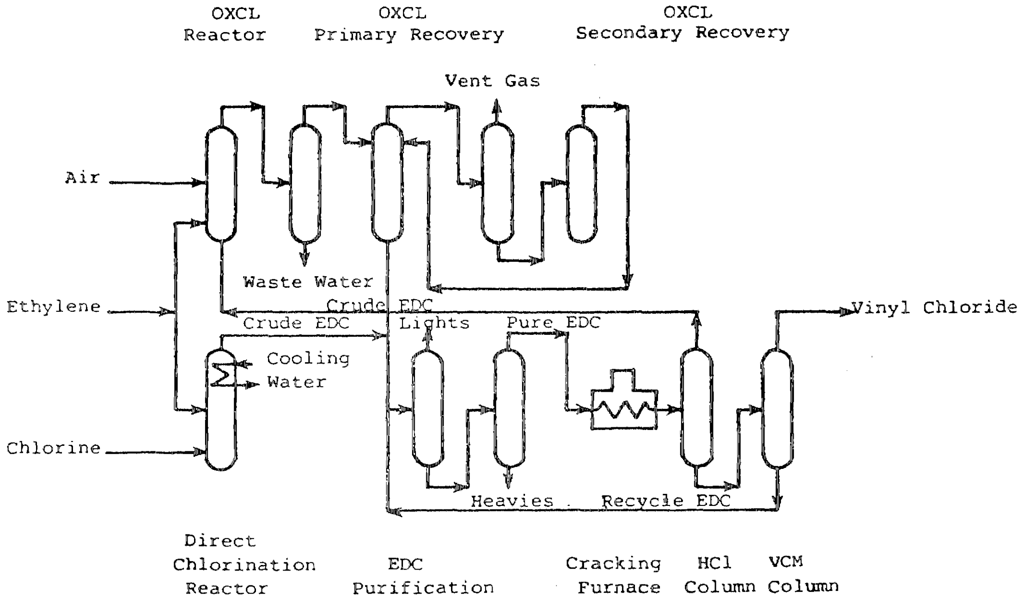

Figure 3-17. Process for the production of EDC amd VCM
(Source: Ref. 50)

The major producers of EDC are:

- Continental Oil Company, Conoco Chemicals
- Dow Chemical, U.S.A.
- Ethyl Corporation
- B. F. Goodrich Chemical Company
- I.C.I. United States, Inc.
- PPG Industries, Inc.
- Shell Chemical Company
- Stauffer Chemical Company
- Vulcan Materials Company

All were contacted and most indicated that no EDC was shipped here for any purpose. Two, however, acknowledged that some EDC was sold in California for minor uses, such as considered in this subsection. Specific amounts were furnished by Stauffer but not by Vulcan. It was obvious from the Stauffer delivery points, which were few in number and not major industrial terminals, that the minor uses of EDC were probably confined to a relatively few users. KVB estimates that a half million lbs/yr of EDC is consumed in California for such minor EDC applications (see Sec. 3.8.6.E).

3.8.6 Emission Factors

A. Gasoline Production--

Unlike the monitoring work done to establish atmospheric levels of EDB downwind of refineries, similar data could not be found for EDC. The vapor pressure of these haloethanes differ by over a factor of six in favor of EDC and the mol fraction of EDC in gasoline is just twice that of EDB. The rough approximation, based on Henry's law, was that only 1.3 lbs/yr of EDB evaporated from the Douglas refinery in Paramount and 22 lbs/yr from the State's largest refinery - Chevron U.S.A., Richmond. Taking into account the higher vapor pressure and higher mol fraction (with respect to EDB), the corresponding releases would be 9 and 149 lbs/yr, respectively. These releases are again too low to be of concern.

B. Gasoline Marketing and Consumption--

An area-source type of effect, EDC losses from gasoline haulers, service stations and user vehicles may all occur. Again, considering the relative partial pressures of EDB and EDC, levels as high as 0.5 $\mu g/m^3$ of EDC may occur in areas well travelled and populated with gasoline stations (see Table 3-23). Tail pipe emissions of uncombusted EDB and EDC could contribute significantly. In this case, however, the expectable concentration ratios of emitted EDB/EDC would be different, since partial pressure ratio would not control. EDC tail pipe emissions would likely still be higher than those for EDB, however, since the latter is more labile and probably would combust more completely.

C. Pest Control--

Again using Hartley's equation (see Section 3.7.5.C), one calculates that EDC will be released at a rate 7.6 times faster than moisture evaporating from the soil or 4.7 times faster than EDB. A plot of assumed soil conditions is shown in Figure 3-18 with estimated EDC release rates. Estimated loss rates are so high as to explain the limited usage of EDC as a soil fumigant.

D. EDC Synthesis--

On an EPA program (Ref. 55), emissions of the Stauffer Chemical Company plant in Carson were measured in 1973 when it was operated as the American Chemical Company. Unfortunately, only VCM (just then of prime concern) was quantitated. Data published by EPA's Patrick (Ref. 43) show 0.012 lb nonmethane hydrocarbons (NMHC) emitted for each pound of EDC produced by the oxychlorination process,* which is what is employed at Carson. The materials comprising the NMHC fraction of emissions should include some ethylene gas. This emission factor is thus in possible variance with that of John's (Ref. 53), which predicts 0.015 lb <u>of EDC</u> emitted per lb produced. Assuming, however, that only 10% of the NMHC emissions from EDC production estimated by Patrick are of the compound itself, then an emission range representing the two different estimates is 0.0012-0.015 lb/lb EDC produced. For the Carson plant, this would suggest atmospheric release of EDC of roughly 0.3 to 3.2 x 10^6 lbs EDC per year, assuming 70% capacity production. At either rate of release, the Stauffer plant would clearly constitute a "hot spot".

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*Actually a combination of the oxychlorination and direct chlorination process (See Page 3-101).

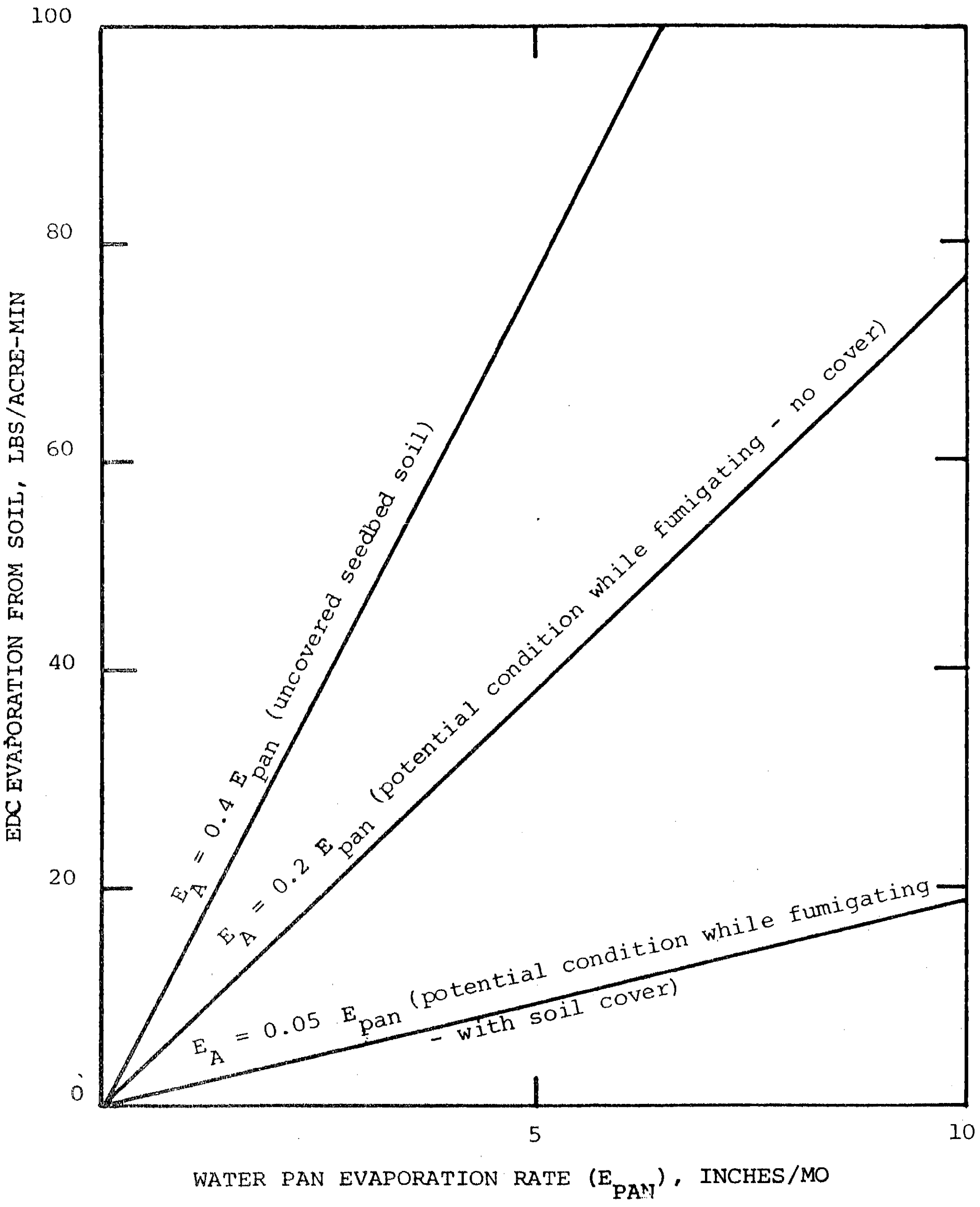

Figure 3-18. Estimated EDC Evaporation Rates from fumigated soil under different moisture conditions.

E. Other Minor Industrial Uses of EDC--

The other minor industrial uses of EDC have been very roughly estimated here as 0.5 x 10^6 lb/yr. User points are probably highly separated but may not involve a great number of facilities. These small users may be involved in releases in which all of the EDC used is vented to the atmosphere.

The EDC estimated consumption in minor industrial uses is based on Stauffer's sales data* for 1978, which shows 230,000 lb. going to unidentified users at Redwood City (172,000), San Diego (38,000) and La Mirada (20,000). Because of the locations of these cities and the absence of sales at major distribution points, it may be assumed that single businesses were users at each place. The Bay Area and South Coast AQMD's were not able to identify the users in their jurisdictions. San Diego APCD did locate an EDC consumer†. This was the ENCOM Division of Illinois Tool Works in the Sorrento Valley District of San Diego. EDC is used to disperse ceramic paste that is applied to electronic components and fixed by kiln firing. EDC emissions could be in excess of 80% (the amount evaporated from the components prior to firing). Use of EDC at this plant will be discontinued shortly when the binder it is used in is withdrawn and an aqueous emulsion binder is substituted. EMCON was of the opinion that this shift will also affect competitor plants, since the process is rather standard within the industry.

The only other EDC supplier identified with servicing minor industrial uses was Vulcan Materials Co., Birmingham, AL. This firm regarded their distribution data as "quite confidential." For the purposes of this study, it was assumed that Vulcan's minor-use EDC sales were about the same as Stauffer's to give the rounded estimate of 0.5 x 10^6 lb/yr. It may further be assumed that Vulcan sales were to a relatively few specialty users, as appears to be the case with Stauffer.

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*Which does not include sales to gasoline producers.
†Stauffer later stated that the customer was not theirs.

Another user of EDC (supplier unknown) is the Keysor-Century Co. in Saugus. This plant polymerizes vinyl chloride (see next section) and uses EDC to clean the primary reactor. The quantities of EDC used are unknown as is the fate of the wastes produced by this practice.

F. EDC Emissions Associated With Polyvinyl Chloride (PVC) Production--

Emission factors for various pollutants released during PVC production have been tabulated by Monsanto workers (Ref. 57). These estimates include a release rate for EDC (4×10^{-5} g/kg PVC produced), which is coincident with the release rate for VCM multiplied by the level of EDC (0.1-2.0 ppm) found in VCM as impurity.

Three VCM polymerization plants operate in California, according to the Monsanto report. These are tabulated below.

TABLE 3-27. VINYL CHLORIDE
POLYMERIZATION PLANTS IN CALIFORNIA
(SOURCE: REF. 57)

Company	Location	Estimated Annual PVC Capacity, 10^3 tons	
Stauffer Chemical Co.	Carson	75	
B. F. Goodrich Co.	Long Beach	58	(See Text Below)
Keysor-Century	Saugus	17.5	

It can be seen that the Monsanto-estimated EDC releases associated with VCM polymerization are trivial. Stauffer, the largest PVC producer, would release only 6 lbs/yr from this particular effect. As pointed out earlier, very significant EDC releases could be occurring at the same plant from EDC conversion to VCM. Also, as previously mentioned, Keysor-Century uses EDC as a solvent in the VCM polymerization process, which could result in significant releases of EDC. The B. F. Goodrich plant in Long Beach once used EDC as a cleaning solvent but discontinued that practice for health reasons. The PVC capacity shown in Table 3-25, incidentally, is low according to B. F. Goodrich. They pointed out that plant capacity and production is about 75×10^3 tons/yr.

3.9 NITROSAMINES

3.9.1 Occurrence Summary

The three major uses for nitrosamines are rubber processing, organic chemicals manufacturing, and alkylhydrazines (rocket fuel) production. The patent literature suggests many other uses comprising or involving dyestuffs, gasoline additives, lubricating oils, explosives, insecticides, fungicides, dielectric fluids, plasticizers, industrial solvents, etc. (Ref. 58).

Despite this suggestive enumeration, nitrosamines have relatively little application in the State.

In rubber production, N-nitrosodiphenylamine (Uniroyal Retarder J, R.T. Vanderbilt's Redax) serves as a "scorch" inhibitor. It is actually a polymerization inhibitor extending the mixing and extrusion life of the worked rubber, thus avoiding the scorching associated with early-setting batches. Most of the N-nitrosodiphenylamine is used in natural rubber processed into off-road vehicle tires. In addition to supplying the above comments, a Uniroyal technical representative estimated West Coast Sales of Retarder J at less than 20,000 lbs/yr.

In organic syntheses (rocket propellants arbitrarily excluded), a variety of intermediate roles exist for nitrosamines. The survey literature, however, suggests no products made in California that could involve such chemistries. Besides N-nitrosodiphenylamine, the scorch inhibitor, only N-nitrosodimethylamine (DMN)* is produced in the U.S. in quantities exceeding 1000 lbs/yr (Ref. 59). The latter is principally used in the production of rocket fuel (see below). DMN is only known to be manufactured in Baltimore by FMC (Ref. 58). A reported minor use of a nitrosamine is as a blowing agent for microcellular rubber production. The material used is dinitrosopentamethylenetetramine (Ref. 60). The Uniroyal technical representative mentioned above was familiar with the process but believed that it is now obsolete and never widely used.

The Teledyne-McCormick-Selph facility in Hollister produced about a million lbs of unsym-dimethylhydrazine (UDMH) annually for the U. S. Air Force.

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*From the Synonym, dimethylnitrosamine

This synthesis finishes with the conversion of N-nitrosodimethylamine to the product. Although the most volatile of the nitrosamines, even DMN boils at 153 °C. In any case, Teledyne fulfilled its contractual commitments and went off stream in August, 1978. They do not contemplate any further manufacture of UDMH, according to the company's environmental specialist.

Aside from direct manufacturing use of nitrosamines, potential or confirmed sources of incidental releases of nitrosamines include (Ref. 58) combustion of hydrazine-based rocket fuel, fish meal processing, tobacco smoke, power plants (using amine additives to modify fly ash resistivity), any source emitting secondary amines, and vehicles (gasoline or diesel engines). Of these possibilities, the sources amenable to control are utility power plants, vehicle engines, and fish meal factories.

EPA's John Bachman (office of Air Quality Planning and Standards) was consulted in this matter as that agency's identified expert on atmospheric nitrosamine pollution. He stated that as a result of work done at Mitre Corporation (Ref. 61) and subsequent information studied, the EPA concluded that, as a class, nitrosamines do not constitute an atmospheric hazard that warrants development of control strategies. Furthermore, there has been no conclusive evidence to indicate that either fossil-fueled power plants or Diesels (or gasoline engines) emit detectible amounts of either amines or nitrosamines.

3.9.2 Secondary Sources (Secondary Amines)

Concern is developing over the possibility that nitrosamines may be formed in significant quantities in the atmosphere in reactions between nitrogen oxides and terrestrially released amines. This effect has been demonstrated in troposphere simulators (Ref. 62) with secondary and tertiary ethyl and methyl amines. Believing that only secondary amines are nitrosable, the EPA listed sources for such emissions (Ref. 58). These EPA findings are discussed in the following subsections. The omission of tertiary amines as precursors of nitrosamines by that agency does not likely represent a scientific position, but, rather, possession of incomplete information.

