

6.0

SOURCE TESTS - JOHNS MANVILLE SALES CORPORATION

6.1 SITE OVERVIEW - JOHNS MANVILLE SALES CORPORATION

Johns Manville, Stockton, was identified as the largest asbestos user in the state (Margler, 1979) excluding mining and milling operations. Total suspended particle emissions from this plant are 19 tons per year, according to the CARB Emission Data System (EDS); the proportion of these emissions represented by asbestos is not stated. The applicable NESHAPS regulation stipulates zero visibility asbestos emissions. In order to determine the relative importance of various potential emission sources within the plant and develop a first-hand familiarity with plant operation, program staff conducted a literature review, made a pre-test site visit, and held discussions with plant and company personnel and researchers at several state and federal agencies. In conversations with company personnel it was determined that the EDS quantity should be considered an estimate with great uncertainty.

6.1.1 Facility Description

On 5 December 1980 program staff met with Johns Manville (JM) personnel to conduct a pre-test review of plant activities and processes, a plant inspection, and particulate monitoring. Basic operation and emission controls are described below.

JM purchases a variety of grades of asbestos from its Quebec mines and other suppliers to produce asbestos-cement pipe. Asbestos bags, shown in Figure 6.1-1, are slit and dry loaded into a willow which performs a fiber separation. Fiber storage, ingredient blending (asbestos, sand, cement) and formation of a water slurry follow. Slurry is transported on wide belts and deposited in thin layers onto a mandrel. After a sufficient thickness is built-up the mandrel is withdrawn, the pipe is usually kiln dried, cut, its ends are machined and other finishing and warehousing operations are performed. Composition of the product material is approximately 15 percent asbestos. Waste, baghouse dust and broken pipe are recycled. Previously, large pipe rejects were broken by earthmoving equipment and accumulated in an onsite refuse pile prior to recycle. However, a larger pipe crusher is now used to break up large pieces for recycling.



Figure 6.1-1 Johns Manville, Stockton, Asbestos Feed Warehousing Area

6.1.2 Emission Sources

All major processes and plant areas are tied into one of nine baghouses. These are delineated below along with their primary function and specified air flow rates in cubic feet per minute (cfm).

<u>System</u>	<u>Process</u>	<u>Flow</u>
D-1	No. 1 - No. 3 Willow (Fiber)	18,000
D-2	No. 1 - No. 3 Pipe Machines	26,000
D-3	No. 4 Willow (Fiber)	8,000
D-4	No. 4 Pipe Machine	13,000
D-5	Cutoff Machinery	53,000
D-6	Pipe Lathes	32,000
	Silica Grinding No. 1 Mill	2,500
	Silica Grinding No. 2 Mill	3,600
	Ball Mill Scrap Silex Unloading	8,500

Each baghouse vents through separate ducts to the atmosphere. Figure 6.2-1 illustrates the plant location of each baghouse.

There are no significant process operations not tied into bag houses. Area intakes are located throughout the plant. However, the facility is neither sealed nor operated under a pressure differential with respect to the outside.

Figure 6.1-2 to 6.1-4 illustrate several views of the D-1 bag-house. Figure 6.1-2 shows the upper level with the exhaust manifolds for the four individual baghouse compartments. Dampers which permit facility air to enter a baghouse compartment during the mechanical shake cycle are at the underside of each exit duct. Shake cycles for each baghouse compartment occur at roughly four-hour intervals and last less than one minute. Figure 6.1-3 illustrates the lower baghouse level where material is picked up by a worm gear train and transferred for recycle. Figure 6.1-4 shows the clean air exhaust duct between the baghouse (above) and the fan.

6.2 EMISSION MEASUREMENT APPROACH

6.2.1 Choice of Measurement Points

Three basic potential emission sources were postulated: baghouses, fugitives from within the plant area, and the exterior scrap storage area. It



Figure 6.1-2 Asbestos Fiber Baghouse, Upper Level



Figure 6.1-3 Asbestos Fiber Baghouse, Lower Level

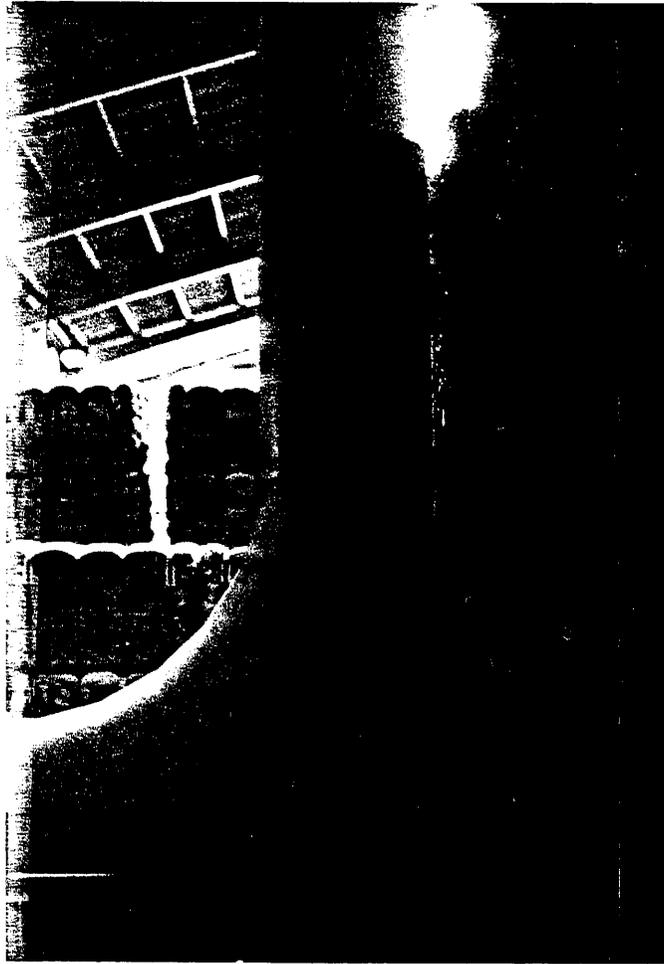


Figure 6.1-4 Asbestos Fiber Baghouse, Clean Air Side
Exhaust Duct

was decided that the third source could be eliminated because use of a scrap storage area was to be discontinued and also because asbestos emissions should be relatively small from what little material might be present as part of the scrap recycle chain. (It was stated that no significant pipe crushing will be carried out by crushing with earth moving equipment). At the time of inspection a significant amount of material had been accumulated in the scrap storage area. After discussion with plant personnel, we assumed that this situation was temporary.

The three bag houses associated with the silica grinding and silex unloading are small and handle a relatively insignificant amount of fiber since approximately 10 percent of plant throughput is scrap recycle and, of that 10 percent, the asbestos content is 15 percent. Furthermore the asbestos present is no longer free fiber but rather is bound into a cement matrix.

Systems D-2 and D-4 are associated with wet process components, i.e. rolling of sheeted slurry onto steel mandrels, and were assigned secondary importance in comparison to dry process baghouses. Systems D-5 and D-6 are large airflow volume baghouses. However, they see only the 15 percent fiber content product. Furthermore, the material expected to comprise the D-5 and D-6 flows should be coarse since the fibers present are bound in the cement matrix. It was therefore expected that the D-1 and D-3 systems would carry nearly all of the asbestos fiber burden. D-1 receives the airflow from as many as three willows i.e. corresponding one-to-one with each of the three pipe machines. Typically, only one pipe machine is operating at a time and therefore only the corresponding willow is active. Results of asbestos measurements need only be scaled to the asbestos throughput handled during the collection period in order to develop a plant emission factor applicable to a specified production level.

In order to evaluate the importance of fugitive emissions from the plant and to assist another CARB sponsored program, "An Inventory of Asbestos Emissions in California," airborne asbestos sampling was planned immediately adjacent to the plant, simultaneously upwind and downwind, during periods of normal operation. The samplers were positioned to locate an upwind area at the border of the JM property line and the downwind site represented an area encompassing possible emissions from the transite pipe storage area and adjacent areas other than the baghouse plume itself. A 10 meter meteorological

tower was erected to provide continuous recording of wind speed, direction and temperature. Wet bulb temperature was manually taken. Figure 6.2-1 illustrates the spatial relationship among the detectors and the plant. The baghouse exhaust duct releases material at approximately 100 feet elevation and emissions were not expected to be detected at the ground level downwind detector.

Particle counter readings were taken at all sampling locations as part of our internal program to examine the relationship between asbestos fiber counts and particle counts for several size ranges. A Royco Model 225 light scattering particle counter was used with a paper tape recorder.

Summary

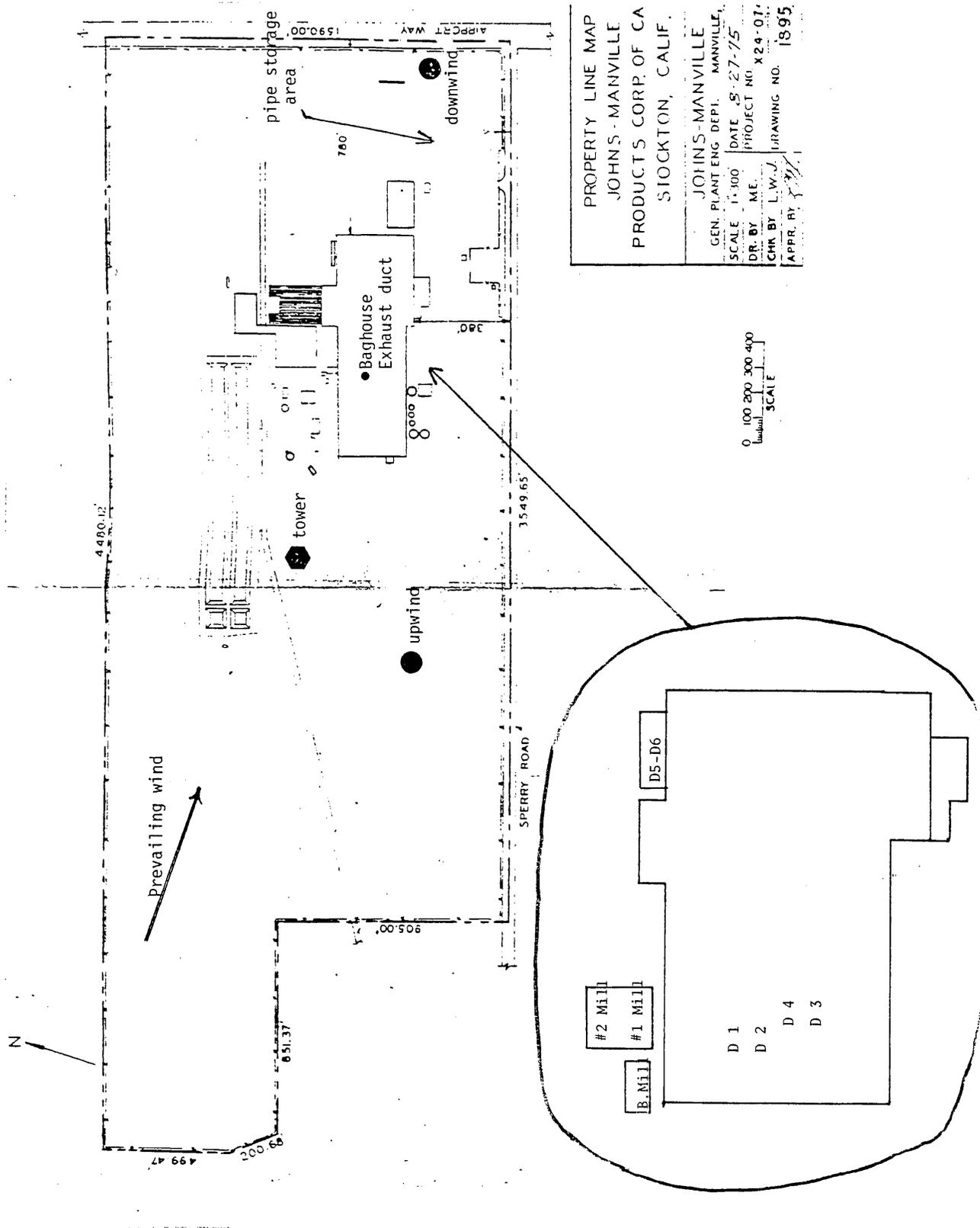
In this study the highest priority was given to determining the emissions of respirable fibers. Baghouse D-1 (or D-3) has the highest priority for measurement. Asbestos emissions leaving the baghouse should account for greater than 90% of total respirable fibers from processes since they are the only baghouses which handle fiber before it is combined into a slurry and becomes part of a blended matrix. Ten percent will be assumed as a conservative bound for miscellaneous process emissions. Although it is expected that most airflow within the main plant passes through a controlled ventilation system, it is still necessary to estimate the importance of miscellaneous fugitive sources by performing close-in area ambient sampling. Specifically, ground based simultaneous upwind and downwind ambient samples were taken adjacent to the plant with the latter detector established to see direct fugitive emissions from key plant access and material storage areas.

6.2.2 Measurement Approach

6.2.2.1 Baghouse

Samples were taken on polycarbonate membrane filters using a cyclonic pre-filter separator as specified by Dr. W. John of the California Air Industrial Hygiene Laboratory. The cyclone effectively eliminates the contribution of the larger nonfibrous materials (aerodynamic diameters ≥ 3.5 micrometers). The sampler is designed to run at a constant flow rate of 15.5 liters/minute to provide a 50 percent deposition of particles in the 2.5 to 3.5 micrometer aerodynamic size range. The filter collection media consisted of a 47 mm diameter Nuclepore filter of 0.2 micrometer pore size with a Millipore

Figure 6.2-1 Meteorological Tower and Asbestos Sampling Locations at Johns Manville



backing filter. Each collector is enclosed as a filter cassette and is self contained in its own sealed box and stored in a specially constructed box designed to transport 50 samples in an upright position with a minimum of vibration. All loading and changing of filter cassettes in the field were conducted under a portable clean bench with HEPA^{*}-filtered air. The cyclone filter assemblies were totally disassembled and cleaned with Freon 113 between each sample run. Figure 6.2-2 illustrates the cyclone sampler. Air is drawn in through the underside of the protective hat down the duct and up through the cone shaped-cyclone. The filter cassette is situated horizontally at the cyclone top and the flow controller/pump rests on the ground at the bottom of the exit tube. Thus the cyclone acts to perform a separation process for coarse particle removal and those fibers remaining will have a sufficiently small aerodynamic diameter to be respirable.

Samples were taken from within the baghouse on the clean air side. The plant was operating in a normal condition somewhat under full capacity and samples were taken over a time expected to produce optimal filter loadings. The sampling time was chosen to be compatible with plant operation and observed baghouse particulate concentrations as determined by the Royco particle counter. Asbestos feed was observed during sampling in order to verify the level of plant activity. The number of willows and/or pipe machines operating is readily observed and directly confirms the level of plant activity.

Figure 6.2-3 shows the monitoring apparatus, which is on the catwalk outside the baghouse. NIOSH Method P & CAM 239 (phase contrast microscopy at 400 X magnification) was used in parallel with electron microscopy. The NIOSH method pumps were placed both on the replacement door and on the SIERRA pump. Sampling lines extend into the clean air side of the baghouse by passing through sealed openings in the substitute door. NIOSH sampling was conducted as specified by the method at a flow rate of 1.5 L/min with a 0.8 micrometer Millipore filter material. The SIERRA pump/flow controller was used to drive the cyclone separator sampling apparatus.

Samples were obtained by replacing the baghouse door with a fabricated substitute (see Figure 6.2-3) having sampling probe access. The cyclonic filter holder and all NIOSH filters were placed centrally inside the baghouse and all pumps and flow meters remained outside of the baghouse. The airflow velocity in the exhaust duct from baghouse D-1 was measured with a standard

* High efficiency particulate air filter

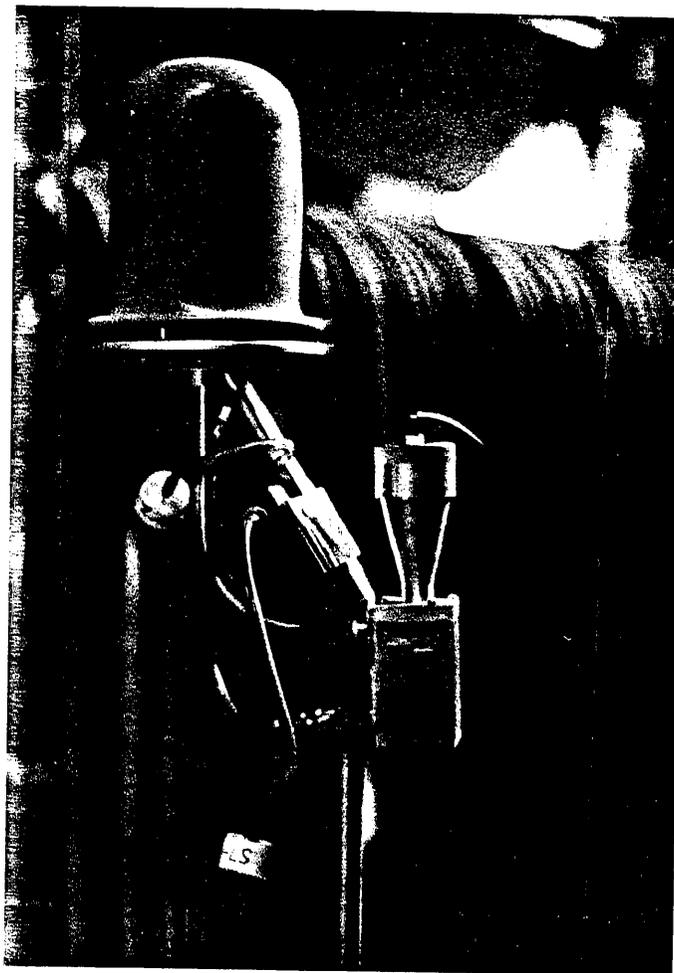


Figure 6.2-2 Asbestos Cyclone Sampling Apparatus

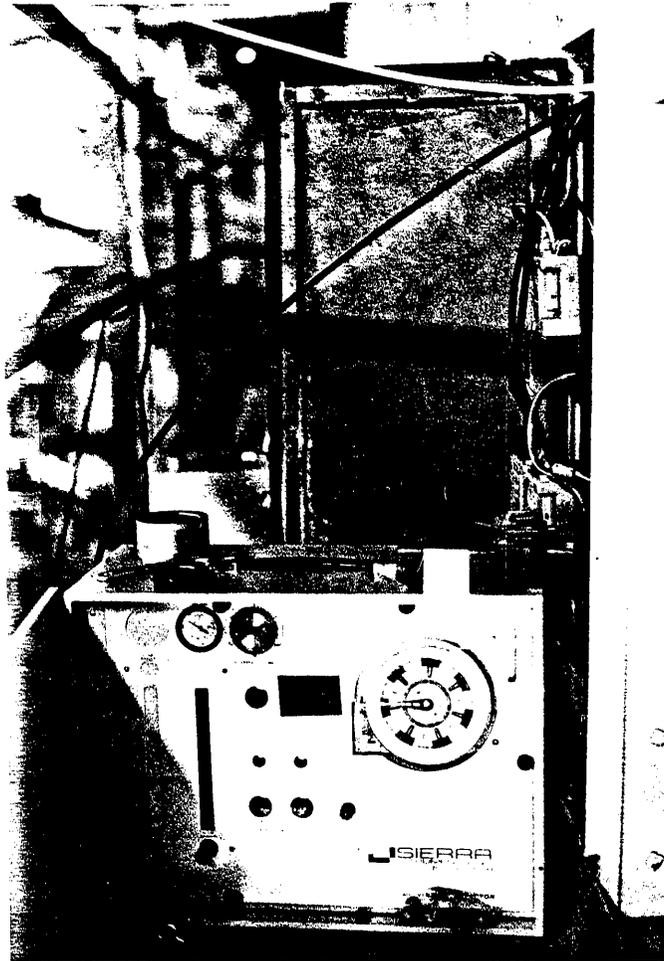


Figure 6.2-3 Asbestos Sampling Equipment Pumps

stainless steel pitot tube and a slant tube manometer. The temperature of the duct was measured with a mercury-in-glass thermometer. The average velocity of the stack gas was 39.071 ft/s and the actual flow at stack conditions was determined to be 14,781 acfm. Velocity traverses were made in the exit duct at eight points in each of two directions in conformance with EPA Methods 1 and 2. The exhaust stack area was 6.3 ft². The exhaust had a temperature of 111⁰F, and barometric pressure 29.9 in. Hg.

6.2.2.2 Upwind/Downwind Plant Area

For ambient sampling, we used the same cyclonic head and pump/flow controller equipment as for the baghouse approach. Samples were simultaneously upwind and downwind for about four hours to assure adequate filter loading and steadiness of meteorological conditions. Filters were handled only in the field laboratory and were thus protected from ambient contamination. Sampling sites were isolated from vehicular activity and other emission sources.

Weather conditions during the sampling period are shown in Figure 6.2-4. Skies were clear and humidity was low. The wind was consistently from the northwest (approximately 290 degrees). Wind speeds reached a maximum of 5 to 10 m/s by mid-afternoon. The temperature ranged from 10 to 30⁰C. the steadiness of the wind direction validated the choice of upwind and downwind sampling locations.

Ambient sampling was conducted on 23 July 1981 by placing the sampling pump assembly on the ground with the cyclone filter assembly fastened directly above. Both upwind and downwind samples were taken essentially at eye level. The upwind sample A-7 (See Table 6.2-1) was taken between 8:31 a.m. and 12:18 p.m. at a flow rate of close to 15.5 L/min. The downwind sample, which was located approximately 75 feet east of the transite pipe yard, was taken between 9:56 a.m. and 1:30 p.m. for 3331.7 L at the same flow.

6.3 DETERMINATION OF EMISSION FACTORS

Sampling was performed on 22-23 July 1981. Plant operations were close to normal although it was estimated that the effects of a labor dispute reduced the level of activity and caused recycle material to accumulate in the outdoor storage yard. Since only one pipe machine was in operation it is appropriate to apply a scale factor of two to measured emission values to account for a more typical baseline operating level. Table 6.3-1 is a summary

Weather Data
for Ambient Air Sampling at
Johns - Manville Transite Pipe Plant

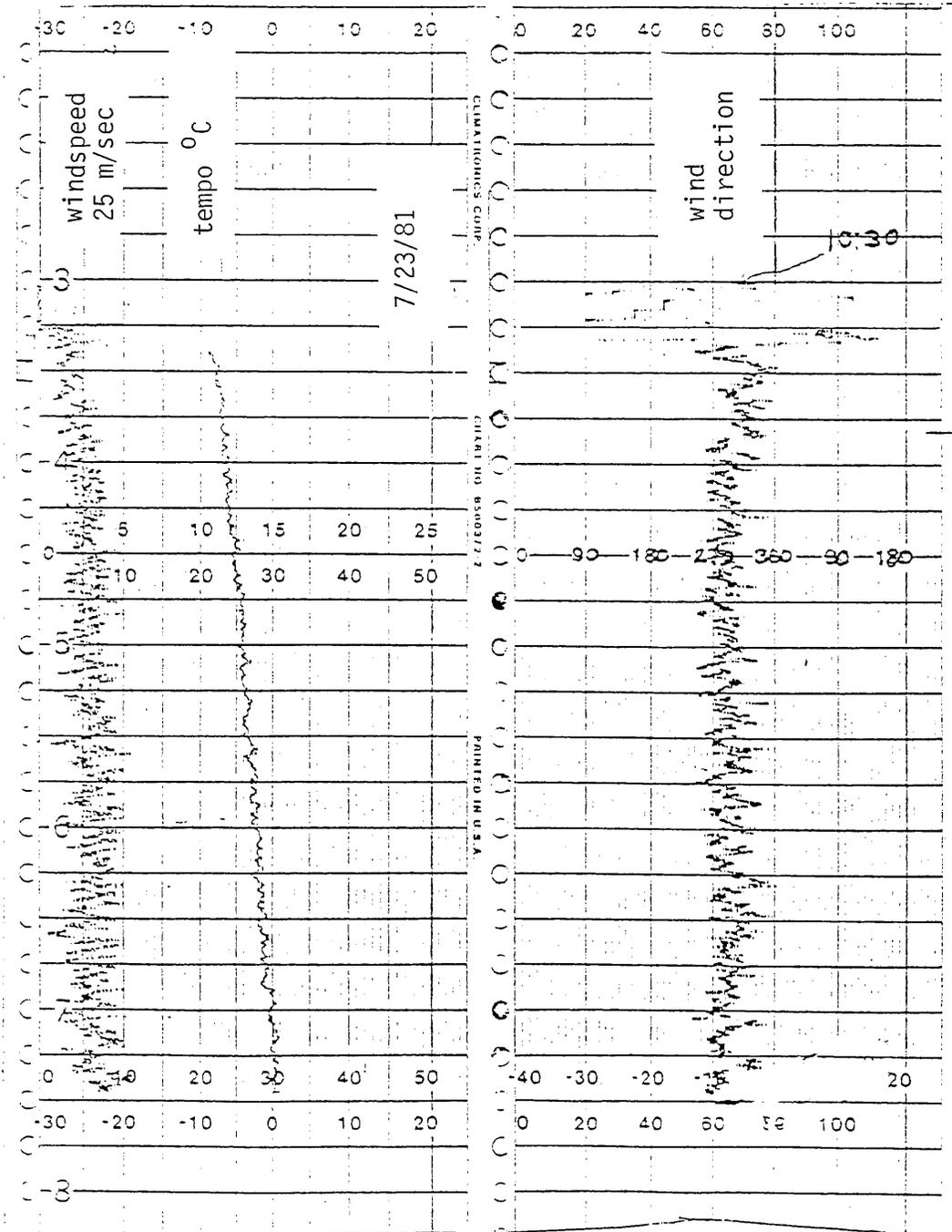


Figure 6.2-4

Table 6.2-1 JM Sample Collection Summary

<u>Sample #</u>	<u>Location</u>	<u>Date</u>	<u>Sample Start Time</u>	<u>Nuclepore Samples</u>		<u>Millipore Samples</u>	
				<u>Liters Sampled</u>	<u>Flow (ℓ/min)</u>	<u>Liters Sampled</u>	<u>Flow (ℓ/min)</u>
A-7	upwind	7/23/81	8:31 a.m.	3516	15.5		
A-8	downwind	7/23/81	9:56 a.m.	3331.7	15.5		
A-9	D-1 baghouse	7/23/81	1:41 p.m.	1497.3	15.5	144.9/140	1.5/1.45
A-10	D-1 baghouse	7/23/81	3:47 p.m.	2573	15.5	144.9/140	1.5/1.45

Table 6.3-1 Johns Manville Fiber Concentration Summary*

Sample#	Analysis Instrument	Location	Total Fibers/m ³			Non-Asbestos
			Chrysotile	Amphibole	Indeterminate	
A-7A	SEM	Upwind	---	---	2.7×10^5	8.9×10^4
A-7B	SEM	Upwind	---	---	1.3×10^5	1.8×10^5
A-7TEM	TEM	Upwind	---	2.5×10^3	7.5×10^3	2.2×10^4
A-8A	SEM	Downwind	1.0×10^5	---	1.0×10^5	1.0×10^5
A-8B	SEM	Downwind	1.0×10^5	---	1.0×10^5	---
A-8TEM	TEM	Downwind	1.8×10^4	3.7×10^3	3.3×10^4	3.7×10^3
A-9A	SEM	Baghouse	6.0×10^5	6.2×10^4	---	---
A-9B	SEM	Baghouse	5.7×10^5	---	---	---
A-9TEM	TEM	Baghouse	5.7×10^5	2.5×10^4	---	---
A-10A	SEM	Baghouse	4.4×10^5	5.1×10^4	---	---
A-10B	SEM	Baghouse	6.3×10^5	2.5×10^4	---	---
A-10TEM	TEM	Baghouse	4.4×10^5	5.0×10^4	1.9×10^4	---

* Any table entries less than approximately 5×10^4 should be considered below the practical limit of detection and assigned the inequality less-than-or-equal-to (\leq).

of the collection data. Only data taken on 23 July 1981 were used for determining emission factors. Baghouse measurement data from 22 July were archived because program staff had some concern that air flow from the plant may have mixed with the clean-side baghouse flow and would thus make differentiation of the latter's contribution impossible to quantify.

6.3.1 Electron Microscopic Analyses of Filter Samples

Measurement and verification of chrysotile fibers conformed to EPA procedure 600/2-77-178, Revised June, 1978. EM analyses were conducted on the Hitachi H-500 scanning transmission electron microscope at 100 KV beam voltage and calibrated with magnification standards. SEM (scanning electron microscope) analysis was performed on an International Scientific Instruments Super IIIA with a Kevex 5100 x-ray energy dispersive spectrometer.

The upwind, downwind, and D-1 baghouse samples were analyzed using both the Scanning Electron Microscope and the Transmission Electron Microscope to provide a comparison of both modes and also a quality control check on the primary (TEM) analysis.

6.3.2 SEM Analysis

The ambient upwind and downwind samples (A-7 and A-8) were coated with gold and a minimum of 100 fields were counted at a magnification of 10,000. Asbestos particles were confirmed using dispersive X-ray. The actual visual counting was conducted on the microscope using a slow raster scan rate (i.e. electron beam sweep rate) of approximately 4 seconds. A slow sweep rate was chosen to provide the best contrast for visual counting of fibers. The samples were analyzed according to the EPA counting procedure (EPA-600/2-77-178) with one modification involving the reporting of true fiber length. Due to the statistical calculation of mass, only the fiber length within the field of view is recorded using EPA's format. The partial length observation is correct in determining mass calculations but limits the recording of length data to the field of view when using the scanning electron microscope. Erroneous length data will be obtained unless another column of data is provided to note the true length of fibers when they extend beyond the field of view. When a fiber extends beyond the field of view the magnification is reduced so it is contained within the field. The true length is recorded along with a notation indicating that the process was performed. SAI's

computer program then accounts for this and the recording of mean length is calculated from the true length data. Mass calculations, on the other hand, are based upon dividing the true fiber length by a factor of two for this subgroup of fibers.

Two sections of filter were analyzed separately for each sample. The results are presented in Table 6.3-1. As noted in the table, fiber concentrations less than 5×10^4 fibers/m³ should be considered below the limit of detection. This limit is primarily a function of the air volume sampled and the number of fields counted in the analysis. It therefore varies from sample to sample and should be considered as the fiber concentration corresponding to finding less than one fiber among the prescribed number of fields counted. The D-1 baghouse samples (A-9 and A-10) were analyzed for 100 fibers and/or 100 fields at a magnification of 5000x. The reasons for the difference in the magnification in the baghouse analysis results stem from an attempt to increase the filter area being analyzed. Unlike the ambient samples, the baghouse asbestos fibers consist mainly of fiber bundles with mean diameters of 0.15 micrometers and mean lengths of 2.6 micrometers. These fibers are clearly visible at magnifications even lower than 5000x. Note that the Table 6.3-1 entry "indeterminate" applies to fibers which could not be positively identified and thus cannot be ruled out as asbestos. Sample notations A and B refer to analyses of independent sections of the same collected sample by SEM.

6.3.3 TEM Analysis

The filter sections for TEM analysis were prepared on 300 mesh copper grids using the modified Jaffe-Wick method outlined in the EPA provisional methodology EPA-600/2-77-178.

Both ambient and baghouse samples were counted at a magnification of 20,000. Ten grid holes per grid on three grids for each sample were counted for both ambient samples. A total of 100 fibers and/or 30 grid holes on 3 grids for each baghouse sample were counted. Confirmation of chrysotile and crocidolite (i.e. amphibole) asbestos was done using selected area electron diffraction.

6.3.4 Comparison of SEM and TEM Baghouse Analyses

The results of the SEM and TEM analyses are compared in Table 6.3-2. Fiber counts for both chrysotile and amphibole asbestos are well within

Table 6.3-2

JM BAGHOUSE ANALYSIS

Sample A-9 (7/23 @ 1:41 - 3:18) mid-point in baghouse

INSTRUMENT	MAGNIFICATION	Chrysotile		Amphibole	
		TOTAL FIBERS/m ³	MASS (pg/m ³) ⁺	TOTAL FIBERS/m ³	MASS (pg/m ³) ⁺
TEM	20,000x	5.7 x 10 ⁵	1.2 x 10 ⁵	2.5 x 10 ⁴	1.2 x 10 ⁴
SEM	5,000x	5.9 x 10 ⁵	3.1 x 10 ⁶	3.1 x 10 ⁴	2.3 x 10 ⁴

Sample A-10 (7/23 @ 3:47 - 6:33)

TEM	20,000x	4.4 x 10 ⁵	2.0 x 10 ⁵	5.0 x 10 ⁴	3.4 x 10 ³
SEM	5,000x	5.4 x 10 ⁵	3.4 x 10 ⁶	3.8 x 10 ⁴	6.0 x 10 ²

TOTAL STATISTICAL SUMMARY

INSTRUMENT	Chrysotile		Amphibole	
	FIBERS/m ³	pg/m ³ +	FIBERS/m ³	pg/m ³ +
TEM	5.1 x 10 ⁵	1.6 x 10 ⁵	3.8 x 10 ⁴	7.7 x 10 ³
SEM	5.7 x 10 ⁵	3.3 x 10 ⁶	3.5 x 10 ⁴	1.1 x 10 ⁴
			MEAN LENGTH *	MEAN DIAMETER *
		2.6	.15	.18
		12.3	.36	.16

* in microns

+ pg/m³, pico grams per cubic meter

statistical variation even for samples analyzed on the same instrument. The acceptable variation for an analysis of fiber counts is approximately 30 percent. The total statistical summary (average over A-9 and A-10) for the D-1 baghouse yield fiber count differences between the SEM and TEM of only 11% for both chrysotile and amphibole. The mass values are approximately one order of magnitude higher in the SEM analysis than the TEM analysis. The disagreement is somewhat to be expected due to the differences in sample preparation, lower resolution of the SEM (70 angstroms as compared to 2 angstroms in the TEM), and the way the electron image is actually generated. In TEM preparation, the samples are coated with carbon, but because the fibers are viewed in a transmitted fashion similar to an X-ray, the actual particle diameter is visible and accurately measured. In the SEM preparation, the filters are coated with gold and then analyzed on the SEM in an essentially reflected mode. The image measurement of the fiber diameter is a total of the actual fiber diameter and the thickness of the gold coating. In large diameter particles (0.5-1.0 micron) this is insignificant; but very small particle diameters can be significantly affected. It must be remembered that in calculating the mass of a fiber, the diameter measurement is squared and therefore mass value errors are drastically compounded.

6.3.5 Calculation of Mass Emission Rate

Fiber counts by SEM, TEM and optical microscopy (from the NIOSH samples) are compared in Table 6.3-3. Note that the optical sample analyses are of two separate filters taken simultaneously rather than of sections of one filter, as in the case of the SEM. Table 6.3-4 compares the fiber mass concentrations as a function of fiber size for SEM and TEM. The average TEM derived mass density for runs 9 and 10 is 1.6×10^5 pg/m³. This, coupled with the actual measured exit duct flow rate of 14,781 cfm (473 m³/min) yields an annual mass emission rate of approximately 40 g. Fiber concentration is in the neighborhood of 0.5×10^6 f/m³ at the release point. TEM, rather than SEM, measurements were used as the primary analysis tool for quantifying mass emissions, as discussed in the previous section on SEM analysis. Assuming the plant might typically operate at twice the activity level that was observed on 22-23 July (i.e. an average of two pipe machines rather than one) yields an emission rate of 80 g at a fiber concentration of approximately 1.0×10^6 fibers/m³. This is a conservative assumption since emissions would be less than doubled if the two pipe machines

Table 6.3-3
 COMPARISON OF FIBER COUNT CONCENTRATION AMONG ANALYTICAL METHODS
 (All concentration in fibers/cm³)

<u>Sample^a</u>	<u>Fiber Size <5 micrometers</u>		<u>Fiber Size >5 micrometers</u>		
	<u>SEM</u>	<u>TEM</u>	<u>Optical</u>	<u>SEM</u>	<u>TEM</u>
9A	0.50		0.20	0.14	
9B	0.37	0.50	0.27	0.19	0.05
10A	0.33		0.12	0.11	
10B	0.58	0.42	0.14	0.05	0.02

^a See Table 6.2-1 and 6.3-1 for descriptions of the sample origins.

Table 6.3-4
 COMPARISON OF FIBER MASS CONCENTRATION AMONG ANALYTICAL METHODS
 (All concentration in pg/m^3)

<u>Fiber Size <5 micrometers</u>			<u>Fiber Size >5 micrometers</u>	
<u>Sample#</u>	<u>SEM</u>	<u>TEM</u>	<u>SEM</u>	<u>TEM</u>
9A	2.5×10^5		4.3×10^6	
9B	3.5×10^5	8.1×10^4	1.3×10^6	4.0×10^4
10A	1.9×10^5		3.3×10^6	
10B	1.1×10^5	3.3×10^4	3.8×10^6	1.62×10^5

operating were hooked up to the same baghouse, i.e. both to D-1 rather than one to D-1 and one to D-4.

Fiber counts for the upwind/downwind ambient measurements were listed in Table 6.3-1. Note that, by TEM, the chrysotile fiber density was zero and below the threshold of detection (1.8×10^4), respectively, for the upwind and downwind positions. These values, along with the particle counts by the Royco device and the CARB TSP Stockton monitors, will be incorporated into the analysis of ambient asbestos concentrations being undertaken in a separate CARB sponsored contract. The program findings do not support the determination of an emission factor from plant fugitive releases since TEM, the primary analytical tool, found upwind and downwind fiber densities to be below the practical limit of detection. Although SEM derived downwind concentrations were somewhat higher, so is the practical limit of detection by SEM since the area scanned in analysis is less than by TEM.

In summary, releases from the D-1 baghouse were determined to be equivalent to 80 g/year for average operating conditions. It was concluded previously that such emissions could be assumed to account for 90 percent of all plant ventilation system releases of respirable asbestos fibers and that miscellaneous fugitive emissions would be directly determined separately by simultaneous upwind/downwind ambient sampling. Therefore the overall plant emission rate will be taken to be 89 g/year in accordance with test findings. It is noteworthy that 19 tons/year of total particulate emissions were listed in the state emission inventory system data base.

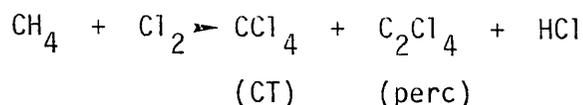
Detailed computer printouts of fiber and mass concentrations from TEM and SEM analyses are provided as Appendix F and may be consulted for examination of the raw data base.

7.0

SOURCE TESTS - DOW CHEMICAL U.S.A.

7.1 SITE OVERVIEW

The Dow facility in Pittsburg, California produces carbon tetrachloride (CT) and perchlorethylene (perc) by the same process. The yield of CT/perc can be varied as a function of feedstock composition. Products are produced by chlorination of methane according to:



After reaction, the process involves various stages of separation and purification and eventually storage and shipment.

Since the system is virtually closed to the atmosphere, it was anticipated that CT and perc would be emitted through fugitive losses from valves, flanges and pump compressor seals. Additionally, emissions from storage tanks and off-loading may be significant. Our recommended approach to determine a site emission factor was to conduct a leak survey of the plant and couple the results with an inventory of the components of interest in order to a mass emission rate. Emissions from storage and off-loading would be estimated from direct measurements (if possible) and calculations.

7.1.1 Facility Description

On 11 December 1980 a meeting was held at the site with Dow personnel. Although some plant information was obtained, it was not possible to tour the plant at that time. It was confirmed that the published process flow diagram of Phase I (Roberts, 1980) was, in fact, a useful representation of the process. Dow staff were sensitive to release of specific information concerning processes and production values. Dow estimated that fewer than 2000 valves, flanges, compressors and pumps exist in the systems which contain hydrocarbons. It was not known what percentage of these devices contain streams with greater than one percent CT or perc. However, no difficulty was anticipated in proceeding through the plant and identifying all such streams during testing. It was clear that numerous streams of CT and perc exist within

the process under a variety of physical states and in combination with other substances.

7.1.2 Emission Sources

Because we were unable to observe plant processes or obtain specifics on control system configurations, i.e., storage tank ventilation and turn-over rate, it was not possible to identify, at the time of the pretest visit, the most important emission measurement priorities beyond what was known in Phase I. The approach taken was to identify the system components of potentially greatest importance, i.e., to emphasize enriched stream compositions and historically important component types. If possible, 100 percent of streams containing greater than one percent product would be tested. It was not known whether storage systems would likely be of primary or secondary importance; we would however, measure only tank working emissions, i.e., displacement of product laden vapor during filling operations. Tank breathing emissions, i.e., equilibrium evaporative emissions, would be considered, if necessary, by calculation.

7.2 MEASUREMENT APPROACH

A secrecy agreement signed with Dow cleared the way for further information exchange and plant access. A protocol was developed which covered the proposed fugitive leak test procedure at Dow and three other synthetic organic chemical plants. This protocol is detailed below. The measurement approach at Dow was to leak test as large a sample as possible of CT- and perc- enriched lines and key component types with a Foxboro Systems Organic Vapor Analyzer (OVA) portable hydrocarbon vapor detector. A mass emission rate based upon knowledge of the leak rate, distribution of line compositions in the applicable sections of the plant, and a plant inventory of possible fugitive emission sources would then be derived. SAI developed OVA response functions for individual substances at various concentrations as well as for selected mixtures. These response functions were used to validate the approach to derive mass emission rates from observed OVA response. The field measurement approach, laboratory calibration and response function procedures, and determination of leak rate are described in Section 7.2.1 and apply to fugitive emission testing at Stauffer, DuPont and Allied as well as Dow.

It was our understanding that although emission from storage and check tanks are currently essentially uncontrolled, plans for future control are under way. Since the tanks are vented to the atmosphere, their emissions due to normal tank breathing was determined by calculation based upon their physical configuration, substance properties and the relationships given by AP-42. Off-loading procedures would be observed and if vented to the atmosphere, their emissions would be initially determined by calculation as follows:

$$L_w = 2.4 \times 10^{-2} M P K_n K_c$$

where: M = molecular weight
P = true vapor pressure at bulk liquid conditions (psia)
K_n = turnover fraction (expressed as a function of the ratios of annual throughput to tank capacity)
K_c = crude oil fraction (1 for CT and perc)
L_w = working loss (lb)/10³ gal

Alternatively the working loss was calculated explicitly for each displacement transfer and combined to determine the annual working loss.

If the working loss was determined to be significant with respect to the normal tank breathing, direct measurement of working loss was planned, if practical, to validate calculational estimates. This would be done by obtaining and analyzing head space samples during off-loading. A sampling tube would be inserted into tank head space and a time integrated sample collected in a large 100L evacuated Tedlar bag. Contents of the Tedlar bag would be transferred to smaller glass bulbs, transported to the SAI laboratory and analyzed directly by gas chromatography. This is useful toward generating as accurate an emissions estimate as possible.

It is believed that the determination of emission factors by direct measurement and/or calculation is the method of choice. Despite the fact that a primary use of these emission factors would be to develop population exposure estimates in the offsite environment, it was concluded that direct ambient concentration determinations would be inappropriate. It was considered more important to unambiguously determine the emission source strength rather than establish, through an elaborate monitoring strategy, that, under a set of particular meteorological conditions, there is or is not a detectable concentration of CT or perc present downwind from the plant. Furthermore at

least two additional issues concerned us: low concentrations as expected off-site would present significantly greater problems to detect and having done so to calculate the emission source. All synthetic organic chemical plants were measured in this manner.

Finally it should be noted that all sites being studied are potential emission sources of substances currently known to be released by other point and area sources. In the case of Dow the clearest example is that of perc releases from dry cleaning operations. Emissions from each site were therefore evaluated within the perspective of other known sources and source types as their relative contribution to background levels.

7.2.1 Fugitive Emission Measurement Approach

Although the processes and even the substances of interest differ among the synthetic organic chemical plants, we were concerned, to some degree, with fugitive emissions from equipment sources including process valves, pump and compressor seals, flanges and relief valves. At some sites other potential emission sources were identified and testing proposed. A standardized approach used to sample fugitive releases is described below. Additional material specific to each plant is provided in corresponding sections. The screening approach is consistent both with previous studies (e.g. Radian Corp, Assessment of Atmospheric Emissions from Petroleum Refining EPA-600/2-80-075; Radian Corp., Frequency of Leak Occurrence for Fittings in Synthetic Organic Chemical Plant Process Units EPA-600/2-81-003) and with proposed standards (e.g. EPA Proposed National Emission Standard for Hazardous Air Pollutants - Benzene Fugitive Emissions 46 FR 1165, Jan. 5, 1981 and EPA Proposed VOC Fugitive Emission Standards for Synthetic Organic Chemicals Manufacturing 46 FR 1136, Jan. 5, 1981). The screening procedure utilizes a portable hydrocarbon detector in a prescribed manner to determine the maximum value of leak concentration at each potential leak site.

In all cases it was expected to be possible to survey nearly 100 percent of all potential equipment sources. Those accessible source types handling at least one weight percent of the substance are of interest. A range of emissions would be determined for each plant based upon the frequency of device leakage found and their magnitudes. Instrument response functions derived in the SAI laboratory would be used to calibrate each substance response to a hexane reference. Nomographs relating hexane (or methane)

response to mass emission would be used to develop a total plant fugitive emission value.

The Foxboro Model OVA-128 (formerly Century Systems) was proposed to determine emissions from plant devices of the following types:

- Process valves
- Pump seals
- Compressor seals
- Relief valves
- Process drains
- Open ended valve lines
- Selected flanges.

The instrument directly analyzes organic vapors in the 1-1000 ppm range and can be extended to 10,000 ppm by means of a dilution system. Additionally the OVA Model-128 optional gas chromatograph and strip chart recorder can be utilized for determining the composition of emissions from multicomponent streams.*

SAI staff met with plant personnel at each site and reviewed the plant processes and equipment components. A proposed test plan was submitted and approved by all parties. As cited above, only those components handling streams composed of greater than 1% content of the substance of interest were proposed to be monitored. Screening procedures to be followed were chosen to correspond to those employed in the Radian survey of thirteen petroleum refineries and twenty four synthetic organic chemical manufacturing plants in order to facilitate the use of nomographs to relate screening value (in ppmv) with total mass emissions.

* It has been our program experience in all sites but one that each plant operator has determined and is aware of, to an acceptable level of precision, the stream composition in nearly all lines of interest. Beyond this and GC characterization we proposed, where necessary, to take compositional samples on Tenax GC at high leakers and confirm composition by analysis at our La Jolla laboratory.

The OVA probe is held as closely as possible to the potential leak source. These locations differ for each device type. In general four points is taken at each source point corresponding to four compass points 90° apart. The probe is rotated around the circumference and if a leak is detected the location of its maximum screening value is taken as a reference for establishing the origin of the four compass points. Specific screening points are:

- valves (gate, globe, control)-stem and the packing gland
- valves (plug) - plug square and under the malleable gland
- flanges (note it is expected that only a fraction of flanges would be sampled from amongst those accessible) - the probe is rotated around the flange perimeter and four points chosen as indicated above
- pump and compressor seals - for single seal types the potential leak source is around the rotating shaft where it enters the pump (compressor) housing; for two seal types - inboard and outboard-each seal will be screened separately. If the seal area is enclosed and vented, the screening location is at a point just inside the end of the vent
- pressure-relief devices (vented to the atmosphere) screening points around the perimeter of the vent and at the center of the vent (as accessible)

Where highly variable leak rates are encountered, sufficient sampling time is allowed to obtain a representative average. Additionally where elevated ambient readings are suspected of contributing to the leak screening reading, average values of ambient hydrocarbon concentrations are determined by using the OVA at points in the proximity but removed from the influence of the source.

Based upon the Radian survey, screening values greater than 200 ppmv, calibrated to hexane,^{*} were defined as leaks and data recorded. However for carbon tetrachloride lines a screening leak threshold of 20 ppmv was defined. It was subsequently determined that leaks with screening values greater than 2000 ppmv contributed greater than 95% to the plant mass emission

* Note that the OVA instrument develops essentially the same response due to hexane and methane. Figure 7.2-1 provided by B. Tichenor of EPA from Radian Corp. documentation illustrates the relationship between the two gases is nearly linear and of unity slope.

Calibrated to Hexane @ 100ppm (Gas Select 393)

Gas Standard	9.5ppm	102ppm	983ppm
OVA 128 Reading	<u>9.2ppm</u>	<u>104ppm</u>	<u>1014ppm</u>
% Difference	3%	2%	3%

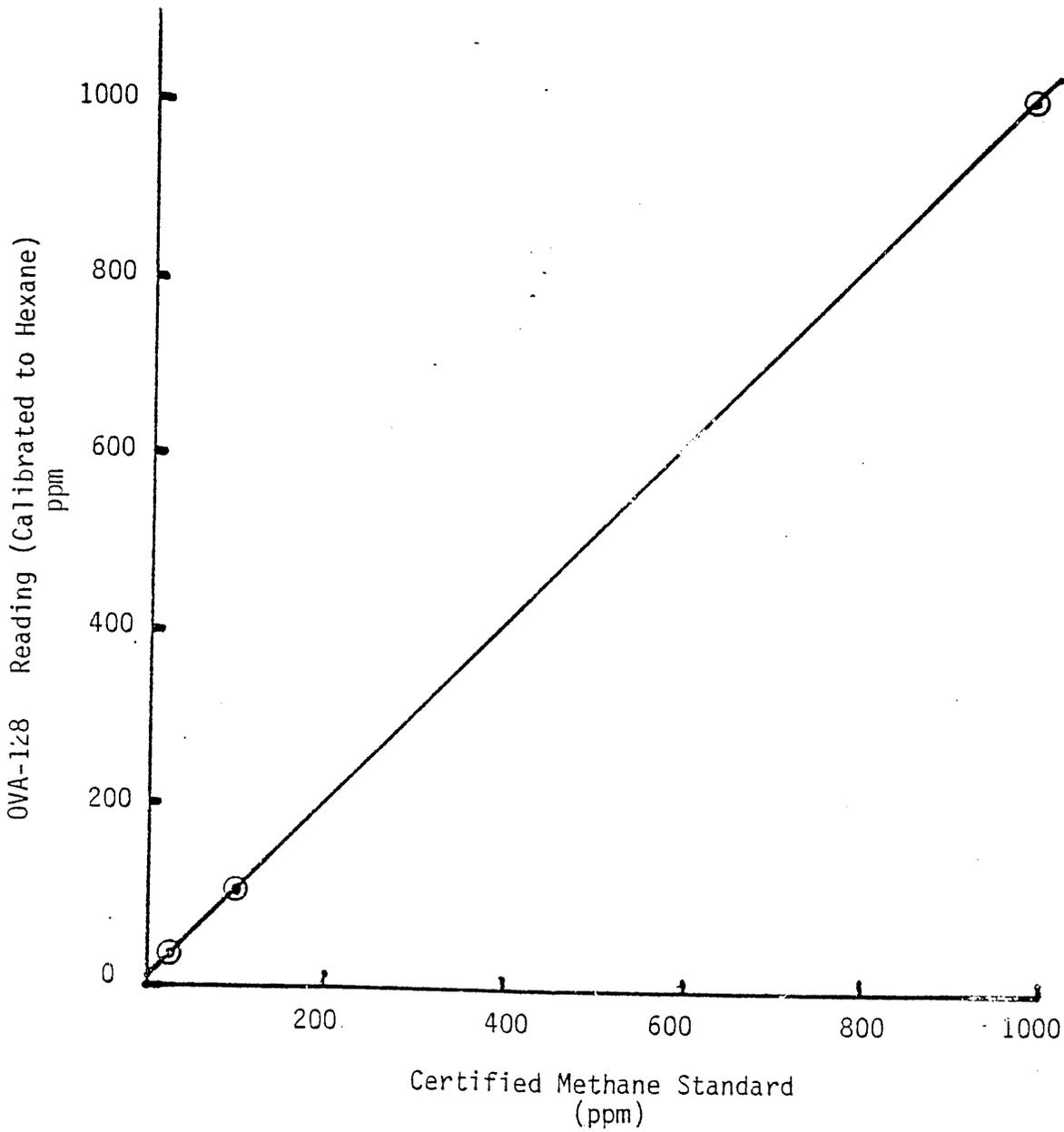


Figure 7.2-1

METHANE VERSUS HEXANE RESPONSE ON THE FOXBORO OVA 128

rate. Mass emissions calculated on both a per unit time basis and as an absolute quantity will be determined. These releases will be further broken out for each device type.

7.2.2 Analysis Approach

In order to determine the hexane response equivalent the OVA 128 was tested in the SAI Trace Environmental Chemistry Laboratory for its response relative to hexane for a number of volatile compounds targeted for measurement. Table 7.2-1 lists the basic data showing the concentration ranges measured, the standard deviations, and the response factors. Table 7.2-2 lists the regression statistics for the meter responses versus concentration. Concentration of each test substance were made by injecting a quantity of the compound into a clean 20 liter glass carboy. The mixture was shaken for 3-5 minutes. The response factor is defined as the ratio of the meter response to the actual concentration with the meter calibrated to read 100 with 100 ppm hexane. The data were taken to gain an appreciation of the absolute variation of response functions among substances and as a function of concentration of each substance in order to assist in field test planning.

Based on the data in Table 7.2-1 a number of multicomponent mixtures were made to determine how well the meter response could be predicted. The component mixtures and the predicted and actual meter responses are shown in Table 7.2-3. As the data indicates, the predicted values are approximately 10% higher than the actual meter responses assuming linear superposition. This is an acceptable error for the program application since the uncertainty, as expressed as 90% confidence interval, is typically greater than 10% and will likely be a greater source of uncertainty.

Figure 7.2-2 is a typical nomograph drawn from the Radian study of fugitive emissions from petroleum refining (Wetherold, 1980). We used such nomographs, after adjustment specific to each device category, as a key step in determining fugitive emission factors. In the EPA petroleum refining data base on the order of 6,000 devices were screened and approximately 700 were bagged to determine mass emission rates. Over 40,000 devices were screened in the EPA sponsored SOCFI surveys. Correlation coefficients between screened and leak rate measured parts were computed for each source type and ranged between 0.68 and 0.77. We recognize that the correlation between screening values and

TABLE 7.2-1
 OVA-128 METER RESPONSE AND G.C. RETENTION TIME - BASED ON METER RESPONSE OF 100 CALIBRATED
 WITH 100ppm HEXANE

Compound	Conc.	Meter Resp.	#Detn.	σ	% σ	Avg. GC Ret. Times T(°C)	RT	Response relative to a Calibration of 100 ppm Hexane
Hexane	10ppm	8.1	1			17°C	2.41min	0.81
	50	48	1			18	2.36	0.99
	100	100.7	8	2.0	2	20	2.10	1.0
	200	190	1			21	2.08	0.95
	300	420	1			22	1.92	1.40
	500	631	3	45	7	23	1.84	1.26
	700	850	1					1.21
	1000	1463	1					1.46
Benzene	10	30.5	2	3.5	11	19	3.35	3.05
	100	231	4	19	8	20	3.24	2.3
	300	822	1			21	3.23	2.74
	400	1040	1			22	2.85	2.60
	500	1145	1			23	2.79	2.29
CCl ₄	100	8.7	4	0.8	9	18	3.67	0.087
	1000	93	3	4.6	5	22	2.95	0.093
	10000	850	1			23	2.90	0.085
CHCl ₃	10	8.9	1					0.89
	100	77	3	0	0	22	1.85	0.77
	500	360	1			23	1.85	0.72
	1000	720	1					0.72
1,2-dichloroethane	10	13	1			21	2.56	1.3
	100	106	3	5.1	5	22	2.29	1.06
	500	572	2	3.5	<1	23	2.28	1.14
Styrene	10	12.2	1					1.2
	100	121	3	14	12			1.2
	500	845	2	35	4			1.69

Table 7.2-1 (Continued)

OVA-128 METER RESPONSE AND G.C. RETENTION TIME - BASED ON METER RESPONSE OF 100 CALIBRATED WITH 100ppm HEXANE (CONTINUED).

<u>Compound</u>	<u>Conc.</u>	<u>Meter Resp.</u>	<u>#Detn.</u>	<u>σ</u>	<u>%σ</u>	<u>Avg. GC Ret. Times T($^{\circ}$C)</u>	<u>RT</u>	<u>Response relative to a Calibration of 100 ppm Hexane</u>
Tetrachloroethylene	10	8.9	1					0.9
	100	101	2	2.8	3			0.9
	500	475	2	21.2	5			0.95
Methane	100	135	1			20	<15sec	1.35

TABLE 7.2-2
 OVA-128 LINEAR REGRESSION BASED ON CALIBRATION WITH 100ppm HEXANE

<u>Compound</u>	<u>Points Discarded</u>	<u>Slope (meter/ppm)</u>	<u>Y-Intercept (meter)</u>	<u>Corr. Coeff.</u>
Hexane	None	1.42	-51	0.9935
Hexane	300ppm, 500, 700, 1000	0.957	+0.53	0.9992
Benzene	None	2.41	+22	0.991
CCl ₄	None	0.0846	-4.1	1.0000
CHCl ₃	None	0.716	3.1	1.0000
1,2-Dichloroethane	None	1.15	-3.12	0.9998
Styrene	None	1.73	-26.3	0.9986
Tetrachloroethylene	None	0.946	2.5	0.9999

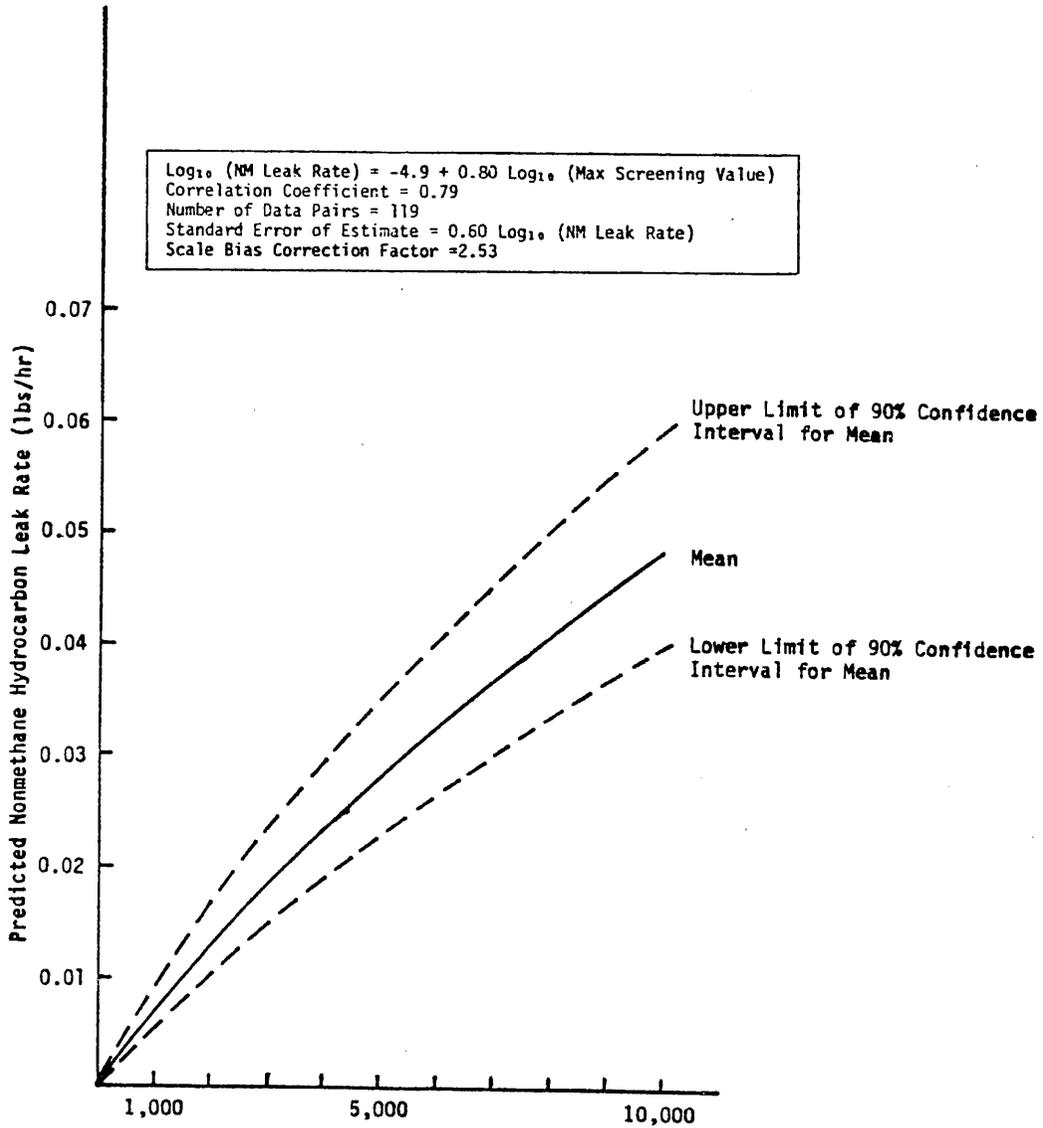
TABLE 7.2-3
COMPONENT MIXTURES

<u>Compound</u>	<u>Concentration (ppm)</u>	<u>Response Factors</u>	<u>Expected Meter Response</u>
Hexane	48	1.0	48
Benzene	70	2.7	190
EDC	78	11	86
CHCl ₃	78	0.77	60
PERC	<u>61</u>	0.99	<u>60</u>
	335 ppm v/v		444
		actual =	495,475
Benzene	250	2.7	685
Hexane	100	1.0	<u>100</u>
			785
		actual =	755,760
PERC	200	0.95	190
CCl ₄	1000	0.093	93
Hexane	100	1.0	<u>100</u>
			383
		actual =	350

*calibrated to 100ppm hexane

Figure 7.2-2

NOMOGRAPH FOR PREDICTING TOTAL NONMETHANE HYDROCARBON LEAK RATES FROM MAXIMUM SCREENING VALUES - VALVES, LIGHT LIQUID/TWO-PHASE STREAMS



Maximum Screening Value (ppmv, calibrated to hexane)
Using J.W. Bacharach TLV Sniffer at the Source.

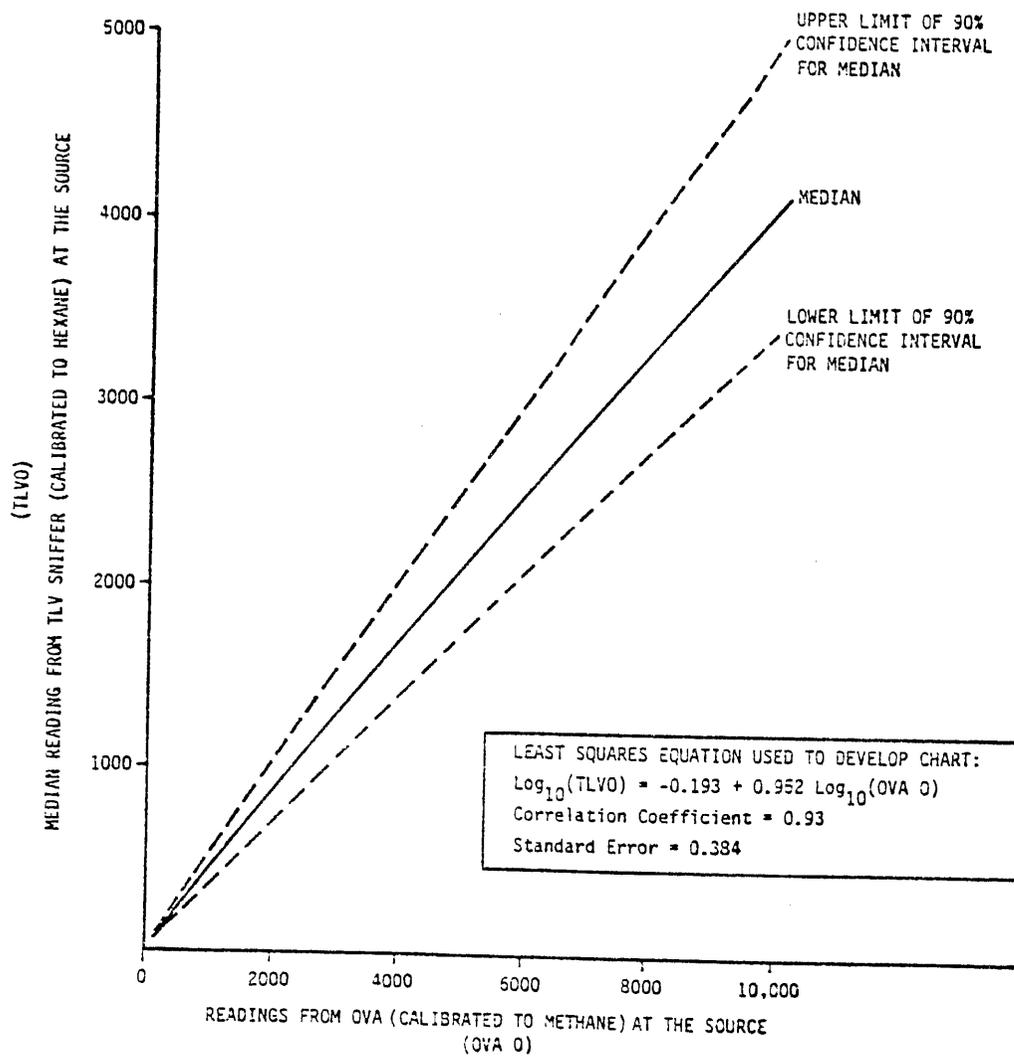
actual leak rates is imperfect. However, it was determined in the Radian studies that prediction of leak rates based upon directly measured data on individual devices would be inappropriate. Clearly at any time an individual device may or may not be found to leak and exhibit a particular relationship between its leak rate and screening value. It is necessary, therefore, to place the sampling emphasis on obtaining screening values for the greatest percentage of process devices and utilize statistically derived mean emission factors and confidence limits. Note that data published by Radian, of the type shown in Figure 7.2-2 corresponds to the Bacharach TLV device. Figure 7.2-3 is included to illustrate the Radian derived correlation between the OVA and TLV devices.