A. Feedlots--

Dimethylamine and various primary and tertiary amines have been identified in air samples taken near feedlots. A survey (Ref. 63) at two Texas beef cattle feedlots showed a concentration of 632 mg/m^3 of dimethylamine at a height of 59 ft. The production of these nitrogenous compounds is associated with the decomposition of livestock and poultry excreta. For beef cattle alone, there are 130 feedlots in California, 80% of which can accommodate over 1,000 head per lot, according to the Department of Food and Agriculture Division of Animal Industry.

B. Rendering Plants--

Animal parts not suitable for human or pet consumption are digested to yield tallow and neat's-foot oil. The wet vapor withdrawn is an odorous stream containing not only secondary amines but such vile-smelling species as putrescine and cadaverine.

Rendering plant digestors are, therefore, necessarily well-equipped with APC systems. The most popular configuration consists of condenser stages followed by a gas incinerator. Liquid scrubbers (three-and-four-stage are also now being permitted by air quality agencies.

Data provided to KVB for a number of rendering plants tested by the SCAQMD showed impressive amine reductions. Expressed as ammonia but not including ammonia itself, 1 lb/hr of amines is volatilized from the digestor for each ton/hr of feed (bones, hooves, horns, hide scraps, and hair). About one tenth of this release fails to collect in the condenser section, but only 6×10^{-4} lb/hr survive the gas incinerator. This represents a control efficiency of 99.94%, which leaves little margin for improvement.

C. Manufacture of Amines and Formulations Containing Amines--

Of the major amine manufacturers listed in the EPA report (Ref. 58), only one is located in California. This is the Shell Chemical Co's Martinez plant. The EPA report stated that amine epoxy hardeners were produced there. According to a Shell spokesman, however, the Martinez plant has not made any kind of amine in over two years. All Shell amine products are now produced at their Houston plant.

According to the EPA report, many products incorporate or utilize amines as snythetic intermediates. These include: (1) vulcanization accelerators (metallic and sulfided thiurams); (2) pharmaceuticals (e.g., ephedrine, chloroquine, Benemide, etc.); (3) morpholine emulsified self-polishing waxes; (4) pesticides (thiurams, triazines, anilines, pyridines, piperazines, etc.); (5) solvents (dimethylformamide); (6) wet strength paper (polyethylenimine); and (7) corrosion inhibitors (morpholine). With the exception of the compounding of waxes and corrosion inhibitors and the manufacture of rubber, the industries involved in the other activities are not known to operate to any appreciable extent in this State.

D. Pesticide Application--

Some pesticides contain secondary amine nitrogens in their molecular structures. Of these, specific individuals have been identified that have been shown to form nitrosamines either in vivo or in vitro (Ref. 64). Six pesticides are listed. Three (carbaryl, propoxur, and benzthiazuron) are N-methyl carbamate structures which additively nitrosate, forming even less volatile structures than the parent compounds. The other three (ziram, thiram, and ferbam) are the zinc, thio and iron (II) bridged forms of bis-dimethyldithiocarbamate. All three of these thiuram pesticides undergo cleavage between the carbamate nitrogen and carbon members to yield dimethylnitrosamine. This is the most volatile nitrosamine (b pt. 153 °C), as mentioned earlier.

Considering the thiuram pesticides as potential precursors of nitrosamine emissions, we see a substantial usage in the 1978 Pesticide Use Report (Table 3-28).

Although no test data are known that demonstrate that field application of these three pesticides actually results in DMN release, a potential site for such a survey is indicated. Almond orchards account for the consumption of 75.5% of the total combined weight used of all three of these thiuram pesticides. The application rate (5.9 lbs/acre), which is only slightly exceeded in ziram-spraying of peach trees, is high for this group of protective fungicides.

TABLE 3-28. REPORTED APPLICATIONS OF THREE THIURAM PESTICIDES IN CALIFORNIA DURING 1978

Pesticide	Application	Pounds	% of Total	Acres
Ferbam				
	Dates	9,952	99.95	2,964
	Residential	5	0.05	-
	Totals	9,957	100.00	2,964
Thiram				
	Strawberries	5,162	30.12	3,763
	Tomatoes	1,993	11.62	743
	Turf	3,687	21.50	974
	Other crops	890	5.19	252,381
	Various agencies	5,414	31.57	-
	Totals	17,146	100.00	257,861
Ziram				
	Almonds	218,954	83.53	36,962
	Apricots	10,540	4.02	1,932
	Peaches	30,906	11.79	5,171
	Other fruit	1,742	0.66	1,079
	Various agencies	7	-	-
	Totals	262,149	100.00	45,144

Source: Pesticide Use Report 1978

E. Miscellaneous Other Secondary Amine Sources--

In the EPA report (Ref. 58), other sources of secondary amine emissions were listed. These are: (1) systems disclosed in patents (amine-type oxidation inhibitors for lubricants and rubber storage environment), (2) synthetic detergent manufacture involving dimethylamine release, (3) uranium oxide extraction with dilaurylamine, and (4) leather tanning using dimethylamine as a liming accelerator. Topic (1) was not pursued because only patent literature was cited; this strongly implies uncertainty as to whether reduction to industrial practice had occurred. Topic (2) concerns the odor problem associated with the release of dimethylamine which occurs as process contaminant in LAS* manufacture. According to Byrd et al (Ref. 65), application of suitable APC equipment has eliminated this problem. This was confirmed in discussions with Pilot Chemical Company of California, a major LAS producer in this State. Topic (3), uranium oxide extraction from yellow cake, was referred to the Bureau of Mines, Spokane, Washington. According to that agency, there is no known uranium ore processing in this State. The last topic deals with leather tanning and the use of dimethyl amine (or sodium sulfide) as liming accelerators. The alkaline properties of this (lime saturated) liquor would render the dissolved amine essentially nonvolatile.

3.9.3 Atmospheric Survey of Nitrosamines--

Unlike most of the other pollutants considered on this program, a systematic sampling for nitrosamines has been conducted in California. This work, under CARB sponsorship, was done by R. J. Gordon of the USC School of Medicine (Ref. 66). The survey included air sampling downwind of: (1) the Teledyne UDMH plant (then operating); (2) the individual chemical and petroleum plants situated between Richmond and Antioch; and (3) selected points representing clusters of chemical plants (and a fish processing plant) in the Vernon-Commerce and Carson-Wilmington districts. Gordon also conducted a systematic sampling program in the southern half of Los Angeles County at about 150 points for comparison with cancer incidence data.

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* Linear alkylsulfonate.

No evidence for any specific point emission source for volatile nitrosamines was observed. The majority of all samples were below detection limits (about 0.03 $\mu g/m^3$ for dimethylnitrosamine (DMN). Several samples reached 0.3 $\mu g/m^3$ or higher, up to a maximim of 1.0 (for a mislabeled sample), but later repeat samples were always lower. The second highest concentration recorded was 0.48 $\mu g/m^3$; the sample was taken on the grounds of the Los Angeles County Hospital.

Gordon concluded that more positive samples were collected in winter. A diurnal pattern was suggested, with maxima around 8:00 a.m. and 6:00 p.m. Diethylnitrosamine was found less frequently than DMN but at similar levels. Traces of a third, less volatile, unidentified nitrosamine were also seen.

Gordon's mapping of DMN data in his cancer correlation study (no apparent correlations found) are shown in Figure 3-19.

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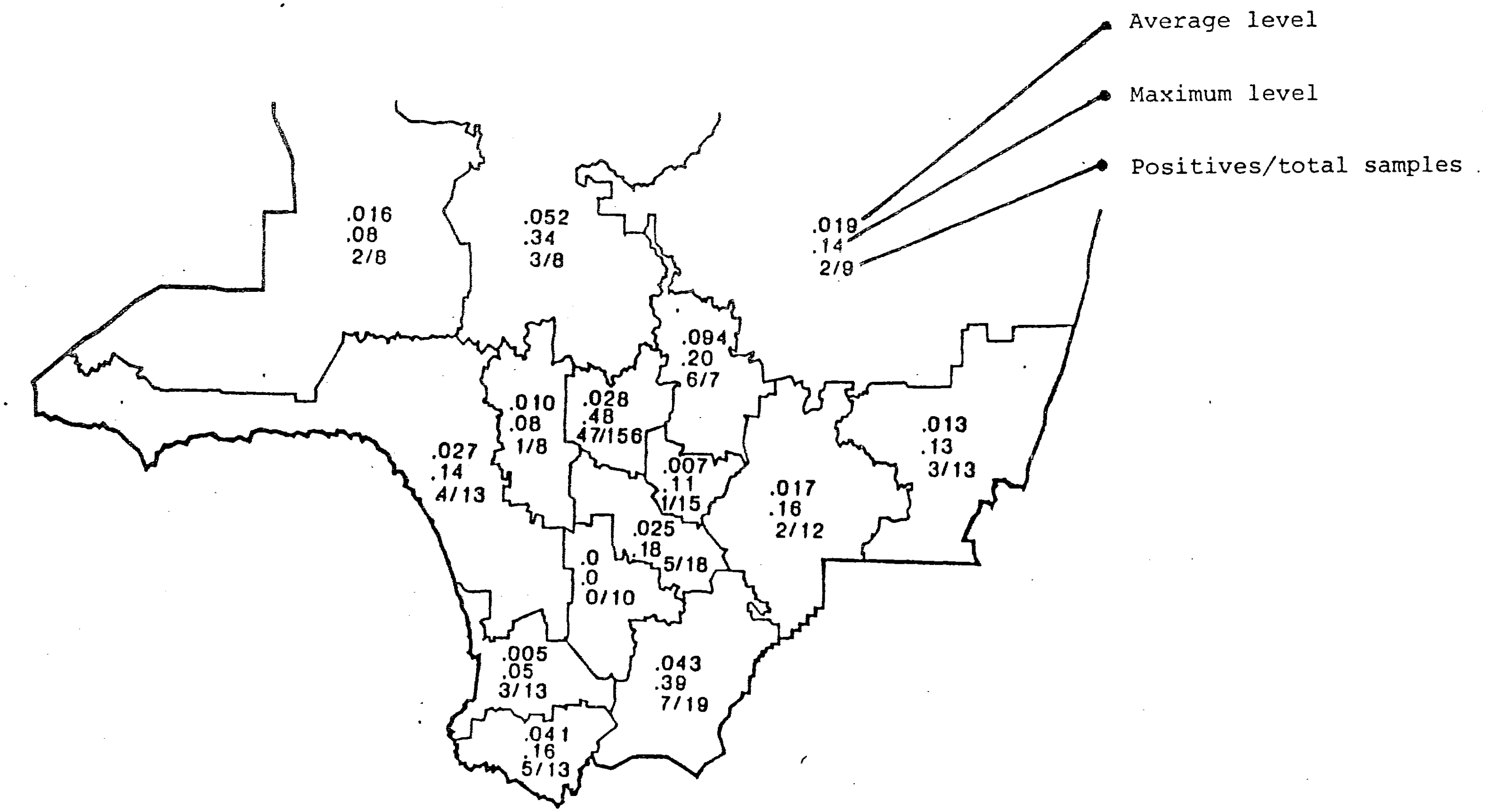

Figure 3-19. Summary of DMN air concentrations (μg/m^3) in health district areas of Los Angeles County (Source: Ref. 66).

3.10 PERCHLOROETHYLENE

3.10.1 Production-Usage Summary

Perchloroethylene (1, 1, 2, 2-tetrachloroethene), which is often referred to as perc, is a widely used solvent. The modes of use, however, are conducive to vapor release such that rather large emission factors have been developed for perc sources.

The estimated 1978 National consumption of Perc has been tabulated by SRI (Ref. 67). These data are shown below with earlier (1971) usage estimates compiled by Mitre Corp. (Ref. 68).

TABLE 3-29. ESTIMATED CONSUMPTION OF PERC IN THE U.S.

Type of Use	SRI Estimated 1978 Consumption, 10^6 lbs	% of Total	
		SRI-1978	Mitre-1971
Dry Cleaning	353	53	70
Textile Processing	44	7	
Chemical Intermediate	88	13	11
Metal Cleaning	110	17	18
Miscellaneous	66	10*	1
	661	100	100

* Includes Perc going into inventory.

The SRI study focused on only two use-categories (dry cleaning and degreasing) and did not explain what consituted miscellaneous use, other than suggested in the table's footnote. In searching the EIS print-outs keyed to perc emitters, no permitted sources could be identified that would fulfill the miscellaneous category in California.

Use of perc as a chemical intermediate (Ref. 67) is predominately for the syntheses of F-113 through F-116 (trichlorotrifluoroethane through hexafluoroethane). No facilities were identified in California that produced other than fluorinated methanes (DuPont, Antioch and Allied Chemical, El Segundo). Thus, it is assumed that chemical intermediate use of perc does not occur in the State.

Use of perc in textile processing is insignificant in California. A search of the EIS print-outs mentioned above, produced only a few hits (e.g., SIC 2283-Wool Yarn Mill; SIC 2262-Finisher of Broad Woven Fibers of Manmade Fiber and Silk, etc.) for the category.

Thus, the present State survey, like the SRI National assessment, focused on just three areas: (1) perc manufacture; (2) dry cleaning, and (3) degreasing operations.

3.10.2 Perc Production

The only producer of perc in the state is Dow Chemical Co., Pittsburg. According to SRI that plant has a rated annual capacity of 44 million lbs and a production last year at half capacity, or 22 million lbs. The process used, which also yields carbon tetrachloride, is described in Section 3.5.1.A.

3.10.3 Dry Cleaning

Three categories of dry cleaning operations can be considered:

- Commercial dry cleaners--the common walk-in garment cleaning service
- Coin-operated machines--located in self-service laundries, apartments, etc.
- Industrial cleaners--supplying cleaned uniforms, wipe rags, safety equipment, dust control devices, etc.

SRI estimates that: (1) about 75% of commercial dry cleaners use perc; (2) coin-operated dry cleaning machines use perc almost exclusively (3% use F-113); and (3) about half the industrial cleaning plants are on perc. Except for the small amount of F-113 used, the balance of cleaning fluid is believed to be Stoddard solvent. The SRI estimated inventory of perc dry cleaning plants in California, broken down by size of operation (based on number of employees), is shown in Table 3-30.

TABLE 3-30. ESTIMATED NUMBER OF DRY CLEANING PLANTS USING PERC IN THE U.S. AND CALIFORNIA

(Source: Ref. 67)

No. of Employees per Plant	Number of Plants (% of Category Total)					
	Commercial		Coin-Operated		Industrial	
	U.S.	Calif.	U.S.	Calif.	U.S.	Calif.
1-4	4,194 (54.1)	566 (58.6)	3,695 (84.3)	269 (80.5)	16 (6.3)	3 (9.1)
5-9	1,906 (24.6)	247 (25.6)	499 (11.4)	47 (14.1)	11 (4.3)	2 (6.1)
10-19	846 (10.9)	101 (10.5)	119 (2.7)	12 (3.6)	18 (7.1)	3 (9.1)
20-49	691 (8.9)	44 (4.6)	57 (1.3)	4 (1.2)	98 (38.4)	12 (36.4)
50+	119 (1.5)	8 (0.8)	12 (0.3)	2 (0.6)	112 (43.9)	13 (39.4)
TOTALS	7,756	966	4,382	334	255	33
(% of total of all three categories)	(62.6)	(72.5)	(35.4)	(25.1)	(2.1)	(2.4)

While the distribution of types of dry cleaning establishments varies somewhat between the Nation and the State, the conformity in size distribution is reasonably good. This composition would then permit the calculation of perc use in the State based on SRI's estimated national perc consumption and the fraction of the national inventory of plants that are operating in the State. This was done with the following results:

TABLE 3-31. ESTIMATED CONSUMPTION OF PERC FOR DRY CLEANING IN CALIFORNIA DURING 1978

Type of Operation	No. of Plants	Estimated Perc Consumption, 10^6 lbs	% of Total Consumed
Commercial	966	33.8	78.7
Coin-operated	334	3.9	7.4
Industrial	33	4.0	13.9
TOTALS	1333	41.7	100.0

3.10.4 Metal Cleaning Operations

Solvent cleaning of metals can be dichotomized into two practices -- cleaning with the hot vapor of the solvent and cleaning with the liquid solvent itself, usually at room temperature. Thus, the terms "cold cleaning" and "vapor degreasing" evolved. Application of these degreasing techniques is predominately batch mode, although conveyorized configurations are dictated for large output operations. The conveyorized degreasers may operate as either cold cleaning or vapor degreasing systems.

In batch cold cleaning, parts are suspended in a tank of solvent with or without spraying, stirring, ultrasound, and other process-accelerating effects. Rejuvenation of the solvent is variously practiced ranging from replacement of the discarded loaded solvent with fresh stock to distillation of the dirty solvent and recycle.