Data to be collected for each device will be:

- source identification number
- source type
- screening value (and liquid droplet leak rate, if applicable)
- type of service (gas, light liquid, heavy liquid)
- composition of the line
- physical properties of the line and the ambient environment.

Properties cited in the final data category will be collected but no attempt will be made at this time to examine interrelationships.

Two procedures were used to obtain a range of mass emissions rates from OVA screening values. For a stream with pure (100%) substance content the relationships derived from SAI's Table 7.2-1 were used to obtain the "true" concentration from the observed OVA response. This "true" concentration was inserted into the Radian derived substance specific relationships to obtain a Bacharach TLV response (Brown, 1980). Using device type nomographs such as Figure 7.2-2 the leak rate is derived. Note that Figure 7.2-2 is not substance specific but rather only device dependent. The nomographs were derived by averaging all the various substances tested in the Radian program. Therefore, for a substance such as carbon tetrachloride to which the OVA is very insensitive the nomograph will significantly underpredict mass emissions. The nomographs were then adjusted by the substance's Bacharach TLV response function to account for this possible underestimate. Comparison of results



02-4245-1

Figure 7.2-3 Nomograph for Relating OVA Readings and TLV Sniffer Readings at the Source - Part I

from these two calculations i.e. device specific-compound averaged and device specific compound-specific, allows the estimation of the range in predicted mass emission rates.

Quality Control

Several quality control procedures were utilized in this program. These include the following:

- equipment calibration
- independent instrument replication
- repeat measurements
- spot confirmation of composition

Specifically the OVA was calibrated immediately prior to and after each set of measurements were made. Arrangements were made in most cases to utilize a second OVA unit for replication of measurements. All screening values above 200 ppmv (hexane equivalent) or less were termed significant for the immediate purposes of the study and were repeated by both instruments. The screening values for each substance and expected known mixtures which define a significant leak (based on laboratory derived response functions) were determined prior to sampling. The instrument was calibrated in the field using hexane both prior to and after sampling and with and without the dilution probe.

7.3 DOW CHEMICAL U.S.A. - DETERMINATION OF EMISSIONS

Approximately 1100 devices were surveyed for fugitive leaks at the facility. This constituted nearly all accessible and active streams containing greater than 1% perc or CT. In order to be certain not to miss any potentially important mass emissions all OVA screening values greater than 100 and 20 ppm were recorded for perc and CT lines respectively. Background values were found to be less than 3 ppm in all areas of the plant surveyed and therefore did not interfere with screening.

All accessible components were surveyed with the exception of flanges of which on the order of 75% were screened. There were relatively few inaccessible components of interest and no attempt was made to account for their potential mass emissions. It was not possible to directly measure

emissions from the product check tanks since maintenance was underway and the area was unavailable for testing. Since these tanks are utilized to store product and are directly vented to the atmosphere with each filled and off-loaded approximately 120 times per year, it was appropriate to calculate working emissions from the tanks since they would be expected to contribute significantly to total tank emissions. Two additional product storage tanks were expected to contribute to emissions by normal tank breathing. Their emissions were determined by calculation.

Thirty one (31) devices were found to leak with screening valves greater than the cutoff thresholds. Twenty eight (28) were valves, one an outer seal on a gas compressor, one a pump seal and the final, a flange. Dow staff independantly performed screening readings of all leaking devices with their own OVA. In addition all readings were repeated by SAI and, as often occurred, values fluctuated with time and maxima were averaged. In all cases Dow staff were able to identify the approximate stream composition, physical state and parameters of temperature and pressure. Table 7.3-1 presents the OVA screening value data and the parameters utilized to determine the range of mass emissions rates for the most significant leakers among the 28 devices. The SAI response factors were derived from data presented in Table 7.2-1. Radian constants relating actual concentration to observed Bacharach TLV response are from Brown, 1980, and take the form

$$IR_C = \exp (a + b \ln C + Se^2/2)$$

where IR_C is the TLV response and C the actual concentration. Device source functions of Table 7.3-1 are given by the codes -

- A. Pump Seals (Light Liquid/Two-Phase Streams) Compressors and Relief Valves (Gas/Vapor Streams)
 $\text{Log}_{10} (\text{leak rate}) = -4.4 + 0.83 \text{Log}_{10} (IR_C)$
- B. Valves + Compressor Seals, Hydrogen Streams
 $\text{Log}_{10} (\text{leak rate}) = -7.0 + 1.06 \text{Log}_{10} (IR_C)$
- C. Valves, Gas/Vapor Streams
 $\text{Log}_{10} (\text{leak rate}) = -7.0 + 1.23 \text{Log}_{10} (IR_C)$
- D. Valves, Light Liquids/Two Phase
 $\text{Log}_{10} (\text{leak rate}) = -4.9 + 0.80 \text{Log}_{10} (IR_C)$

Table 7.3-1
 DOW CHEMICAL U.S.A.
 MASS EMISSION PREDICTION FROM OVA SCREENING VALUES

Compound	OVA Response*	SAI Response Factor	Actual Conc.*	a	b	Se	IRc*	Source Function	Leak Rate lb/yr	Upper Bound Leak Rate lb/yr
PERC	10,000	0.95	10,526	0.32	0.69	0.47	904	D	23.3	161
	3,500		3,684				439		13.1	74
	7,000		7,368				707		19.2	119
	4,000		4,210				401		14.1	78
	4,000		4,210				401	A	53.6	304
CT	900	.085	10,588	4.66	0.093	0.739	329	D	10.4	168
CT	700	.085	8,235	"	"	"	322	D	10.2	133
60% CT	5,000		6,961(CT)	"	"	"	317	D	10.1	116
40% PERC			4,640(PERC)	0.32	0.69	0.47	514	D	14.9	86

* ppm

E. Drains

$$\text{Log}_{10} (\text{leak rate}) = -4.9 + 1.10 \text{ Log}_{10} (\text{IR}_c)$$

F. Flanges

$$\text{Log}_{10} (\text{leak rate}) = -5.2 + 0.88 \text{ Log}_{10} (\text{IR}_c)$$

G. Pump Seals, Heavy Liquid Streams

$$\text{Log}_{10} (\text{leak rate}) = -5.1 + 1.04 \text{ Log}_{10} (\text{IR}_c)$$

Finally the upper bound leak rate was determined by utilizing the true concentration rather than the Bacharach TLV response in the relationship between screening value and leak rate e.g. in A above $\text{Log}_{10} (\text{leak rate}) = -4.4 + 0.83 \text{ Log}_{10} (C)$. This was done because relationships such as Figure 7.2-2 are based upon screening data on a range of substances which may significantly underpredict the leak rate, for a substance less responsive to detection by OVA or TLV than methane or hexane.

Incorporating the remaining 20 leaking devices yields approximately an equal contribution to the mass emission rate found for the 8 heaviest leakers. Thus, for the entire plant the emissions are estimated to range between 338 and 2478 lb/yr or between 0.033 and 0.242 lb/day/leaking valve. Approximately 2% of all valves inspected were found to leak above the detection threshold. Thus, factoring in the nonleakers one has between 9.3×10^{-4} to 6.8×10^{-3} lb/day/plant valve of CT or perc emissions. By way of comparison in 1978 the Dow plant was among several sampled by the CARB to determine plant fugitive emissions. Almost 2400 valves and flanges were surveyed and four (4) valves among 1080 were found to leak with a combined averaged (assumed) mass emission rate of 3942 lb/year. Leaks were found in the butadiene storage and service areas (not considered in the present study) and not in the CT or perc areas.

Calculation of Working Emissions from Dow Check Tanks

Four check tanks are on-site with two each for CT and PERC. Ordinarily three days are required to fill one tank while the second is being off-loaded. Dimensions of each tank are 12 ft diameter and 21 ft height for a volume of 2375 ft³. Filled is typically 70% volume or 1662 ft³. Assuming an average temperature of 20°C the vapor pressures of CT and perc are approximately 92 and 20 mm respectively. therefore head space vapor composition at equilibrium is 92/760 = 12% for CT and 20/760 = 2.6% for perc. During one

complete fill cycle the volumes of CT and perc emitted are $0.12 \times 1662 = 200$ and $0.026 \times 1662 = 43 \text{ ft}^3$ respectively. The vapor density of CT and perc at 20°C are

$$\rho_{\text{CT}} = \frac{PM}{RT} = (1) (154) / (.082) (293) = 6.4 \text{ g/L} = 0.4 \text{ lb/ft}^3$$

$$\rho_{\text{perc}} = (1)(165.8) / (.082) (293) = 6.9 \text{ g/L} = 0.43 \text{ lb/ft}^3$$

Therefore the displacement weight of CT per tank fill for CT is $200 \text{ ft}^3 \times 0.4 \text{ lb/ft}^3 = 82 \text{ lb}$ and for perc = $43 \text{ ft}^3 \times 0.43 \text{ lb/ft}^3 = 18.5 \text{ lb}$. Since the number of fills per year are approximately 120^+ the total emissions become

$$\text{CT: } 80 \times 120 = 9600 \text{ lb}$$

$$\text{perc: } 18.5 \times 120 = 2220 \text{ lb}$$

Alternatively using the working loss emissions relationship of Section 7.2 for CT one has for each of the two check tanks:

$$L_w = 2.4 \times 10^{-2} M P K_n K_c$$

$$= (2.4 \times 10^{-2}) (154) (92/760) \times 14.7 (0.6) (1) = 3.946 \text{ lb/} 10^3 \text{ gal}$$

Where the turnover fraction K_n is taken as 0.6 corresponding to 60 throughputs per year by AP-42.

Since each fill volume is $1662 \text{ ft}^3 = 12.4 \times 10^3 \text{ gal}$ and there are 60 fills per year, then the annual emission for each CT tank is 2936 or 5872 lb. total for both tanks. For perc

$$L_w = (2.4 \times 10^{-2}) (165.8) (20/760) \times 14.7 (0.6) (1) = 0.923 \text{ lb/} 10^3 \text{ gal}$$

This corresponds to 1374 lb/year from both per tanks.

Normal tank breathing emissions were computed using the AP-42 emission formula for fixed roof tanks (as described in Section 9.1). The two check tanks for each substance are used in a coordinated fashion, i.e., one being filled while the other emptied. Therefore, the normal breathing emissions for both tank were equivalently modeled as a complete year's emission from one tank assumed

⁺ Tank emission calculations are based upon the displacement volume and number of fills cited by Dow (Anderson) during plant visits. It is recognized that year to year changes occur.

half full. Then L_B , the breathing loss in pounds per day for CT becomes:

$$\begin{aligned} L_B &= 6.19 \times 10^{-5} M \left(P/(14.7-P) \right)^{0.68} D^{1.73} H^{0.51} T^{0.5} F_P C K_C \\ &= (6.19 \times 10^{-5}) (154) \left(1.78/(14.7-1.78) \right)^{0.68} (12)^{1.73} (10)^{0.51} (26)^{0.5} (1)(0.6) \\ &= 1.78 \text{ lb/day} = 652 \text{ lb/year} \end{aligned}$$

For perc $P = .386$ $M = 165.8$ and $L_B = 231$ lb/year. The diurnal temperature variation, T , was obtained from Dow site average annual meteorological data (Anderson, Personal Communication) and the small tank adjustment factor from an AP-42 (EPA, 1981) plot.

The check tank emissions are not based upon actual measured values of head space product concentrations. Measurements taken at DuPont for CT showed that saturation vapor pressure concentration values were not attained in the relatively quick fill (5 hours) monitored. However in the absence of direct measurements and the longer fill time the saturation vapor pressure derived quantities are appropriate for use in determining the upper bound of plant emission factors. The AP-42 derived numbers will be used to determine the lower bound.

Calculation of Emissions from Dow Storage Tanks

In addition to the check tanks there is a large permitted CT storage tank and evidently also a perc storage tank (W. Anderson, Personal Communication). Tank dimension for CT are $D = 48$ ft and $H = 50$ ft while for perc $D = 42$ ft and $H = 30$ ft. Utilizing the AP-42 (EPA, 1981) emission formula for fixed roof tank breathing (see Section 9.1 for definition of terms) one has in lb/day:

$$L_B = 6.19 \times 10^{-5} M \left(P/(14.7-P) \right)^{0.68} D^{1.73} H^{0.51} T^{0.5} F_P C K_C$$

For CT, taking the vapor pressure at 20°C , the average diurnal temperature variation as 26°F , and the average vapor space height based upon a 50% liquid fill, one has

$$\begin{aligned} L_B &= (6.19 \times 10^{-5}) (154) \left(1.78/(14.7-1.78) \right)^{0.68} (48)^{1.73} (25)^{0.51} (26)^{0.5} \\ &= 52.8 \text{ lb/day} = 19,285 \text{ lb/year} \end{aligned}$$

For perc

$$\begin{aligned} L_B &= (6.19 \times 10^{-5}) (165.8) \left(.386/(14.7-.386) \right)^{0.68} (42)^{1.73} (15)^{0.51} (26)^{0.5} \\ L_B &= 11.5 \text{ lb/day} = 4,186 \text{ lb/year} \end{aligned}$$

The working emissions are calculated using AP-42's fixed roof working loss equations and the same parameter values and throughput assumed for the check tanks. Then for CT

$$L_w = 2.4 \times 10^{-2} MP K_n K_c$$

$$= (2.4 \times 10^{-2})(154)((92/760) \times 14.7)(1.0)(1) = 6.58 \text{ lb}/10^3 \text{ gal}$$

where the turnover fraction $K_n \approx 1$. Since the total assumed throughput is $12.4 \times 10^3 \text{ gal} \times 120$ (check tank fills), the total emission are 9802 lb. Similarly for perc total emissions become 2293 lb.

Summary of Dow Emission Source Strength

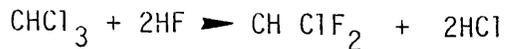
Emission from the plant sources surveyed are tested below. All quantities are in lb/year.

	<u>perc</u>	CT
1. Fugitives	225 lower estimate 1600 upper estimate	113 lower estimate 800 upper estimate
2. Check Tanks- working Emissions	1374 lower estimate 2220 upper estimate	5872 lower estimate 9600 upper estimate
3. Check Tanks- Breathing Emission	231	652
4. Storage Tanks - Breathing	4,186	19,285
Working	2,293	9,802
	8,309 lower estimate 10,530 upper estimate	35,724 lower estimate 51,883 upper estimate
<hr/>		
Total CT and perc	44,033 lower estimate	62,413 upper estimate

SOURCE TESTS - ALLIED CHEMICAL

8.1 SITE OVERVIEW

Allied Chemical, El Segundo, has a fluorocarbon synthesis plant. It either uses carbon tetrachloride or chloroform as feed and produces Genetron 11, 12, or 22. The plant was projected to be operating with chloroform during the measurement period and producing G-22 according to:



Chloroform is offloaded from tank cars to a storage tank for feed to the reactor. Chloroform enriched streams (>0.5%) occur prior to the reactor and just beyond. Based upon venting and process configuration it is concluded that fugitive emissions from valves, flanges and pump seals constitute the potential emission sources. The number of components of interest is less than 100 and therefore 100% can be leak tested. When the plant feed is switched to carbon tetrachloride a storage tank vented to the atmosphere is incorporated into the process and emissions must be accounted for.

Basic Process Equipment

The plant produces fluorocarbons from either carbon tetrachloride or chloroform feedstock. Emissions of carbon tetrachloride will be estimated indirectly in this study since the site was operating on chloroform feed throughout the testing period.

Chloroform is offloaded from tank cars and stored in closed unvented tanks. As the storage tank is filled the air space displaced is fed back to the tank car. The storage tank is not vented in its breathing mode and is part of a closed feed system to the reactor. Material is fed to a reactor and reacted with hydrogen fluoride in the presence of an antimony pentachloride catalyst. Unreacted product is recycled in a closed system. Process steps beyond the reactor and recycled loop do not contain appreciable concentrations of chloroform nor do reconcentration mechanisms or controls exist.

It is expected that fugitive emissions from the valves, flanges and pump seals will constitute the bulk of chloroform emissions. Less than 100 components are involved.

Emission sources associated with carbon tetrachloride feed include the storage tank since it is equipped with a breather and vented to the atmosphere. Offloading as well as breathing modes of operation would be emission processes.

8.2 MEASUREMENT PROGRAM

The basic approach toward the measurement of fugitive emissions is by use of the Foxboro OVA Model 128 portable hydrocarbon analyzer as was described in Section 7.2.

Plant management was cooperative and advised us 72 hours prior to beginning chloroform off-loading activity. Measurements were conducted of fugitive emissions from components involved in off-loading and reactor feed/recycle. It was possible to sample 100% of the pump seals, valves and flanges associated with components handling chloroform. Based upon our laboratory characterization of chloroform response we identified an instrument reading of 100 ppmv as a threshold concentration which was recorded to determine the mass emission rate. Above this threshold concentration all survey readings were recorded and line compositions determined. Based upon our laboratory derived response factors, stream composition and the Radian nomographs, resulting leak rates were determined.

Comparisons were made with Allied Chemical Company data taken by the CARB in a previous study of fugitive emission from the plant. These data will provide a useful data base with which to examine the historical rate of device leakage found.

Carbon tetrachloride emissions cannot be measured directly because plant operations were switched to chloroform feed. However, based upon the rate of device leakage found and the frequency of operation with CT feed, a fugitive emissions factor will be derived.

Emissions of CT associated with the storage tank vented breather will be determined based upon the emission factor relationships specific in AP-42*. We will consider both modes of emission from storage tanks: (a) loss due to tank breathing and (b) working loss due to tank filling. According to AP-42, the relationship between working loss and vapor pressure is given by:

* AP-42-ED-3-PT-B Compilation of Air Pollution Emission Factors - Environmental Protection Agency, Research Triangle Park, NC.

Where: $L_w = 2.4 \times 10^{-2} M P K_n K_c$
 M^w = molecular weightⁿ
 P = true vapor pressure at bulk liquid conditions (psia)
 K_n = turnover fraction $\left[\frac{\text{annual throughput}}{\text{tank capacity}} \right]$

K_c = crude oil fraction
 L_w = working loss (lb/10³ gal)

For normal tank breathing the AP-42 emission formula is:

$$L_B = 6.19 \times 10^{-5} M \left(\frac{P}{14.7-P} \right)^{0.68} D^{1.73} H^{0.51} T^{0.5} F_p C K_c$$

Where: L_B = breathing loss lb/day
 M = molecular weight
 P = true vapor pressure at bulk liquid condition (psia)
 D = tank diameter (ft)
 H = average vapor space height (ft)
 T = average ambient temperature change, diurnal (°F)
 F_p = paint factor
 C = small tank adjustment factor
 K_c = crude oil factor

The formula is estimated to be within $\pm 10\%$ of actual measured values.

8.3 DETERMINATION OF EMISSIONS

8.3.1 Fugitive Releases

Ninety (90) devices were surveyed with the OVA. This constituted 100% of the chloroform service. Six leaks above 100 ppm were detected. Background response was less than 3 ppm and therefore did not interfere with leak detection measurements. Table 8.3-1 summarizes the fugitive emissions testing. Chloroform has a response factor of about 0.25 i.e. IR_c divided by the actual concentration and the upper bound on mass emission worked out to between 2 and 13 times the Radian derived baseline estimate. Leaks in two (2) valves, two (2) couplings and two (2) flanges were found. One liquid leak dominated the mass emission. It was important that the off-loading procedure was functioning since four leaks were associated with this operation. If the plant was assumed to operate the entire year on chloroform feedstock, Allied estimates 412 hours of off-loading activity. Therefore the first four leaks are scaled to 412 hours/year and the final two are at 8760/year.

Table 8.3-1

ALLIED CHEMICAL MASS EMISSION PREDICTION FROM OVA SCREENING VALVES

Device/ Location	OVA Response (ppm)	SAI Response Factor	Actual Conc. (ppm)	a	b	Se	IRC	Source Function	Leak Rate Tb/yr	Upper Bound Leak Rate Tb/yr
Off-loading coupling	700	0.72	972.	1.13	0.64	0.27	258.	D	0.4*	1.3*
Off-loading coupling	200	0.75	267.				113.	D	0.2*	0.4*
Flange-off- Loading	100	0.77	130.				72.	F	0.1*	0.2*
End Fitting- Valve Drain Hose	Liquid leak 2.1 m ³ /min	---	---	---	---	---	---	---	155. *	155. *
Relief Valve Plug-Storage Tank Area	2000	0.72	2778.	1.13	0.64	0.27	504.	D	14.6	63
Flange-Heat Exchanger at Reactor	1000	0.72	1389.	"	"	"	323.	F	8.2	105

All emissions 100% chloroform

* Based upon an estimated yearly off-loading time of 412 hours

Valve leakage rate was approximately 7% (2/28), while for flanges it was nearly 4% (2/52). The couplings were of the quick disconnect type and 40% (2/5) of those tested were found to be leaking. Excluding the liquid leak the remaining five devices were determined to emit between 23 and 170 lb/year of chloroform. Note that the liquid leak was repaired during the test day and should have been easily spotted as part of a routine inspection procedure.

Total fugitive leaks range between 178 lb and 325 lb with the liquid leak included.

8.3.2 Storage Tank Emissions

Calculations rather than a direct experimental determination were made because the plant was currently operating on chloroform feedstock. It is known that the chloroform off-loading and storage system is fully closed and recycled back through the railcar. The carbon tetrachloride tank is vented to the atmosphere. Allied is permitted to operate the tank at a maximum temperature of 61.9⁰F. The displacement volume of carbon tetrachloride is 13,000 gal. For the purposes of bounding the calculation it will be assumed that between 4 and 9 million pounds per year of CT are consumed.

The vapor pressure of 76 mm H_g at 60⁰F is applied. The saturation vapor pressure at equilibrium is 72/760 = 9.5% by volume or approximately 1.4 psi.

Displacement volume during fill is:

$$13,000 \text{ gal} = 1738 \text{ ft}^3$$

The volume of CT emitted is;

$$0.095 \times 1738 = 165 \text{ ft}^3$$

The density of CT vapor is given by,

$$\rho_{CT} = (1) (154) / (0.082) (293) = 6.41 \text{ g/L} = 0.41 \text{ lb/ft}^3$$

Therefore, the displacement weight of CT per off-load is equal to $165 \text{ ft}^3 \times 0.41 \text{ lb/ft}^3 = 65.9 \text{ lb}$

Maximum number of loads per year is

$$\frac{9 \times 10^6 \text{ lb/yr}}{1.72 \times 10^5 \text{ lb/load}} = 52 \text{ loads/year}$$

$$1.72 \times 10^5 \text{ lb/load}$$

where the product of the displacement volume (1738 ft^3) and the specific gravity (99.3 lb/ft^3) is $1.72 \times 10^5 \text{ lb/load}$.

Therefore the maximum quantity of emissions per year are:

$$65.9 \text{ lb/load} \times 52 \text{ loads/yr} = 3427 \text{ lb.}$$

Assuming 4 million pounds feed this becomes 1523 lb.

Alternatively AP-42 (EPA, 1981) can be utilized to calculate working emissions. For 9×10^6 pounds feed and 52 turnovers per year one has

$$L_w = \text{lb}/10^3 \text{ gal} = 2.4 \times 10^{-2} M P K_n K_c$$

$$= 2.4 \times 10^{-2} (154) 72/760 \times 14.7 (0.7)(1)$$

$$= 3.83 \text{ lb}/10^3 \text{ gal.}$$

For 9×10^6 lb of carbon tetrachloride one has 678×10^3 gal. Therefore, total working emissions become 2596 lb/year. For 4×10^6 pound feed the turnover factor K_n for 23 loads per year is nearly 1.0 and $L_w = 5.47 \text{ lb}/10^3$ gal. Therefore, annual total working emissions become 1648 lb.

For the normal tank breathing emissions utilizing the AP-42 formula given in Section 8.2 and approximate tank dimensions of 24 feet diameter, an average vapor level of 5 feet, CT vapor pressure at 20°C and a diurnal

temperature variation of 26⁰F, one has:

$$\begin{aligned}
 L_B &= (6.19 \times 10^{-5}) M \left(\frac{P}{(14.7-P)} \right)^{0.68} D^{1.73} H^{0.51} T^{0.5} F_P^{0.51} C K_C \\
 &= (6.19 \times 10^{-5})(154) \left(\frac{1.4}{(14.7-1.4)} \right)^{0.68} (24)^{1.73} (5)^{0.51} (1)(1)(1) \\
 &= 5.81 \text{ lb/day} \\
 &= 2123 \text{ lb/year}
 \end{aligned}$$

Summary

Therefore total emission for chloroform feed are fugitive and range between 23.5 (no liquid leak assumed) lb. and 325 lb. For year long operation on carbon tetrachloride, total emissions are fugitive plus storage tank releases and range between 3669 lb/yr (no liquid leak; 4 million pounds CT consumption; and computation of tank working emissions by saturation vapor displacement) and 5875 lb/yr (liquid leak; 9 million pounds CT consumption level; computation of tank working emissions by assuming saturation vapor displacement). If it is assumed that plant activity is divided into 50% chloroform and 50% carbon tetrachloride operation, then predicted emissions are between 1847 and 3099 pounds.

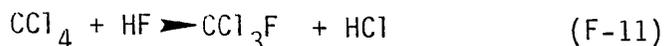
9.0

SOURCE TESTS - DUPONT DeNEMOURS AND COMPANY

9.1 SITE OVERVIEW

Summary

Dupont, Antioch produces Freon 11 and 12 from carbon tetrachloride feed according to the reactions:



Carbon tetrachloride (CT) is off-loaded primarily from bottom emptying railroad rail cars and stored in a tank vented to the atmosphere. Process feed pumps transport CT into a reactor which is operated in a continuous manner. Reactor output is fed into a distillation column with recycle back to the reactor.

Emission sources of CT are expected to be the storage tank and the fugitive emissions from valves, flanges and pump seals.

Facilities Descriptions

Tank cars containing 200×10^3 lbs of CT are off-loaded into a 570×10^3 lbs capacity storage tank on the order of 250 times per year. CT is fed from the tank car by bottom unloading and pumped into the storage tank. A feed pump delivers CT to the reactor where it is reacted with hydrogen fluoride. Since the HF is highly corrosive, considerable care is taken to contain all reactants. Material is output to the distillation column and chlorocarbons are recycled to the reactor from the column bottom. Beyond this point there are no enriched CT streams as hydrogen chloride absorbing, caustic scrubbing, and scrubbing and distillation are accomplished.

The single CT storage tank has a 3-inch U-leg vent to the atmosphere and thus has no vapor recovery system. Fittings associated with CT flow are inspected for leaks and maintained according to plant practices and Bay Area Air Quality District rules on volatile organic emissions. The total number of fittings are less than 100.

It is felt that the single most important source of CT emissions is the storage tank. There are two kinds of emission from storage tanks: (a) loss due to tank breathing and (b) working loss due to tank cleaning and filling. Dupont has made measurements of head space concentrations of CT during tank filling and also performed theoretical calculations based on vapor pressure. These compliment one another and are 18,800 and 24,000 lbs/yr respectively. Specifically for the calculations the vapor pressure was taken at 20⁰ C bulk liquid temperature. According to AP-42, the relationship between working loss and vapor pressure is given by:

$$L_w = 2.4 \times 10^{-2} MP K_n K_c$$

where: M = molecular weight
P = true vapor pressure at bulk liquid conditions (psia)
 $K_n = \text{turnover fraction} \left(\frac{\text{annual throughput}}{\text{tank capacity}} \right)$
 $K_c = \text{crude oil fraction} (=1 \text{ for CT})$
 $L_w = \text{working loss (lb)}/10^3 \text{ gal}$

Dupont did not predict the loss due to normal tank breathing during the year. Vapor is expelled from two primary mechanisms: (1) thermal expansion of existing vapors and (2) vapor expansion caused by barometric pressure changes. The AP-42 emission formula (EPA, 1981) is:

$$L_B = 6.19 \times 10^{-5} M \left(\frac{P}{14.7-P} \right)^{0.68} D^{1.73} H^{0.51} T^{0.5} F_p C K_c$$

where - $L_B = \text{breathing loss lb/day}$
M = molecular wt.
P = true vapor pressure at bulk liquid condition (psia)
D = tank diameter (ft)
H = average vapor space height (ft)
T = average ambient temperature change, diurnal (⁰F)
 $F_p = \text{paint factor}$
C = small tank adjustment factor
 $K_c = \text{crude oil factor}$

The formula is estimated to be within $\pm 10\%$ of actual measured values. Fugitive emissions from leaks in the relatively few (approximately 100) valves, flanges and pump fittings are likely to be of secondary importance to the storage tank emissions. These, however, will be directly measured in the field monitoring.

9.2 MEASUREMENT APPROACH

Top priority is the determination of storage tank emissions. This can be done for tank working loss by obtaining and analyzing head space samples during tank car unloading. It was proposed to insert a sampling tube into tank head space and collect a time integrated sample over the off-loading period. The sample would then be transferred to the La Jolla laboratory of SAI and analyzed directly by gas chromatography. Normal tank breathing can be determined sufficiently precisely ($\pm 10\%$) by utilizing AP-42 with accurate tank dimensions and meteorology.

Since relatively few fugitive source components exist, it unlikely that such emissions would be significant with respect to the storage tanks. However, it would be cost effective to screen 100% of the fittings with the Foxboro OVA since a team would be on site to perform the tank measurements. The fugitive screening approach would follow the procedure described in Section 7.2.

9.3 DETERMINATION OF EMISSIONS

9.3.1 Fugitive Releases

Approximately 110 devices were screened and six leaks above the established threshold of 20 ppm were recorded. Table 9.3-1 summarizes the screening data and mass emission projections. Since carbon tetrachloride is poorly detected by the OVA and TLV instruments factors between approximately 5 and 14 were applied, based on response functions to determine the upper bound of the leak rate mass emissions. Total fugitive emissions range between 58 and 610 lb/year.

9.3.2 Storage Tank Emissions

Head space samples were taken during the nearly six hour off-loading interval in order to directly determine the CT concentration in the displaced

Table 9.3-1

DUPONT MASS EMISSION PREDICTION FROM OVA SCREENING VALVES

Device/ Location	OVA Response (ppm)	SAI Response Factor	Actual Conc. (ppm)	a	b	Se	Irc	Source Function	Leak Rate 1b/yr	Upper Bound Leak Rate 1b/yr
Gate Valve Storage Tank Pump Area	300	0.09	3333.	4.66	0.09	0.74	296.	D	9.5	70
Gate Valve Storage Tank Pump Area	700	0.09	7778.				320.		10.2	140
Gate Valve Feed Pump Exit Area	350	0.09	3889.				300.		9.7	81.5
Gate Valve Feed Pump Exit	700	0.09	7778				320.		10.2	140
Gate Valve	600	0.09	6667.				315.		10.0	127
Valve-Reactor Heat Exchanger	200	0.09	2222				285.		9.3	52

All measurements are for 100% CT streams

air space. Saturation concentration at 20°C is approximately 12%. Measured values were 6.9 and 7.4%. These values resulted from gas chromatographic analyses of transferred samples from the 100 liter Tedlar bag time integrated sample. For the tank car displacement of 2008 ft³ the total CT emitted, based on the average, is 2008 x 0.072 = 144 ft³.