In batch vapor degreasing, the coated pieces are suspended in a vapor reflux configuration. Under the load, the solvent is boiled and above the load the solvent vapors are condensed on cooled surfaces. The clean refluxate flows back into the pot while some vapor condenses on and drips off the parts themselves, providing the cleaning effect. Most large vapor degreasers are fitted with quick-operating lids and charcoal vapor recovery systems.

The most popular synthetic degreasing solvent is 1, 1, 1 - trichloroethane (methylchloroform) followed, up until recently, by trichloroethylene and then perc. Halogenated solvents (the above three plus methylene chloride and F-113) accounted for about 59 wt-% of the degreasing fluids used in 1974 (Ref. 68). The balance of the materials used in degreasers were petroleum solvents (37 wt-%) and the various oxycarbons (4 wt-%).

Trichloroethylene, a photochemically active substance, is now falling in popularity as a degreasing solvent in some states (certainly in California). This has resulted from local APC regulation and, perhaps, the carcinogenicity issue. There is, however, no pending OSHA action for lowering the MAC for trichloroethylene and the EPA is only now tentatively considering trichloroethylene for inclusion on the list of hazardous pollutants. In any case, most California degreasers who used that solvent have converted their trichloroethylene degreasers to methylchloroform service. The boiling point of the latter (74 °C) is closer to trichloroethylene (87 °C) than any of the other halocarbon degreasing solvents. Perc (b. pt. 121 °C) sales have also apparently benefited somewhat from the reduced usage of trichloroethylene here. The above observations resulted from discussions with technical representatives of Baron-Blakeslee and Delta Industries, leading degreaser manufacturers.

In a study for the CARB, Eureka Laboratores (Ref. 69) canvassed a sampling of California industries operating degreasers to determine solvent types used. The field represented 45 different SIC codes, covering all possible categories of degreaser users. Although the canvass reached only 5.8% of the selected field, statistically this is a generous sample and should promote a high confidence level in the results.

SRI (Ref. 67) analyzed the work sheets from the Eureka survey to determine perc preference among the polled group. Some manufacturers in 17 of the 45 SIC codes canvassed were found to degrease with perc. The fractions within this subgroup using perc and their estimated annual consumption of the solvent are shown in Table 3-32. KVB obtained from SRI (B.E. Suta) the population of plants within the 17 SIC categories (according to size) that SRI had extracted from the 1976 Bureau of Census report on 1974 County Business Patterns.

This matrix represented a total of 6,550 plants that operated degreasers. The fraction using perc was then multiplied for each corresponding population element and the SRI-estimated perc usage (Table 3-32) for that particular SIC and plant size. The breakdown is shown in Table 3-33. Using Mitre Corporation's (Ref. 68) estimated National consumption of perchloroethylene for degreasing in 1975 (108 million lbs), the Table 3-32 estimate for California is 11.9% of that total.

Several interesting aspects of the Table 3-33 perc consumption estimates are apparent. Small business operations using degreasers account for a very minor part of the total. The aircraft and aircraft equipment manufacturing industries account for almost 36% of the total degreasing perc used. The larger companies (greater than 100 employees) account for over 67% of the perc consumed in degreasing, although only 62 plants comprise that grouping.

A print-out from the Emission Inventory Subsystem (EIS) of firms operating perc degreasers and dry cleaning equipment was also requested and received from the CARB. These data were fragmentary, there being no information included for such important counties as most of those littoral to San Francisco Bay. Although listed, no permits were recorded for Riverside and San Bernardino Counties. Thus, the discrepancy in the total count of

TABLE 3-32. ESTIMATED FRACTIONAL AND INDIVIDUAL PLANT PERCHLOROETHYLENE USAGE FOR DEGREASING IN CALIFORNIA BY PLANT SIZE AND SIC TYPE

(Source: SRI and Eureka Laboratories - Refs. 67 & 69)

		% Using Perc No. of Employees		Amount of Perc Used Per Plant, 10^3 lbs/yr No. of Employees		
SIC Code	Industry Description	< 20	> 20	< 20	20-100	> 100
331	Basic steel	0	11	0	24.4*	136
336	Non-ferrous foundry	0	6	0	0.6*	3.4
339	Misc. primary metal	0	14	0	163	911*
342	Gen. hardware	0	9	0	36.0*	200
343	Plumbing and gas heating	0	14	0	37.3	209*
344	Structural metal	0	8	0	4.8	26.6*
345	Metal fasteners	0	18	0	11.7*	65*
347	Plating and engraving	8	11	4.5	71.3	231
349	Misc. metal products	0	14	0	17.8	99*
352	Farm and garden eqpt.	0	11	0	1.2*	6.8*
361	Elec. transmission eqpt.	0	7	0	2.0*	11.2
362	Elec. industrial apparatus	17	0	3.0	0	0
364	Elec. lighting and wiring	0	7	0	1.0*	5.5
366	Communications eqpt.	0	11	0	2.4*	13.3
367	Electronic components	6	0	10.0	0	0
371	Vehicles and eqpt.	0	5	0	1.5	8.4*
372	Aircraft and eqpt.	10	22	0.14	6.6	348

* These estimates are extrapolations based on number of employees.

TABLE 3-33. ESTIMATED TOTAL PERCHLOROETHYLENE USAGE IN CALIFORNIA DEGREASERS BY PLANT SIZE AND TYPE

SIC Code	Industry Description	Amount of Perc Used Per Category 10^3 lbs/yr Number of Employees < 20	20-100	> 100
331	Basic steel	0	97	358
336	Non-ferrous foundry	0	3.2	5.5
339	Misc. primary steel	0	911	637
342	Gen. hardware	0	191	774
343	Plumbing and gas heating	0	177	438
344	Structural metal	0	117	145
345	Metal fasteners	0	145	281
347	Plating and engraving	201	1,411	534
349	Misc. metal products	0	482	696
352	Farm and garden eqpt.	0	5.5	6.0
361	Elec. transmission eqpt.	0	4.7	17.2
362	Elec. industrial apparatus	53	0	0
364	Elec. lighting and wiring	0	6.3	15.7
366	Communication eqpt.	0	40.9	139
367	Electronic components	219	0	0
371	Vehicles and eqpt.	0	1.2	25.5
372	Aircraft and eqpt.	2.3	113	4,597
	TOTALS	475	3,706	8,669

GRAND TOTAL = 12,850,000 lbs

degreasers shown in the EIS and the SRI data was expectable. For the South Coast Air Basin, for example, the EIS lists only 128 degreasers, while the SRI compilation shows about 250. The latter count represented a population within a matrix consisting of 17 SIC (three digit) codes. These were identified by SRI within the 45 SIC codes canvassed by Excelsior Laboratories as including any degreaser-operating companies employing perc. In the EIS printout, however, 41% of the SCAB perc users involved SIC codes other than those 17. Of these extraneous sources, almost 60% did fall within the other 28 codes considered by Eureka. The balance were extraneous to the overall matrix of 45 considered by that contractor.

While these overlooked SIC's represented 41% of the total permitted and EIS-listed firms operating perc degreasers, emission-wise their contribution was only 29% of the EIS total. If one assumes that there is a direct relationship between perc consumption and release, then the total perc consumption figure shown on Table 3-32 is possibly low by 29%. If this were the case, total consumption of degreasing perc in California would be just over 18 million lbs/yr.

3.10.5 Emission Factors

A. Perc Production--

The Dow Chemical plant at Pittsburg is estimated by SRI (Ref. 67) to emit 44,000 lbs/yr of perc. This is less than is released by a single, large, open-top degreaser. The factor applied was 0.002 lb emitted/lb produced. This factor was estimated for the direct chlorination process by the EPA (Office of Air Quality Planning and Standards) on the basis of "several very limited studies of perc losses during production". The estimates were provided to SRI in a personal communication (December 1978) from J. K. Greer, Jr. of that agency. An earlier SRI estimate (Ref. 70) placed the emission factor at 7.5 times higher than that cited above.

Excerpts of the later SRI report were presented to Dow Chemical for review. After studying the material, Dow returned the material without comment.

B. Dry Cleaning--

It is generally assumed (e.g., AP-42) that all of the perc consumed by the dry cleaning business community is lost to the atmosphere. Based on the Table 3-31 consumption estimate, this would amount to 41.7×10^6 lbs/yr of perc emissions in California.

Fisher of the International Fabricare Institute (IFI) estimated (Ref. 71) a per capita perc release of 1.75 and 1.99 lb/year based on reported and calculated perc consumption, respectively. The Census Bureau estimated the state's population at 22,294,000 as of July 1978. This would represent perc releases of 39.0 and 44.4×10^6 lbs/yr for the above two conditions. The average of the two IFI estimates is 41.7×10^6 lbs/yr, which happens to be the same value as calculated from Table 3-31.

A CARB draft report (Ref. 72) dealing with solvent (petroleum and synthetic) emissions from dry cleaning operations was obtained from that agency. In the report, per capita emissions were estimated at 1.5 lb and included both petroleum and synthetic species. This was based on AQMA surveys of dry cleaning plants in the various jurisdictions. Although over one-third of the state was not included, most of the state's population was inclusive of the area inventoried. A survey was also conducted to determine usage rates of petroleum solvent. This was found to average 3,840 gal/yr in commercial plants and 37,200 gal/yr in industrial plants. Synthetic emissions were calculated according to the following formula:

$$E\ \text{synth} = 1.5\ p - (3{,}840 \times d\ \text{lb/plant-yr} \times N_c) + \left(\frac{37{,}200\ d}{2}\ \text{lb/plant-yr} \times N_i\right)$$

where:

N_c = number of commercial cleaning establishments using petroleum solvents

N_i = number of industrial cleaning establishments using petroleum solvents

p = county population in 1976

d = average density of petroleum solvent (6.5 lb/gal)

The first term (1.5 p) calculates the total petroleum and synthetic emissions for the county (or State). The balance of the expression is intended to subtract out the petroleum solvent used in industrial and commercial operations (coin-operated facilities can be ignored as using no petroleum solvent), and then add back half the solvent consumed in industrial plants as being for the cleaning of non-clothing items (drapes, rugs, uniforms, cleaning rags, etc.). It was apparently assumed that the 1.5 lb per capita emission factor did only include solvent releases from wearing apparel.

The formula, however, fails to accomplish the stated scenario. While the second term does subtract out petroleum solvent usage in commercial plants, the third term does not accomplish this for industrial plants or add back half the synthetic solvent used to clean non-clothing items. As written, the formula defines estimated emissions to include all the synthetic solvent used in all dry cleaning operations plus 150% of the petroleum solvent used in industrial facilities.

A breakdown by county of perc emissions was included in the CARB report (Ref. 72). The total for the entire state was 27.4 x 10^6 lbs/yr. The estimate may be on the low end of the probable range.

The distribution of the sources responsible for these considerable perc emissions are doubtless consistent with population densities. The small (approx. 14%) fraction of the total perc emitted by industrial cleaning establishments is probably concentrated in non-residential zones of the major California cities. The general effect, however, should still be one in which perc dry cleaning emissions are distributed according to and are directly proportional to urban population concentrations.

C. Degreasing Operations--

The EPA (Ref. 73) estimates the average emission rate for cold cleaners at 662 lbs/yr, although the rates vary widely. Most losses occur because of bath evaporation, solvent carry-out, agitation, waste solvent evaporation, and spray evaporation. In sharp contrast, the same report estimates the average solvent loss for an open top vapor degreaser at 80,650 lb/yr. Most of the losses are directly out of the opening, there being relatively small losses occasioned by carry-out or waste solvent evaporation. Conveyorized degreasers are mostly of the vapor type, only about 15% being designed to operate with cold solvent. Although typically of larger capacity, the conveyor vapor degreasers are of enclosed design and thus release less solvent than the open top configuration. The EPA estimates the average conveyorized vapor degreaser to emit 55,620 lb/yr of solvent. The cold conveyorized degreasers are estimated to release about 105,000 lb/yr per unit on the average. The more recent designs are far more efficient, however.

The EPA report estimates that only 10 to 20% of the solvent input to conveyorized degreasers and 20 to 25% of the solvent input to open top vapor degreasers are disposed of as waste solvent. In California, most vapor degreasers distill and recycle this material in-house. APCD permit charges are based on solvent purchases. The incentive is thus to recycle solvent internally, rather than to sell off dirty solvent to outside reclaimers, according to the degreaser manufacturers cited earlier.

Emissions from degreasing operations are generally regarded (e.g., AP-42) as being equal to the solvent purchased. The Eureka study (Ref. 69) subtracts out solvent sent to reclaimers, which involved a small fraction. Mitre Corp. (Ref. 68) estimates that 98% of the solvent purchased is lost to the atmosphere.

The Eureka study, which involved the polling of a generous sampling of degreaser users, resulted in emissions for nine different solvents in the principal California air basins by 45 SIC plant categories. The latter was assumed to embrace all probable classifications that would be employing degreaser equipment. As pointed out earlier, this is not the case, but the error involved is not great. The results obtained by Eureka for perc emissions in 1976 are given in Table 3-34. They have also been cited in a recent CARB model rule proposed (Ref. 74) within that agency.

TABLE 3-34. ESTIMATED PERC EMISSIONS FOR MANUFACTURING INDUSTRY DEGREASING OPERATIONS FOR 1976

(Source: Eureka Laboratories, Ref. 68)

Air Basin	County	Perc Emissions, 10^3 lbs/yr	% of State
Sacramento Valley	Sacramento	14.6	0.09
San Diego	San Diego	1,343	8.1
San Francisco Bay Area	Alameda	263	
	Contra Costa	21.9	
	Marin	197	
	Santa Clara	453	
	San Francisco	58.4	
	TOTAL	993	6.0
San Joaquin Valley	Fresno	29.2	
	Kern	7.3	
	San Joaquin	321	
	Stanislaus	--	
	Tulare	--	
	TOTAL	358	2.2
South Central Coast	Santa Barbara	307	
	Ventura	--	
	TOTAL	307	1.9
South Coast	Los Angeles	11,592	
	Orange	1,854	
	Riverside	29.2	
	San Bernardino	80.3	
	TOTAL	13,556	81.8

State total 16,571,600 lbs/yr.

It will be noted that the State total emissions of perc are considerably larger than the consumption rate estimated in Table 3-33. The data presented in that table are, however, based on SRI statistics which considered only 17 of the 45 SIC codes canvassed by Eureka. SRI felt that all of the perc users were inclusive of that grouping. As pointed out earlier, it was estimated that their figures may be low by 29% because, based on SCAB perc emissions data (EIS), many other SIC categories had been overlooked. Thus, if the Table 3-33 data are increased by 29%, the estimated release for the state would be 16.58 x 10^6 lbs/yr. This extremely close agreement with the Eureka estimate (16.57 x 10^6) is extraordinary. Although SRI worked with Eureka's questionnaire results, KVB adjusted the Table 3-33 total using EIS emission factors (and for only one air basin) rather than Eureka's findings. The one air basin -- SCAB -- does, however, furnish an estimated 81.8% of the total perc emissions in the state.

Just 90% of the total perc emissions are identified with four counties: Los Angeles (70.0%), Orange (11.2%), San Diego (6.0%), and Santa Clara (2.7%).

Because of the high concentration of perc emissions in Los Angeles County, the EIS printouts were searched to detect the possible existence of hot spots. It was noted that 12 aircraft/aerospace and two other companies were responsible for 22% of the perc emissions in the County. Of that fraction, 45% were contributed by one firm, the Day and Night Manufacturing Co., City of Industry (SIC 3822 - automatic controls for regulating residential and commerical environmental control systems and related appliances). The annual release of perc from that plant is listed as 1,180,000 lbs/yr in the EIS. These sources are plotted on Figure 3-20. The distribution of the balance of the perc degreasers generally covered the industrialized areas of greater Los Angeles.