Then for a density of $\rho = PM/RT$

$$\rho = \frac{(1)(154)}{(.082)(293)} = 6.4 \text{ g/L} = 0.41 \text{ lb/ft}^3$$

Therefore the displacement weight of CT per off-load is equal to 144 ft³ x 0.41 lb/ft³ = 57.6 lb. For 250 off-loadings annually we have 14,400 lbs. This compares with DuPont's measurements of 9.3% vapor content and 18,800 lb/yr emissions. Saturation vapor pressure concentration emission would yield 24,000 lb.

Breathing loss from the tank can be calculated from AP-42 as:

$$\begin{aligned} L_B(\text{lb/day}) &= 6.19 \times 10^{-5} M \left(\frac{p}{14.7-p} \right)^{0.68} D^{1.73} H^{0.51} T^{0.5} F_p C K_c \\ &= (6.19 \times 10^{-5})(154) \left(\frac{1.73}{14.7-1.73} \right)^{0.68} (15.5)^{1.73} \\ &\quad (16)^{0.51} (26)^{0.5} (1)(1)(1), \\ &= 5.63 \text{ lb/day} \end{aligned}$$

where a working range of 200 x 10³ to 400 x 10³ lbs were used to determine an average liquid height. Annually emissions would be 2057 lb. Therefore working losses dominate the total emissions from the plant.

Summary

The upper and lower bounds of carbon tetrachloride emission were determined as 21,467 lb/year (upper bound on fugitives; DuPont measurement of storage tank working emissions; normal tank breathing) and 16,515 lb/year (lower bound on fugitives; SAI measurement of storage tank working emissions; normal tank breathing).

SOURCE TESTS - STAUFFER CHEMICAL COMPANY

10.1 SITE OVERVIEW

Summary

Stauffer is located in the Carson area of Los Angeles County. It is a manufacturer of polyvinyl chloride from the monomer (VCM) which is produced on site. Stauffer is the only California producer of ethylene dichloride (EDC) which is converted to VCM. The VCM is regulated by several standards including Cal. OSHA, EPA (emission standard) and CARB (ambient).

During Phase I, the plant was inspected and possible emission sources were identified. These consisted of EDC storage tanks, fugitive emissions from valves, flanges and pumps, process water content, gas incinerator effluents and the loading of outbound tankers.

Since the completion of Phase I several events have transpired which affected the test program to determine facility emissions. These were:

- the completion of a vent gas incineration system tied to all significant EDC storage tank breathers.
- the completion of a comprehensive study by SAI staff to develop a nationwide material balance for EDC.
- inactivity in EDC importation for the plant and elimination of EDC exportation from the plant.

Based upon this input and the plant inspection of February 3, 1981, it was expected that a plant emission factor for EDC can be determined with relatively little uncertainty. It is further expected that significant atmospheric release of EDC due to plant operation may not occur at the plant itself but rather offsite. These would arise from two sources - the process water discharge from the plant and several off site EDC storage tanks.

Facilities Description

Ethylene dichloride is being produced at Stauffer by two processes: direct chlorination and oxychlorination. In the former, EDC is produced by direct chlorination of ethylene in the presence of an FeCl_3 catalyst. In the latter process EDC is produced by the oxychlorination of ethylene with hydrogen chloride and oxygen in the presence of a catalyst, typically CuCl_2 .

The plant purifies EDC after the primary reactions by separation and distillation. Product is stored and used as feed for VCM production. All sources agree that emission of EDC is of concern in its production/storage process stages and of little importance in VCM production steps. (JRB, 1980).

At the time of plant inspection some storage of EDC existed at three leased storage tanks located at the Port of Los Angeles. Material has not been withdrawn from these tanks during the last year and there had been discussion to consolidate material into a single tank.

All process components handling EDC storage are now tied to a closed ventilation - incineration system. It is expected that virtually all chlorinated hydrocarbons including EDC will be effectively destroyed since the system must demonstrate VCM concentrations are reduced below 1 ppm. Firebox temperature is 2200⁰F and residence time greater than 1.5 seconds under heaviest flow conditions. Note that by way of comparison combustion performance data for PCB's are 99.995% destruction at 1832⁰F and 1 second residence time and 99.999994 at 2 seconds and 2372⁰F (N. Flynn, SAI, Personal Communication).

Fugitive emissions from valves and flanges are monitored by the plant according to the requirements of SCAQMD Rule 466.1. Pumps and compressor follow Rule 466. Emission and control requirements for vinyl chloride are specified by Rules 1005 and 1005.1. EDC concentrations in wastewater are monitored several times daily in the primary EDC steam stripper stream and once daily in the composite plant outflow stream. Daily water discharge limits are 25 ppm with typical monthly averages being in the 8 ppm vicinity. The discharge limit is embodied in the discharge permit (number 5061) with the Los Angeles County Sanitation District.

There are a number of points at which the EDC can be released to the atmosphere and they are similar for both direct chlorination and oxychlorination. These include the following along with their emissions factors for direct chlorination:

- | | | |
|-----------------------------|--------------------|---------------------------------|
| A. chlorinator vent | 2×10^{-5} | mass per unit mass EDC produced |
| B. light end column vent | 2×10^{-5} | |
| C. distillation column vent | 2×10^{-5} | |
| D. storage tank breathing | 7×10^{-5} | |

E. storage tankworking loss	2.7×10^{-6}
F. fugitive emission	$6. \times 10^{-5}$
G. wastewater	1.5×10^{-3}

Emission factors are similar for oxychlorination processes.

Emission factor values are taken from the literature (JRB, 1980) and assume 98% efficiency for incineration (A-E). It is also assumed above that EDC emissions to water are 29% of emission to air and that in wastewater treatment 100% of EDC discharged to water is released to air. These emission factors were used to prioritize releases but were clearly crude approximations to the plant. Because of the incineration system it was anticipated that factors A-E would be reduced. Factor F might be reduced since a monitoring program had been in force almost one year. Factor G and the off site storage tanks, which are not tied into an incinerator system might dominate emissions.

Emission limits and concomitant regulations embodied in Rule 1005 of the SCAQMD have necessitated the incineration system. Ninety gas chromatograph probes are located throughout the plant including the stack of the primary incinerator. Concentrations of VCM are reported essentially below the regulatory limit of 10 ppm and in fact below the limit of detection somewhat less than 0.1 ppm.

10.2 MEASUREMENT APPROACH

The objective of the program is to determine a plant emissions for EDC. It is not acceptable to develop such information based upon published industry wide estimates of plant control efficiencies. Fortunately, it was possible to design a monitoring and calculational program to determine EDC emissions for the site and not absorb a disproportionate share of program resources.

There are three modes of release from the plant and a fourth offsite.

- Post-Process Incineration

Processes A-E of Section 10.1 are all vented into the plant incineration system. The concentration of VCM continuously measured in the stack as gas output represents a reasonable upper limit to apply for EDC concentrations since its efficiency of incineration is at least equal to that

of VCM. Therefore, knowledge of the system airflow and VCM concentration are the necessary and sufficient conditions for determining the bounds of EDC release. The plant expressed willingness to provide these data in order to support the calculations.

- Fugitive Emissions - Valves, Flanges, Seals and Other Sources

Fugitive emission from the valves, pumps and flanges can be determined more precisely than was anticipated since Stauffer has completed a comprehensive leak inventory of all such components in compliance with Rule 466, 466.1, and 1005. The inventory delineates all leaks uncovered by their three man crew throughout the year and indicates the screening level in ppmv and component identity. In consultation with Stauffer we will be able to identify the total number of components associated with EDC handling systems (700), the distribution of substance composition streams, the distribution and incidence of leaks by hardware component type and leak rate. We will utilize this information to provide historical data to compliment our Foxboro OVA sampling at the site. Based upon this monitoring we predict an EDC mass emission rate for the fugitive releases. The plant has agreed to provide the necessary information. We propose to meet with plant personnel prior to the start of monitoring and finalize the sampling strategy to accomplish 100% coverage of the lines of highest EDC composition. The sampling approach and calculation of mass emission are described in Section 7.2.

- Wastewater

From examination of the emission factors derived from published literature (see Section 10.1) it is clear that EDC release from wastewater to air is potentially several orders of magnitude higher than any other plant source. Based upon plant measured concentrations of 8 ppm EDC in water a more realistic emission factor would be 2.4×10^{-4} mass/unit mass EDC produced. Clearly this could still be the dominant source. Furthermore, the release point would be expected to be located between the plant and the sanitary district treatment site which is 5 km. from the plant at 24501 S. Figueroa. We believe it is necessary to independently confirm the average 24 hour EDC concentration in the discharge water by obtaining the refrigerated composite sample. We have identified the lines of interest and received agreement to sample and analyze for EDC in the stream. We propose to draw a duplicate sample from the compositor and analyze for its EDC content. This will be

compared with Stauffer's parallel analysis. It is not reliable to obtain direct readings of EDC by survey instrument in the air above the water flow since concentrations at any single point will be in the near ambient range.

Emissions will be calculated using the plant's volumetric daily flow and assuming that complete degassing of the effluent will eventually occur. This assumption is based upon the relative volatility of EDC and the distances involved. However, it should be noted that no direct experimental or monitoring data is available with which to confirm this. The composition of the discharge stream is unknown since it merges into a large multisource flow. Conversation with the L.A. County Sanitation District (J. Milne) reveals the stream to be both exposed and covered. Vents exist where EDC measurements could be made to assess gross leakage at key points.

We will obtain samples of several plant process discharge streams in 40 ml bottles with no head space. Transit time from sample collection to analysis will be minimized and will not exceed 24 hours. This time frame is conservative although EDC is a volatile material and will undergo concentration degradation and outgassing. Analysis will be performed in the SAI Trace Environmental Chemistry Laboratory utilizing purge and trap analysis FID gas chromatography. A trial analysis was conducted and the EDC characteristic peak was distinctive down to the ppb level. Therefore, the analysis should easily confirm concentrations in the 8 ppm range.

- Offsite Storage Tanks

Three EDC leased storage tanks are located offsite at the Port of Los Angeles and are owned by another firm. Annual emissions from the tanks were very roughly estimated based on AP-42 (JRB, 1980) as 44 kkg/year based on preliminary estimates of stored quantities

Considering the magnitude of this source these storage tanks must be investigated. We will gather information about their configuration and control in order to calculate their emissions.

10.3 DETERMINATION OF EMISSIONS

10.3.1 Incinerator

Vinyl chloride concentration is monitored at approximately 90 locations throughout the plant (Langner, 1981) including the incinerator output. Concentrations are reported by Stauffer as less than 0.1 ppm at a flow rate between 10,000 and 12,000 SCFM. Although no direct monitoring of EDC is conducted, it is possible to conservatively bound the concentration of EDC at 0.1 ppm. That concentration is a suitable choice since it represents a conservative bound on the VCM levels measured near the stack output. Furthermore, the molar volume will be taken as 22.4 L rather than the higher value it would have because of the slightly elevated temperature at the detector location.

$$\begin{aligned} & \text{Using 12,000 SCFM one has the annual emission of EDC as } 12 \times 10^3 \\ & \text{SCFM} \times 28.3 \text{ L/SCF} \times 5.26 \times 10^5 \text{ min/yr} \times \frac{1 \text{ mole}}{22.4 \text{ L}} \times 97 \text{ g/mole} \times 10^{-7} \text{ v/v} \\ & = 77.3 \times 10^3 \text{ g} \end{aligned}$$

Therefore incinerator emissions of EDC are thought to be bounded by 77.3 kg or 170 lb/year.

10.3.2 Fugitive Emissions

Seven hundred (700) sources were surveyed comprising nearly 100% of EDC service. All accessible plant areas with streams containing greater than 1% EDC were screened except for a small number of devices located in areas where active maintenance was being conducted. It is believed unnecessary to perform any emission factor adjustment since it is estimated that greater than 95% of the requisite components were screened.

Three leaks above an arbitrary OVA reading threshold of 20 ppm were detected. Table 10.3-1 summarizes their screening values, calculation parameters and mass emission numbers. The upper bound leak rate was determined to be close to twice the nominal leak rate which accounted for the response factor of approximately 0.5 by Radian for TLV detection of EDC (Brown, 1980).

Stauffer found and reported approximately 10 leaks in the EDC service during 9 months previous to the plant testing. Assuming nominal leak

Table 10.3-1

STAUFFER CHEMICAL MASS EMISSIONS PREDICTION FROM OVA SCREENING VALUES

Device/ Location	OVA Response (ppm)	SAI Response Ractor	Actual Conc. (ppm)	a	b	Se	IRc	Source Function	Leak Rate Tb/yr	Upper Bound Tb/yr
Gate Valve Unit P1559A	300	1.1	273	-0.35	0.96	0.17	153	D	6	11
Valve Heavy Ends Column Unit 14439	500	1.14	439	"	"	"	241	C	1	1
Compressor Seal EDC Storage Unit T1062	2000	~1.1	1818	"	"	"	939	A	93	187.

All emissions 100% EDC (1,2-Dichloroethane)

values, in the neighborhood of 2000 lbs. total could be emitted annually. Therefore it appears that major reductions in the mass emissions were achieved by the company run inspection program and the fugitive emission source has now become of secondary importance as a fraction of total plant emissions.

10.3.3 Wastewater Discharge

Wastewater samples were collected in duplicate from four sites within the plant for determination of ethylene dichloride (EDC) concentration. The samples were collected in EPA standard 40 ml VOA vials on July 1, 1981. Analyses were performed using standard purge and trap techniques coupled with flame ionization detection gas chromatography. The results are given in the table below.

Sample description	EDC concentration range ($\mu\text{g/ml}$)	EDC concentration average ($\mu\text{g/ml}$)	Approximate flow (gpm)
PVC Interceptor Box	8.2 - 10.8	9.5	200
EDC Stripper, number 2 Chlorination area, C1404	0.11 - 0.14	0.12	25
Final collection site for pH adjustment, P663	34.9 - 38.2	36.6	350
Final discharge site, sanitary sewer	6.2 - 25.4	15.8	500

The water in the PVC Interceptor Box was warm and represents washings from the PVC reactor which travels to the Interceptor Box in a concrete drainage ditch. Water from the EDC stripper was very hot, and because of its heat was difficult to collect. The heat of the water may in part account for the relatively low concentration of EDC here as the EDC would out-gas from the hot water more readily. The final collection site for pH adjustment is a large concrete container with mixers in it located just prior to the final discharge site. Water at the final discharge site is being constantly aerated due to the speed that it flows through the concrete drainage trough. This aeration could account for the relatively large range in the EDC content found here. The average EDC concentration at the final discharge site is below the daily discharge requirement of 25 $\mu\text{g/ml}$ EDC.

Plant personnel indicated monthly average readings are typically on the order of 8 ppm but daily averages can reach greater than 20 µg/ml. In addition L.A. County Sanitation District staff (J. Milne, 1981) indicated that an on-site impoundment pond can become laden with EDC during certain abnormal operating periods and discharge variances are requested by Stauffer. This might occur on the order of once each year and therefore is not expected to significantly impact average annual discharge values. It is not expected at this time that evaporative emissions from this pond are significant except infrequently during upset conditions and spill control operations. Program staff were unaware of any periods when EDC content in the ponds could be appreciable and therefore no sampling was performed.

Utilizing the average of the two final discharge concentration readings (15.8 micrograms/ml) and 500 gpm flow one has 34,600 lb/year of EDC released into the sanitary sewer. For the purposes of calculating population exposures from plant releases it will be assumed that the EDC is locally emitted from the wastewater streams. There are no monitoring data available with which to develop a more accurate release profile.

However, emissions of EDC from the plant wastewater discharge can be calculated according to the method of Mackay (1975) as modified by Dilling (1977). It should be noted that this must be considered an estimate since conditions of flow and the presence of other substances will influence emission rates.

Using Dilling (1977) for nonaerated flow first recalculate Henry's law constant (dimensionless-mg of chemical per liter of air divided by mg of chemical per liter of water) as:

$$H_i = \frac{16.04 P_i^* M_{wi}}{TS_i}$$

where

- H_i = Henry's law constant, dimensionless,
- P_i^* = the compound's pure component vapor pressure in mm Hg at T,
- M_{wi} = the molecular weight,
- T = the absolute temperature of the wastewater in K,
- S_i = the compound's solubility in mg/liter at T.

Then for EDC

$$H_i = \frac{(16.04)(72)(99)}{(294)(8690)} = 0.0447 \text{ with}$$

the solubility of EDC in water given at 20°C is 8690 and the vapor pressure 1.4 psi (72mm) at 70°F.

The overall liquid mass-transfer coefficient K_{i1} is given by Dilling (1975) as

$$K_{i1} = \frac{(221.1)(0.6)}{\frac{1.042}{H_i} + 100 (M_{wi})^{1/2}} \text{ in m/hr}$$
$$= 0.108 \text{ m/hr}$$

Then from Mackay the percent desorption is given by:

$$\frac{C_i}{C_0} = \exp(-K_{i1} t/L), \text{ where}$$

C_i = the concentration at time t of EDC

C_0 = the initial concentration

L = the liquid depth (m)

t = the retention time (in hr) of the liquid in the wastewater system.

Retention time is based upon a flow velocity range of 3 ft/sec as estimated by the Los Angeles County Sanitation District (J. Milne) over a distance of approximately 5 km to the Joint Water Pollution Control Plant. Sewer flow depth throughout the entire route have been estimated by J. Milne as typically 1 foot (0.30m) to the Davison Pump Plant and 3 feet (0.9m) to the Joint Treatment Plant distances assumed to be 1 mile and 2 miles respectively. Transit time becomes between 0.5 and 1.0 hours sequentially. Then computing the net emission reduction as the product of each leg:

$$\frac{C_i}{C_0} = \exp\left[(-0.108)\left(\frac{0.5}{0.30}\right)\right] \times \exp\left[(-0.108)\left(\frac{1.0}{0.9}\right)\right] = 0.74$$

Therefore, 26% of the EDC is emitted between the plant and the Joint Water Pollution Control Plant. Residence time and conditions at the plant account

for additional releases and residual content is further emitted between the plant and the ocean discharge point. Wherever the flow is retained, aerated, or shallow, emissions will be accentuated.

10.3.4 Offsite Storage Tank Emissions

There are three storage tanks leased by Stauffer for EDC storage located at 22nd and Gaffey Sts. in San Pedro. These tanks are used for long term storage rather than providing feed on a routine basis. Therefore breathing loss rather than working loss is of concern. All tanks are white, two being 67 ft in diameter while the third is 57 ft. All are 40 ft 3 inches high and have capacities of either 1,050,000 (2) or 840,000 gallons. The tanks are cone roof type and are not tied into vapor recovery systems. The South Coast Air Quality Management District has based their estimate of emissions on the specification of 7 1/2 foot vapor level. Using the AP-42 formula for breathing loss with the vapor pressure of EDC at 20°C and an average diurnal temperature variation of 26°F one has for each of the two larger tanks:

$$\begin{aligned}
 L_B &= (6.19 \times 10^{-5}) M \left(\frac{P}{14.7-P} \right)^{.68} D^{1.73} H^{.51} T^{.5} F_p C K_C \\
 &= (6.19 \times 10^{-5}) (98.9) \left(\frac{1.16}{14.7-1.16} \right)^{.68} (67)^{1.73} (7.5)^{.51} (26)^{.5} (1) (1) \\
 &= 23.6 \text{ lb/day}
 \end{aligned}$$

Thus for the two larger tanks $L_B = 47.2 \text{ lb/day}$

For the third tank $D=57$ and $L_B = 17.8 \text{ lb/day}$.

The total emissions become 23,724 lb/year. Since the plant is in the process of shutdown it is not clear what the liquid levels currently are. Note that if the material in the three tanks were combined into one, total emissions would be reduced markedly. Exposure to a population from this site was determined separately since it is located over six miles from the plant.

11.0

ASSESSMENT OF POPULATION EXPOSURE

11.1 OVERVIEW

A major program goal was to compare emissions from the various sources and identify and rank any "hot spots" in California where the general population was exposed to elevated concentrations of carcinogens. A simple Gaussian dispersion model was therefore used to obtain order-of-magnitude estimates of exposure of the general population surrounding each source. Since this was essentially a screening study, use of more sophisticated models was not appropriate.

It cannot be emphasized too strongly that most California residents are exposed to emissions of hazardous substances from a variety of natural and manmade sources. Urban dwellers are typically exposed to greater concentrations than rural residents; however, all are subjected to so called "background" levels from multiple sources. In order to place stationary source exposures in perspective, the typical ambient levels of each substance were identified from the literature and compared with the concentrations due to the emissions from each plant. Exposures were thus expressed both as absolute quantities and as increments above "background."

Comparison of plants presents a further difficulty in that various substances are being considered. No attempt was made to evaluate the relative importance of exposure to two different substances, such as chloroform versus carbon tetrachloride, other than by ambient concentration.

11.2 DATA SOURCES

11.2.1 Meteorological Data

The dispersion model to be described in Section 11.3 required input of annual average wind speed and frequency of occurrence of wind from each compass direction. These data were obtained for most of the sites from the South Coast Air Quality Management District (SCAQMD). In other cases (Kaiser, Johns-Manville, Dow and DuPont), only daily average wind speed and frequency data were available. In all cases, we used data from the meteorological station nearest the modeled emission source. Table 11.2-1 summarizes the

Table 11.2-1
METEOROLOGICAL DATA BASE

Plant	Observation Site (Distance from Plant)	Data Source	Period of Observation	Remarks
Allied Chemical, El Segundo	Lennox (3 miles)	SCAQMD	1971-1974	Averaged hourly readings available
Stauffer Chemical, Carson	Long Beach (3 miles)	SCAQMD	1962-1974	Averaged hourly readings available; offsite storage tanks approximately 5 miles from meteorology site
Dow, Pittsburg DuPont, Antioch	Pittsburg (<5 miles to Antioch)	Dow	1956-1974	Daily and averaged wind rose only-no hourly data available
Kaiser Steel, Fontana	Fontana <3 miles	SCAQMD	1978-1979	Two years of hourly/daily data printout made available (33000 entries); daily averages estimated as only practical alternative
Johns Manville, Stockton	Stockton (1 mile)	NOAA	1941-1970	No hourly data, estimates based on monthly prevalence of directions and speed
RSR, City of Industry	Whittier (4 miles)	SCAQMD	1969-1973	Averaged hourly readings available

meteorological data base for each site. Wind speed and wind direction frequency data used in the model are provided in Appendix G.

11.2.2 Population Data

In order to assess population exposure in the same way for all the sources, we defined a 10-square mile "impact area" around each plant. This size was chosen since it was found in most cases to include all distances at which incremental ground level concentrations due to plant emissions would exceed general urban ambient levels for the pollutant in question. In most cases, the plant was placed at the center of the impact area. Where winds were predominantly from one sector or a few adjacent sectors, or where an unpopulated area (e.g., the Pacific Ocean) adjoined one side of a plant, the impact area was defined to lie immediately downwind of the site.

Once the impact areas were defined, we obtained Thomas Brothers maps of all census tracts within them. These maps are provided in Appendix H. Census tract populations were obtained from the 1980 U.S. Census. The population of each tract was assumed to lie at the centroid, except when the tract was large and most of the population was concentrated away from the centroid; in the latter case, the best-defined population center was used. Radial and angular distances from the sources to the population centers were then determined.

11.3 DISPERSION MODELING APPROACH

In order to estimate population exposures in the census tracts surrounding each source, a simple Gaussian dispersion model was used. Use of a more sophisticated model was inappropriate given the uncertainty in our emission rate estimates. It is questionable whether any real gain in accuracy would have resulted.

The well-known Gaussian dispersion formula is (Porter, 1976):

$$C = \frac{10^6 Q}{\pi u \sigma_z \sigma_y} \exp \left[-\frac{1}{2} \left(\frac{H}{\sigma_z} \right)^2 \right] \exp \left[-\frac{1}{2} \left(\frac{y}{\sigma_y} \right)^2 \right] \quad (11.3-1)$$

where

- C = ground level concentration in ($\mu\text{g}/\text{m}^3$)
- Q = emission rate (g/s)
- u = average wind speed at the physical stack height (m/s)
- σ_z = standard deviation of the vertical concentration distribution

- σ_y = standard deviation of the horizontal concentration distribution
- H = effective stack height (m)
- y = is the crosswind distance from the plume centerline to the receptor point (m)

This equation was assumed to provide hourly average ground level concentrations (Ranzieri, 1982). The values for the standard deviations σ_y and σ_z are functions of the downwind distance, x:

$$\sigma_z = ax^b \quad (11.3-2)$$

$$\sigma_y = cx^d \quad (11.3-3)$$

where a, b, c, and d are constants that fit the function to the empirical curves presented in Turner (1970). The wind speed at physical stack height is given by the equation:

$$u = u_0 \left(\frac{h_s}{h_0} \right)^p \quad (11.3-4)$$

where

- u = wind speed at physical stack height (m/s)
- u_0 = measured wind speed (m/s)
- h_s = physical stack height (m)
- h_0 = the height at which the known wind speed was measured (m) and
- p = an empirical constant which varies with stability class*

Lacking data on the heights at which the all known wind speeds were measured, we followed common practice and assumed a value of 10 m for h_0 .

Trial calculations showed the value of the plume rise for all the sources except RSR, Johns-Manville and the Kaiser final cooler cooling tower to be negligible (i.e. less than one meter). Plume rise formulas developed by Christiansen (1975) and cited by Porter (1976) were used for the exceptions. The rise was assumed to be momentum-dominated for RSR, Johns-Manville and Kaiser cooling tower, and bouyancy-dominated for the Kaiser coke ovens.

As was discussed above, the radial and angular distances from a source to each surrounding census tract were determined. Wind direction and

*See Busse, 1973

speed data, meanwhile, were obtained for each of the 16 major compass points. To calculate the concentration at a given point, it was first necessary to determine the compass sector in which the point lay. Figure 11.3-1 gives an example for a census tract at r km from a source and at 30 degrees from a reference angle, which we defined as north (0 degrees). As seen in the figure, this point lies in a sector bounded by the NNE (22.5 degrees) and NE (45 degrees) compass directions. The calculation was performed once for every hour of the day since annually averaged values of hourly wind speed were available. The following schedule of hourly stability class was determined to be consistent with the relationships summarized by Turner (1967), given the observed distribution of wind speeds at our meteorological measurement stations. The schedule was modified slightly at the suggestion of the ARB (Ranzieri, 1982).

Hour	Class	Hour	Class
0	F	13	B
1	F	14	B
2	F	15	B
3	F	16	B
4	F	17	B
5	F	18	DN
6	F	19	DN
7	DD	20	F
8	B	21	F
9	B	22	B
10	B	23	B
11	B		
12	B		

Using the above equations and adjustments, the concentration at the point of interest was then calculated as the sum of the concentrations resulting from plumes having the bounding compass directions as centerlines. If the angular distance to the point was congruent with a compass direction, then only one calculation was necessary. Let $C(\theta_1, t_i)$ and $C(\theta_2, t_i)$ be the concentrations calculated at hour i for compass directions θ_1 and θ_2 , respectively. As discussed in Section 11.2, our meteorological data in most cases included the frequency of wind direction for each hour of the day. Let $f(\theta_1, t_i)$ and $f(\theta_2, t_i)$ be the probabilities of occurrence of wind in the

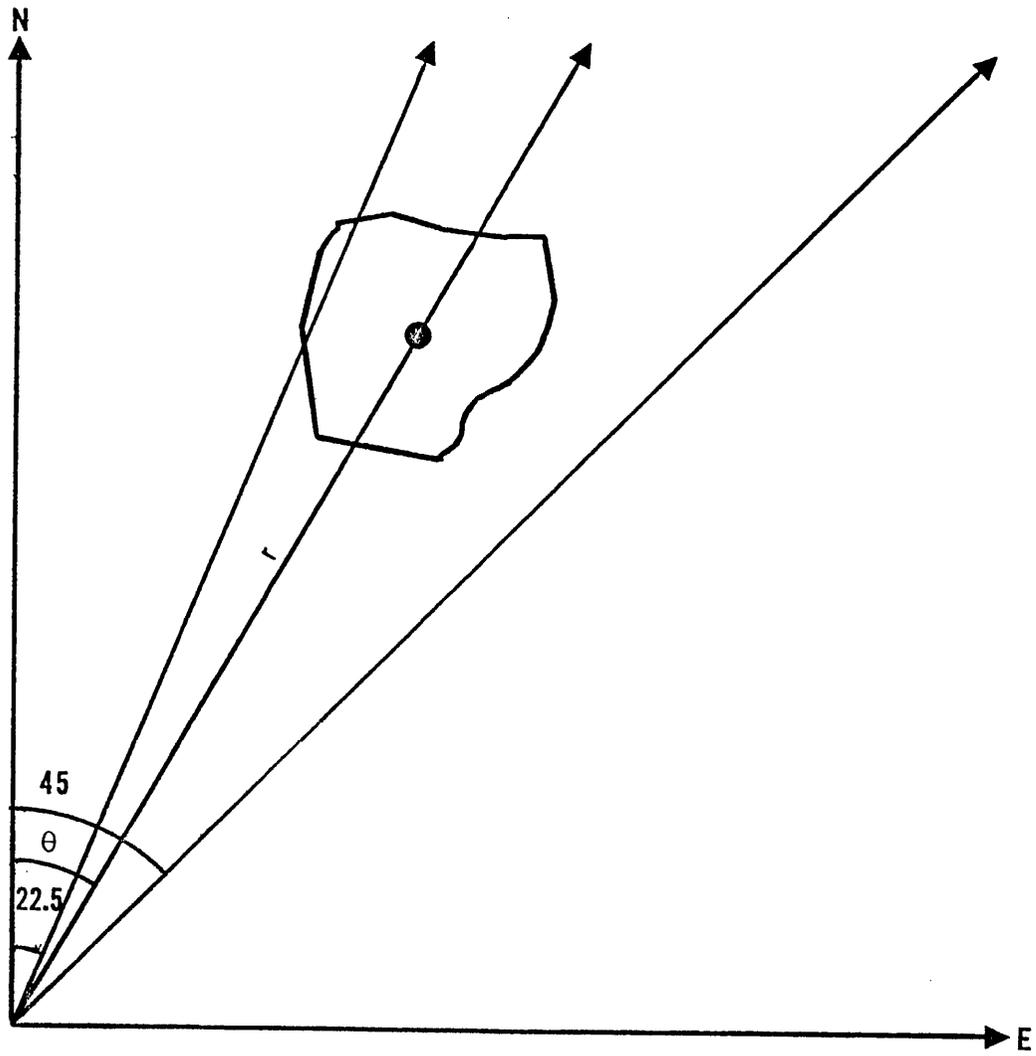


Figure 11.3-1 Determination of Compass Position of Census Tract Centroid.

directions θ_1 and θ_2 , respectively at hour i . Then the expected value of the concentration at the point in question at hour i is:

$$C(t_i) = f(\theta_1, t_i)C(\theta_1, t_i) + f(\theta_2, t_i)C(\theta_2, t_i) \quad (11.3-5)$$

The average annual exposure was then calculated as the average exposure on this composite day:

$$C = (1/24) \sum_{i=0}^{23} C(t_i) \quad (11.3-6)$$

The model was programmed in Applesoft BASIC on an Apple II microcomputer having 48 K bytes of random access memory and a disk storage capability. The program, which is included as Appendix I, was compiled with an On-Line Systems, Inc. Expediter II BASIC compiler, in order to decrease running time.