D. Ambient Air Measurements--

In 1972, Simmonds, et al (Ref. 75) obtained ambient perc measurements on three different dates at mostly non-repeated station sites throughout

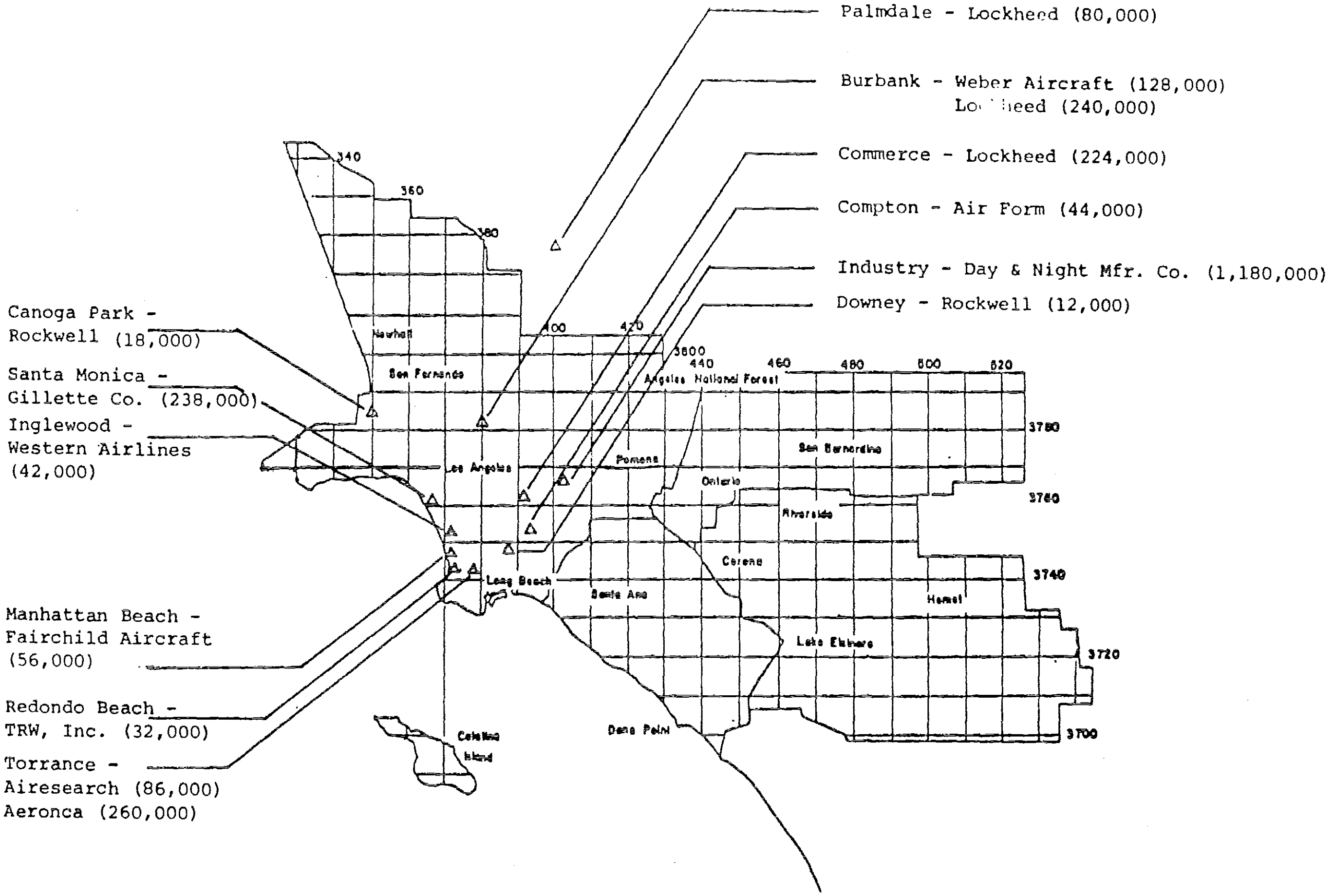

Figure 3-20. Location of 14 degreaser-operating firms estimated to be contributing 22% of the perchloroethylene released in Los Angeles County by such operations (emission factors in lbs/yr).

Los Angeles County. On a fourth date, samples were taken in the San Bernardino Mountains to characterize background. The weather conditions were somewhat mixed. In the first survey (industrial eastern Los Angeles), perc levels ranged from 1.3 to 2.5 ppb. The second survey ranged from the area of the first survey west through central Los Angeles to Santa Monica Bay. At the beach station a value of 0.01 ppb was obtained, while the high value proved to be 3.8 ppb (central Los Angeles). The third survey ranged south into Orange County, triangulating from the extreme eastern and western stations of the first two surveys. On the third survey, perc levels ranged from 0.06 ppb (west central Orange County) to 3.84 ppb (at the coast). The 24 hr average obtained at about 6,000 feet in the San Bernardino Mountains was 0.09 ppb.

The one station (industrial eastern Los Angeles) that was sampled on all three surveys produced an average for the three samples of 1.4 ± 0.3 ppb perc. This site, incidentally, was probably less than ten miles distant from the Day and Night Manufacturing Co. plant, which alone is estimated to realease 7% of all the perc emitted by degreasers in the state.

3.11 POLYCYCLIC ORGANIC MATTER (POM)

3.11.1 General Nature of the Pollutant Category

A. Definition--

Some confusion exists as to the specific chemical class(es) represented by the POM category. The tendency is to assume that the precedent expressions PAH, PNA* and PNAH are all the same classification. The latter three abbreviations refer, however, to fused polycyclic (polynuclear) hydrocarbons (carbon and hydrogen only) which exhibit a maximum number of non-cumulative double bonds (or aromaticity). The narrowness of this classification is raised since saturated and heteroatomic derivations of the polynuclear aromatics certainly occur with them in the polluted media. Such other forms, perhaps no less potent carcinogens, are therefore brought into the category, the definition of which has been semantically broadened under the title, "Polycyclic Organic Matter."

The National Academy of Science first used the title (Ref. 76), and the EPA eventually defined it (Ref.77). This definition is somewhat confusing because of the terminology used. Included in the POM category are the true PNA's, plus aza and imino (the terms are synonymous), arenes (generic term for <u>monocyclic</u> as well as fused ring aromatic hydrocarbons), and so on. The intent, however, was to bring in a broader class of compounds that allows nitrogen, oxygen, sulfur, and oxycarbon ring-atoms as well as PCB's and appropriate pesticides. The last two subgroupings were not considered in the present study. Collectively, PCB's now comprise a banned substance category. Pesticides represent a commodity rather than a chemical class. Many pesticides could be shown to fit the imprecise EPA definition of POM, the determination of which would clearly be outside the intent of the study.

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*The expression PNA will be used in this discussion to refer to the true hydrocarbon fused ringed aromatic compounds.

B. Occurrence--

With the exceptions of PCB's and pesticides, the use of technical-grade chemicals that are generically POM's is limited to a few materials in commerce. Very small amounts of true PNA's are used as organic semi-conductors. In the broader POM concept, cholesteric liquid crystalline materials can be considered; they are widely employed in numeric registers for calculators and wrist watches. Naphthalene (the simplest fused ring aromatic but not a polynuclear aromatic) is heavily used (75% of that produced) in the synthesis of phthalic anhydride, dyestuffs, and various specialty chemicals (Ref. 59). California apparently does not share in this area of manufacture.

The principal occurrence of POM arises as a result of combustion processes. Minor releases are associated with asphalt-product manufacture, carbon black production, bauxite reduction, and tire-wear (carbon back release), according to the EPA (Ref. 77).

In combustive processes, the major concern, POM's are typically pyrogenically formed. Benzene itself is very refractory and can survive thermal environments in which other hydrocarbons completely oxidize. The presence of this aromatic in a reactive zone with nonaromatic radicals can produce accreted, cyclized structures. These can then molecularly condense with each other to produce a wide variety of fused ring species. On leaving the hot zone of the sponsoring process, the POM vapors must physically condense, which process is promoted by any particulate matter capable of nucleating the effect. Ordinary soot or fly ash from boilers, Diesels, jet engines, forest fires, etc., serve this function.

C. Measurement of POM--

The measurement of POM's is also an imprecise if highly challenging technical art. It is virtually impossible at the present time to identify and quantify all of the class species in any given POM sample. It is also quite inadequate to apply many of the extant sampling techniques to the collection of these substances, and expect 100% recovery for analysis. This situation is generally acknowledged by the community of analytical chemists.

The family of chemical analytes comprising POM's is simply too numerous, too extensive of range in physical and chemical properties, and so involatile at the higher boiling end that it frustrates facile specific analyses.

At present, considerable POM testing is being done with the computerized GC/MS. This is a semiquantitative analysis which furnishes reasonable resolution of species but shows deteriorating recovery as molecular weight and/or polarity of the eluted compounds increase. High performance liquid chromatography (HPLC) is suggested for more accurate results. It is a more reliable quantitative procedure and does tend to overcome the inadequacies of GC/MS in eluting the lower vapor pressure POM's. HPLC does not furnish the resolution available from an efficient (60,000 to 70,000 effective theoretical plates) capillary GC column. It also cannot identify the substances triggering the detector (s). Analysis is thus an inadequately developed art for this difficult mixture of chemicals that, until recently, was of relatively little interest to the analyst.

Because the POM family is a very complex chemical group and the analytical chemistry being applied is far from optimum, compromise procedures have been adopted. A favored technique is to measure the PNA, benzo[a]pyrene (BaP) as being the representative or "surrogate" for the entire class. This resulted because BaP analysis was theretofore reasonably developed, favoring its use as an indicator POM substance.

In some cases, the values of BaP determined for a particulate sample can be related to data available from the same sampling for benzene soluble organics (BSO) and a fraction loosely defined as "POM". The last is usually the sum of ten (and sometimes more) PNA species (pyrene, BaP, BeP, perylene, benzo[ghi]perylene, anthracene, caronene, anthranthrene, phenanthrene, and fluoranthene) collected on the front and back portions of the EPA Method 5 sampling train. While this group of ten PNA's does not possibly represent all of the POM in the sample, the BSO will conversely include most or all of the POM but other matter as well. Thus, the actual POM content lies somewhere between the yield of ten or more PNA's and BSO. A comparison of BaP values with BSO and the totalled PNA's will afford the extremes of the range in which the ratio of BaP to POM should fall. These data are shown in Table 3-35.

TABLE 3-35 ESTIMATES OF RATIOS FOR BaP, BSO, AND TEN PNA's FOR VARIOUS PROCESSES BASED ON GEOMETRIC MEANS OF COLLECTED DATA

Process	BSO/BaP	PNA's[*]/BaP	Reference
Coke Production			
Wet coal charging	500	--	78
Quenching	300	--	78
Door leaks	167	2.9[†]	78
Battery stacks	133	--	78
Residential Fireplaces			
(Wood burning)	--	28	79
Oil Fired Intermediate Boilers			
Steam atomized	80,900	21	80
Low pressure, air atomized	15,500	21	80
Forest Fires			
Heading	--	264[§]	81
Backing	--	47[§]	81
Mobile Sources			
Autos (diesel)	3,250	--	82
Trucks (diesel)	--	810	83
Gas Fired Intermediate Boilers			
Process steam	> 800	> 3.5	80
Hospital heating	2,760	145	80
Gas Fired Residential Heaters			
Double shell boiler	19,500	23	80
Hot air furnace	11,000	13	80
Wall heater	20,000	110	80
Petroleum Catalytic Crackers[#]			
Regenerator outlet	12,160	68	80
CO waste heat boiler	> 89,000	24	80
Asphalt Production			
Saturators (controlled)	--	4	84
Air blowing (controlled)	--	50	84
Hot road mix (controlled)	> 180,000	> 70	80

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[*] Ten PNA's were determined and summed unless otherwise specified.

[†] Fourteen PNA's determined and summed.

[§] Eighteen PNA's determined and summed.

[#] All types weighted by population.

D. POM Emission Sources--

Some 17 categories of POM sources have been identified by Energy and Environmental Analysis, Inc. (EEA) as emitters of POM (Ref. 85). A number of these source types do not exist in California or are so limited in number as to be inconsequential. These sources include coal-fired power plants, industrial boilers, and residential furnaces; municipal and commercial incinerators; bauxite reduction plants; open burning dumps; and burning coal refuse banks. The balance of the source types and the estimated National emissions of BaP included in the EEA report are shown in Table 3-36.

These estimates are described as being quite coarse by EEA. Also, by utilizing BaP as the indicator or surrogate substance, the actual POM emission factors are speculative and certainly considerably higher. Nonetheless, concern for all source categories listed in Table 3-36 below "Iron and Steel Sintering" can be dismissed as minor in nature by comparison.

In the higher BaP emission categories, the estimates point to dispersed sources in all cases except the dominant one. This is coking for steel production and the related practice of iron ore sintering. In California, this occurs at only one site, the Fontana steel mill of the Kaiser Steel Co. Although the estimated POM emissions for coking shown in Table 3-36 are National, one must assume that, until source testing is accomplished, releases at Fontana are proportional in terms of coke output.

Another factor in coking to be noted is that the BSO/BaP and PNA/BaP ratios for coking operations are the lowest for any of the source categories shown in Table 3-35. This suggests, although not convincingly, considering the measurement methodology, that coking oven POM emissions are comparatively enriched in BaP with respect to other types of POM species.

Whatever attention again focuses on the Kaiser plant in this present topic, the other designated POM sources should also be considered. The next section therefore deals with all the categories listed in Table 3-36 with the exception of those previously eliminated as being minor in nature.

TABLE 3-36. ESTIMATES OF TOTAL BaP EMISSIONS IN THE UNITED STATES BY SOURCE TYPE

(Source: Energy and Environmental Analysis, Inc. - Ref. 85)

			Estimated BaP Emissions, Tons		
Source	Annual Production or Fuel Consumption	Date Year	Minimum	Maximum	Geometric Mean
Coke Production	56.5 x 10^6 tons	1975	0.06	330	120
Residential Fireplaces (wood)	47.5 x 10^6 tons	1975	57	120	80
Oil Fired Intermediate Boilers					
Commercial/ Institutional	522.6 x 10^6 tons	1973	--	--	21
Industrial	377.1 x 10^6 tons	1973	0.25	0.75	0.41
Forest Fires	8,000 sq miles	1976	10.5	140	110
Mobile Sources					
Tire wear	217 x 10^6 pop'n	1977	0	12	--
Motorcycles	512 x 10^6 gals	1975	--	--	6.2
Autos (gasoline)	78 x 10^9 gals	1975	1.7	3.6	3.0
Autos (Diesel)	10 x 10^6 gals	1975	0.007	0.03	0.01
Trucks (Diesel)	9 x 10^9 gals	1975	0.009	6.8	0.14
Iron & Steel Sintering	40.8 x 10^6 tons	1977	0.024	45	0.69
Gas Fired Intermediate Boilers					
Commercial/ Institutional	2.8 x 10^{12} cu ft	1973	--	--	0.67
Industrial	5.3 x 10^{12} cu ft	1973	--	--	0.02
Gas Fired Residential Furnaces	7.6 x 10^{12} cu ft	1973	0.13	1.7	0.47
Petroleum Catalytic Crackers					
Fluid cat	28.8 x 10^6 cu ft	1977	0.00002	0.003	0.0003
Thermofor	1.6 x 10^6 cu ft	1977	negl	0.04	0.001
Houdriflow	0.1 x 10^6 cu ft	1977	--	--	0.005
Carbon Black Production	1.3 x 10^6 tons	1976	0.043	0.096	0.096
Asphalt Production					
Saturators	4.8 x 10^6 tons	1976	negl	0.019	0.005
Air blowing	4.8 x 10^6 tons	1976	0.002	0.027	0.005
Hot road mix	21.5 x 10^6 tons	1976	--	0.014	0.001

3.11.2 Emission Factors

A. Coking Operations and Ore Sintering--

The coal and coke estimates developed by SRI (Ref. 86) show 1975 coke production at Fontana at about 1.3 x 10^6 tons. This was produced in 315 ovens organized within seven batteries. Comparing this coke production with the National output and the average BaP (Table 3-36) emission, the factor for Fontana would be 5,500 lbs/yr of BaP. The ratios given in Table 3-35 would suggest that the release of PNA's (14 species, including BaP) would be about three times that amount, and of BSO about 300 times (based on a rounded average of Table 3-35 BSO/BaP ratios).

B. Residential Wood Burning Fireplaces--

As the Table 3-36 estimates suggest, the burning of wood is a relatively rich source for the emissions of POM. This may arise from the aromatic nature of lignin, a characteristic fraction of woody plants and trees.

Of the sources listed in Table 3-36, the home fireplace emerges as the third largest source of BaP emissions in the United States. Assuming that California homeowners burn wood in the fireplaces in proportion to their fraction of the National population (∿10%), then the BaP emissions from these sources would be 16,000 lbs/yr POM. The California Housing and Community Development Department estimated that, as of January 1978, there were 8,613,388 residential units in the State. Although not all of these housing units have fireplaces, a fireplace emission factor of 840 mg BaP/yr. per unit is calculated. This is based on the data given in Ref. 79 for ten PNA's measured in home fireplace emissions. Assuming that these ten PNA's (including BaP) represent the entire POM class, then the POM emission factor would be 23.7 g POM/yr per unit. The BaP fraction in the ten PNA's measured was 3.54%.

C. Oil Fired Intermediate Boilers--

The two types of boilers considered in this class, as shown in Table 3-36, are industrial and institutional/commercial boilers. The former are employed in manufacturing processes to furnish process steam and electricity. The industrial boilers are of higher energy capacity ($> 20 \times 10^6$ Btu/hr) and are more efficient combustors than the smaller institutional/commercial boilers ($< 10 \times 10^6$ Btu/hr). As shown in Table 3-36, the BaP emissions of industrial boilers are relatively low even though their fuel comsumption is similar to that of institutional/commercial boilers. Their emissions are also a small fraction of the total and are therefore not considered further.