11.4 POPULATION EXPOSURE FROM SURVEYED SOURCES

11.4.1 Modeling Results

Using the modeling parameters listed in Table 11.4-1, the incremental population exposure due to each of the stationary sources was computed. Tables 11.4-2 through 11.4-12 show the modeled annual average incremental exposure for each census tract around each plant. Census tract numbers appear on the maps in Appendix H). The cumulative population column specifies the total population exposed to all concentrations equal to or greater than the corresponding source weighted concentration entry of the table. Figures 11.4-1 through 11.4-11 illustrate the cumulative population exposure versus incremental concentration above ambient background concentrations. Table 11.4-13 lists ranges of typical urban ambient concentrations for each substance. These were used to assess the incremental contribution of the plant emissions. Table 11.4-14 summarizes the incremental population exposure due to each source. These were based upon annual average source strengths and do not reflect transients in emissions or worst case meteorological conditions. Note that no attempt was made to assess the potential health effects or risks to the public due to the resultant combined exposure.

Table 11.4-1
VALUES OF MODELING PARAMETERS USED FOR POPULATION EXPOSURE ESTIMATES

Source	Initial Source Height(m)	Plume Rise Domination	Exit Velocity (m/s)	Exit Temperature (°K)	"Stack" Radius (m)	Emission Rate (g/s)
RSR/Quemetco	18	Momentum	17.8	NN ^a	0.54	5.1 x 10 ⁻⁴ (As)
Kaiser Steel Corp. - Coke Ovens	19	Buoyancy	1.0	589	1.33 ^c	0.12 (PAH) 1.25 (benzene) 3.23 (benzene)
- Cooling Tower	15	Momentum	2.7	NN ^a	3.38 ^c	
Johns Manville	30	Momentum	11.9	NN ^a	0.43	2.8 x 10 ⁻³ (asbestos)
Dow Chemical	10	NC ^b	NC	NC	NA	0.38 - 0.47 (perc & carbon tet)
Allied Chemical	10	NC	NC	NC	NC	0-0.0047 (chloroform) 0.053 - 0.084 (carbon tet) 0.026 - 0.044 (combined)
Dupont	10	NC	NC	NC	NC	0.024 - 0.031 (carbon tet)
Stauffer Chemical - Onsite Tanks - Offsite Tanks	0 0	NC NC	NC NC	NC NNC	NC NC	0.50 (EDC) 0.34 (EDC)

^a NN = Not necessary for calculation of plume rise.

^b NC = Plume rise not calculated.

^c Effective radius assumed equal to that of a circle having the same horizontal area as the source.

Table 11.4-2
ESTIMATED POPULATION EXPOSURE TO ARSENIC FROM RSR
SECONDARY LEAD SMELTER, CITY OF INDUSTRY

Census Tract	Concentration for 1 g/s Emission Rate ($\mu\text{g}/\text{m}^3$)	Source-Weighted Concentration (ng/m^3)		Census Tract Population	Cumulative Persons Exposed
		Low	High		
4068.0	0.578	0.068	0.29	3,532	117,268
4074.0	0.696	0.082	0.35	1,533	113,736
4069.0	0.696	0.082	0.35	6,369	112,203
4067.0	0.705	0.083	0.36	7,079	105,834
4071.01	0.720	0.084	0.37	4,357	98,755
4075.0	0.828	0.097	0.42	5,442	94,398
4086.01	0.829	0.097	0.42	7,099	88,956
4084.01	0.832	0.098	0.42	3,531	81,857
4085.01	0.878	0.10	0.45	2,472	78,326
4073.0	0.963	0.11	0.49	7,220	75,854
4071.02	0.965	0.11	0.49	4,547	68,634
4070.0	1.103	0.13	0.56	8,158	64,087
4082.02	1.110	0.13	0.56	2,112	55,929
4077.0	1.113	0.13	0.56	8,893	53,817
4076	1.855	0.22	0.94	6,267	44,924
4072	1.873	0.22	0.95	6,195	38,657
4340	2.101	0.25	1.1	9,168	32,462
4083.01	2.150	0.25	1.1	3,809	23,294
4085.02	2.223	0.26	1.1	6,496	19,485
4083.02	3.078	0.36	1.6	3,356	12,989
4083.03	3.149	0.37	1.6	3,893	9,633
4084.02	3.984	0.47	2.0	5,740	5,740

Table 11.4-3
ESTIMATED POPULATION EXPOSURE TO BENZENE FROM KAISER
STEEL CORPORATION STEEL MILL, FONTANA

Census Tract	Concentration for 1 g/s Emission Rate ($\mu\text{g}/\text{m}^3$)		Source-Weighted Concentration (ng/m^3)	Census Tract Population	Cumulative Persons Exposed
	Cool. Tower	Coke Oven			
20.0	0.162	0.162	0.73	39,428	72,196
28.0	0.721	0.779	3.3	4,404	32,768
23.0	0.921	0.957	4.2	5,698	28,364
24.0	1.292	1.678	6.3	6,058	22,666
31.0	1.496	1.626	6.9	4,890	166,608
22.0	1.433	1.997	7.1	5,773	11,718
25.0	2.483	3.155	12.0	5,945	5,945

Table 11.4-4
ESTIMATED POPULATION EXPOSURE TO CARCINOGENIC POLYCYCLIC AROMATIC
HYDROCARBONS FROM KAISER STEEL CORPORATION STEEL MILL, FONTANA

Census Tract	Concentration for 1 g/s Emission Rate ($\mu\text{g}/\text{m}^3$)		Source-Weighted Concentration (ng/m^3)	Census Tract Population	Cumulative Persons Exposed
	Cool. Tower	Coke Oven			
20	0.162		19	39,428	72,196
28	0.779		93	4,404	32,768
23	0.957		115	5,698	28,364
31	1.626		195	4,890	22,666
24	1.678		201	6,058	17,776
22	1.997		240	5,773	11,718
25	3.155		379	5,945	5,945

Table 11.4-5
ESTIMATED POPULATION EXPOSURE TO ASBESTOS FROM
JOHNS-MANVILLE PLANT, STOCKTON

Census Tract	Concentration for 1 g/s Emission Rate ($\mu\text{g}/\text{m}^3$)	Source-Weighted Concentration (pg/m^3)	Census Tract Population	Cumulative Persons Exposed
51.03	0.559	1.6	5,435	15,907
24.0	1.038	2.9	4,909	10,472
23.0	1.076	3.0	3,816	5,563
28.0	2.150	6.0	1,747	1,747

Table 11.4-6
ESTIMATED POPULATION EXPOSURE TO CARCINOGENS FROM TWO
CHEMICAL PLANTS IN CONTRA COSTA COUNTY, CALIFORNIA

Census Tract	Concentration for 1 g/s Emission Rate ($\mu\text{g}/\text{m}^3$)	Source-Weighted Concentration (ng/m^3)		Census Tract Population	Cumulative Persons Exposed
		Low	High		
Dow, Pittsburg (carbon tetrachloride and perchloroethylene)					
3060.0	1.511	945	1335	7,817	20,309
3131.02	1.550	978	1372	1,696	12,492
3050.0	1.920	1211	1692	5,241	10,796
3072.01	2.207	1393	2030	2,986	5,555
3072.02	2.241	1410	2068	2,569	2,569
DuPont, Antioch (carbon tetrachloride)					
3020.0	2.471	59.0	77.0	7,098	7,098

Table 11.4-7
ESTIMATED POPULATION EXPOSURE TO CHLOROFORM FROM
ALLIED CHEMICAL PLANT, EL SEGUNDO

Census Tract	Concentration for 1 g/s Emission Rate ($\mu\text{g}/\text{m}^3$)	Source-Weighted Concentration (ng/m^3)	Census Tract Population	Cumulative Persons Exposed
6500.02	1.174	6	6,276	161,278
6037.02	1.626	8	4,859	155,002
6005.02	1.634	8	3,078	150,143
6041.0	1.650	8	5,065	147,065
6037.01	1.676	8	6,181	142,000
6205.01	1.842	9	5,716	135,819
6020.02	1.889	9	2,893	130,103
6040.0	1.932	9	7,077	127,210
6205.02	2.108	10	6,667	120,133
6208.0	2.190	10	7,074	113,466
6025.03	2.224	10	4,612	106,392
6025.01	2.339	11	5,886	101,780
6038.0	2.359	11	5,754	95,894
6021.01	2.422	11	7,430	90,184
6025.02	2.785	13	4,983	82,710
6021.02	2.816	13	6,561	77,727
6039.0	3.102	15	5,564	71,166
6024.01	3.425	16	7,453	65,602
6209.02	3.630	17	3,142	58,149
6204.0	4.361	20	3,835	55,007
6024.02	4.473	21	5,296	51,172
6022.0	4.677	22	4,662	45,876
6209.01	6.036	28	2,651	41,214
6023.01	6.833	32	5,494	38,563
6201.0	7.835	37	7,482	33,069
6200.0	8.899	42	6,210	25,587
6023.02	11.547	54	3,352	19,377
6203.02	21.153	99	6,546	16,025
6203.03	22.574	106	4,250	9,479
6202.0	24.521	115	1,185	5,229
6203.01	43.056	202	4,044	4,044

Table 11.4-8
ESTIMATED POPULATION EXPOSURE TO CARBON TETRACHLORIDE
FROM ALLIED CHEMICAL PLANT, EL SEGUNDO

Census Tract	Concentration for 1 g/s Emission Rate ($\mu\text{g}/\text{m}^3$)	Source-Weighted Concentration (ng/m^3)		Census Tract Population	Cumulative Persons Exposed
		Low	High		
6500.02	1.174	62	99	6,276	161,278
6037.02	1.626	86	140	4,859	155,002
6005.02	1.634	87	140	3,078	150,143
6041.0	1.650	87	140	5,065	147,065
6037.01	1.676	89	140	6,181	142,000
6205.01	1.842	98	160	5,716	135,819
6020.02	1.889	100	160	2,893	130,103
6040.0	1.932	100	160	7,077	127,210
6205.02	2.108	110	180	6,667	120,133
6208.0	2.190	120	180	7,074	113,466
6025.03	2.224	120	190	4,612	106,392
6025.01	2.339	120	200	5,886	101,780
6038.0	2.359	120	200	5,754	95,894
6021.01	2.422	130	200	7,430	90,184
6025.02	2.785	150	230	4,983	82,710
6021.02	2.816	150	240	6,561	77,727
6039.0	3.102	160	260	5,564	71,166
6024.01	3.425	180	290	7,453	65,602
6209.02	3.630	190	300	3,142	58,149
6204.0	4.361	230	370	3,835	55,007
6024.02	4.473	240	380	5,296	51,172
6022.0	4.677	250	390	4,662	45,876
6209.01	6.036	320	510	2,651	41,214
6023.01	6.833	360	570	5,494	38,563
6201.0	7.835	420	660	7,482	33,069
6200.0	8.899	470	750	6,210	25,587
6023.02	11.547	610	970	3,352	19,377
6203.02	21.153	1,100	1,800	6,546	16,025
6203.03	22.574	1,200	1,900	4,250	9,479
6202.0	24.521	1,300	2,100	1,185	5,229
6203.01	43.056	2,300	3,600	4,044	4,044

Table 11.4-9
 ESTIMATED POPULATION EXPOSURE TO CARBON TETRACHLORIDE AND
 CHLOROFORM FROM ALLIED CHEMICAL PLANT, EL SEGUNDO
 (Six months/year assumed for each feedstock)

Census Tract	Concentration for 1 g/s Emission Rate ($\mu\text{g}/\text{m}^3$)	Source-Weighted Concentration (ng/m^3)		Census Tract Population	Cumulative Persons Exposed
		Low	High		
6500.02	1.174	31	52	6,276	161,278
6037.02	1.626	42	72	4,859	155,002
6005.02	1.634	42	72	3,078	150,143
6041.0	1.650	43	73	5,065	147,065
6037.01	1.676	44	74	6,181	142,000
6205.01	1.842	48	81	5,716	135,819
6020.02	1.889	49	83	2,893	130,103
6040.0	1.932	50	85	7,077	127,210
6205.02	2.108	55	93	6,667	120,133
6208.0	2.190	57	96	7,074	113,466
6025.03	2.224	58	98	4,612	106,392
6025.01	2.339	61	100	5,886	101,780
6038.0	2.359	61	100	5,754	95,894
6021.01	2.422	63	110	7,430	90,184
6025.02	2.785	72	120	4,983	82,710
6021.02	2.816	73	120	6,561	77,727
6039.0	3.102	81	140	5,564	71,166
6024.01	3.425	89	150	7,453	65,602
6209.02	3.630	94	160	3,142	58,149
6204.0	4.361	110	190	3,835	55,007
6024.02	4.473	120	200	5,296	51,172
6022.0	4.677	120	210	4,662	45,876
6209.01	6.036	160	270	2,651	41,214
6023.01	6.833	180	300	5,494	38,563
6201.0	7.835	200	350	7,482	33,069
6200.0	8.899	230	390	6,210	25,587
6023.02	11.547	300	510	3,352	19,377
6203.02	21.153	550	930	6,546	16,025
6203.03	22.574	590	990	4,250	9,479
6202.0	24.521	640	1,100	1,185	5,229
6203.01	43.056	1,200	1,900	4,044	4,044

Table 11.4-10
 ESTIMATED POPULATION EXPOSURE TO CARBON TETRACHLORIDE
 FROM ALLIED CHEMICAL PLANT, EL SEGUNDO, DURING SIX-HOUR
 OFFLOADING FROM MIDNIGHT TO 6 A.M.

Census Tract	Source-Weighted Concentration ^a ($\mu\text{g}/\text{m}^3$)	Census Tract Population	Cumulative Persons Exposed
6500.02	2.6	6,276	161,278
6037.02	3.6	4,859	155,002
6005.02	4.1	3,078	150,143
6041.0	3.7	5,065	147,065
6037.01	3.7	6,181	142,000
6205.01	4.3	5,716	135,819
6020.02	4.7	2,893	130,103
6040.0	4.3	7,077	127,210
6205.02	4.9	6,667	120,133
6208.0	4.9	7,074	113,466
6025.03	5.1	4,612	106,392
6025.01	5.1	5,886	101,780
6038.0	5.2	5,754	95,894
6021.01	6.0	7,430	90,184
6025.02	6.1	4,983	82,710
6021.02	7.0	6,561	77,727
6039.0	6.8	5,564	71,166
6024.01	7.5	7,453	65,602
6209.02	8.0	3,142	58,149
6204.0	10.0	3,835	55,007
6024.02	10.0	5,296	51,172
6022.0	11.0	4,662	45,876
6209.01	13.0	2,651	41,214
6023.01	15.0	5,494	38,563
6201.0	17.0	7,482	33,069
6200.0	19.0	6,210	25,587
6023.02	25.0	3,352	19,377
6203.02	45.0	6,546	16,025
6203.03	47.0	4,250	9,479
6202.0	50.0	1,185	5,229
6203.01	91.0	4,044	4,044

^a Assuming 1.0 g/s emission rate from 0000 to 0600 hours.

Table 11.4-11
 ESTIMATED POPUATION EXPOSURE TO ETHYLENE DICHLORIDE
 FROM STAUFFER CHEMICAL PLANT, CARSON

Census Tract	Concentration for 1 g/s Emission Rate	Source-Weighted Concentration ($\mu\text{g}/\text{m}^3$)	Census Tract Population	Cumulative Persons Exposed
5724.0	1.801	0.90	1,153	58,821
5440.0	2.190	1.1	6,085	57,688
5438.01	5.048	2.5	3,683	51,583
5727.0	5.069	2.5	4,499	47,900
5726.0	5.944	3.0	4,068	43,401
5723.0	6.674	3.3	5,764	39,333
5725.0	7.892	3.9	2,892	33,569
5439.01	11.917	6.0	3,732	30,677
5437.03	14.197	7.1	3,295	26,945
5438.02	14.687	7.3	6,153	23,650
5433.03	17.273	8.6	6,578	17,497
5439.02	19.230	9.6	3,329	10,919
5437.02	20.801	11.0	4,683	7,590
5437.01	23.220	12.0	2,907	2,907

Table 11.4-12
 ESTIMATED POPULATION TO ETHYLENE DICHLORIDE FROM
 STAUFFER CHEMICAL OFF-SITE STORAGE

Census Tract	Concentration for 1 g/s Emission Rate	Source-Weighted Concentration ($\mu\text{g}/\text{m}^3$)	Census Tract Population	Cumulative Persons Exposed
2961.0	1.926	0.65	1,029	60,873
2966.0	3.921	1.1	4,043	59,844
2965.0	4.497	1.5	3,171	55,801
2962.0	4.561	1.6	5,518	52,630
2964.0	4.709	1.6	6,143	47,112
6099.0	7.657	2.6	1,988	40,969
2971.0	8.404	2.9	6,079	38,981
2967.0	9.887	3.4	1,949	32,902
2974.0	14.249	4.8	3,989	30,953
2968.0	17.235	5.9	3,311	26,964
2969.0	28.211	9.6	6,043	23,653
2973.0	39.992	14.0	2,587	17,610
2975	44.669	15.0	3,303	15,023
2976	402.159	140.0	4,960	11,720
2972.0	408.785	140.0	6,760	6,760

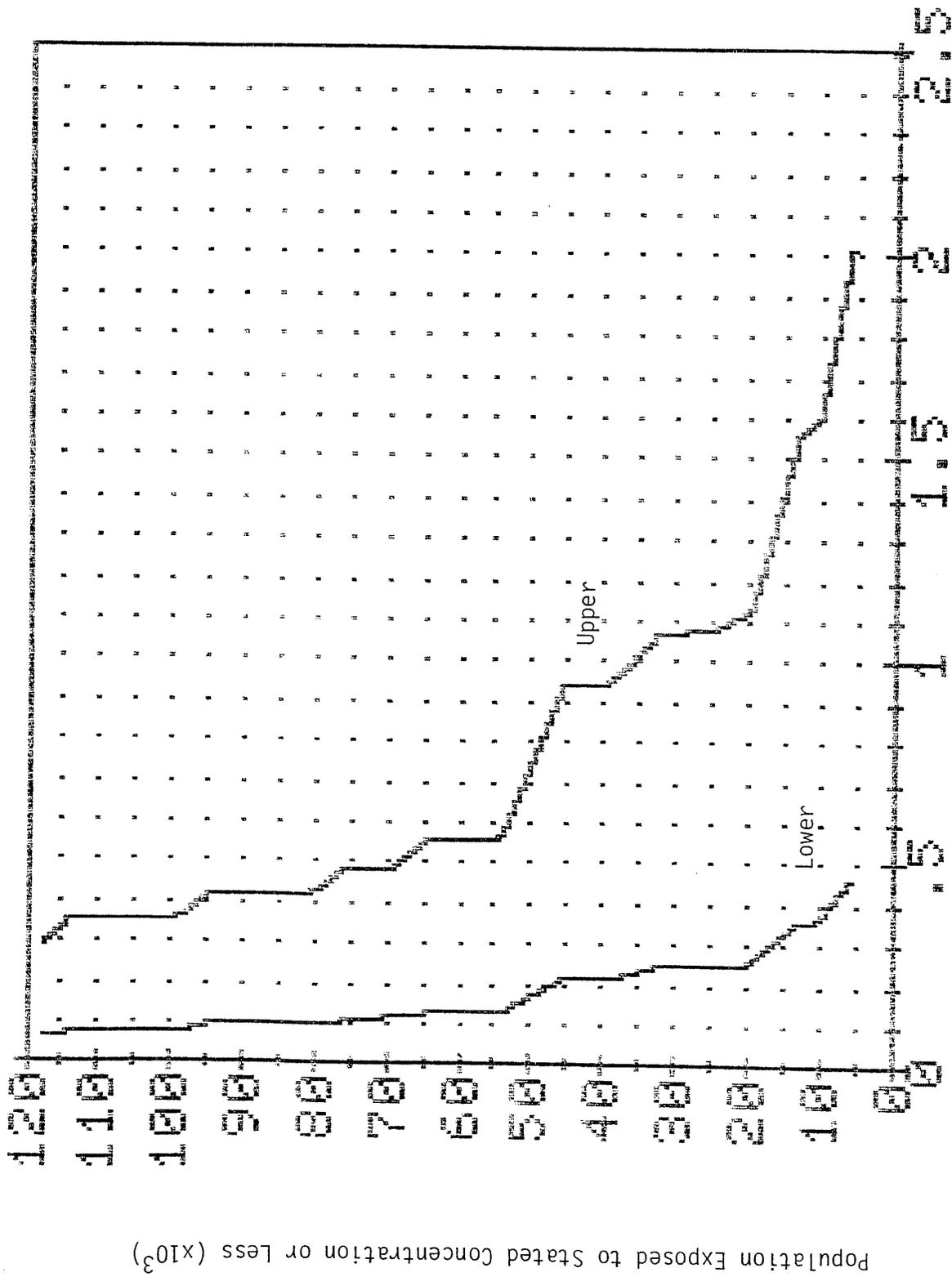


Figure 11.4-1 Cumulative Population Exposure to Arsenic from RSR Secondary Lead Smelter, City of Industry. (Curves Correspond to Upper and Lower Bounds on Emission Rate Estimate.)

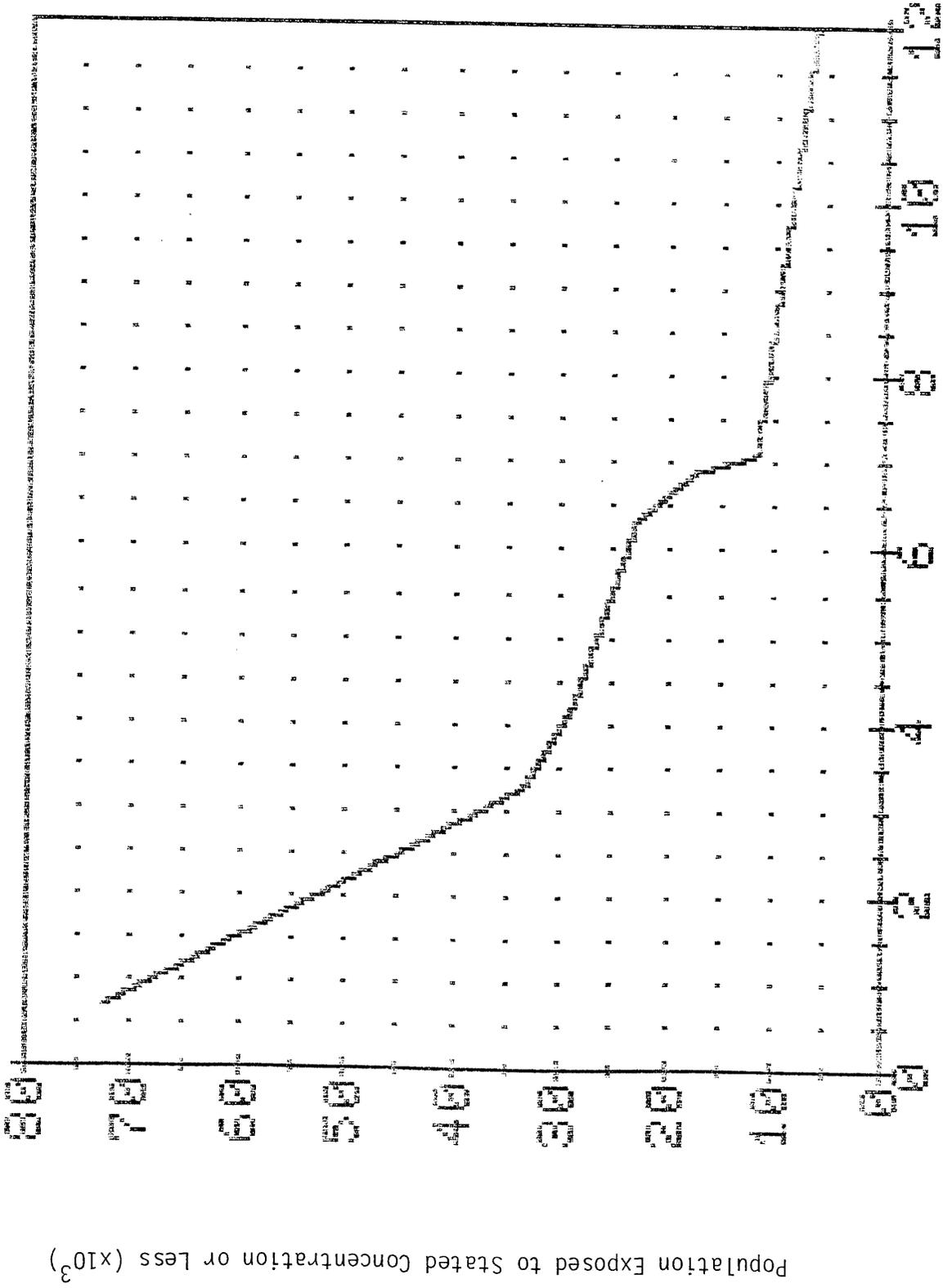


Figure 11.4-2 Cumulative Population Exposure to Benzene From Cooling Tower and Coke Ovens at Kaiser Steel Corporation Steel Mill, Fontana

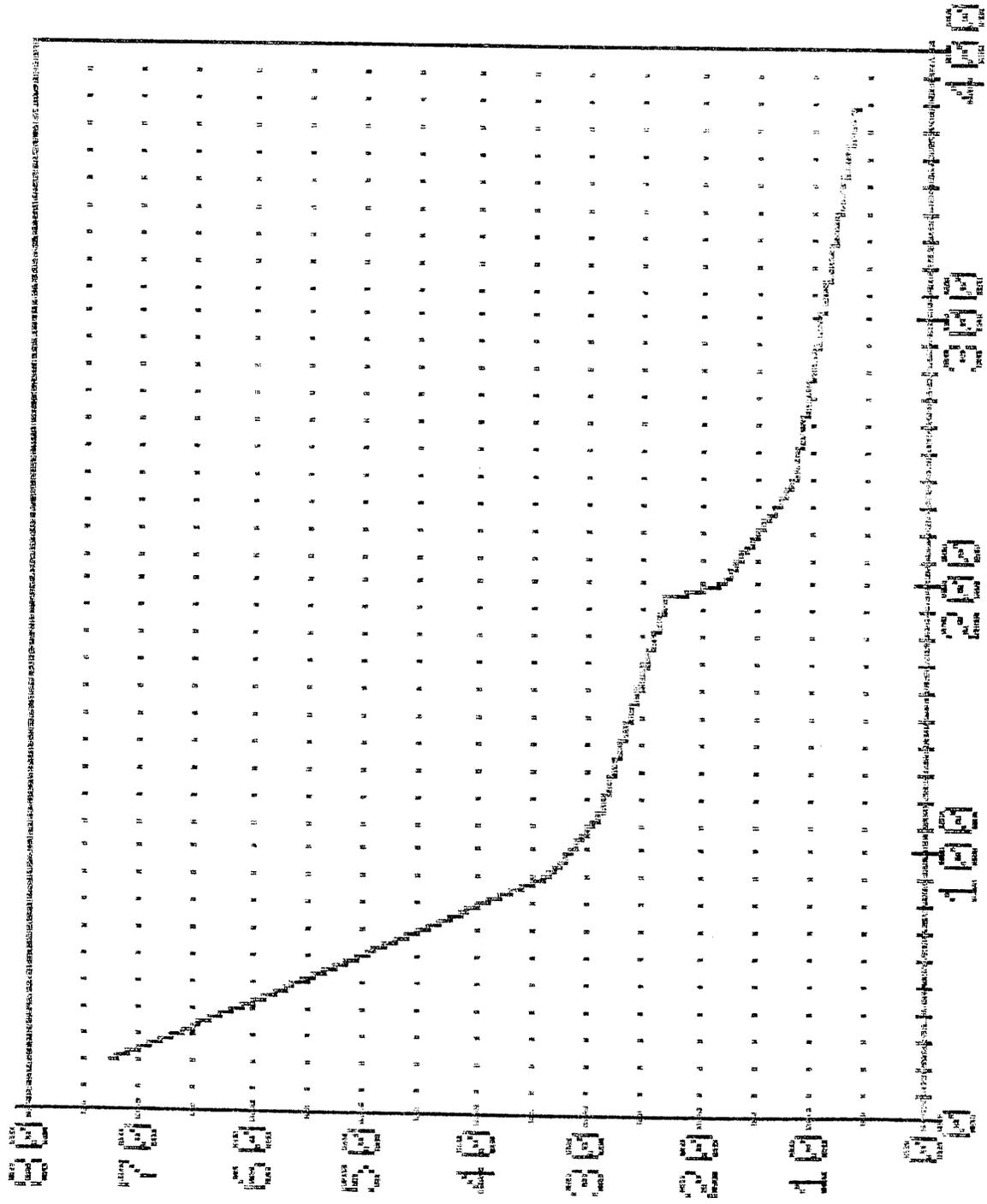
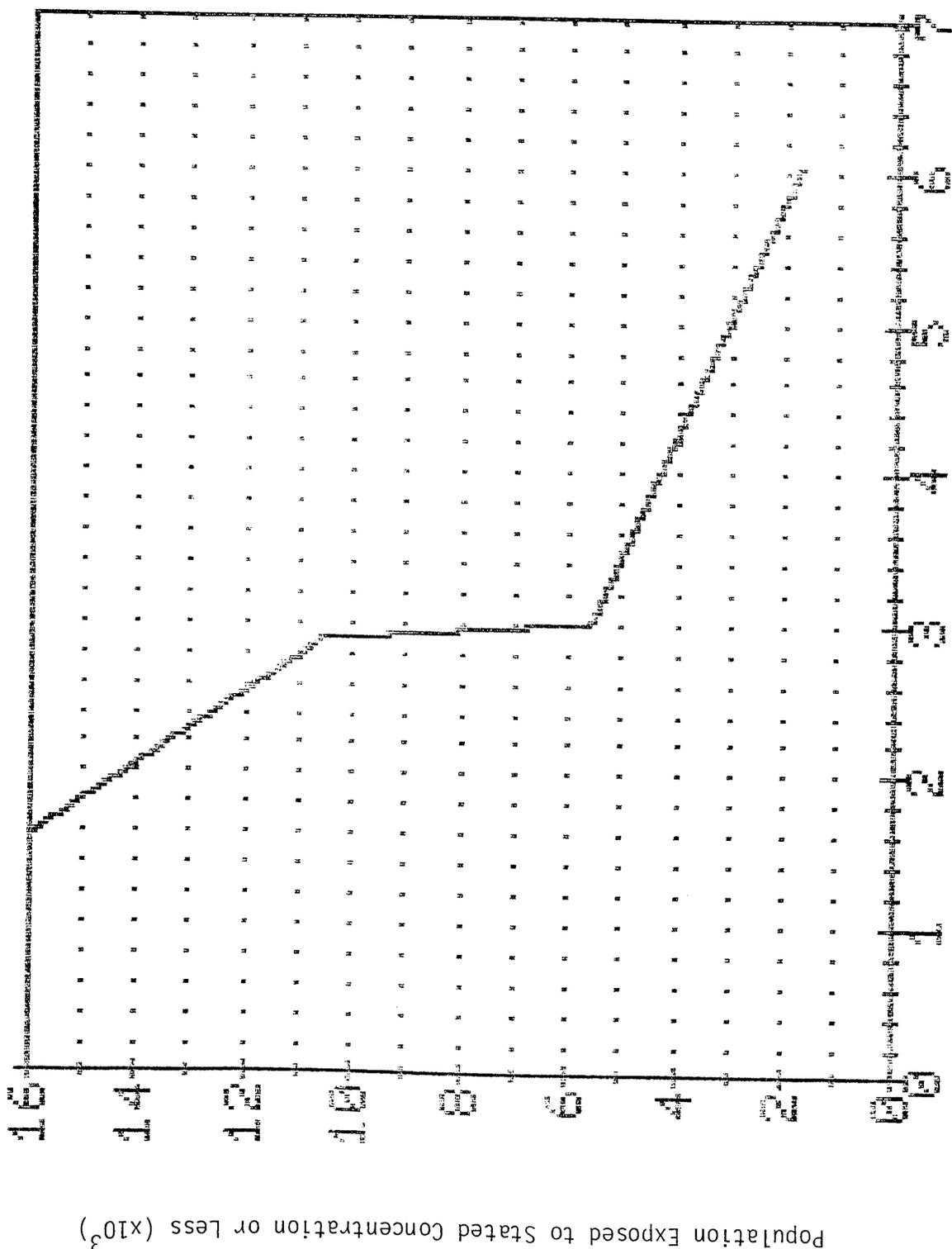


Figure 11.4-3 Cumulative Population Exposure to Carcinogenic Polycyclic Aromatic Hydrocarbons From Coke Ovens at Kaiser Steel Corporation Steel Mill, Fontana



Incremental Concentration (pg/m³)

Figure 11.4-4 Cumulative Population Exposure to Asbestos From Johns-Manville Plant, Stockton

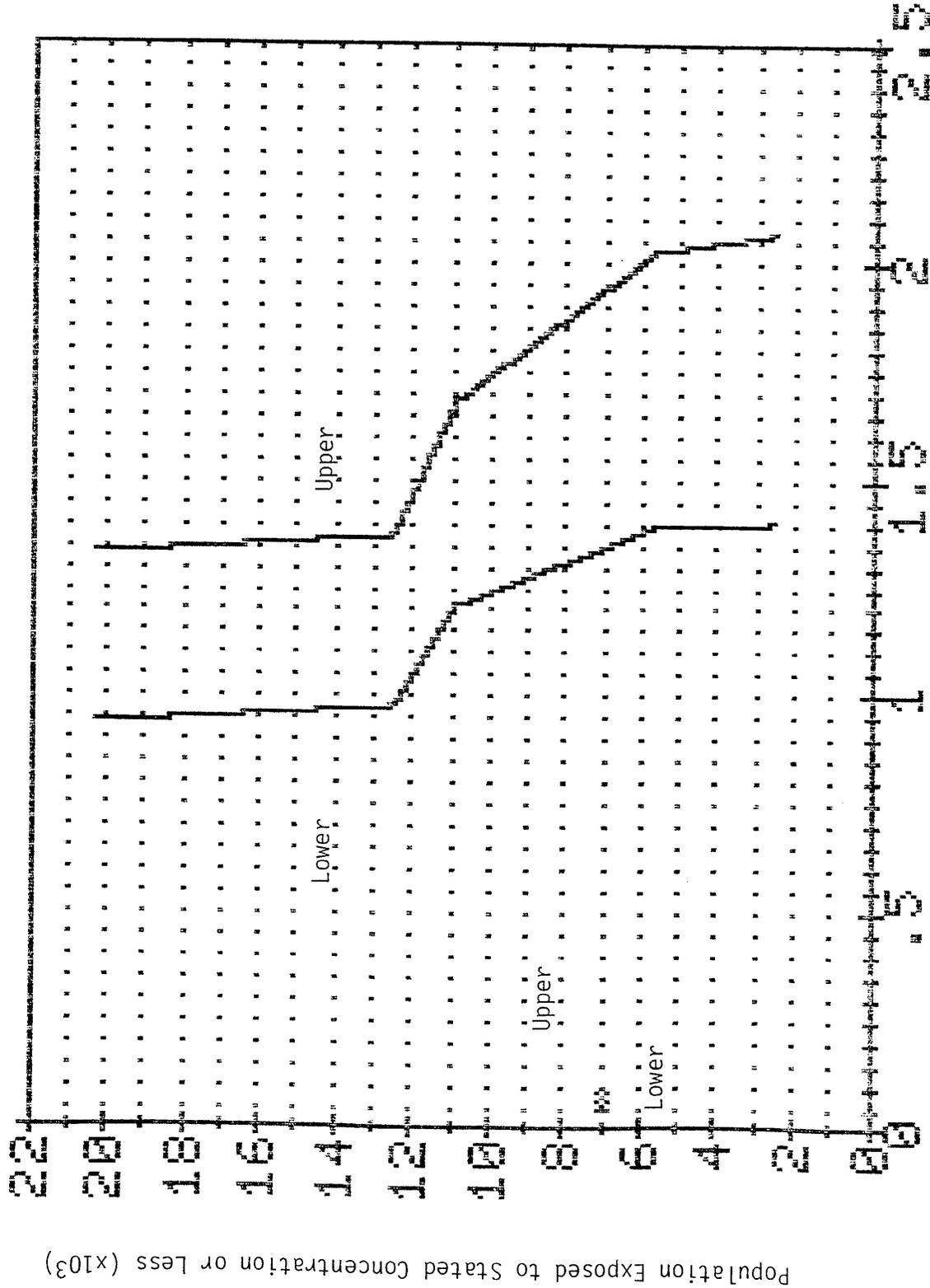


Figure 11.4-5. Cumulative Population Exposure to Perchloroethylene and Carbon Tetrachloride From Dow, Pittsburgh (Solid Lines) and to Carbon Tetrachloride From DuPont, Antioch (Xs). Results For Upper Lower Bounds on Emission Estimates Are Shown.

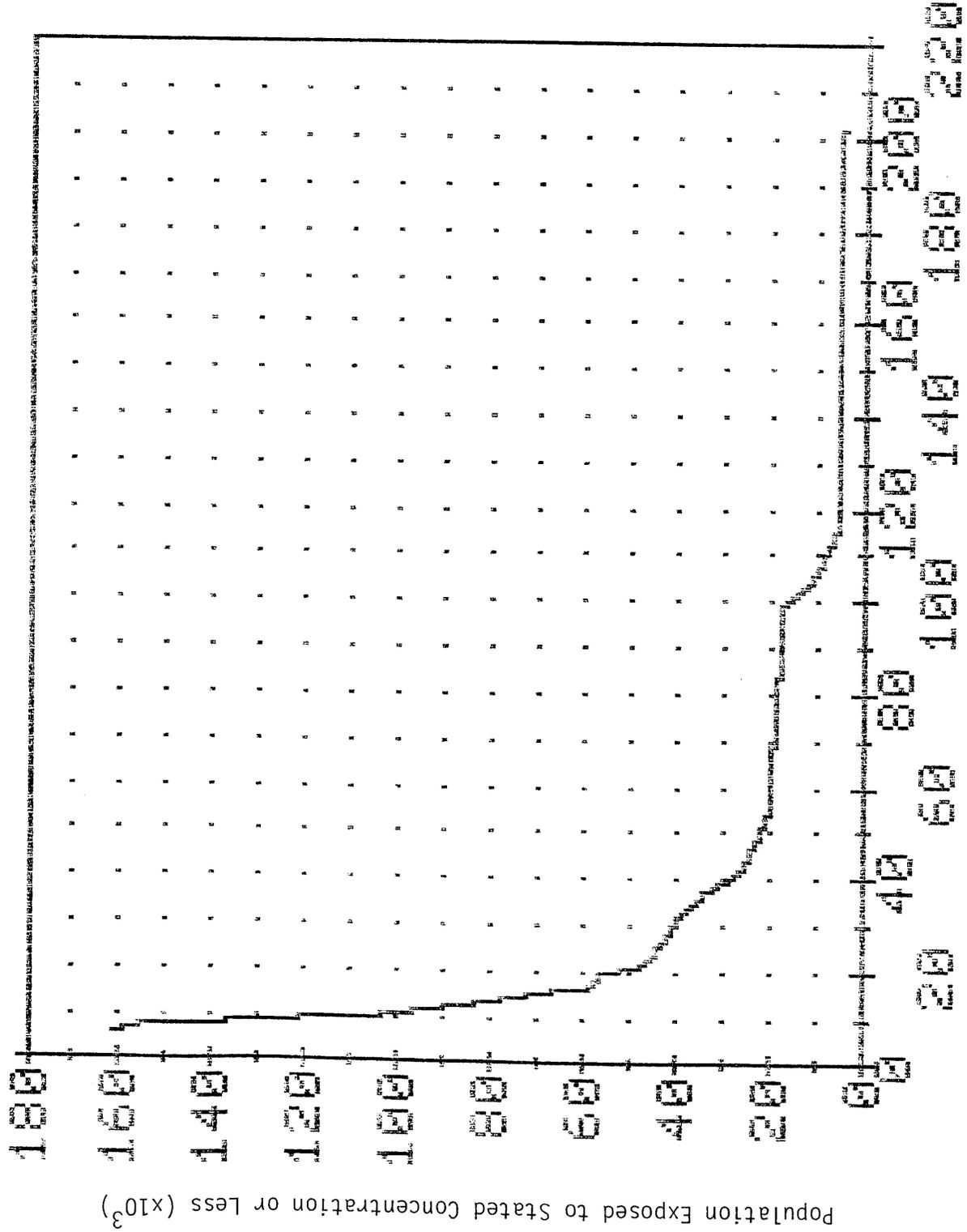


Figure 11.4-6 Cumulative Population Exposure to Chloroform From Allied Chemical, El Segundo

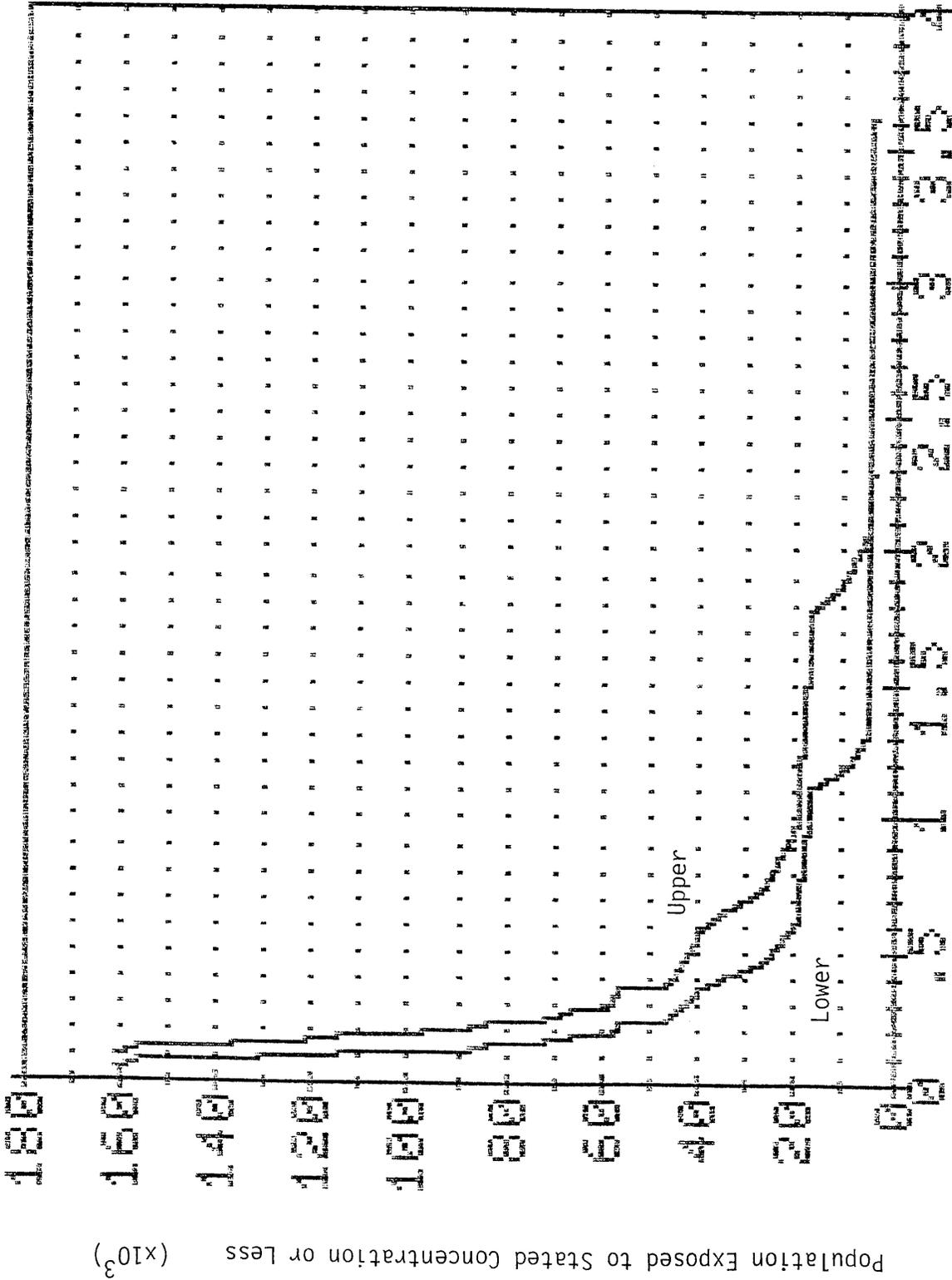


Figure 11.4-7 Cumulative Population Exposure to Carbon Tetrachloride From Allied Chemical, El Segundo. (Curves Correspond to Upper and Lower Bounds on Emission Rate Estimate.)

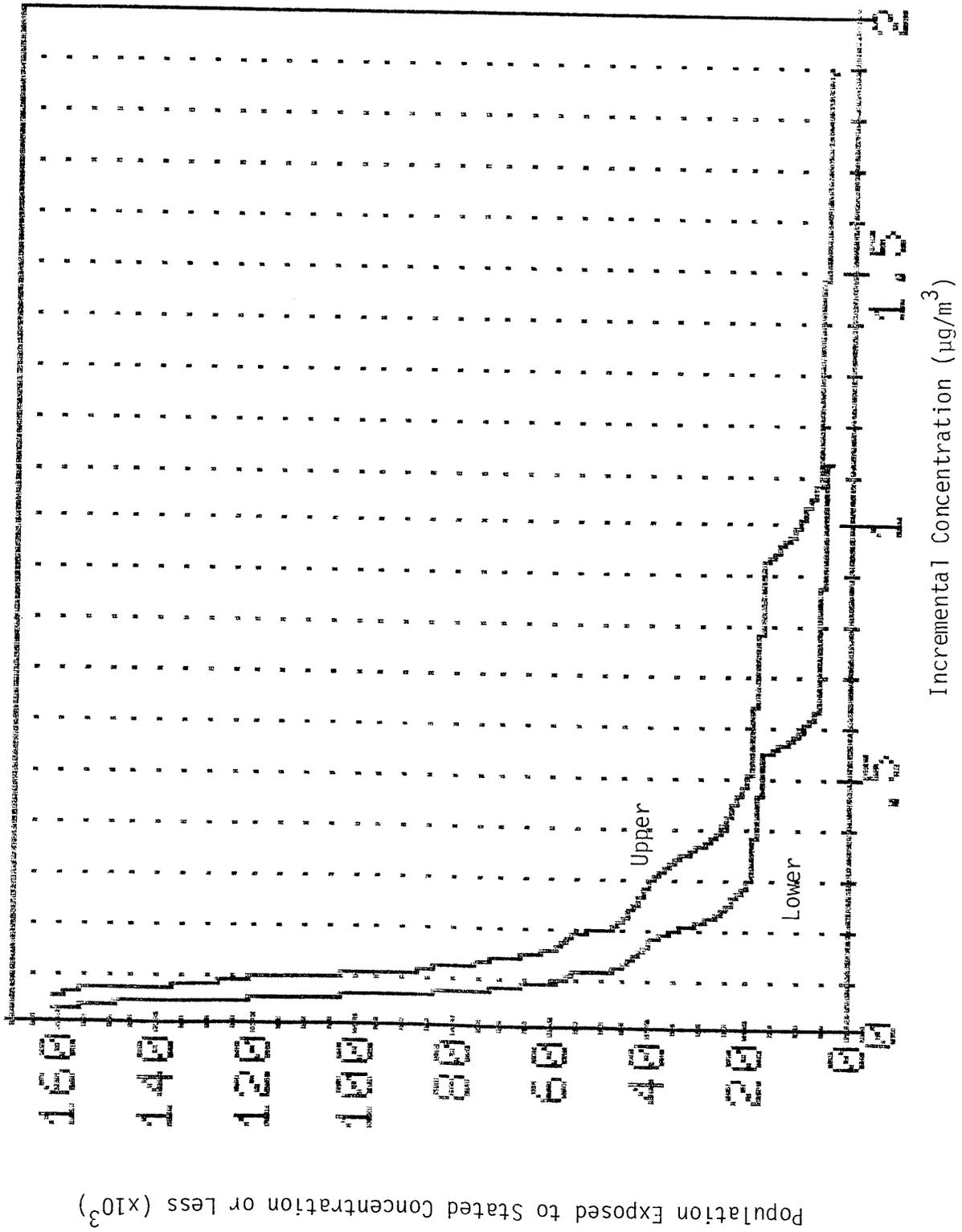


Figure 11.4-8 Cumulative Population Exposure to Carbon Tetrachloride and Chloroform From Allied Chemical, El Segundo, Assuming six-months Operation With Each Feedstock. (Curves Correspond to Upper and Lower Bounds on Emission Rate Estimate.)

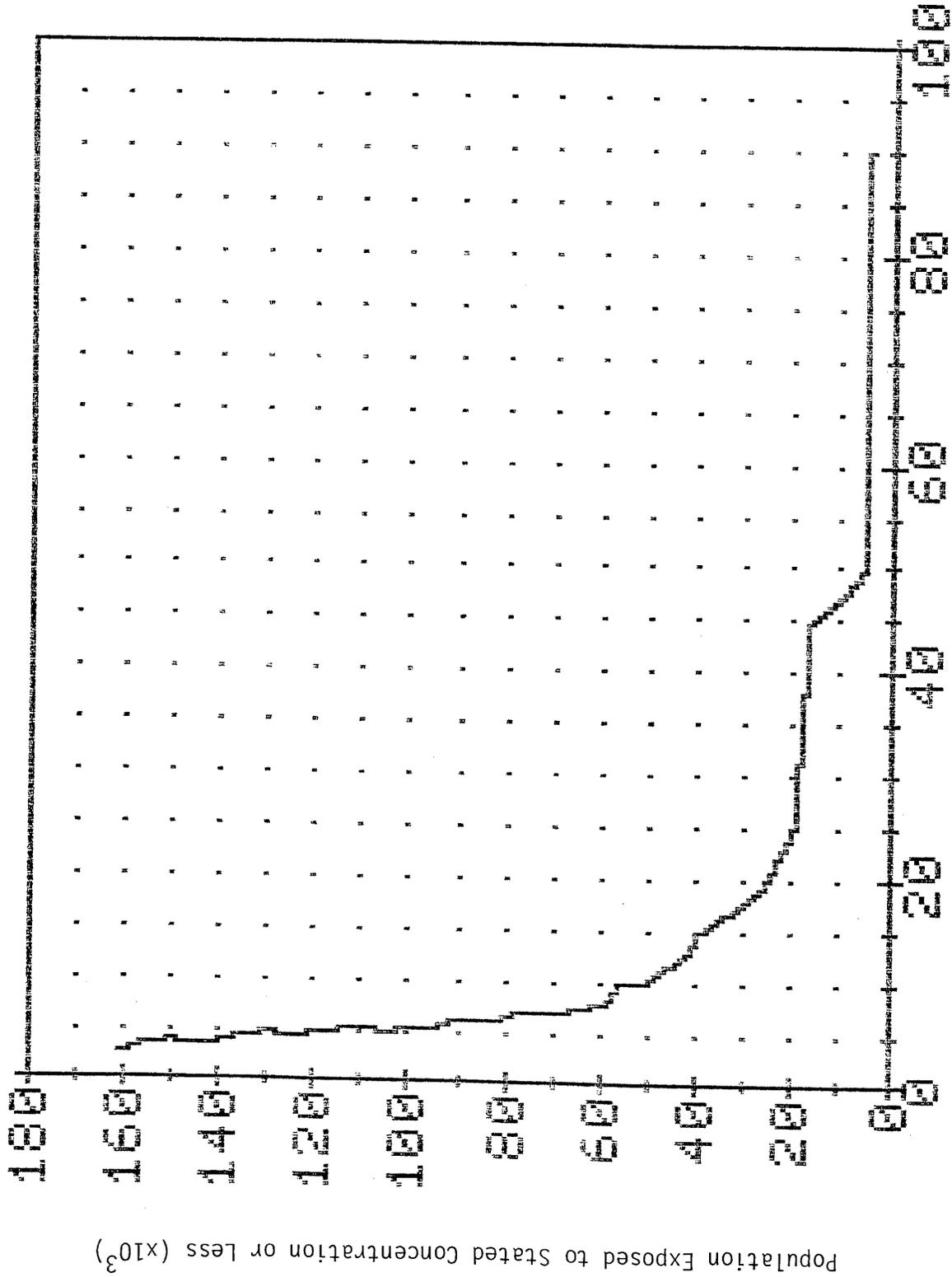


Figure 11.4-9 Cumulative Population Exposure to Carbon Tetrachloride From Allied Chemical, El Segundo, During Offloading From Midnight to 6 a.m.

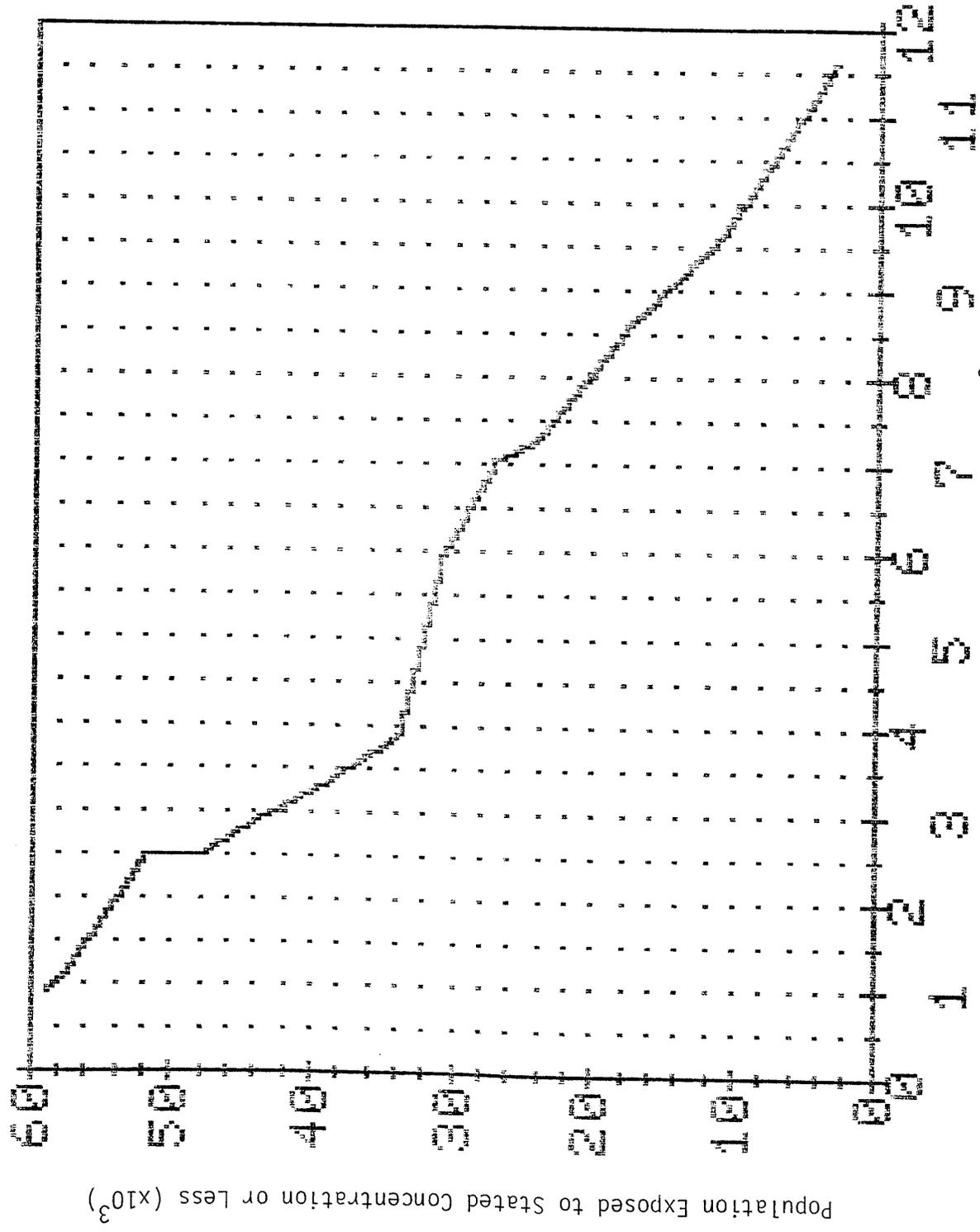


Figure 11.4-10 Cumulative Population Exposure to Ethylene Dichloride From Stauffer Plant, Carson.

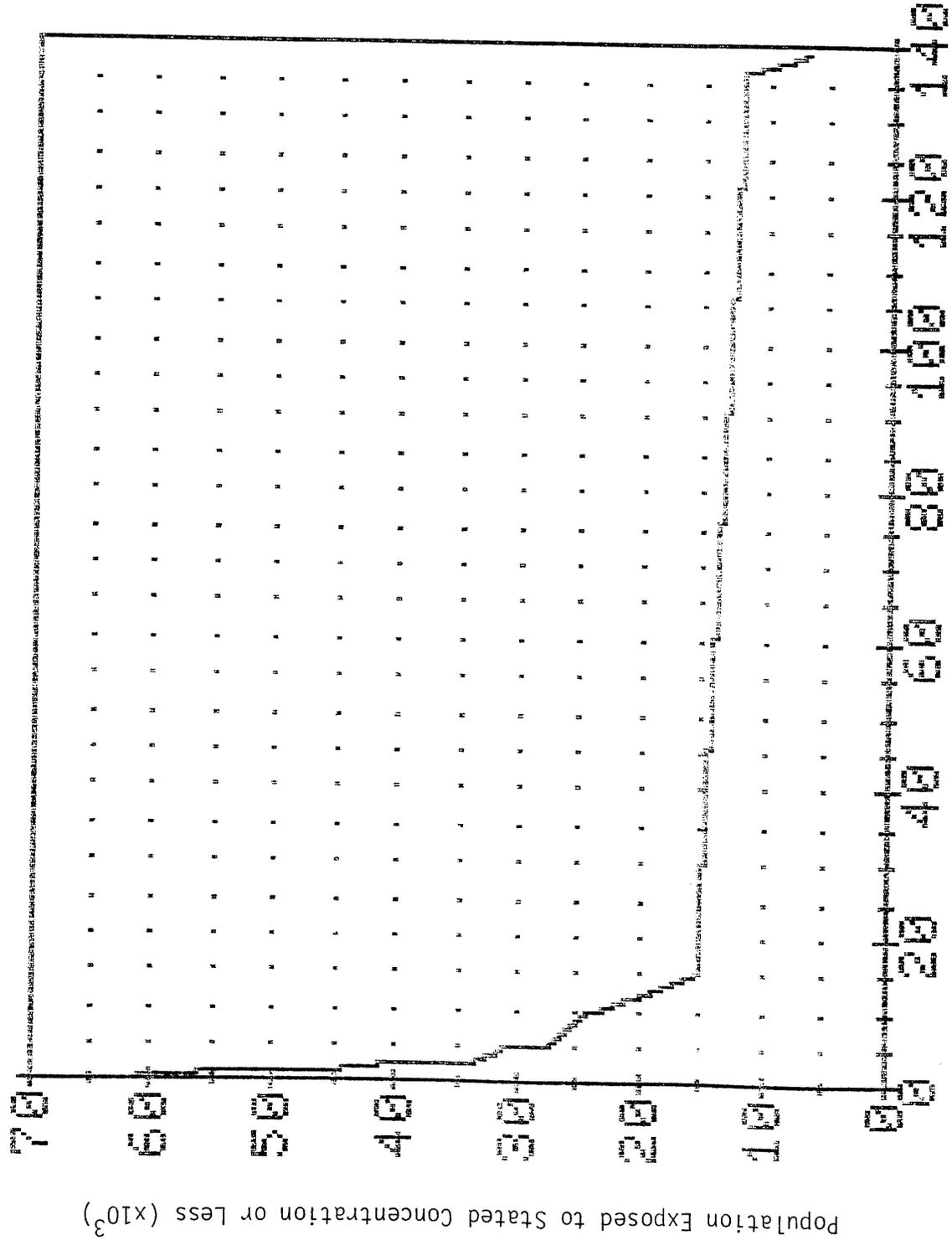


Figure 11.4-11 Cumulative Population Exposure to Ethylene Dichloride From Stauffer Off-Site Storage Tanks.

Table 11.4-13
TYPICAL URBAN AMBIENT LEVELS OF STUDY CARCINOGENS

Substance	Ambient Concentration	Environment	Reference
Arsenic	4-6 ng/m ³ 20-90 ng/m ³	General urban Heavy industrial	Braman, 1976 National Research Council, 1976
Cadmium	3 ng/m ³ <0.4 ng/m ³	Typical urban Remote areas	EPA, 1977 EPA, 1977
Asbestos	200-5,700 fibers/m ³ 20-100 fibers/m ³	Typical urban Desert	Murchio, 1978 Murchio, 1978
Ethylene Dichloride	3.7 ppb trace 0.08, 0.11, 0.51ppb	Dominguez, CA 8 N.J. industrial sites Oakland, Upland, Los Angeles	Barber, 1977 Pellizzari, 1977 Pellizzari, 1979
Chloroform	0.1 ppb 0.02 ppb	Urban background rural background CA & elsewhere	Barber, 1977; Holzer 1977
Carbon Tetrachloride	0.11 ppb 0.13 ppb 5.95 ppb 0.22 ppb (ave) 0.175 ppb (ave)	8 industrial sites, N.J. Tuscaloosa, AL (average) Riverside, CA rural background Los Angeles average Torrance, CA Southern California (60 readings) Riverside, CA	Barber, 1977; Grimrud, 1975; Russell, 1977 Pellizzari, 1977 Holzer, 1977 Singh, 1982 Barber, 1977; Russell, 1977; Grimrud, 1975 Barber, 1977 Pellizzari, 1977 Simmonds, 1974 Singh, 1982
Perchloroethylene	0.7 ppb <0.04 ppb 1.25 ppb .36	Los Angeles average Rural background Russell, 1977 Los Angeles average Riverside, CA	Barber, 1977; Barber, 1977 Grimrud, 1975; Simmonds, 1974 Singh, 1982

Table 11.4-13
 TYPICAL URBAN AMBIENT LEVELS OF STUDY CARCINOGENS
 (continued)

Substance	Ambient Concentration	Environment	Reference
Benzene	1.1 ppb	8 N.J. industrial sites	Pellizzari, 1977
	0.6-34 ppb	28 samples in industrial areas with benzene consumption facilities	R.T.I., 1977
	4.2 ppb	Torrance, CA	Pellizzari, 1977
	16-60 ppb	Tuscaloosa, AL	Holzer, 1977
	0.2-1.3 ppb	National Forest	Holzer, 1977
	13 ppb	1000 samples-Toronto	Pilar, 1973
	4.8 ppb	Azusa, CA	EPA, 1980a
	6.7 ppb	El Monte, CA	EPA, 1980a
	5.5 ppb	Long Beach, CA	EPA, 1980a
	6.3 ppb	Upland, CA	EPA, 1980a
8.2 ppb	Los Angeles, CA	Calvert, 1976	
3.9 ppb	Riverside, CA	Singh, 1982	
Benzo(a)pyrene	0.31-2.1 $\mu\text{g}/\text{m}^3$	Los Angeles, 1971	Colucci, 1971
	0.46 ng/m^3	Los Angeles, 1976	Gordon, 1976
Benzo(e)pyrene	0.90 ng/m^3	Los Angeles, 1976	Gordon, 1976
Benz(a)anthracene	0.5-2.8 ng/m^3	Los Angeles, 1971	Colucci, 1971
	0.18 ng/m^3	Los Angeles, 1976	Gordon, 1976
Chrysene	0.60 ng/m^3	Los Angeles, 1976	Gordon, 1976
Indeno [1,2,3-cd]pyrene	1.34 ng/m^3	Los Angeles, 1976	Gordon, 1976

Table 11.4-14

INCREMENTAL POPULATION EXPOSURE TO CARCINOGENS FROM STATIONARY SOURCES

Site	Substance	Typical Urban Background Level	Population Exposed to	
			100% Increment Over Background	50%
Allied ⁺	Chloroform	0.1 - 0.7 ppb (>497 ng/m ³)	0	0
Allied ⁺	Carbon Tetrachloride	0.15 ppb (942ng/m ³)	<4,044	25,587 - 41,214
Dow ⁺	Perchloroethylene	0.7 ppb (4830 ng/m ³)	0	0
Dow ⁺	Carbon Tetrachloride	0.15 ppb (942 ng/m ³)	10,796 - 20,309	20,309
Du Pont	Carbon Tetrachloride	0.15 ppb (942 ng/m ³)	0	0
Johns Manville	Asbestos	1000 fibers/m ³ (313 ng/m ³)	0	0
Kaiser	Benzene	10ppb (32,500 ng/m ³)*		
Kaiser	PAH 5 compounds	3.5 ng/m ³	72,196	72,196
Kaiser	Cadmium	3 ng/m ³	0	0
Kaiser	Arsenic	4 ng/m ³	0	0
RSR	Arsenic	4 ng/m ³	0	0
Stauffer	Ethylene Dichloride	0.51 ppb (2100 ng/m ³)	92,552	117,532

+ Assumes all year operation on either feedstock. If plant operates 50% on each feed, the population exposed to greater than 50% increment over background goes to 16,025 - 19,377 and 4,044 - 16,025 for 100%.