The institutional/commercial boilers are typically low pressure, air-atomized devices that are used for space heating. In California, most are operated with natural gas although all must have standby oil firing capability. When gas service is interrupted, the oil systems are of course used. Practically all boilers in this category purchase gas at curtailable service rates. Curtailment is very infrequent, however, such that oil firing occurs for only several days a month during the winter months. Thus, the State's fraction of the oil burned in these smaller boilers throughout the nation (523 million tons, per Table 3-36) is far below the population ratio. For this reason, development of an emission factor was not attempted.

D. Forest Fires--

Considerable variability in the output of POM is seen in burning timber stands (Ref. 81). Smoldering fires emit three to four times the BaP as do flaming forest areas. Fires burning into the wind (backing) emit eight to ten times the BaP as do wind-driven (heading) fires. These ratios are considerably higher for the comparative yields of PNA's (18 determined in the case of the data considered here). The estimated average emissions for forest fires are therefore quite coarse.

In Table 3-36 the area consumed by forest fires is listed at 8,000 square miles in 1976. Comparative forest area loss in California is considerably less than the National population ratio. The six year average furnished by the State Dept. of Forestry includes all State fire control jurisdictions (California Dept. of Forestry, U.S. Forestry Service, Bureau of Land

Management, U.S. Park Services, and five counties contracted to protect State forests), is 378 square miles annually destroyed. This is less than 5% of the National loss figure.

This fractional area loss figure permits estimation of BaP emissions in the amount of 10,400 lbs/yr based on Table 3-36. The amount of PNA's that would be measured (18 species including BaP, according to Ref. 81) would weigh somewhere between 50 to 250 times as much.

E. Mobile Sources--

1. Tire wear--The National Academy of Science (NAS) points out (Ref. 76) that the carbon black (a rich source of POM) incorporated in vehicle tires as opacifier releases that matter with wear. Relevant statistics on particulate releases are cited in Section 3.4.6C of this report. The NAS estimated emissions range from zero to 12 tpy (Table 3-36). The California fraction, based on vehicle population would be less than 3,000 lbs per year. The effect would be highly dispersed.

2. Motorcycles--Most lower horsepower motorcycles are equipped with two cycle engines. These engines combust a premixed fuel of gasoline and oil. Combustion is less efficient than that in a four cycle engine since the exhaust remains in the firing chamber after each cycle. The presence of oil results in high emissions of POM (Ref. 76).

The NAS estimates the national release of BaP from motorcycles at 6.2 tpy. Assuming the state motorcycle population ratio to National count corresponds with the human population ratio of about 10%, the BaP release from this source in California would be less than one ton per year.

3. Other vehicles--The POM emissions of gasoline engine automobiles have been characterized by Gross (Ref. 87). Based on his data and the estimates for gasoline consumption, the release shown in Table 3-36 was derived by EEA (Ref. 85). The fractional amount released in California would be about 1,000 lbs/yr, roughly one-half the amount released by motorcycles. This is notable in that automobiles consume over 150 times the gasoline used in motorcycles.

The contributions of Diesel engines to the POM burden are minor. What is interesting in the estimates presented in the Table 3-36 is the disparity of emission factors between the gasoline and Diesel engine automobiles and trucks. On a unit volume of fuel, the Diesel truck emits only 40% of the BaP attributed to the gasoline engine car. The latter, in turn is estimated to produce only 2.5% BaP of the Diesel car. Per gallon, the latter emits 90 times the BaP than does a truck equipped with the same type engine.

3.11.3 Ambient Levels of BaP and BSO

As might be expected from the previous discussion, POM emissions of integrated steel plants are of greatest concern. Thus, average BaP and BSO data obtained from the National Air Surveillance Network (NASN) are compared with respect to cities in which such mills are located to those not hosting such operations. This comparison was prepared by SRI (Ref. 74) and is shown in Tables 3-37 and 3-38.

These data can be compared with the levels measured at seven Southern California cities, all of which are 75 miles or less from Fontana (Table 3-39). The data suggest several things. Emissions of POM, as indicated by BaP measurements may have dropped over the past decade. The levels of ambient BaP in U.S. cities hosting coking plants appear to be higher than in those which do not.

TABLE 3-37. SUMMARIZATION OF NATIONAL AMBIENT BaP AND BSO DATA FROM NATIONAL AIR SURVEILLANCE NETWORK (NASN)

Pollutant	Statistic	Cities with Coke Ovens	Cities without Coke Ovens	Rural Areas
BaP (ng/m^3) 1975 data	Average	1.21	0.38	< 0.10
	Sample size*	21	13	3
	Range	0.3-4.7	0.03-0.9	< 0.10
BSO (μg/m^3) 1971-72 data	Average	4.21	3.75	0.95
	Sample size*	25	12	2
	Range	2.1-7.3	1.9-5.6	0.8-1.1

* Number of cities providing averaged annual concentration data.

Source: Ref. 85

TABLE 3-38. CHRONOLOGICAL BaP AVERAGES FOR SELECTED U.S. CITIES (NASN DATA) (ng/m^3)

Year	Cities with Coke Ovens	Cities without Coke Ovens
1966	4.74 (15)*	2.76 (7)
1967	5.34 (15)	2.29 (8)
1968	3.75 (18)	2.64 (8)
1969	4.41 (23)	2.14 (11)
1970	3.02 (21)	1.41 (11)
1971	2.18 (11)	1.22 (8)
1972	2.14 (19)	0.64 (11)
1975	1.21 (21)	0.38 (13)
1976	0.93 (20)	0.41 (13)

* Number of cities included in average.

Source: Ref. 85

TABLE 3-39. ATMOSPHERIC BaP AND BSO CONCENTRATIONS FOR CHESS AND CHAMP SITES IN CALIFORNIA*

Location	Distance from Fontana, Miles	BaP (ng/m^3) Mean	BaP (ng/m^3) Range	BSO ($\mu g/m^3$) Mean	BSO ($\mu g/m^3$) Range
Vista	65	1.03	0.1-4.9	2.07	0.8-6.7
Santa Monica	64	1.46	0.2-3.5	3.91	1.1-6.1
Thousand Oaks	75	0.63	0.1-1.4	2.31	1.1-4.8
Garden Grove	37	2.42	0.3-7.5	3.86	0.8-11.9
Glendora	23	0.91	0.1-2.2	4.13	0.5-6.5
West Covina	29	1.98	0.2-5.0	5.85	2.6-9.5
Anaheim	34	2.36	0.4-7.1	4.77	1.6-11.2

* Data collected in 1975 over a 12 month period (except Santa Monica, which was for six months); all samples are 24 hour averages.

Source: Ref. 85

The pattern in Southern California for seven cities in 1975 shows BaP and BSO levels that are higher than the National average for cities having steel mills (BaP 1.80 vs 1.20 ng/m^3 and BSO 4.40 vs 4.21 $\mu g/m^3$, respectively). The effect of the Fontana coking plant in this is not clear. The CHESS/CHAMP data are for cities off the prevailing wind (westerly) at Fontana. Glendora, the nearest city to Fontana exhibits the next to lowest BaP value for the set. It would be of interest to measure BaP levels east of Fontana at, say, San Bernardino or Redlands.

SECTION 4.0

POPULATION DENSITIES RELATIVE TO POLLUTANT SOURCES

4.1 SOURCE MAPPING

A number of the pollutants studied were found to be used in a manner that resulted in their being released as area sources. Figure 1-2 presented early in this report was included to show this effect for sources exhibiting some geographic definitions. Other pollutant sources considered are so highly dispersed, however, that even this treatment is not possible.

In contrast to the dispersed area sources that offer no recognizable "hot spots," a number of materials and point sources were described. Assuming that the emissions factors associated with these point sources are significant, these can be mapped to show relationship with population density. This has been done here using a Bureau of Census map (stock no. 0324-00214) section.

In overlaying the point sources of interest, a single map was originally considered. This proved too cluttered, so that two separate maps have been prepared. The display of "hot spots" on the two maps was arbitrarily segregated into displays of sources for the inorganic and organic classes of materials. Explanatory tables furnish firm names and estimated emissions rates. The technique for reading the population density map was given earlier with Figure 1-2.

In the following discussions, comments are also offered on the micrometeorology/topography of the locales in which various souces or groups of sources are situated. These observations derive from the general knowledge of the project staff and should not be construed as being products of the study itself.

4.2 INORGANIC POLLUTANTS

4.2.1 Arsenic

From Figure 4-1 and Table 4-1, it can be seen that 90% of the arsenic emissions emitted (mostly from the secondary lead smelters) is released into the South Coast Air Basin (SCAB). Most of the pollutant is released in the heaviest populated area of the State. The topography of the basin and its historical lack of air drainage are well known. The balance (10%) of the arsenic released in the State is from reasonably well ventilated shore sites.

4.2.2 Asbestos

All three of the asbestos mining and milling areas are located in very lightly populated areas, although each is near a small city or town. The micrometeorology and topography in each case favors the dispersion of particulate matter. This probably is not altogether an advantage in view of the great amount of surface-exposed facies bearing asbestos.

4.2.3 Cadmium

This air pollutant is associated principally with the Kaiser steel mill at Fontana. Also located in the SCAB, this locale suffers from deficient vertical air movement and prevailing (light) winds are westerly. The topography comprising a tank framed by the (clockwise) San Gabriel, San Bernardino, San Jacinto, Lakeview, and Santa Ana Mountains, entraps polluted air masses in the moderately populated areas around San Bernardino, Redlands and Riverside. The Kaiser mill contributes cadmium (and three other of the materials of interest) to this pocket of polluted air.

Another source of significant cadmium emissions is the highway vehicle tire. Conceptualization of traffic density patterns with respect to population densities was given earlier in Figure 1-2. This map overlay, however,

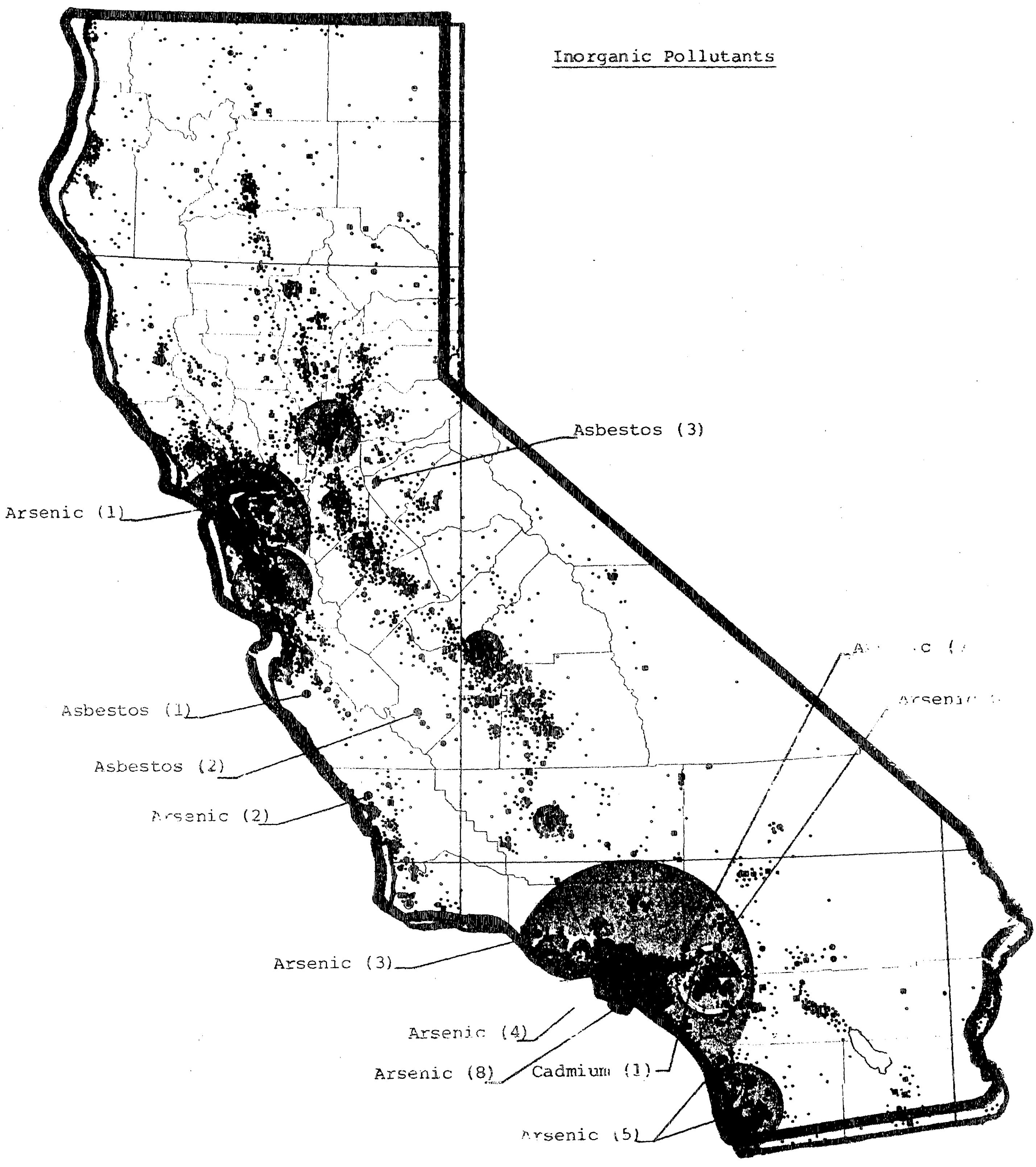

Figure 4-1. Location of inorganic carcinogen emission sources relative to California population concentrations.

TABLE 4-1. INORGANIC POLLUTANT SOURCE INFORMATION CORRESPONDING TO FIGURE 4-1

	Map Code		Firm Name	Type Operation	Estimated Annual Emissions, Lbs
ARSENIC	1	Antioch	Pac. Gas & Elect.	Pwr Plt	1,225
		Pittsburg	" " "	" "	2,085
	2	Morro Bay	" " "	" "	1,172
	3	Oxnard	So. Cal. Edison	" "	1,189
	4	Redondo Beach	" " "	" "	1,134
		El Segundo	" " "	" "	809
		Hermosa Beach	" " "	" "	645
		Long Beach	" " "	" "	1,561
		Seal Beach	LA Dept W&P	" "	1,216
		Carson	ALCO Pacific	Lead Smelt.	4,400
		Vernon	Gould, Inc.	" "	44,000
	5	Carlsbad	San Diego G&E	Pwr Plt	677
		San Diego	" " "	" "	744
	6	San Bernardino	Southwest Smelt.	Lead Smelt.	4,400
	7	Etiwanda	So. Cal. Edison	Pwr Plt	800
	8	Fontana	Kaiser Steel Co	Steel Mill	1,480
ASBESTOS					
	1	King City	Union Carbide	Asb.mine	26,500
	2	Coalinga	Atlas Asbestos	" "	17,500
	3	Copperopolis	Calaveras Asb	" "	34,000
CADMIUM					
	1	Fontana	Kaiser Steel Co	Steel Mill	14,000

shows flow densities for only the State highway systems. This represents roughly half the highway miles driven. The other half, operated by county and city jurisdictions, lies mostly within the densest population zones.

4.3 ORGANIC POLLUTANTS

4.3.1 Benzene

Before considering the point sources emitting this chemical, the reader is again referred to Figure 1-2 As pointed out earlier, the automobile is a major source of benzene pollution.

The "hot spots" identified with benzene emissions are the two producers (ARCO-Carson and Chevron - El Segundo), the three benzene converters (Chevron-El Segundo, Chevron-Richmond and Witco-Carson), the refinery community and the Kaiser steel plant. These are shown on Figure 4-2 with emission factor tabulations included in Table 4-2. With the estimated high release from the Kaiser plant, together with emissions from thirteen refineries (two of which produce benzene) and two of the State's three benzene converters (one of which is not a refinery), the SCAB is again recipient of the bulk (57%) of this carcinogenic burden.

Because of the presence of the Chevron U.S.A. refinery at Richmond, the largest in California, the community of refineries in the area (Carquines Straights) emit a substantial (37%) fraction of the estimated State total. The locale, however, is spotty in populated areas (east of Richmond) and is reasonably well ventilated much of the time. Richmond itself is situated in a topographical arrangement which involves the buildup of polluted air in the Berkeley/Oakland area when winds are unfavorable. The population density southwesterly of the Chevron-Richmond plant is quite dense.

The final grouping of benzene emissions sources is around the city of Bakersfield. This area is seldom becalmed, enjoying the prevailing winds out of the north (San Joaquin Valley). Terrain-induced wind-flows associated with the nearby Sierra Nevada Mountains play a relatively minor role at Bakersfield. Thus, stagnant air conditions are infrequent in this area.