* Ambient concentrations of benzene vary over one order of magnitude in the literature and therefore make this calculation questionable. For Kaiser therefore the carcinogenic PAH assessment was used to evaluate incremental population exposure above background.

+ The partition of emissions from Dow are 78% carbon tetrachloride and 22% perchloroethylene by weight.

11.4.2 Comparison of Incremental and Background Concentrations

Those sites which elevate background concentrations greater than 50% to surrounding population are discussed below.

11.4.2.1 Stauffer Chemical

The Stauffer chemical plant has two principal sources of EDC emissions, the off-site storage tanks and the waste water discharge stream. Each contributes about equally to the population exposure figures as shown in Tables 11.3-11 and 11.4-12. The ambient measurements by Pellizzari (1979) of 2100 ng/m³ as the Los Angeles background was used as the typical urban background. Pellizzari notes that urban readings generally remain under 2500 ng/m³ while plant proximity concentration have been observed as high as 700,000 ng/m³. Other ambient data noted by Pellizzari are Birmingham, Alabama 205-400; Phoenix, Arizona 157-5870; Dominguez, California 14,814; Calvert City, Kentucky 6600. The latter two are associated with EDC plants. Data taken in service stations and traffic areas in various cities range from 300-3640 ng/m³. As previously mentioned the Stauffer plant is discontinuing operations. These two sources should be examined as part of any possible start-up permitting activity.

11.4.2.2 Kaiser Steel Corporation

The Kaiser steel plant polycyclic aromatic hydrocarbon (PAH) emissions arise from the coke oven operations. Comparison of the cumulative population exposure Figure 11.4-3 and Table 11.4-4 with the specified background levels for urban areas illustrates the breadth of the exposure distribution. The five known PAH carcinogens that were isolated in the coke oven emissions were quantified in the ambient air of Los Angeles by Gordon, 1976:

Benzo[a]pyrene	0.46 ng/m ³
Benzo[e]pyrene	0.90
Benz[a]anthracene	0.18
Chrysene	0.60
Indeno [1,2,3-cd]pyrene	1.34

Although these concentrations are low compared with a number of other cities cited in the literature and represent a very limited data base, the predicted concentrations from the Kaiser plant generally exceed these levels by a

significant margin i.e. greater than 30,000 are predicted to be exposed to greater than 10 x the ambient background of 3.5 ng/m³. It is likely that benzene exposures in the area are also elevated over ambient however, since background concentrations of benzene show large variation, no population calculation was specified.

11.4.2.3 Dow

Carbon tetrachloride releases from Dow constitute approximately 78% of the total CT plus perc emissions in Table 11.4-6 and were found to elevate urban background concentrations greater than 50% in five census tracts. Emissions are predominately from storage and check tank working and brething releases.

11.4.2.4 Allied Chemical

The Allied plant was modeled several ways since the plant can operate with chloroform or carbon tetrachloride feed. The cases presented in Tables 11.4-7 and 11.4-8 represent annual operation with either feed. Partial year operation with each feed can be scaled from the individual annual modes and is presented for equal half year operation in Table 11.4-9. As with the Du Pont plant carbon tetrachloride emissions arise from feed tank working loss. Table 11.4-10 illustrates peak exposures predicted to arise during an off loading cycle. As expected concentrations in that six hour period far exceed annual average values. Insufficient data were available to contrast levels with background transient concentrations.

AVAILABLE CONTROL TECHNIQUES

Alternative control approaches for the most significant emission sources among the various plants are described in the following subsections. Emphasis has been placed in dealing with those sources of greatest absolute magnitude (lb/yr) and those constituting the largest increment to the background concentration of the emitted substance. No attention will be given to the secondary sources within each plant or to the case of Johns-Manville since the major source is less than 200 lb/yr and is not predicted to raise background exposure levels to the general population. Furthermore all emission sources at Kaiser Steel which were directly dealt with in this program are related to the coke oven operations. These facilities are to be closed down and all primary steel mill operations discontinued. Kaiser forecasters have predicted further deterioration of the plant economics and the phased closure has been accelerated for primary steel making operations. Note that this closure is essentially irreversible since differential expansion and contraction of the coke oven structure occurs in the cooling process and it would be improbable that ovens could be reheated without extensive rebuilding at major expense.

12.1 STORAGE TANK EMISSIONS - STAUFFER, DOW, DUPONT AND ALLIED

At all four sites emissions from storage tanks constitute either the primary or near dominant (Stauffer) source of carcinogen release and/or general population exposure. Currently the tanks of interest at each site are permitted by the local Air Quality Districts however they do not require emission control systems for various reasons. The estimated releases, grounds for exemption, and other pertinent information are given in Table 12.1-1.

In order to appreciate the practical alternatives for emission controls the provisions of SCAQMD Rule 463 are listed below which specify the acceptable alternatives for tanks requiring controls i.e. tanks having capacities greater than 39,630 gal. with substances of true vapor pressure

Table 12.1-1-1

STORAGE TANK SUMMARIES

<u>Site</u>	<u>Approx. Capacity(gal)</u>	<u>Substance</u>	<u>Emission Mode</u>	<u>Vapor Pressure</u>	<u>Grounds for Exemption</u>
Stauffer Off-Site Tanks (3) (San Pedro)	1.05×10^6 (2) $.84 \times 10^6$ (1)	Ethylene Dichloride	Tank breathing	1.4 at 70°F psi	Exempt from control requirements to SCAQMD Rule 463 since vapor pressure does not exceed 1.5 lb at storage conditions.
Allied (El Segundo) - Raw Material Feed Storage	<39,630	Carbon Tetrachloride	Tank working Tank breathing	1.78 psi at 68°F	Exempt from Rule 463 since tank capacity is under 39,630 gal. (150 m ³)
Dow (Pittsburg)-Product Check Tanks (4)	18,000 each	Perchlone- thylene and Carbon Tetra- chloride	PERC-working PERC-breathing CT-working CT-breathing	1.78 psi at 68°F (CT) 0.39 psi at 68°F (perc)	Exempt from Regulation Rule 85300 because tank capacity is under 39,630 gal. and/or substances are not classified as organic liquids.
Dow - product storage	700,000 300,000	CT perc	Tank breathing Tank breathing	1.78 psi at 68°F	Exempt from Rule 85300 because substance is not classified as an organic liquid according to Regulation-Rule 81203.
DuPont (Antioch) - Raw Material Feed Storage	30,000 working 42,636 liquid full	Carbon Tetrachloride	Tank working Tank breathing	1.78 psi at 68°F	Exempt from Rule 85300 because substance is not classified as an organic liquid according to Regulation-Rule 81203.

exceeding 1.5 psi at storage conditions.

- floating roof tanks
- fixed roof tanks with an internal floating type cover
- a vapor recovery system with vapor collection and return (or disposal) processing exceeding 95% efficiency.

In a chemical plant a typical vapor recovery system (K.R. Evans, SCAQMD) might consist of a collection manifold to a recovery system (such as a vapor sphere) to a compression system and subsequently to absorption and recovery systems. The absorption system consisting possibly of scrubber, stripper, or activated carbon.

In dealing with specific carcinogenic substances such as vinyl chloride highly efficient vapor control system performance has sometimes been stipulated necessitating incineration systems.

For the cases of concern realistic alternatives are as follows:
Stauffer Off-Site Tanks - There are a number of options which can markedly reduce emissions from these tanks from the calculated value of over 20×10^3 lb/yr. One alternative is to consolidate the material in the three tanks. One of the large tanks can contain the currently stored material and reduce emissions to approximately 13.0×10^3 lb/yr. Another alternative is to transfer all EDC to a single floating roof tank. Various types of such tanks exist and are reviewed in the EPA report Organic Chemical Manufacturing Volume 3: Storage, Fugitive, and Secondary Sources EPA-450/3-80-025 e.g. internal and external floating roofs and a variety of seal design configurations. Generally such designs would be expected to reduce emissions to the order of one-fourth to one-fifth the current level. Cost of installing a contact single seal internal floating roof was estimated by B.B. Lumquist, Pentrex, for EPA as \$27,770 in 1980 dollars for 70 ft diameter tank. Cost to build an external floating roof tank was estimated by G. Stilt of Pittsburg Des Moines for EPA as \$140,000 for D=67 H=40ft. Another common approach is to utilize carbon adsorption. This works well with nonpolar hydrocarbons as VOC is removed from the vapor phase. A basic system consists of two carbon beds and a regeneration system. Regeneration is typically performed with steam or vacuum. Figure 12.1-1 illustrates the systems (Basdekis, 1980). Steam raises the VOC vapor pressure. The resulting steam-VOC mixture is condensed and

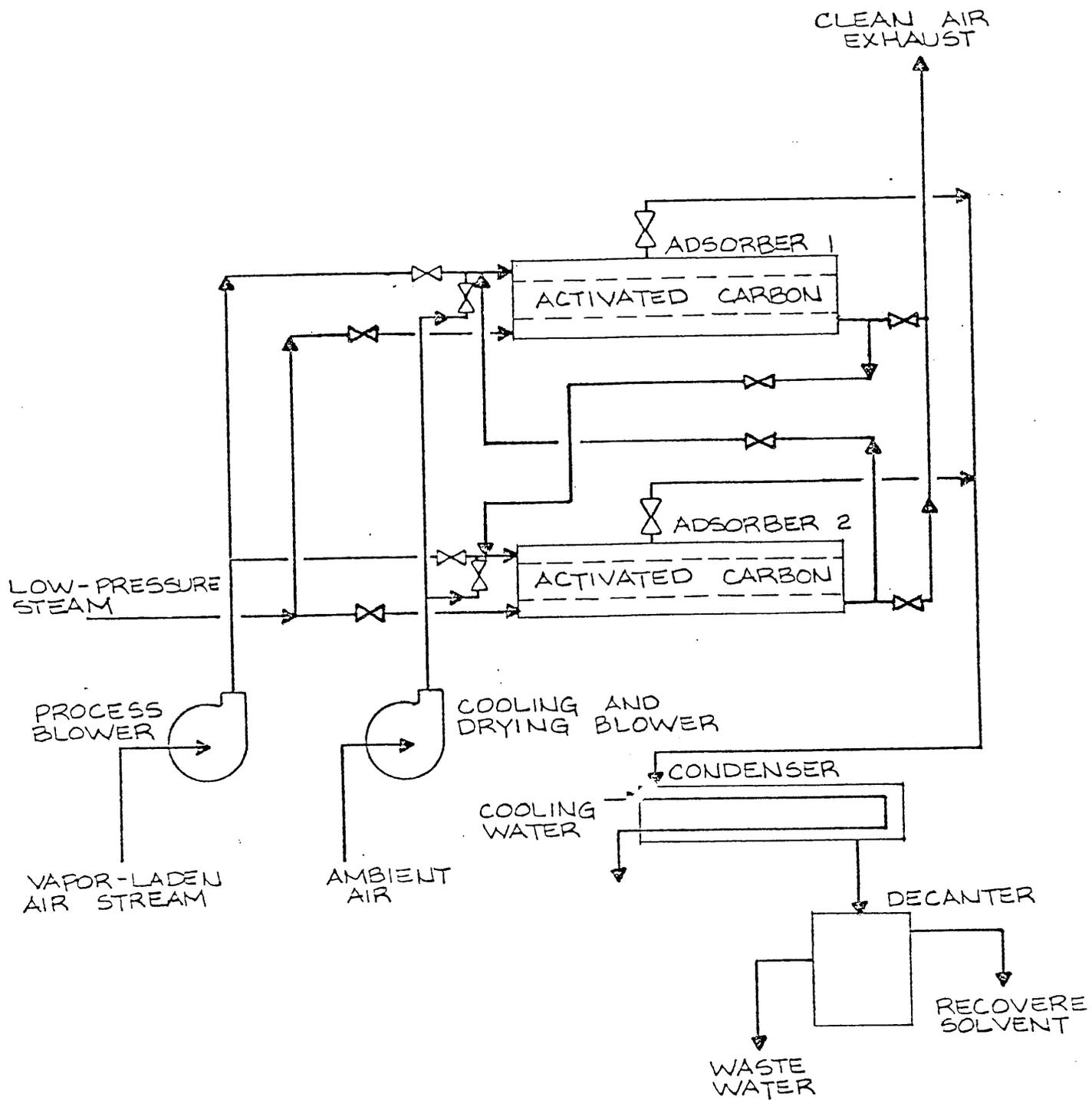


Figure 12.1-1 Activated-Carbon Adsorption System

routed to a separator, decanted and returned to storage. In vacuum regeneration VOC vapor is desorbed by pulling a vacuum on the carbon bed then condensed and returned. System efficiency is estimated at 96% reduction from fixed roof levels (EPA 450/3-80-025).

Refrigerated vent condensers are one of the most common emission reduction processes for controlling fixed-roof storage tank VOC. Figure 12.1-2 illustrates a unit (Erikson, 1980) efficiency of recovery is rated between 60-90% for the vapor pressure range of concern. For such a large tank the capital costs would be high. Figure 12.1-3 illustrates EPA estimates (EPA, 1980b) for the condenser section. Condenser system area would be in excess of 1000 ft².

It should be noted that Stauffer Chemical has announced the closure of its VC/PVC plant. Previously they had planned to purge the off-site tanks of EDC. Since any future possible plant start-up will necessitate a comprehensive SCAQMD review this document can assist in evaluating proposed control measures.

Allied and DuPont Feed Tanks - In both of these cases the more significant quantity of emissions arise from tank working, i.e. during the off-loading activity, rather than tank breathing. Control measures taken for working emissions are thus of primary concern. Therefore, no detailed discussion will be provided on the alternatives for control of breathing emissions. Additionally both tanks are in the range of 20,000 gallons which is a capacity where floating roof tanks are almost nonexistent. Out of 670 floating roof tanks surveyed by EPA less than 1.5% were smaller than 30,000 gallons in capacity. Therefore, the utilization of any floating roof concept and seal combination will not be considered.

Commercially it is estimated by DuPont that carbon tetrachloride feed costs approximately \$0.17/lb (E. Taylor, personal communication). Therefore, less than \$2500 is lost to DuPont annually as a result of working level emissions and less from Allied. Thus, it is unlikely that any appreciable economic incentive exists to develop a vapor recovery system. However, a candidate system could be patterned after the chloroform feed-storage unit currently at Allied. This is a dedicated vapor balance system. Chloroform is off-loaded from tank cars and stored in a closed unvented tank. As the storage tank is filled the air space displaced is fed

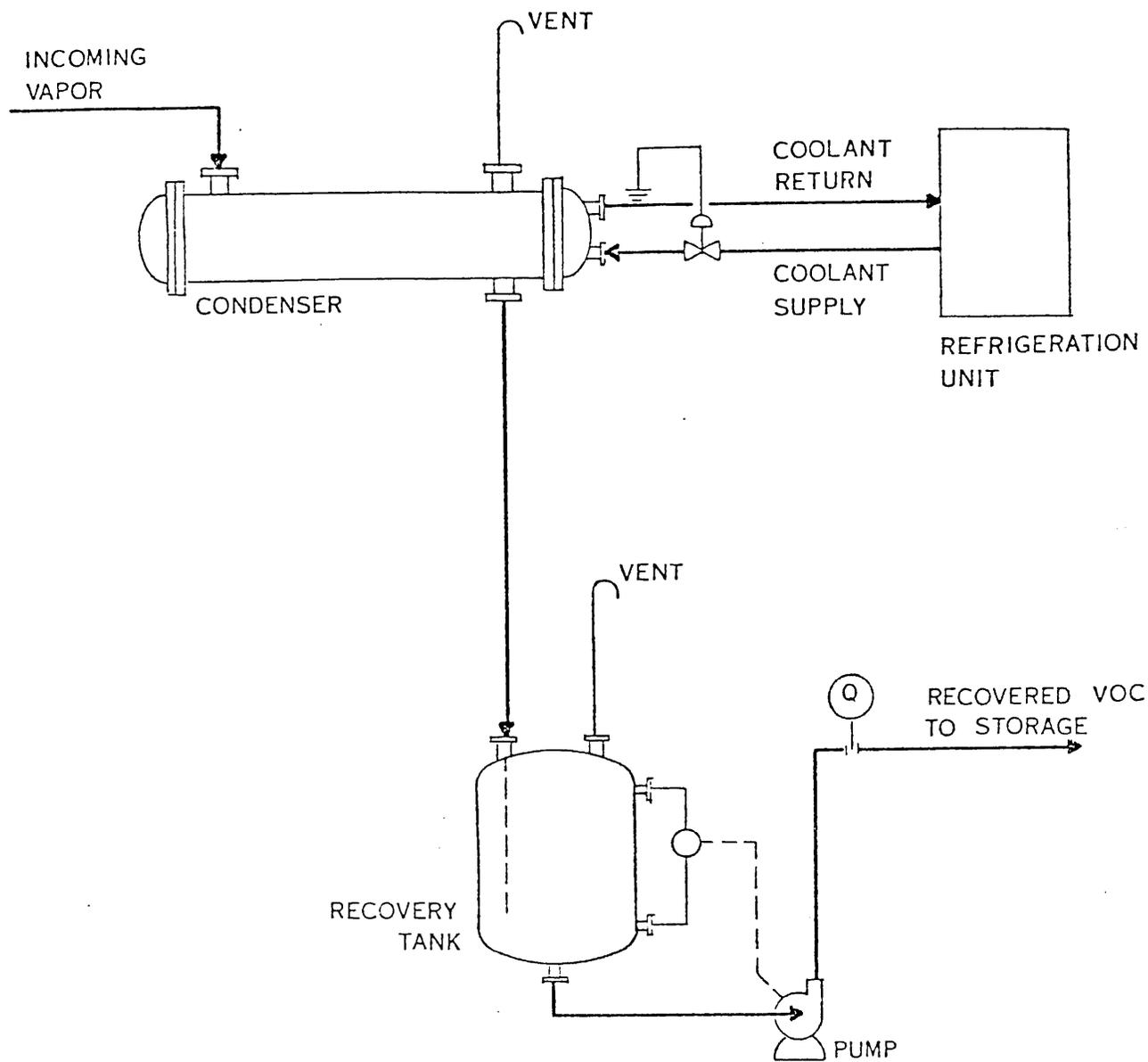


Figure 12.1-2 Refrigerated Vent Condenser System

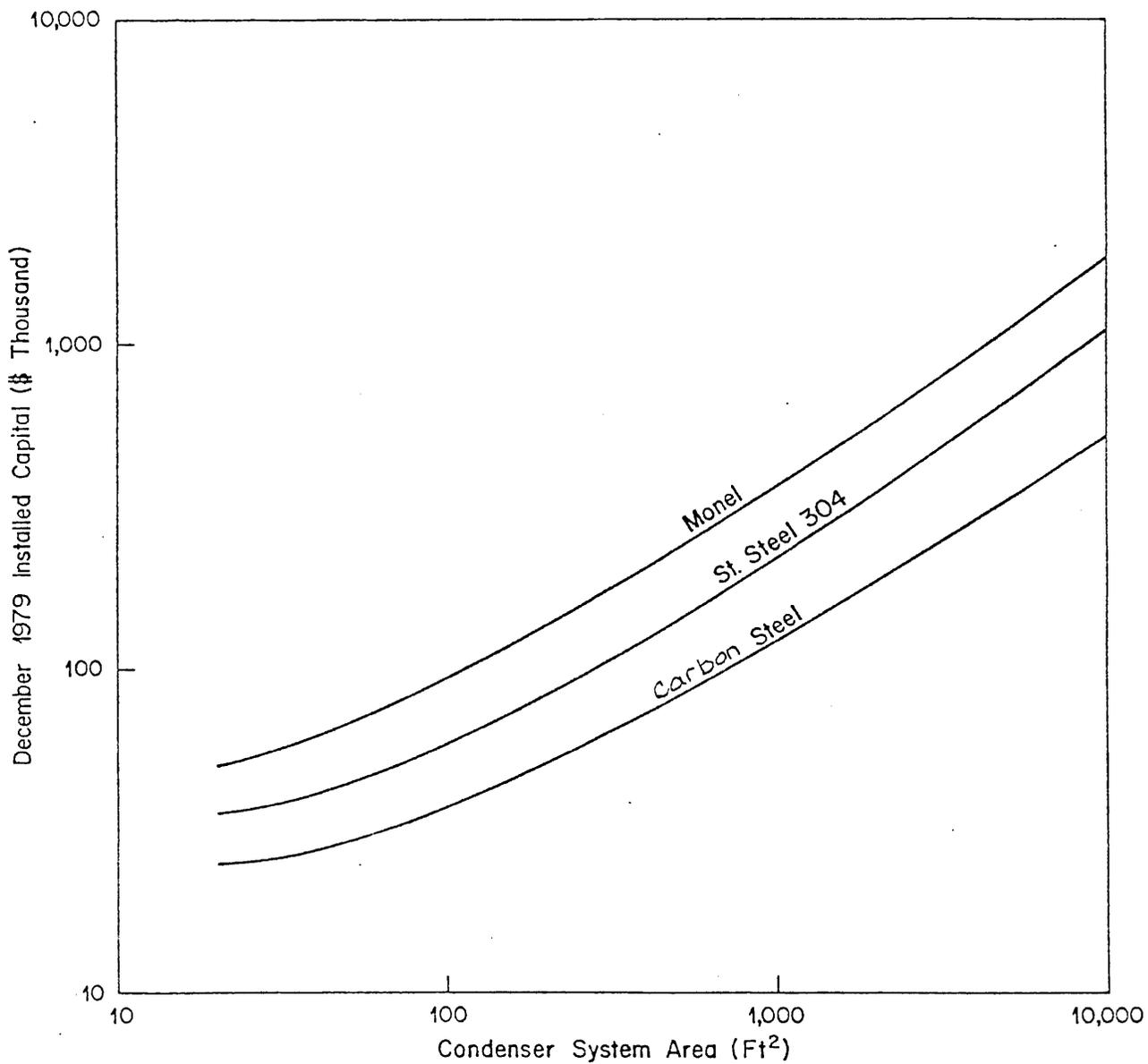


Figure 12.1-3 Installed Capital Cost vs Condenser Area for Various Materials of Construction for a Complete Condenser Section

back to the tank car. Also in this case the storage tank is not vented in its normal breathing mode and is part of a closed feed system to the reactor.

Vapor recovery system alternatives which are particularly effective in loading and handling include refrigeration, adsorption and/or absorption. Control efficiencies are estimated in the range of 90-95% (EPA, 1980b) and, of course, depend on the specific substance and equipment used. Carbon adsorption systems were discussed above. The smallest capacity carbon adsorption system priced by EPA (EPA, 1980b) has 2 vertical beds of carbon (900 lbs - 4ft diameter by 3 ft depth) with an installed capital cost of \$135,000 based on December 1979 dollars.

Dow Tanks - Dow has two pair of product check tanks which alternately are filled and off-loaded. Emissions from these tanks were calculated based upon operating cycle (3 day fill) saturation vapor pressure and physical characteristics. Direct head-space testing was planned however it could not be accommodated because of restricted access due to unscheduled maintenance on the field test day.

Dow has indicated that they are studying the option of installing a vapor control/recovery system in these and their larger product storage tanks.

The extent of their engineering and assessment work is unknown as are their current plans. It may be possible to incorporate a vapor balance design into the system whereby the displaced vapor is transferred to another process point within the system. Alternatively a vapor recovery system such as carbon adsorption is feasible. However, since emissions for the check tanks are primarily due to working loss, the use of a conservation vent or an adjustment of its operational differential pressure would be ineffective for the reduction of the bulk of such emissions. Furthermore, since check tank size is relatively small no consideration was given to conversion to a floating roof configuration for those tanks. Conversion would be possible for the large storage tanks.

12.2 WASTEWATER EMISSIONS - STAUFFER

Emissions of EDC through wastewater discharge are the largest single source identified at the plant sites. The discharge limit was set at 25 ppm by the Los Angeles County Sanitation District and was established with the occupational limit in mind of 50 ppm over an 8 hour work shift at the District.

treatment center. There had been some discussion between parties of possibly raising the discharge limit since it is felt by Stauffer that dilution of the stream is sufficient to allow it. It should be noted however that NIOSH has recommended the permissible exposure limit be reduced to 5 ppm averaged over a work period of 10 hours per day, 40 hours per week with a ceiling level of 15 ppm averaged over a 15-minute period.

It is not certain at what rate EDC will be released from the wastewater stream. At the plant discharge points wastewater is both hot and aerated thus favoring release. No measurements have been taken downstream of the plant after considerable dilution has occurred. The distance to the water treatment plant is approximately 5 km at which point anaerobic digestion is conducted. It is presumed that all EDC will be released before final ocean discharge.

A possible emission control process for reduction of the EDC in the effluent is by process adjustments or additions. For example process modifications to the EDC stripping stage could dramatically reduce discharge levels. A control alternative is the use of activated carbon or XAD-2 resin to recover EDC in the discharge stream. Tests of Gulf South Research Institute on XAD-2 and activated carbon (Coco, 1980) show high recovery yields for nonpolar organic carcinogens under a range of concentrations. Viable suggested alternatives by Smith included regeneration of the trapping materials and even consideration of burning the concentrate carbon media (at greater than 1000 ppm).

Control approaches to reduce emissions from so called secondary sources in general and waste water emissions in particular fall into four categories - waste source control, resource recovery, alternative disposal and add-on controls. Alternative control processes which were considered but appear to be inappropriate to this case include: chemical means e.g. neutralization, precipitation, coagulation and chemical oxidation; thermal destruction of the unconcentrated waste stream is impractical; biological treatment e.g. aeration and biomass-wastewater contact, generally relates to the treatment of soluble degradable organics in the concentration range between 0.01 and 1%; terminal storage e.g. landfilling, surface impoundment and deep well injection are either inapplicable or impractical. Therefore in summary the possible control approaches for this case include the improvement

of separation efficiencies in steam stripping; the internal recycle of waste streams; and the adsorption by activated carbon. The design configuration, efficiency and cost obviously depend upon numerous plant specific factors and their determination would require detailed analyses.

The wastewater system of a model chemical production plant based upon the average properties of a composite of 30 chemicals was evaluated for EPA by IT Enviroscience (EPA, 1980b). Included prominently among the 30 was EDC with the highest uncontrolled secondary emission wastewater release rate i.e., 9 percent of the production and 34 percent of the emission. Cost and impact analyses were evaluated for alternative control systems to reduce secondary VOC emissions from wastewater. Four systems were considered: a carbon adsorption system (CAS) for recovery of the VOC from the wastewater, a cover to reduce secondary VOC emissions from the wastewater clarifier, a cover for the clarifier plus a carbon desorption system; and a cover for the clarifier plus a CAS system using a fume incinerator. The scale of the model system was greatly in excess of the Stauffer plant thus further making detailed comparison impractical. However emission reduction factors were given as 99% and cost effectiveness per 10^6 g reduction generally ranged between \$450 to 1733. These factors would likely grossly underestimate the system cost if scaled down to the range of the Stauffer plant i.e. the order of 34,600 lb annual discharge.

The alternative approaches of improved steam stripping efficiency and internal recycling of the stripper discharge stream with a reduction in makeup requirements could decrease net EDC wastewater content release.

12.3 CONTROLS FOR SECONDARY LEAD SMELTER STACK EMISSIONS

Given our finding of low (16 kg/yr) emissions of arsenic from the reverberatory furnace at RSR, it would appear that the arsenic content of the lead feedstock is low and/or that the plant's system for reducing lead emissions is also quite effective for arsenic. RSR, it will be recalled from Section 3.2, uses a quenching chamber and baghouse filters to remove particulate matter and a carbonate scrubber to remove sulfur dioxide.

There are no federal new source performance standards for lead emissions per se; however, the Standards of Performance for Secondary Lead Smelters (40 CFR 60.122) limit total particulate emission from a blast furnace

or reverberatory furnace to 50 mg/m^3 . According to Augenstein et al. (1978), who reviewed the technology for controlling lead emissions from these sources, baghouse filters or wet scrubbers are generally used to control particulate emissions. When fabric filters are used to control blast furnace emissions, they are normally preceded by an afterburner, which incinerates hydrocarbons that would otherwise blind the fabric. Afterburners are not necessary for reverberatory furnace emission, since the excess air and temperature are usually sufficient to oxidize the hydrocarbons.

According to Augenstein et al., "shaker-type baghouse filters are the most effective means of controlling lead fume emissions from secondary furnace operations." Collection efficiencies can exceed 99 percent. One advantage to this control approach is that lead oxide dust can be recovered easily and recycled in the smelter. Flue gases must be cooled to below $300 \text{ }^\circ\text{F}$ for dacron bags and to below $500 \text{ }^\circ\text{F}$ for fiberglass bags (High et al., 1977).

Although wet scrubbers are effective under some circumstances in controlling lead emissions, it is more difficult to recover the lead oxide for recycling. In addition, sulfur dioxide present in the flue gases becomes oxidized to sulfuric acid and can cause corrosion problems. For this reason, sodium carbonate, or other basic reagents are added to the scrubber solution.

Although it concerns a gold smelter, an approach described by Marchant and Meek (1980), provides an example of an arsenic control alternative which might be applicable to secondary lead smelters. At the Campbell Red Lake Gold Smelter in Balmerton, Ontario, Canada, Smelter gases are first passed through a hot electrostatic precipitator (ESP). The ESP is heated so that the arsenic (which is principally in the form of As_2O_3) remains gaseous and is not yet collected. This exclusion of arsenic allows the ESP to recover particulate gold more easily. The ESP exhaust is then quenched with ambient air to condense the arsenic trioxide. Baghouse filters then remove the arsenic, along with other particulate matter.

12.4 CONTROLS FOR STEEL MILL EMISSIONS

Given the imminent and irreversible cessation of coking activities at Kaiser Steel Corporation, a review of technologies for controlling emissions from the coke ovens and the coke byproduct recovery plant was not deemed to be necessary. This is the only primary steel mill in California.

REFERENCES

- Allen Jr., C.C. 1980a. A model to estimate hazardous emissions from coke oven doors, prepared by Research Triangle Institute for U.S. Environmental Protection Agency, Office of Air Quality and Standards, Research Triangle Park, North Carolina, RTI/1736/2-01.
- Allen Jr., C.C. 1980b. Estimation of charging emissions for by-product coke oven, prepared by Research Triangle Institute for U.S. Environmental Protection Agency, Office of Air Quality and Standards, Research Triangle Park, North Carolina, RTI/1736/2-02.
- Allen Jr., C.C. 1980c. "Environmental assessment of coke by-product recovery plants" Proceedings: First Symposium on Iron and Steel Pollution Abatement Technology, Chicago, Illinois, 30 October - 1 November 1979, EPA-600-9-80-012 pp. 75-88.
- Anon. 1978. "Coke quench-tower emissions tests," Environ. Sci. Tech. 12(10): 1122-1123.
- Augenstein, D.M., T. Corwin et al., 1978. Control techniques for lead air emissions, prepared by PEDCO Environmental, Inc. for U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, EPA-450/2-77-012-B (NTIS: PB80-197551).
- Barber, W.C., 1977, "Interim air pollution assessment for eight high-volume industrial organic chemicals," U.S. Environmental Protection Agency memorandum to Air and Hazardous Materials Division, Regions, I, III-X and to Director Environmental Programs Division, Region II.
- Barrett, R.E., W.L. Margard et al. 1977. Sampling and analysis of coke-oven door emissions. Prepared by Battelle-Columbus Laboratories for U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina, EPA-600/2-77-213.
- Barrett, R.E. and P.R. Webb, 1978. "Effectiveness of a wet electrostatic precipitator for controlling POM emissions from coke oven door leakage." Presented at 71st Meeting of the Air Pollution Control Association, Houston Texas, 25-29 June 1978.
- Basdekis H.S., 1980, "Carbon Adsorption Control Device Evaluation," IT Enviroscience, Inc. report in preparation for U.S. Environmental Protection Agency, ESED.
- Bee, R.W. et al. 1974. Coke oven charging emission control test program, Vol. I and II, U.S. Environmental Protection Agency, EPA-650/2-74-062.
- Beimer, R.G. 1978. Air pollution emission test. Analysis of polynuclear aromatic hydrocarbons from coke oven effluents. Prepared by TRW Defense and Space Systems Group for U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, EMB Report 78-CK0-12.