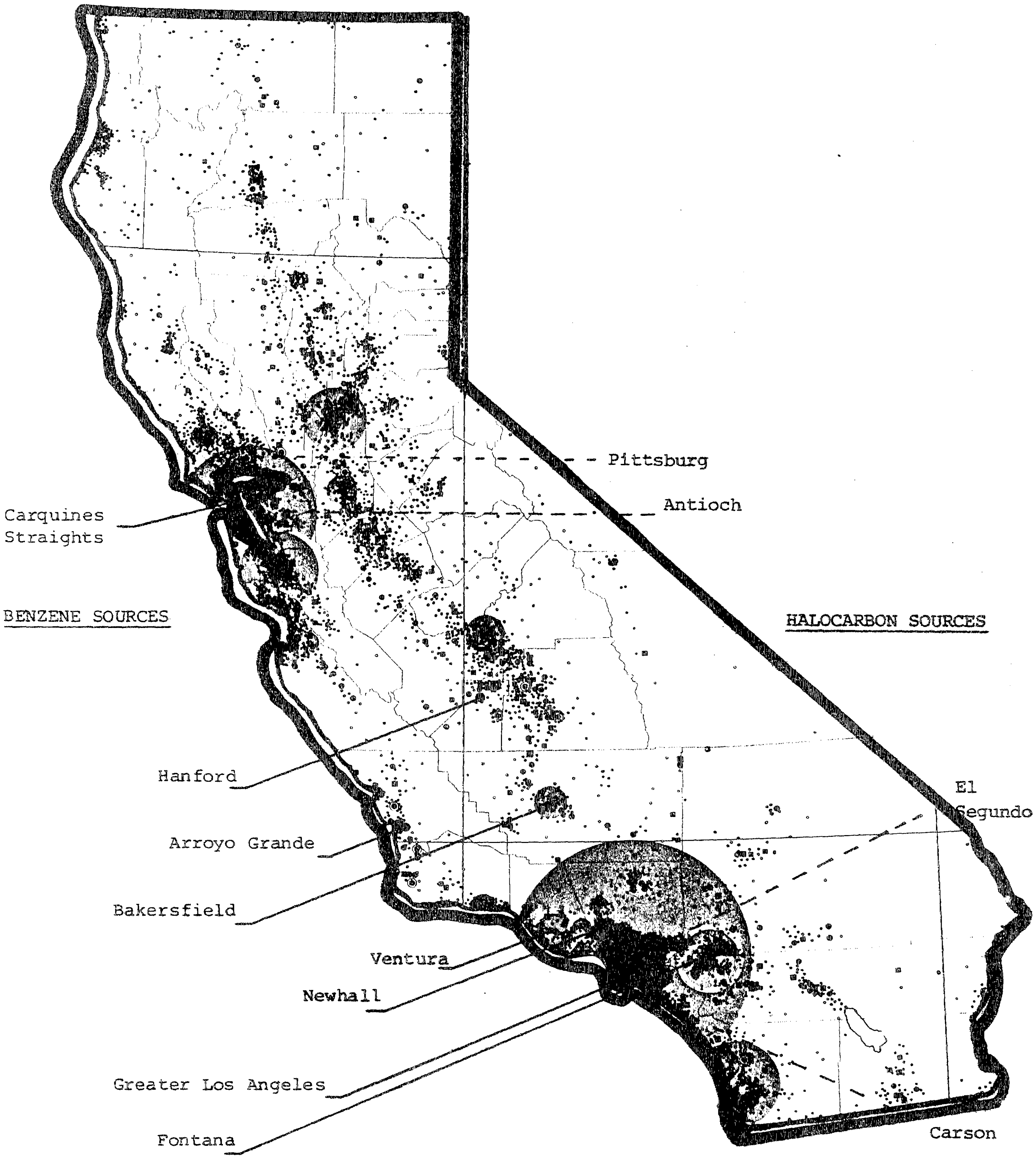

Figure 4-2 Location of Organic Carcinogenic Emission Sources Relative to California Population Concentrations

TABLE 4-2. ORGANIC POLLUTANT SOURCE INFORMATION
CORRESPONDING TO FIGURE 4-2 (BENZENE OVERLAY)

AREA	LOCATION	FIRM NAME	TYPE OPERATION	ESTIMATED ANNUAL EMISSIONS, LBS
Carquines Straights				
	Richmond	Chevron USA	Ref/Conv	217,600
	Benicia	Exxon Oil Co	Refinery	20,000
	Avon	Lion Oil Co	"	28,500
	Hercules	Pacific Ref Co	"	12,000
	Martinez	Shell Oil Co	"	19,700
	Rodeo	Union Oil Co	"	15,900
Arroyo Grande		" " "	"	9,200
Ventura		USA Pet Co	"	3,400
Los Angeles Basin				
	Carson	ARCO	Ref/Prod	30,300
	"	Fletcher Oil Co.	Refinery	4,500
	"	WITCO	Converter	27,500
	Wilmington	Champlin Pet	Refinery	2,800
	"	Shell Oil Co	"	20,400
	"	Texaco, Inc	"	14,200
	"	Union Oil Co	"	4,500
	El Segundo	Chevron USA	Ref/Prod/Con	61,600
	Long Beach	Edgington Oil Co	Asphalt Plt	6,500
	Sante Fe Springs	Gulf Oil Co	Refinery	11,700
	" " "	Powerine Oil Co	"	9,900
	Torrance	Mobil Oil Co.	"	50,800
	South Gate	Lunday Oil Co	Asph Plt	1,100
	Paramount	Douglas Oil Co	Refinery	10,500
Fontana		Kaiser Steel Co	Steel Mill	223,400
Hanford		Beacon Oil Co	Refinery	2,800
Bakersfield/Oildale				
	Bakersfield	Chevron U.S.A.	"	5,900
	"	Kern Cty Ref Co	"	3.600
	"	Lion Oil Co	"	9,100
	"	Mohawk Petro Co	"	5,000
	"	Road Oil Sales	Asph Plt	400
	"	Sunland Ref Co	Refinery	3,400
	"	West Coast Oil Co	"	3,600
	Oildale	Golden Bear Co	"	2,400
	"	San Joaquin Refining Co	"	3,800
Newhall		Newhall Refining Co	"	1,700

TABLE 4-3. ORGANIC POLLUTANT SOURCE INFORMATION CORRESPONDING TO FIGURE 4-2 (HALOCARBON OVERLAY)

LOCATION	FIRM	HALOCARBON	ESTIMATED ANNUAL EMISSIONS, LBS
Carson	Stauffer Chemical Co	EDC	300,000-3,200,000
Pittsburg	Dow Chemical Co	Perc	44,000
"	" "	Carbon Tet	320,000
Antioch	DuPont	" "	20,000- 520,000
El Segundo	Allied Chemical Co	" "	7,000- 175,000

4.3.2 Halocarbon Pollutant Sources

The broken lines in Figure 4-2 site the four plants in California associated with the release of three different halocarbons (ethylene dichloride, perchloroethylene and carbon tetrachloride). Each of these plants is located in an area which has already been discussed in this section, namely the SCAB and the Carquines Straights. Emission data are shown in Table 4-3.

4.4 SELECTION OF CANDIDATE "HOT SPOTS" FOR TASK IV SOURCE TESTING PLAN

The use of the population density map permits the direct visualization of the potential impact of sources on the surrounding communities. It does not, however, provide an adequate scaling of the "hot spots" relative to one another. In planning for source testing for specific pollutants, all of the "hot spots" cannot be immediately included. Thus, the need to establish a scaling factor was indicated. This would properly include certain of the factors already described in Task I screening effort. For convenience, these are repeated here:

R_1: Extent of present use in California
R_2: Projected growth in use in California
R_3: Potential for emission during production and use
R_4: Stability in ambient air
R_5: Dispersion potential
R_6: Evidence of carcinogenicity

These factors were intended to scale pollutants rather than sources with respect to each other. Thus certain modifications would be needed to render them compatible to source ranking. Term R_1 would be inapplicable and term R_3 should be replaced with the emission rate for the source considered that was actually estimated. Finally, a term should be introduced that would reflect the human population density in the area surrounding the source. As with the Task I rating factors, these terms would again be combined using a multiplicative approach. In the present formula, however, the term R_6 has been emphasized by exponentiation.

$$\text{Scaling factor} = E \times p \times R_2 \times R_4 \times R_5 \times \exp(R_6)$$

where: E = specific pollutant emissions, tpy
p = human population in area of source

The values for the R terms are the same as used in Task I, and are repeated here for convenience in Table 4-4. The emission factors are those discussed in the various subheadings of Section 3.0.

The population term employed is the estimated population of a 10 km. grid in which the source is centered. For the SCAB area, population data were available from KVB computer printouts serially organized by UTM coordinates. These were prepared from CARB computer files on a SCAB

TABLE 4-4. TASK I RATING FACTOR ASSIGNMENTS

	R_2	R_4	R_5	R_6
Arsenic	3	5	3	5
Asbestos	1	5	5	5
Benzene	3	5	5	5
Cadmium	3	5	5	5
Carbon Tetrachloride	3	5	5	4
Chloroform	3	5	5	4
Ethylene Dibromide	1	5	5	4
Ethylene Dichloride	3	5	5	4
Nitrosamines	3	3	5	5
Perchloroethylene	3	5	5	4
POM	4	5	5	5

hydrocarbon survey (Ref. 22). The UTM coordinates of the emission sources were determined from Geological Survey map.

The emission sources were never found to lie directly in the center of the UTM grids. It was necessary, therefore, to use the population data for the four decade-numbered UTM grids that enclosed the 10 km. grid in which the source centered. Homogenous distribution of people in each of the four grids was assumed and the people within the four rectangular fractions added to obtain the estimated total for the source-centered grid.

Computer print-outs of populations by UTM coordinates were not readily available for the rest of the State. The Bay Area AQMD accessed their tapes to furnish KVB 5 km. grid populations. These corresponded to UTM-source coordinates for Richmond, Antioch, and Pittsburg that were given KVB by the Contra Costa County Planning Commission. In order to develop source-centered 10 km. grid populations, populations for six pentad-numbered grids were used. In the case of the du Pont Antioch Works, it was found that the UTM coordinates obtained were incorrect. Therefore, the population for the grid centered on the close-by Dow plant at Pittsburg was used.

Populations for the 10 km. grids centered on the Stockton John-Mansville plant and the Salinas PG&E power plant were estimated from Census Bureau maps. These estimates were provided by the Planning Commissions of the counties of San Joaquin and Monterey, respectively. In the case of the three State asbestos mines, the populations of the nearby cities, Copperopolis, King City, and Coalinga, were used. Telephone calls to the City Halls of the last two cities and the Fire Department (there being no City Hall) at Copperopolis were used to obtain the population data. The individuals contacted acknowledged that each of the towns would completely fit within a 10 km. grid centered on the nearby mills. They also estimated that the number of people within that zone that did not live in the towns would be less than 10% of the populations of King City and Coalinga. In the case of Copperopolis (population 110 at last count), an additional hundred or so people were estimated to be scattered throughout the out-of-town area.

The results of the scaling exercise were presented earlier in Section 2.0 as Table 2-1. Included therewith are the conclusions arrived at, which will serve as the basis for designing the Task IV recommended source testing plan.

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APPENDIX A

MAJOR MANUFACTURERS OF ASBESTOS CONTAINING PRODUCTS IN CALIFORNIA

APPENDIX A

MAJOR MANUFACTURERS OF ASBESTOS PRODUCTS IN CALIFORNIA

(Source: U. S. EPA-1973)

A & D Gasket Mfg. Co.
2643 E. 124th Street
Compton, CA 90222

ACAP Gasket & Washer Co.
219 S. Mednick Avenue
Los Angeles, CA 90022

Accro Gasket Co., Inc.
4535 N. Baldwin Avenue
El Monte, CA 91731

Acme Gasket, Inc.
16322 Garfield Avenue
Paramount, CA 90723

Airseals Corp.
1045 S. Wall
Los Angeles, CA 90015

Airseals Company
1834 Overland Avenue
Los Angeles, CA 90025

Alcan Western Products
3016 Kansas Avenue
Riverside, CA 92502

Aluminum Company of American
1450 Rincon Street
Corona, CA 91720

AMAX Alum Mill Products
1495 Columbia Avenue
Riverside, CA 92507

Anchorlik Division, Royal Industries
9530 W. Jefferson
Culver City, CA 90230

Andersen Mfg. Co.
5442 Vineland Avenue
No. Hollywood, CA 91601

Armstrong Cork Company
5037 Patata
South Gate, CA 90280

Amsted Industries, Inc.
10661 Etiwanda Avenue
Fontana, CA 92335

Asbestos Cloth Products Co.
766 Merchant
Los Angeles, CA 90021

Asbestos Products & Fabricators
2316 San Fernando Road
Los Angeles, CA 90065

Atlas Asbestos Co.
1145 Westminster Avenue
Alhambra, CA 91802

Atlas Minerals Corp.
P.O. Box 805
Coalinga, CA 92112

Bass Chemical Company
70 15th Street
San Diego, CA 92112

Borg-Warner Corp.
2300 E. Vernon Avenue
Los Angeles, CA 90058

Walter D. Burt Mfg. Co.
McNears Point
San Rafael, CA 94901

California Gasket Corp.
1601 W. 134th Street
Gardena, CA 90249

Cellulo Company
124 "M" Street
Fresno, CA 93721

Certain-Teed Products Corp.
1695 W. Crescent
Anaheim, CA 92801

Certain-Teed Products Co.
2100 Avalon Avenue
P.O. Box 706
Riverside, CA 92502

Certain-Teed Saint Gobain Insulation
1700 S. El Camino Real
San Mateo, CA 94402

Chevron Chemical Co.
200 Bush Street
San Francisco, CA 94120

Childers Products Co., Inc.
1150 S. Vail
Montebello, CA 90640

Coalinga Asbestos Co.
P.O. Box 1045
Coalinga, CA 93210

Darcoid Company of California, Inc.
234 Ninth Street
San Francisco, CA 94103

DeSoto, Inc.
4th & Cedar Streets
Berkeley, CA 94710

Duro-Well Liner Co.
591 S. Walnut
La Habra, CA 90631

El Dorado Limestone Co., Inc.
Old Highway 50
Shingle Springs, CA 95682

Esco Rubber Co.
130 N. Brea Boulevard
Brea, CA 92621

Featherock, Inc.
6331 Hollywood Boulevard
Los Angeles, CA 90028

Federal-Mongul Corp.
11634 Patton Road
Downey, CA 90241

Filtering Materials, Inc.
860 S. 19th Street
Richmond, CA 94804

Flintkote Com.
P.O. Box 2218
Terminal Annex
Los Angeles, CA 90054

Fortifiber Corp.
4489 Bandini Boulevard
Los Angeles, CA 90023

Foundry Service & Supply
1906 Oak
Torrance, CA 90501

GAF Corp.
P.O. Box 1768
2340 E. Artesia
Long Beach, CA 90801

T. H. Garner Co., Inc.
177 S. Indian Hill
Claremont, CA 91711

Gasket Shop, Inc.
435 Brannan Street
San Francisco, CA 94107

Gasket Manufacturing Co., Inc.
P.O. Box 26
18001 S. Main Street
Gardena, CA 90247

Gasket Manufacturing Co.
320 Venice Boulevard
Los Angeles, CA 90015

GRAFCO, Inc.
Lomita, CA 90717

Grefco, Inc.
630 Shatto Place
Los Angeles, CA 90005

Golden State Stamping Gasket
8654 Helms Avenue
Cucamonga, CA 91730

HSG Company
435 Brannan Street
San Francisco, CA 94107

Johns-Mannville Sales Corp.
Exploration Department
P.O. Box 1045
Coalinga, CA 93210

Johns-Mannville Corp.
2420 E. 223rd Street
P.O. Box 9067
Los Angeles, CA

Johns-Mannville Corp.
East Third Street
P.O. Box 591
Pittsburg, CA 94565

Johns-Mannville Corp.
P.O. Box 1587
Stockton, CA 95201

Head Gasket Company
465 Bryant Street
San Francisco, CA 94107

Hill Bros. Chemical Co., Inc.
15017 East Clark Avenue
City of Industry, CA 91744

Huntington Tile, Inc.
9223 Bolsa Avenue
Westminster, CA 92683

House of Rubber
2522 East 54th Street
Huntington Park, CA 90255

Industrial Building Materials, Inc.
6417 Bandini
Los Angeles, CA 90022

Kaiser Gypsum
300 Lakeside Drive
Oakland, CA 94612

Kennedy Industries
4447 47 1/2 Alger
Los Angeles, CA 90039

Krasne Division
Royal Industries
3171 East 12th Street
Los Angeles, CA 90023

LASCO Industries, Inc.
1561 Chapin Road
Montebello, CA 90640

Leed Insulator Corp.
793 East Pico Boulevard
Los Angeles, CA 90021

Local Co., Inc.
3440 East 14th Street
Los Angeles, CA 90023

Lasco Brake Products Corp., Ltd.
26th & Magnolia Street
Oakland, CA 94600

M. G. Industries, Inc.
1427 West 16th Street
Long Beach, CA 90813

D. W. Mack Co.
8124 Secura Way
Santa Fe Springs, CA 90670

Miller Gasket Mfg. Co.
1020 South Azusa Boulevard
City of Industry, CA 91744

Miller Gasket Mfg. Co.
5100 District Boulevard
Los Angeles, CA 90058

Milton M. Minear
1839 Preuss Road
Los Angeles, CA 90035

Mobar Industrial Supply Co.
1106 Van Ness Avenue
Torrance, CA 90507

Monogram Industries, Inc.
10889 Wilshire Boulevard
Los Angeles, CA 90024

Nicolet of California, Inc.
544 McCray
Hollister, CA

North American Asbestos Corp.
139 South Beverly Drive
Beverly Hills, CA 90212

North American Rockwell
Autonetics Division
3370 Miraloma
Anaheim, CA 92803

O. G. Supply, Inc.
700 Palm Avenue
Alhambra, CA 91803

Joseph P. Occhipinti
11779-1/2 East Slauson
Santa Fe Springs, CA 90670

Pacific Asbestos Corp.
Obyrns Ferry Road
P.O. Box 127
Copperopolis, CA 95228

Pacific States Felt & Mfg. Co.
23850 Clawiter Road
Hayward, CA 94545

Paramount Gasket Mfg. Co.
15553 Vermont Street
Paramount, CA 90723

Parker Hannipin Company
10567 Jefferson Boulevard
Culver City, CA 90230

Raybestos-Manhattan, Inc.
1400 East Orangethorpe
Fullerton, CA 92634

Raybestos-Manhattan, Inc.
1825 East 22nd Street
Los Angeles, CA 90058

Riverside Cement Co.
1500 Rubidoux Boulevard
Riverside, CA 92502

Royal Industries, Inc.
947 North Vignes Street
Los Angeles, CA 90012

SACOMO-Sierra Mfg. Co.
1559 Custer Avenue
San Francisco, CA 94124

Searle Leather & Packing Co.
2101 15 North Marianna
Los Angeles, CA 90032

Serra Manufacturing
3039 East Las Hermanas
Compton, CA 90221

Silver Line Products, Inc.
4615 Bandini Boulevard
Los Angeles, CA 90022

Silverline Brake Lining Corp.
Davie Avenue & Fleet Street
Los Angeles, CA 90022

Simpson Drag Chute Safety Equip.
22638 South Normandie
Torrance, CA 90502

Southern Pacific Milling Co.
P.O. Box 71
San Luis Obispo, CA 93401

Southern Pipe & Casting Co.
P.O. Box C
Azusa, CA 91702

R. H. Strever Mfg. Co.
3032 Enterprise Street
Costa Mesa, CA 92626

Thorpe Insulation Company
2741 South Yates
Los Angeles, CA 90022

Thorpe Insulation Company
24300 Broad
Wilmington, CA 90744

Tilley Manufacturing Co., Inc.
900 Industrial Way
San Carlos, CA 94070

Union Carbide Corp.
P.O. Box K
Highway 101 South
King City, CA

Uniroyal, Inc.
5901 Telegraph Road
Los Angeles, CA 90022

Walker Products, Inc.
3600 South San Pedro Street
Los Angeles, CA 90011

Weber Pipe Diapers
1024 East Foothill Boulevard
Claremont, CA 91711

Western Aircraft Supply, Inc.
815 Moraga Drive
Los Angeles, CA 90049

Western Chemical & Manufacturing Co.
3270 East Washington Boulevard
Vernon, CA 90058

Western Gasket & Packing Company
3007 Fruitland Avenue
Los Angeles, CA 90058

Western MacArthur Company
3150 Third Street
San Francisco, CA 94124

Western States Brake Mfg. Co.
1224 West 130th Street
Gardena, CA 90247

Anchor Packing Company
22600 South Avalon
Carson, CA 90744

Berg-Nelson Company
1633 West 17th Street
Long Beach, CA 90813

Douglas Oil Company
Attn: F. N. Dawson
Dir. of Manufacturing
14708 Downey Road
Paramount, CA 90723

Edgington Oil Company
2400 East Artesia Road
Paramount, CA 90723

Griffith Company
1380 Arrow Highway
Irwindale, CA 91706

Industrial Asphalt
6840 Hayvenhurst
Van Nuys, CA 91406

Livingston-Graham Company
5500 North Peck Road
El Monte, CA 91732

Lunday-Thagard Oil Company
9301 South Garfield
South Gate, CA 90280

Owl Rock Products
5435 North Peck Road
El Monte, CA 91732

Standard Oil Company
324 West El Segundo
El Segundo, CA 90245

Sully-Miller Contracting
5500 North Peck Road
El Monte, CA 91732

APPENDIX B

HYDROCARBON EMISSIONS MEASURED AT THE DOUGLAS OIL COMPANY REFINERY IN PARAMOUNT, CALIFORNIA ON KVB HYDROCARBON SURVEY PROGRAM

(CARB Contract ARB 5-1323)

SECTION B-1.0

OVERVIEW

The objectives of the refinery tests conducted as part of the KVB hydrocarbon survey were to: (1) obtain emission profile data, (2) check emission factors in AP-42 and (3) evaluate ambient testing as a means of characterizing refinery emissions. The fugitive emission rates from eight major refineries had been measured in the late 50's by the LA APCD in a joint Federal, State and District project. These test results became the basis for most emission factors in AP-42. It was felt that the testing permitted by the ARB program budget for the hydrocarbon survey would be sufficient to validate the AP-42 emission factors or determine that current maintenance practices and sealing technology had caused a reduction in emission factors. Also by sampling and analyzing the emissions from typical refinery processes an emission profile for various refinery processes could be obtained.

One major refinery was tested primarily for device type emission factors. The smaller Douglas Oil refinery was tested to evaluate correlations between ambient and source testing results. Another small independent refinery was used for some preliminary testing to check out test procedures. Because the work done at the Douglas refinery furnished data that would best support the development of a hydrocarbon emission factor for an entire refinery, that data has been referenced in the present report.

The effort included stack tests on process heaters and FCC units plus fugitive emission tests on valves, fittings, pumps, compressors, cooling towers and oil/water separation pools. Fugitive emissions from process hardware were determined by spraying the components with soap solution and characterizing the leak rates by the rate of bubble formation. By measuring a number of small, medium and large leaks, a characteristic leak rate was determined for each of these leak sizes. Emissions from cooling towers and pools were estimated by determining organic evaporation rates from samples taken from these sources.

Although GC/MS data were obtained for many of the samples acquired, insufficient compositional information is available to attempt a benzene emission factor for the entire refinery. By using data obtained from major refinery sources together with extrapolations and estimates derived from the leak and evaporation rates discussed in the preceding paragraph, total hydrocarbon releases can be estimated. Applying a separately derived value for the benzene content, which will vary considerably, depending on the nature of the crude being processed, will then furnish a benzene emission factor for the plant. This was done in Section 3.3.7.C.2 of this report.

SECTION B-2.0

SURVEY RESULTS

The layout of the Douglas Oil Co. refinery is shown in Figure B-1. For the three principal categories of emitters (stack, fugitive, and tank storage and transfer), total hydrocarbon releases are summarized and compared with data obtained by the LA APCD and published in AP-42.

TABLE B-1. DOUGLAS OIL COMPANY HC EMISSION SUMMARY (LB./HR.)

	SC APCD	AP-42	KVB/ARB (Ref. 3) 24 Hr. Av.	KVB/ARB (Ref. 3) Night
Stack Emissions	11	26	13	13
Fugitive Emissions	84	123	54	54
Tank Storage and Transfer	90	95	95	67
TOTAL	185	244	162	134

A breakdown of the unit emissions for each of the categories of refinery components are summarized in Table B-2.

TABLE B-2. DOUGLAS OIL CO. HC EMISSION (LB/HR.) BY COMPONENT TYPES

Emission Category	SC APCD	AP-42	KVB/ARB
Stack Emissions			
Heaters	9	14	10
Boilers	2	2	2
Flaring	Neg.	10	<1
Asphalt Blowing	Neg.	Neg.	NT
SCOT Incinerators	Neg.	N/L	1
Fugitive Emissions			
Reformer Unit	12	16	14
Naphtha Unit	12	13	Neg.
Crude Units (2)	44	54	25
Asphalt Plant	15	--	--
Oil/Water Separators	1	20	1
Cooling Towers	--	20	14
Tank Storage and Transfer			
Crude Storage (3 F/R; 1 C/R)	58	48	48
Gasoline Storage (9 F/R)	16	22	22
Other Petroleum Storage (6 C/R)	14	9	9
Gasoline Transfer and Mixing	1	16	16
Other Petroleum Transfer	1	--	--
TOTAL			162

Legend: Neg. = negligible; NT = not tested; N/L = not listed;
F/R - fixed roof; C/R = cone roof

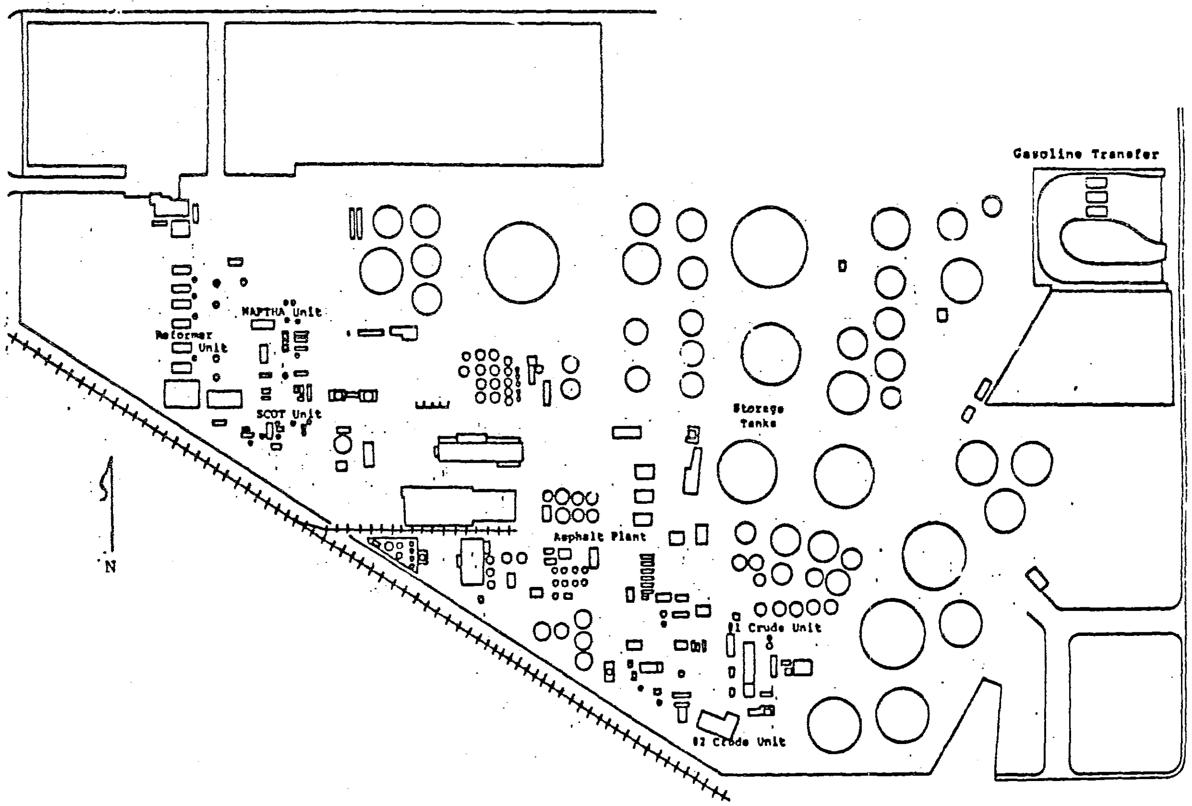

Figure B-1. Layout of Douglas Oil Co. Refinery in Paramount, CA

Stack emissions were determined in the convential manner, except that grab samples were also taken to permit speciation. Fugitive emissions estimates were based on coarse leakage testing which results were expressed as heavy (0.15 cu. ft./min.), medium (0.025 cu. ft./min.) and small (0.002 cu. ft./min.). The number of valves, flanges and pumps inventoried for the reformer unit, naphtha unit and the two crude units are shown in Table B-3. This table also indicates the percentage of these components that were tested on the program and the number of leakers, graded by size, found. Where less than 100% of the components were tested, the number of leakers found is extrapolated to the full population.

In the case of the testing of Douglas tankage, compositional data only were acquired. Mass flows of emissions were calculated using AP-42 (thus the agreement for this category in Table B-2 for AP-42 and KVB data columns). The assumptions used in rendering these calculations are as follows:

Fixed Roof (API 2518)

Assumptions: Av. temp. 75°F
Point Factor 1.0
$\Delta T = 20^{\circ}F$
Tank Ullage = 1/3 Tank Height
Tank Turnovers - Crude 35
Gasoline 10

Floating Roof (API 2517)

Assumptions: Av. temp. 75°F
6 mph wind (4 mph at night)
Welded, old, white

TABLE B-3. DOUGLAS OIL COMPANY VALVE, FLANGE AND PUMP INVENTORY

	Reformer Unit	Naphtha Unit	Crude Unit
Valves	500 (100%)	318 (100%)	475 (80%)
Heavy Leaks	-0-	-0-	2
Medium Leaks	26	-0-	9
Small Leaks	13	5	7
Flanges	852 (70%)	889 (70%)	1,319 (80%)
Heavy Leaks	-0-	-0-	-0-
Medium Leaks	13	-0-	7
Small Leaks	7	-0-	11
Pumps	12 (100%)	7 (100%)	30 (100%)
Heavy Leaks	-0-	-0-	1
Medium Leaks	1	-0-	-0-
Small Leaks	1	-0-	2

APPENDIX C

ESTIMATION OF SOURCE STRENGTH USING REVERSE DIFFUSION CALCULATIONS

ETHYLENE DIBROMIDE EMITTED BY REFINERY GASOLINE TRANSFER AND LOADING OPERATIONS

In Section 3.7.5.A of this report, ethylene dibromide (EDB) measurements at a refinery are discussed. These were made on an EPA-sponsored study (Ref. 50) downwind of bulk transfer and tank truck loading operations. The values obtained were 165 and 0.23 mg/m^3 at 50 and 400 ft., respectively, from the designated centerpoint of the operations.

It was desired that these measurements be related to EDB release rate at the source complex. The use of reverse diffusion calculations has been employed before, although not always with notable success (Ref. 22--Appendix A). In any case, a very rough approximation would serve in making comparisons with estimates derived by other approaches.

In the present case, the Gaussian distribution model, modified by Gifford (Ref. 88), was used. This is expressed as follows:

$$\chi(x, y, z, H) = \frac{Q}{2\pi\sigma_y\sigma_z U} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] . \left\{\exp\left[-\frac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2\right]\right\}$$

χ is the concentration of the indicator substance at point x,y,z, the coördinates being relative to the ground level wind vector. Q is the source strength or emission factor. H is the effective plume height, which includes source elevation. Wind speed is U and the σ terms are vertical and horizontal dispersion coefficients.

In the present exercise, assumptions were necessary since actual conditions were not known. First, it was assumed that the measured values were taken directly on the wind vector. Thus y = 0 and the first exponentiated term of the equation becomes unity. Sampling height (or z) was assumed to be 2m and the wind speed 2.24 m/sec. (5 mph).

The dispersion coefficients were taken from Reference 88, using Class C stability category. This corresponds, at the given wind speed, to daytime air stability with moderate solar radiation. The values would thus be:

Station Distance from Source		Dispersion Coefficients, m	
Feet	Meters	σ_z	σ_y
40	15	1.3	1.5
400	122	9	15

The effective plume height was assumed to be 10 m. for the 400 ft. station since there would be no propelling forces operating in the vertical direction (as from conventional stacks) and the sources involved in the present refinery analysis are largely close to the ground (tank trucks, etc.). In the case of the close-in station at 50 ft., the plume height was assumed to be 5 m. This derived from the assumption that the mean height of the source complex was rather low and, since the station was so close in, that vertical plume lift by any propelling effect would be small.

The Gifford equation was exercised using these variously estimated values. The source strength (Q) results were 1.7 mg. EDB/sec. at 400 ft. and 65 mg./sec. at 50 ft. The discrepancy, while not small, is consistent with measurements that had been taken off the wind by the same angular displacement. The closer in source would be more influenced by this, yielding larger values if the y term is set at zero, as was done here.

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

TASK IV

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

PREPARED FOR
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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, the last of which, Task IV, is described in this volume. The overall organization of these tasks is as follows:

TASK I (SAI) - Identify a limited number of carcinogens posing the greatest potential hazard as ambient atmospheric pollutants in California.

TASK II (KVB) - Locate major sources of and estimate emission factors for this list of carcinogens.

TASK III (SAI) - 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 them into the Task I evaluation.

TASK IV (KVB) - Develop a field test plan to verify the more significant factors estimated on Task II.

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 the factors listed above (except as 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 selection process further involved a review by an ad hoc panel of experienced scientists convened by SAI. From this and two 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 IN TASK II

Arsenic	Ethylene dibromide
Asbestos	Ethylene dichloride
Benzene	Nitrosamines
Cadmium	Perchloroethylene
Carbon tetrachloride	Polycyclic Organic Matter (POM)
Chloroform	

On the Task II effort, which is discussed in another volume of this report, sources were identified where the highest concentrations of emissions of these substances were suspected. This was based on the analysis of published data, together with contacts with government agencies and major producers and/or users of these materials. Stationary sources, recognized as "hot spots," were then displayed on maps, whenever practical, and coded according to the ranges of estimated quantities released per unit of time. A number of the pollutants studied were associated with area or dispersed sources. These would thus not emerge as "hot spots," although comparatively large total releases were involved in some cases.

So that "hot spots" identified could 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 used in Task I for the comparison of suspected carcinogens with one another with respect to hazard potential. The application of this formula resulted in the listing of seventeen "hot spots" that are detailed in Table 2—1 of the Task II report. An abbreviated version of that tabulation is presented here as Table 1-2.

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

Site	Pollutant	Estimated Emissions, tpy		Scaling Factor x 10^{-6}
Kaiser Steel Corp., Fontana	Benzene	112		54.5
	Cadmium	7.0		3.4
	Arsenic	1.6		0.5
	POM	27 *		17.5
			Total	75.9
Stauffer Chemical, Carson	Ethylene dichloride	150 †		55.2
Dow Chemical USA, Pittsburg	Carbon tetrachloride	160 §		41.8
	Perchloroethylene	22 §		5.7
			Total	47.5
DuPont de Nemours & Co., Antioch	Carbon tetrachloride	250 #		41.8
Chevron USA, Richmond	Benzene	50		35.0
ARCO, Carson	Benzene	25		21.1
Allied Chemical, El Segundo	Carbon tetrachloride	113 #		17.8
Witco Chemical Co., Carson	Benzene	14		14.0
Chevron USA, El Segundo	Benzene	30		12.0
Gould Inc., Vernon	Arsenic	22		3.5
RSR Corp., Industry	Arsenic	3.3		1.3

TABLE 1-2. (Continued)

Site	Pollutant	Estimated Emissions, tpy	Scaling Factor x 10^{-6}
ALCO-Pacific, Carson	Arsenic	2.2	1.3
Pacific Gas & Elec.,	Arsenic	1.0	0.4
Johns-Manville, Stockton	Asbestos	2.9	0.3
Calavaras Asbestos, Copperopolis	Asbestos	148	0.3
So. Cal. Edison, Long Beach	Arsenic	0.8	0.3
Pacific Gas & Elec., Salinas	Arsenic	1.0	0.02

Notes:

* 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

The Task III effort aimed at expanding the scope of Task I to include sixteen cancer-causing substances regulated by the State under the Occupational Carcinogens Control Act.

These substances were studied in the same manner as the target compounds considered in Task I. Those materials found to be high scoring on being tested with the screening algorithms were then input into Task I for comparative evaluation with the materials of interest in that task that had already been similarly screened. Thus Task III actually represented an expansion of scope of the Task I work. The output of the latter included input target materials for both tasks and became the common focal point for the Task II studies.

The objective of Task IV, which is the topic of the present discussion, was to develop a plan for a source-testing program which, if implemented, would verify or correct the emission factors estimated for the top seventeen "hot spots" in California. The initial requirement was to determine if access to the various plants would be permitted such that at least one site representative of each plant or process type category would be accessible. These categories are listed below. Three of the eleven topical carcinogens are seen not to have been identified as pollutants for any of the seventeen "hot spots."

TABLE 1-3. CATEGORIES OF STATIONARY SOURCES CONSIDERED IN THE TEST PLAN

Plant Category or Subprocess	Number Listed on Table 1-2	Pollutant(s)
Integrated Steel Mill	1	Benzene Cadmium Arsenic POM
EDC-Synthesis	1	EDC
Carbon tetrachloride (CT)/ perc synthesis	1	CT & perc
Carbon tetrachloride converters	2	CT
Benzene synthesis/conversion and/or gasoline refining	4	Benzene
Secondary lead smelter	3	Arsenic
Oil-fired power plant	3	Arsenic
Asbestos-containing product manufacture	1	Asbestos
Asbestos mining	1	Asbestos

With the exception of utility companies and one benzene consumer (Chevron-USA, Richmond), all of these plants were contacted. Omission of contact with the utilities was prompted because power plant access was believed to be readily forthcoming and the sites so familiar as to obviate the need for inspection. Chevron-USA, El Segundo, was contacted in preference to the Richmond plant because it represented a more interesting test site (see Sec. 3.1.2.A). It is the only refinery in the State that both manufactures and consumes benzene.

With one exception, access to a test site within each category was extended, but usually with the provision that the test plan was found to be technically acceptable by the intended host. The one exception was the Dow Chemical plant at Pittsburg; emission factor estimation using the Virtual Source Test Method will thus be required there. In the case of the other categories and where more than a single plant offered access, the best candidates were identified using Task II information. Site visits were then arranged and conducted at most of the "open" plants. Because of the information supplied and the nature of the test work contemplated (see Sec. 3.1.7 and 3.1.9), visits to the asbestos mine and the asbestos/cement pipe works were considered unnecessary.

As a result of the site visits, considerable proprietary information was acquired. In most cases, secrecy or proprietary information agreements were stipulated. It was also required that the preliminary test plan developed for these plants be reviewed for content by the host companies. The present discussions, therefore, avoid process details that are regarded as proprietary by these companies.

Using the information thus gained, a general test approach was next developed for each host plant and submitted for review, where required. Some, but not all, of the comments received back have been incorporated in the present volume.

Additionally, methodology for the overall pertinent analytical chemistry and asbestos counting is examined and optimum techniques recommended. This proved particularly appropriate since measurement of several of the analytes* (arsenic, asbestos and POM) is by no means routinized and/or ruggedized.†

Another section of this volume deals with nonstationary sources which, though not "hot spots," account for releases of significant amounts of materials from dispersed or area sources. This section is called "Special Testing". It briefly itemizes the identified problems and suggests the general type of testing that would be appropriate for each source type.

Section 2.0, which next follows, deals with chemical analytical and other measurement methodology. This is presented first, so that the selection of modalities of sampling for these analytes that is discussed in the test plan will be better appreciated. Section 3.0 presents a discussion of the test approaches recommended for the various plant categories. This is followed by a subsection on "Special Testing."

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* "Analyte" is a term generally used by analytical chemists to describe the thing that is measured by a chemical analytical procedure.

† "Ruggedization" is a term widely used by analytical chemists, particularly in government agencies (EPA, NIOSH, FDA etc.). The term denotes the exercise of an analytical method to the degree adequate to determine its precision and accuracy, and its sensitivity to chemical or other interferences.

SECTION 2.0

LABORATORY PROCEDURES

In the following subsections, the methodology applied in environmental test laboratories for the measurement of the eleven materials of interest is reviewed. Procedures are favored which would furnish adequate sensitivities for trace substances having potentially potent pathogenic properties and which are reasonably available and relatively economic to employ. These include techniques in some degree of use at the EPA, NIOSH, OSHA and other agency laboratories, as well as contractor labs under contract to these agencies.

While the detection limits of the various techniques are discussed in either specific or general terms, the sample size requirements are not. This will be determined by a number of factors, the consideration of which would involve detailing beyond the scope of this study. As a generalization, however, the sample sizing should conform with the formula:

$$V_s \geq 5\ M_D/ca$$

Where:

V_s = Sample volume (vapor equivalent)

M_D = Detectable mass

c = Concentration of analyte in V_s

a = Aliquoting factor (fraction of analyte in V_s actually seen by the detector)

This rule of thumb thus specifies a sample volume that will provide to the detector an analyte mass that is five times, at least, the detection limit of the detector. As will be pointed out, detection limits are not always accurate values, and measurements at levels well below these limits are frequently reported without comment on that fact.

2.1 ARSENIC ANALYSIS

2.1.1 Current Methodology

The techniques in most prevalent usage for environmental arsenic analysis are colorimetric, atomic absorption spectroscopy (AAS), and voltammetry. All require wet ashing of the sample filters, usually with a combination of nitric, perchloric and sulfuric acids. Aside from low temperature ashing in a microwave furnace (Ref. 1), the use of elevated temperature ashings or fusions of arsenic-containing samples are avoided because of the comparatively high volatility of the metal and its salts.

The colorimetric procedure is commonly used and is recommended by EPA (Ref. 2), the NIOSH (Ref. 3), the American Conference of Governmental Industrial Hygienists (ACGIH) (Ref. 4), and the Association of Official Agricultural Chemists (AOAC) (Ref. 5). The solubilized arsenic is converted to arsine with a hydrogen source ($NaBH_4$) (Ref. 6) or the classical Zn/HCl mixture and collected in a pyridine solution containing silver diethyldithiocarbamate. Arsine reacts with the latter to form a colored adduct which is photometrically measured at 560 nm. The detection limit would be about 0.2 $\mu g/m^3$ in air, assuming 60 cu ft is passed through the filter. Use of the method for lead smelter effluents is contraindicated since antimony, a significant constituent in the input scrap, interferes.

Of the AAS techniques, three versions can be employed: (1) direct solution aspiration into the flame; (2) direct hydride aspiration into the flame; and (3) graphite furnace solution injection. Method (1) is not favored for trace-realm work because detectivity* is not impressive (>1 $\mu g/m^3$ - 60 cu ft sample) and accuracy is often compromised by matrix effects (Ref. 7). The hydride/flame AAS technique is more sensitive. Absence of solvent enhances analyte ionizability and, thus, specific responses. Typically a detection limit of less than 50 ng/m^3 (60 cu ft sample) is obtained (Ref. 7). The AAS graphite furnace furnishes a sensitivity of about that of the AAS hydride technique (Ref. 7). It is specified for use by the NIOSH (Ref. 3) and the EPA (Ref. 8).

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* "Detectivity" is the term specified by the American Chemical Society to denote the limit of detection of a measurement, usually assuming a signal to noise ratio of 5:1.

Another technique that has received Government acceptance (Ref. 3) is the voltammetric approach. After conventional wet ashing, pentavalent arsenic is reduced to As(III) with $NaHSO_3/Fe(ClO_4)_2$. The Fe(II) is stabilized by addition of hydrazine and As(III) determined by anodic stripping, using a composite gold-graphite electrode. The detection limit of the procedure is about the same as for the graphite furnace and hydride AAS procedures. Bismuth and antimony interfere but can be corrected for if separately determined.

Another technique that has been adopted by the NIOSH (Ref. 3) involves the measurement of iodide oxidation (by bromate) as controlled by osmium catalysis (Ref. 9-12). Arsenic promotes the catalysis such that iodine concentration is proportional to As(III) level. The former is determined colorimetrically. The detection limit is about 2 ng/m^3 (60 cu ft sample); copper (II) and ammonium ions interfere.

Neutron activation analysis (NAA) has been employed to achieve low detection limit quantitative analysis of arsenic (Ref. 13). Although applied to direct analysis of oil samples, measurement of arsenic in conventionally digested air-filter samples should furnish a lower working limit of about 5 ng/m^3 by the cited NAA approach.

A number of other techniques can be employed for arsenic analysis. These include such approaches as mass spectrometry (spark source and secondary ionization), emission spectroscopy (flame, arc and inductively coupled argon plasma modes), X-ray fluorescence spectroscopy, polarography, various micro-field spectroscopic techniques (Auger, microprobe, X-ray energy dispersive, ESCA), and so on. Due to limitations in the individual cases, these methods are not widely used for the quantitative analysis of arsenic on filters.

2.1.2 Analytical Problems

Either the graphite furnace or hydride AAS analysis would appear to be an acceptable approach for arsenic analysis. Neither is known to be susceptible to matrix or other interferences (Ref. 3); both are widely practiced, offer adequate sensitivity for source-acquired filter samples, and are endorsed by the EPA and the NIOSH.

Robbins et al of Asarco have published (Ref. 14) round robin results that show acceptable precision but poor accuracy in arsenic analyses at levels equivalent to 4.3 and 6.8 $\mu g/m^3$ (60 cu ft sample). The methods employed (ad lib) included the arsine AAS, voltammetry and colorimetric procedures.

The State's Air and Industrial Hygiene Laboratory (AIHL) verified the problem using the graphite furnace AAS approach (NIOSH Method S309). AIHL's Lew stated (Ref. 14) that the poor recovery of 53-61% for the lower and 58-68% for the higher concentration samples obtained by S309 agreed reasonably well with Robbins' round robin results of 62% and 71%, respectively. Lew concluded that NIOSH method S309 would be inappropriate for the current arsenic standard of $10\mu g/m^3$.

When contacted, Lew suggested that because of the low concentration involved, a more sensitive technique, such as voltammetry, would be appropriate. This did not prove convincing, since the voltammetric approach had been employed (with recoveries of 81% and 64% for the two levels cited above) on the Robbins round robin. Also, the arsenic levels were at least two orders of magnitude above the graphite furnace AAS detection limit.

It would appear that the problem is not inherent in the various measurement techniques employed, all of which should have been adequately sensitive, but in the sample preparation. All of the methods involve digestion of the filters under fuming perchloric acid conditions. Such an elevated temperature promotes arsenic volatilization. This is why NIOSH method S309 requires the application of a recovery factor, which is developed (independent of the usual calibration curve preparation) using standards that are carried through the complete procedure. It is not clear that this was done in either the Robbins or the CALOSHA studies. Even if applied, however, the recovery factor use is problematic in that it varies with concentration.

The overall problem has been recognized by the OSHA Analytical Laboratory in Salt Lake City. There, the digestion step involves only the use of nitric acid. Unlike the colorimetric, voltammetric, or hydride AAS methods, nitric acid is compatible with the graphite furnace AAS procedure. Solubilization of arsenic in nitric acid is excellent. The filter is also completely dissolved, if not completely digested (to CO_2).

Arsenic volatilization is supressed by the addition of $Ni(NO_3)_2$. Based on the results at OSHA, Salt Lake, this technique is effective when nitric acid digestion is involved. CALOSHA found it ineffectual at the higher temperature perchloric acid digestion conditions.

Arsenic recoveries at OSHA, Salt Lake, typically exceed 90% when working in the range considered by Robbins. Although not published in the open literature, the procedure is available on request and is recommended for the present requirement.

The analytical chemists at OSHA who supplied the above comments (L. Larson and J. Septon) also noted the work done by D. V. Sweet at NIOSH, Cincinnati. In lieu of the S309 perchloric/nitric acid digestion, that worker dry-ashed her filters in a microwave low-temperature asher. She worked with as little as 30 ng As/filter, which borders on detection limit, but experienced an average arsenic recovery of 101% using a graphite furnace AAS finish. Nickel spiking was not employed.

Sweet presented her results recently (Ref. 15) and the method will be incorporated in the NIOSH Manual of Analytical Methods as P & CAM No. 286. At present, the method is unclassified but will be designated as either Class D (operational) or Class E (proposed). Negotiations are currently underway to retain a contractor who will ruggedize the procedure, that is, fully exercise the procedure against interferants, over the full working range and with equipment variables. If successfully emergent (variance analysis demonstrates acceptable precision and accuracy), the method will be given a Class B (accepted by NIOSH) designation.

2.1.3 Recommended Approach

The OSHA, Salt Lake City, graphite furnace AAS procedure is recommended. The NIOSH P & CAM No. 286 procedure will also be endorsed if proved acceptably rugged in upcoming testing.

The EPA is currently developing a reference method for the sampling and analysis of arsenic in flue gases. While the former portion was complete and appeared satisfactory, the analytical methodology was still not set. Thus, no comment on this agency's procedure can be offered at this time.

2.1.4 Laboratory Qualifications

Assuming that an adequate QA program is effectively in place (see Sec. 2.8), any laboratory offering the requisite AAS equipment should be capable of performing the arsenic measurements. The AA spectrophotometer should have a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the u.v. region. The use of a background corrector is absolutely necessary in order to avoid molecular scattering effects at the working wavelength (193.7 nm). An electrodeless arsenic lamp should be used. A direct readout (metric or recorder) proportional to absorbance units should be provided.

If the P & CAM Method 286 is employed, a suitable low temperature ashing system will be required. The International Plasma Model PM 1604 has furnished satisfactory results in NIOSH tests.