Braman, R.S., 1976, "Application of the arsine evolution methods to environmental analyses," presented at the International Conference on Environmental Arsenic, Ft. Lauderdale, Florida, 5-8 October.

Bratina, J.E. 1979. "Fabric filter applications on coke oven pushing operations," J. Air Poll. Cont. Assoc. 29(9): 916-920.

Buonicore, A.J. 1980. "Environmental assessment of coke quench towers," in proceedings: First Symposium on Iron and Steel Pollution Abatement Technology, Chicago, Illinois, 30 October - 1 November 1979 EPA-600/9-80-012, pp. 112-142.

Busse, A.D. and J.R. Zimmerman. 1973. User's guide for the Climatological Dispersion Model, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, EPA-R4-73-0024.

California Air Resources Board, 1976. Coke oven emissions, miscellaneous emissions, and their control at Kaiser Steel Corporations Fontana Steel making facility, Enforcement Branch, Sacramento, California, L & E-76-11.

Calvert, C.A., 1976. Envir. Sci. & Technol., 10, 256.

Coco, J.H. et al., 1979, "Development of treatment and control technology for refractory petrochemical wastes," Final Report Gulf South Research Institute to U.S. Environmental Protection Agency EPA-600/2-79-080.

Colucci, J.M. and C.R. Begeman, 1971, Polynuclear aromatic hydrocarbons and other pollutants in Los Angeles air, In: Proceedings of the International Clean Air Congress, Vol. 2, Academic Press, pp 28-35.

Cooper, J.A. and J.G. Watson Jr. 1980. "Receptor oriented methods of air particulate source apportionment," J. Air Pollution Control Assoc. 30(10): 1116-1125.

Coutant, R.W., J.S. McNulty and R.D. Grammar, 1975. Final report on determination of trace elements in a combustion system: Prepared by Battelle Columbus Laboratories for the Electric Power Research Institute, EPRI 122-1.

Dilling, W., 1977, "Interphase transfer processes," Envir. Sci. Technol., 11, 4, pp 405-409.

Dowling, M.P., J.D. Jeffry and A.H. Laube, 1978. "Reduction of quench tower emissions." Presented at the 71st Air Pollution Control Association Conference, Houston, Texas, 25-30 June. APCA No. 78-9.2.

EPA, 1977, Multimedia Levels Cadmium, Environmental Protection Agency, 560/6-77-032, September, 1977.

EPA, 1980a, "Review of Criteria for Vapor Phase Hydrocarbons," U.S. Environmental Protection Agency Report, 600/8-80-045.

EPA, 1980b, Organic Chemical Manufacturing Volume 3: Storage, Fugitive and Secondary Source, EPA report 450/3-80-025.

EPA, 1981, Compilation of Air Pollutant Emission Factors (Including Supplements 1-7), Third Edition, Supplement 12, Office of Air Quality Planning and Standards, AP-42-ED-3-Suppl-12.

- Erikson, D.G., 1980, "Control Device Evaluation - Condensation," IT Envioscience, Inc. report in preparation for U.S. Environmental Protection Agency, ESED.
- Ertel, G.L. 1979. Quench tower particulate emissions. J. Air Poll. Cont. Assoc. 29(9): 913-916.
- Evans, K.P., 1981. Personal Communication with R. Ziskind.
- Goodwin, D.R., 1980. "Air pollution emissions standards," in Proceedings: First Symposium on Iron and Steel Pollution Abatement Technology, Chicago, Illinois, 30 October - 1 November 1979, EPA-600/9-80-012, pp. 37-45.
- Gordon, G.E. 1980. "Receptor Models," Environ. Sci. Tech. 14(7):792-800.
- Gordon, R.J., 1976, "Distribution of airborne polycyclic aromatic hydrocarbons throughout Los Angeles," Envir. Sci. Technol., 370-373.
- Great Lakes Carbon Corporation, 1977. Study of coke side coke-oven emissions. Vol. 1: Source testing of a stationary coke side enclosure, EPA-340/1-77-014A.
- Grimsrud, E.P., and R.A. Rasmussen, 1975, Atmos. Envir. 9, 1010.
- Hartman, M.W., 1980. Source test at U.S. Steel Clairton Coke Ovens, Clairton, Pennsylvania. Prepared by TRW Environmental Engineering Division for U.S. Environmental Protection Agency, Emissions Standards and Engineering Division, Research Triangle Park, North Carolina, EMB Report 78-CKU-13.
- Hendriks, R.V. et al. 1979 "Organic air emissions from coke quench towers." Presented at 72nd Annual Meeting of the Air Pollution Control Association, Cincinnati, Ohio, June 1979, Paper NO. 79-39.1.
- High, M.D., M.E. Lukey and T.A. Li Puma, 1977. Inspection manual for secondary lead smelters, prepared by Engineering Science, Inc. for U.S. Environmental Protection Agency, Office of Enforcement, EPA-340/1-77-001.
- Holzer, G. et. al., 1977, "Collection & analyses of trace organic emissions from natural sources," Journal of Chromatography, 142, pp 755-764.
- JRB, 1980, "Materials Balance 1,2-Dichloroethane, Level 1-Preliminary," Science Applications, Inc. Final Report to U.S. Environmental Protection Agency, EPA-560/13-80-002.
- J. Milne, 1981, Personal Communication with R. Ziskind.
- Kemner, W.F. 1979. Cost Effectiveness model for pollution control at coking facilities. Prepared by PEDCo Environmental, Inc. for U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina, EPA-600/2-79-185 (NTIS: PB 80-118706).
- Kessler, T., A.G. Sharkey Jr. and R.A. Friedel, 1973. Analysis of trace elements in coal by spark-source mass spectrometry. U.S. Bureau of Mines Report of Investigations No. 7714.

- Kolak, N.P., J. Hyde and R. Forrester, 1979. Particulate source contributions in the Niagara Frontier. Prepared by New York State Department of Environmental Conservation for U.S. Environmental Protection Agency, Region II, EPA-902/4-79-006.
- Mackay, D. and P.J. Leinonen, 1975, "Rate of Evaporation of low - solubility contaminants from water bodies to atmosphere," Envir. Sci. Technol. 9, 13, pp 1178-1180.
- Magee, E.M., H.J. Hall and G.M. Varga Jr., 1973. Potential pollutants in fossil fuels. Prepared by ESSO Research and Engineering Co. for U.S. Environmental Protection Agency, EPA-R2-73-249. (NTIS: PB 225 039).
- Marchant, G.H. and R.L. Meek. 1980. Evaluation of technology for control of arsenic emissions at the Campbell Red Lake Gold Smelter, prepared for the U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, Ohio, EPA-600/2-80-141 (NTIS PB 80-219363).
- Margler, L., R.A. Ziskind, M.B. Rogozen, and M. Axelrod, 1979, "An inventory of carcinogenic substances released into the ambient air of California: Volume I - Screening and identification of carcinogens of greatest concern," Science Applications, Inc. Final Report SAI-068-80-504 to the California Air Resources Board.
- Milne, J., 1981. Personal Communication with R. Ziskind.
- Murchio, J.C., W.C. Cooper, and A. De Leon, 1978 "Asbestos fibers in ambient air of California," California Air Resources Board, ARB 4-054-1, EHS Report 73-2 (March).
- National Academy of Sciences, 1972. Particulate polycyclic organic matter, Washington, D.C., pp. 4-12.
- National Research Council, 1976. Arsenic, prepared by Subcommittee on Arsenic, Committee on Medical and Biological Effects of Environmental Pollutants, Washington, D.C.
- Oliver, J.F. and J.T. Lane. 1979. "Control of visible emissions at CF&I's coke plant-Pueblo, Colorado," J. Air Poll. Cont. Assoc. 29(9): 920-925.
- Pellizzari, E.D. and J.E. Bunch, 1979, "Ambient air carcinogenic vapors: Improved sampling and analysis technology," EPA Contract #68-02-2764.
- Pellizzari, E.D., 1977 "The measurement of carcinogenic vapors in ambient atmospheres," EPA-600/7-77-055.
- Phelps, R.G., 1979. "AISI-EPA-Battelle coke oven door sealing program. J. Air Poll. Cont. Assoc. 29(9): 908-912.
- Porter, R.A. 1976. Dispersion equation solutions by calculator. A guide for air pollution engineers and scientists, Second edition. Texas Air Control Board (NTIS PB 262 135).

- Ranzieri, A., 1982. Personal Communication with M.B. Rogozen
- Redburn, T. 1980. "Kaiser battles against legacy of woes," Los Angeles Times (7 September 1980), Part VI, pp. 1,11.
- Research Triangle Institute, 1977 "Quantification of benzene in 150 ambient air samples," for U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards.
- Rinkus, S.J. and M.S. Legator, 1979. "Chemical characterization of 465 known or suspected carcinogens and their correlation with mutagenic activity in the Salmonella typhimurium system," Cancer Research 39:3289-3318.
- Roberts, R.M., 1980, "An inventory of carcinogenic substances released into the ambient air of California, Tasks II and IV", KVB Final Report KVB 26900-836 to Science Applications, Inc.
- Rogozen, M.B., L.W. Margler, P. Mankiewicz and M. Axelrod, 1978. Water pollution control for coal slurry pipelines. Prepared by Science Applications, Inc. for U.S. Department of Energy (NTIS: SAI-068-79-516.
- Rogozen, M.B., D.F. Hausknecht and R.A. Ziskind, 1976, "Methodology for ranking elements in fossil fuels according to their potential health impact," Science Applications, Inc. Final Report 260-77-539 to the Electric Power Research Institute.
- Russell, J.W. and L.A. Shadoff, "The sampling and determination of halocarbons in ambient air using concentration on porous polymers."
- Siebert, P.C., C.A. Craig and E.b. Coffey, 1978. Preliminary assessment of the sources, control and population to airborne polycyclic organic matter as indicated by benzo(a)pyrene. Prepared by Energy and Environmental Analyses, Inc. for U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.
- Simmonds, P.G., et al., 1974, "Distribution of atmospheric halocarbons in the air over Los Angeles basin," Atmos. Envir., Vol 8, pp 209-216.
- Singh, H.B., L.J. Salas, and R.E. Stiles, "Distribution of Selected Gaseous Organic Mutagens and Suspected Carcinogens in Ambient Air," in Proceedings Annual Meeting Air Pollution Control Association, 82-65.1, June 20-25, 1982 New Orleans.
- Smith, W.M., 1979. "Evaluation of coke oven emissions," in Yearbook of the American Iron and Steel Institute, pp. 163-179.
- SRI International, 1980, "Assessment of human exposures to atmospheric benzene," S.J. Mara and S.S. Lee, final report to U.S. Environmental Protection Agency, EPA-450/3-78-031.
- Taback, H.J. 1978. Control of Hydrocarbon emissions from stationary sources in the California South Coast Air Basin. Prepared by KVB, Inc. for the California Air Resources Board, KVB No. 5804-714.

Trenholm, A.R. and L.L. Beck, 1978. "Assessment of hazardous organic emissions from slot type coke oven batteries," unpublished paper. U.S. Environmental Protection Agency, Emission Standards and Engineering Division.

Turner, D.B. 1970. Workbook of atmospheric dispersion estimates, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

U.S. Bureau of Mines, 1972. Minerals yearbook: 1970, Vol. I, p. 423.

VanOsdell, D.W., D. Marsland et al. 1979. Environmental assessment of coke by-product recovery plants, prepared by Research Triangle Institute for U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina, EPA-600/2-79-016 (NTIS: PB 293-278).

Westbrook, C.W. 1979a. Level 1 assessment of uncontrolled sinter plant emissions. Prepared by Research Triangle Institute for U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina, EPA-600/2-79-112.

Westbrook, C.W. 1979b. Level 1 assessment of uncontrolled Q-BOP emissions. Prepared by Research Triangle Institute for U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina, EPA-600/2-79-190.

Wetherold, R.G., L.P. Provost, and C.D. Smith, 1980, "Assessment of atmospheric emissions from petroleum refining: Volume 3 Appendix B", Radian Corp. Final Report to U.S. Environmental Protection Agency, EPA-600/2-80-075c.

Ziskind, R.A., D.F. Smith, J.L. Hahn and G. Spivey, (1980), Determinants of Cancer and Cardiovascular Disease Mortality in Asbestos Mining counties of California, SAI Report 068-81-514, 1 May.

Rapid Screening and Identification of Airborne Carcinogens of Greatest Concern in California

Lawrence W. Margler, Michael B. Rogozen,
Richard A. Ziskind, and Robert Reynolds

Science Applications, Inc.
Los Angeles, California

This paper describes a method for establishing a priority list of airborne carcinogens within a state jurisdiction. In this case it was necessary to identify, from among hundreds of potential candidates, the five to ten materials of greatest potential concern in California as airborne carcinogens.

Because no previous inventory of carcinogens in California existed, published lists, rankings, and assessments of national scope were used to identify candidates. By systematic manipulation and comparison of these data sources, 47 materials of some notoriety were chosen for closer scrutiny. This selection was pared to 22 candidates largely by eliminating those which had very little production and use in California. (Substances primarily used as pesticides were excluded from the scope of this study.) The remaining candidates were then ranked by additive and multiplicative algorithms and by a panel of experts. The results of these rankings were combined to produce a single selection of 11 priority candidates. In alphabetical order, they are arsenic, asbestos, benzene, cadmium, carbon tetrachloride, chloroform, ethylene dibromide, ethylene dichloride, N-nitrosoamines, perchloroethylene, and polycyclic aromatic hydrocarbons. In continuing studies, a baseline emissions inventory is being prepared, and a source testing program is being designed.

In recent years, concern has grown over the possibility that certain materials released to the atmosphere through industrial and commercial activity may be responsible for a significant portion of the incidence of cancer in the general population. This concern is manifested at the federal level in the National Emission Standards for Hazardous Air Pollutants (NESHAP), which limit emissions of the known carcinogens asbestos, beryllium, and vinyl chloride.¹

Only a few states, including New Jersey and California, have begun efforts to identify airborne carcinogens of concern to the general public for the purpose of setting state emission regulations for these substances. After reviewing national use data for known and

suspected carcinogens, New Jersey selected ten volatile organic compounds and five heavy metals to be examined further, and is currently measuring ambient atmospheric concentrations of these substances in a variety of areas. In the second year of the study, the state has increased the volatile organics studied to 20 and begun measuring heavier organics associated with particulates.² In California, a very different approach was taken.

Overview of California's Approach

The California Air Resources Board (CARB) is sponsoring a three-stage study of airborne emissions of carcinogens from anthropogenic activities. The

first stage, which is the subject of this paper, was to identify roughly five to ten materials which, of the hundreds of known or suspected airborne carcinogens, are most likely to be of greatest concern to California's general population. Also of interest were those which, in order to satisfy occupational health and safety regulations, might be transferred from the workplace air to the outside atmosphere. The second stage, which is now underway, includes pinpointing of emission sources for each of the carcinogens of importance, quantification of emissions, and design of source-testing methods. A subsequent stage will consist of source testing and measuring public exposures to those substances for which data are unavailable. The basis for regulatory action, if appropriate, will include the results of this program and other related research.

Screening of Candidate Carcinogens

The National Institute for Occupational Safety and Health (NIOSH), lists 1905 chemicals which have reported neoplastigenic or carcinogenic effects and 510 which have otherwise received attention for their neoplastigenic potential.³ The need to select five to ten materials from such a large number of potential candidates dictated that we devise a way to rapidly eliminate from further consideration the vast majority of the substances. Given the paucity of published data on most of the candidate substances, the screening method was designed to make best use of readily

Copyright 1979-Air Pollution Control Association

available information. The screening process was as follows: (1) eight complications of known and suspected carcinogens were reviewed and those substances which were not used in California, were highly unstable in air, or were very doubtfully carcinogenic were eliminated; (2) after more detailed information was obtained for the remaining 25 substances, candidates were rated by two different analytical methods; (3) an expert panel was convened to review dossiers on the candidates and to independently rank them; (4) from the eight to eleven substances ranked highest by all three approaches, eleven were selected for the emission identification and source-testing design stages of the CARB effort.

Initial Screening of Potential Candidate Carcinogens

65 compounds were selected from 642 industrial organic air pollutants compiled by MITRE Corporation for the U.S. Environmental Protection Agency (USEPA).⁴ In that study, pollutants were scored by multiplying four explicitly defined rating factors: annual U.S. production, fraction of production lost to the environment, volatility, and toxicity. To adapt this work to our purpose, we first selected the 114 substances listed as being carcinogenic or neoplas-tigenic. Then, the scores of each of these compounds under the criteria "annual U.S. production," "fraction of production lost," "volatility," and "carcinogenicity" were multiplied together. Selected for further consideration were those substances which had a product score above 50. Another 15 substances listed as being carcinogenic but lacking information for one of the other rating factors were also selected. This list of 65 was then compared with seven other lists of carcinogens.⁵⁻¹¹ Materials common to the reduced MITRE list and at least one of the other lists were chosen for further consideration. Added as candidates were those substances which are regulated as occupational carcinogens by the Occupational Safety and Health Administration (OSHA), and certain inorganic carcinogens.⁹ Finally, substances were added which, in our judgment, should be investigated but had been eliminated at this point. Examples of these are bis(chloromethyl)-ether, epichlorohydrin, and hydrazine.

Next, the refined list, which now contained 47 substances or chemical groups, was pared further by another rapid screening process. Eliminated were all candidates (1) whose production and/or use in California was very low (under 10⁵ lb/yr) and was not thought likely to pose a risk to a localized population; (2) which are very unstable in air; or (3) which should not, on the basis of current evidence, be considered carci-

Table I. Substances reviewed in detail.

Candidate Substances	
Arsenic	Inorganic lead
Asbestos	Alkyl lead
Benzene	Maleic anhydride
Cadmium	Nickel
Carbon tetrachloride	Nitrosamines
Chloroform	Perchloroethylene
Chromium	Phenol
1,4-Dioxane	Polycyclic aromatic hydrocarbons
Epichlorohydrin	Propylene oxide
Ethylene dibromide	Trichloroethylene
Ethylene dichloride	Vinyl chloride
Rejected Substances	
Provisionally Rejected Substances	
Acrylonitrile	
Formaldehyde	
Vinylidene chloride	
Occupationally Controlled Carcinogens	
2-Acetylaminofluorine	4-Dimethylaminoazobenzene
Benzidine	Ethyleneimine
4-Biphenylamine (4-aminodiphenyl)	4,4'-Methylene bis(2-chloroaniline) (MOCA)
Bis(chloromethyl)ether,	
Chloromethyl methyl ether	α -Naphthylamine, β -Naphthylamine
Dibromochloropropane (DBCP)	4-Nitrobiphenyl
3,3'-Dichlorobenzidine	β -Propiolactone
Other Rejected Substances	
Acetamide	Diphenylamine
Aniline	Hydrazines
Auramine	Isonicotinic acid hydrazide
Beryllium	Nitrobenzene
Diethyl sulfate, Dimethyl sulfate	

nogenic. The result of the initial screening was a list of 22 candidate materials, which is presented in Table I.

Ranking Candidates by Additive and Multiplicative Algorithms

Many screening or ranking systems fall into one of two categories: additive and multiplicative. Some systems are a combination of the two, while others combine an "objective" approach with subjective evaluation of the results.¹² The 22 substances surviving the initial screening were ranked independently by the two approaches. If the same substance rated highly under both systems, its importance to California was judged to be more likely than if it had scored highly in only one method.

Additive Approach. In the additive approach, the user identifies one or more criteria and rates each alternative substance against each criterion, while simultaneously deciding the relative importance of the criteria. Eq. (1) shows its mathematical formulation.

$$\text{Rating for pollutant } i = \sum_{j=1}^m W_j R_{ij} \quad (1)$$

Each criterion, or rating factor (R_j) is assigned a value for each pollutant i , and each rating factor is weighted (by W_j) according to its importance relative to the other criteria. The score for pollutant i under criterion j is the product of

the rating under that criterion and the corresponding criterion weight. The overall rating for pollutant i is then the sum of the scores under all the criteria.

The additive approach has several virtues, the main one being that it forces the user to make all assumptions explicit. In the process of setting up such a ranking system, new insights into the problem under consideration may be gained. Once the system is set up, it is relatively easy to use. Where data for scoring pollutants are unavailable, artificial scales can be constructed to quantify subjective factors. Finally, the sensitivity of the results to the system's subjective aspects may be measured. For example, one can determine the effect of changing criteria weights upon the final pollutant ranking. Similarly, an appreciation may be gained of the significance of the range of uncertainty for a particular required data element by varying rating factor values.

A fundamental problem with the approach is that there is no logical basis for adding the individual scores assigned under the criteria, other than the assumption that this simulates, or even improves upon, the user's thought process. A major operational problem is that of weighting the criteria. A common practice is to give all criteria equal weight, but that is in itself a statement about the relative importance of the criteria.

Multiplicative Approach. In the multiplicative approach, the rating for each alternative is the product of the ratings under each criterion:

$$\text{Rating for pollutant } i = \prod_{j=1}^m R_{ij} \quad (2)$$

A multiplicative approach can have some advantages over additive ones. First, in some cases the ratings can be physical parameters such as concentrations or volatilities; there is then no need to weight the criteria and hence less controversy over subjective judgments. Second, multiplication generally provides a wider range of scores than does addition, allowing clearer discrimination among alternatives. Finally, this approach provides results which are more intuitively acceptable. As an example of this last point, suppose that exposure and "harmfulness" levels for candidate substance are each converted to values on a 0 to 10 scale and that a certain substance is both extremely toxic and extremely rare. An additive approach would give the compound a rating of $0 + 10 = 10$, which is equivalent to that of a moderately prevalent substance (rated, say, at 5) which is moderately harmful (rated also at 5). A multiplicative approach, on the other hand, would rate the first substance at 0 and the second at 25.

Criteria. The six criteria used in the additive and multiplicative ranking procedures are defined in Table II. Assignment of values to the R_{ij} was based upon data gathered from published literature, personal communications, and panel discussion, and has been fully documented.¹³

Because the purpose of this exercise was to determine the relative importance of the suspected candidate carcinogens, R_1 was scaled to the most heavily used candidate substance, benzene, whose annual production and use in California is nearly 10^9 lb. Materials with a use under 10^5 lb/yr would be rated zero for R_1 and rejected. However, before rejecting a substance by this criterion, we considered whether its emissions could in particular circumstances result in high exposures to a localized population.

R_2 takes into account the fact that the chemical industry is in continual change. Substances of concern today may be phased out, while the use of others may rise dramatically, increasing their importance as pollutants. Information on developments which could likely result in a change in the growth rate was factored into the choice of a value for R_2 . As an example, asbestos consumption in California has been stable in recent years. However, the pending phaseout of asbestos in motor vehicle friction materials will hasten the decline in asbestos consumption; hence we assigned a value of 1 for R_2 .

Ideally one could use pollutant emission as a criterion. However, in this case emissions were to be estimated in detail only for the five to ten carcinogens finally selected. Therefore a measure of emission potential was used, based upon knowledge of the substance's manufacture and use, for R_3 . The highest rating went to substances which are widely used, especially in consumer products. A slightly lower rating went to substances which are routinely emitted from industrial processes during production and use. Some materials are employed in such a way that emissions are quite low even though tight emission control may not be required by law. Materials in this category were assigned a value of two for R_3 . Substances which, under federal or state regulations, may not be discharged to the exterior environment but which could be discharged by accident received the lowest rating.

Each candidate was evaluated on the basis of its propensity to decompose in ambient air. Materials with half-lives greater than eight hours were considered moderately to highly stable and rated five for R_4 . Low to moderate stability was assigned to substances with half-lives between zero and eight hours. Compounds known to exist in air for only a few minutes would be rated zero

and rejected. Even though their oxidation state or anion associations may change in the atmosphere, metals do not degrade and were considered stable. Asbestos is likewise stable. Many of the decomposition reactions of organic molecules are mediated by light. Such substances, if released at night, would have several hours to disperse in the surrounding area.

A rapid way of assessing the relative potential of different substances to spread from a release point is to note their physical state under normal ambient conditions. Accordingly, we scored materials emitted as vapors or fine particulates the highest for R_5 and coarse particulates the lowest. Intermediate values are possible for varying amounts of fine and coarse particulate emissions from the same source or from different sources.

There is as yet no widely agreed upon measure of the relative potencies of carcinogens, although some ranking systems have been proposed.¹⁴ Extrapolating data from *in vitro* techniques such as the Ames bacterial mutagenicity test and from laboratory animal studies to humans is problematic. Therefore a less quantitative measure of the carcinogenic potential of each candidate substance was used. The candidates receiving the highest scores for R_6 would be those for which there is strong evidence of carcinogenesis in humans. Examples are asbestos, which is implicated in mesothelioma; vinyl chloride, which has been identified as the agent of liver cancer in exposed workers; and bis-(chloromethyl)ether, shown by epidemiological studies to cause lung cancer in resin workers. The next highest rated substances are those for which human carcinogenicity is unknown but which have produced cancer in one or more mammalian species in laboratory tests. Next are those which have not been shown to be carcinogens, but which have proven to be mutagenic in test animals. Substances for which the only knowledge of carcinogenic potential is a positive Ames test (producing mutations in histidine-requiring strains of *Salmonella*) are rated 2. Finally, substances which are implicated only as precursors or co-carcinogens would be rated lowest.

Substances unequivocally associated with carcinogenesis were considered as carcinogens in this study. Conditions of emission and exposure, including the presence of co-carcinogens, were factored into the evaluation of each candidate where possible. Carcinogenic substances derived from the metabolism of a precursor were considered as carcinogens. However, ubiquitous substances which have been hypothesized to be precursors (e.g., secondary amines, nitrous acid, and nitric oxide, which combine under certain circumstances to

Table II. Definitions of the criteria used.

R_1: Present use in California	
100% of max. (10^9 lb/yr)	5
10% of max. (10^8 lb/yr)	4
1% of max. (10^7 lb/yr)	3
0.1% of max. (10^6 lb/yr)	2
0.01% of max. (10^5 lb/yr)	1
<0.01% of max. (< 10^5 lb/yr)	0
R_2: Growth in California use	
+ 20%	5
+10% to +20%	4
Positive growth to 10%	3
Stable or unknown	2
Decline	1
Being phased out	0
R_3: Emission potential	
Widespread use in consumer products	5
Relatively poor control over emissions	4
Relatively good control over emissions	2
Tightly controlled	1
R_4: Stability in ambient Air^a	
Moderate to high stability ($t_{1/2} > 8$ hr)	5
Low to moderate stability ($t_{1/2} \sim 0-8$ hr)	3
Unstable ($t_{1/2} \sim$ few minutes)	0
R_5: Dispersion Potential	
Emitted largely as vapor or fine particulate	5
Emitted largely as coarse particulate	1
R_6: Evidence of Carcinogenicity	
Known or suspected human carcinogen	5
Known mammalian carcinogen	4
Suspected mammalian carcinogen or known mammalian mutagen	3
Ames test positive	2
Precursor or co-carcinogen	1

^a $t_{1/2}$ is the half-life.

form N-nitrosoamines) were not considered because of uncertainties in the importance of their link to the carcinogenic compound and the practical considerations demanded by the scope of the study.

It was beyond the scope of this study to judge the validity and interpretation of the experimental and epidemiological evidence upon which the carcinogenicity of candidate substances has been established. We accepted the conclusions about carcinogenicity drawn by the International Agency for Research on Cancer or the National Cancer Institute and did not consider dosage or route of administration of tested substances. However, considerations of test validity did enter into the subjective evaluation by the panel of experts.

Weight. In the additive ranking scheme, each rating criterion is weighted according to its importance relative to the other criteria. Little precedent exists for assigning these weights. In our judgment, and as generally agreed by the panel of experts (see below), R_1 , R_3 , and R_6 are more important than the other criteria. Evidence of carcinogenicity was considered to be the most important criterion of all, so W_6 was assigned a value of 3. W_1 and W_3 were set at 2, and W_2 , W_4 , and W_5 were set at 1. In order to discern the potential sensitivity of the rankings to the weight assignments, the candidates were also ranked using equally weighted criteria.

Ranking Candidates by Panel of Experts

A nine-member panel of experienced governmental, industrial, and academic scientists, whose disciplines included organic and physical chemistry, industrial hygiene, toxicology, epidemiology, and regulatory control of toxic substances, was convened to provide additional data for our ranking algorithms,

to discuss our candidate substances and rejections, to suggest possible new substances for consideration, and to rank the candidates independently of our own ranking. Two weeks before the meeting, panel members were given one-to three-page dossiers on each candidate substance.

At the start of the meeting, before any group discussion, the panel was asked to rate each candidate substance with a score from 0 to 5. Next, each candidate was discussed at length. We provided an overview and summarized critical issues identified up to that point. Through materials brought to the meeting and their personal experience, panel members were able to provide much useful information on the candidates and additional insight into our rating criteria. At the end of the two-day session, the panel again rated the candidates.

Results and Discussion

Final Selection

Table III shows the highest-scoring substances as determined by the additive and multiplicative approaches and by the panel. In the additive approach, a single ranking was obtained by averaging the two rankings resulting from using equal and unequal weights. The rankings of most candidates were unaffected, but carbon tetrachloride, chloroform, chromium, and inorganic lead changed more than three positions. Because uncertainties in the data base preclude imputing significance to small differences in the final ordering, the lists in Table III are presented in alphabetical order. However, it is of interest to point out that benzene consistently ranked highest.

Because some candidates had equal rating scores, we could not choose exactly ten candidates from the additive and multiplicative rankings. Instead, the

top nine and eleven were selected from the two exercises, respectively. We also considered the ten substances scored highest by the panel at the end of the session. The final consensus selection consisted of the 11 candidate substances appearing on at least two of the three lists. For the substances included in the consensus ranking, a baseline emissions inventory is being conducted, and a source testing program is being designed.

Rejected Substances

Some comments about certain substances not appearing on the final list are in order, inasmuch as they include known carcinogens and compounds which have received considerable attention in recent years as occupational carcinogens.

Provisionally Rejected Substances. Appended to the consensus ranking (Table III) were vinyl chloride, gasoline and engine exhausts, tobacco smoke, and pesticides. No further action by the CARB is recommended at this time for vinyl chloride because it is already subject to the USEPA emissions standard, a CARB ambient air quality standard, and an OSHA standard.

Gasoline and tobacco smoke were appended to this list because each occurs very widely and contains several of the candidate substances reviewed in this study, some of which are in the final listing. For example, gasoline contains benzene, ethylene dibromide, ethylene dichloride, and alkyl lead compounds, the last three being in leaded grades only. Both gasoline and diesel combustion products include PAH's. Tobacco smoke contains, among other neoplastic substances, nitrosamines, PAH's, nickel, arsenic, cadmium, and other heavy metals. Many individuals are involuntarily and, in many situations,

Table III. Highest ranked candidates from each ranking method.^a

Additive	Multiplicative	Panel of experts	Highest consensus ranking	Highly ranked but no inventory recommended at this time
Asbestos	Arsenic	Arsenic	Arsenic	Vinyl chloride
Benzene	Asbestos	Asbestos	Asbestos	Gasoline and engine exhausts
Cadmium	Benzene	Benzene	Benzene	Tobacco smoke
Ethylene dibromide	Cadmium	Carbon tetrachloride	Cadmium	Pesticides
Ethylene dichloride	Carbon tetrachloride	Chloroform	Carbon tetrachloride	
Nitrosamines	Chloroform	Ethylene Dibromide	Chloroform	
Perchloroethylene	Chromium	Ethylene Dichloride	Ethylene dibromide	
Polycyclic aromatic hydrocarbons (PAH)	Ethylene dichloride	Nitrosamines	Ethylene dichloride	
	Nitrosamines	Perchloroethylene	Nitrosamines	
	Perchloroethylene	PAH	Perchloroethylene	
	PAH		PAH	

^a Listed alphabetically.

virtually unavoidably exposed to tobacco smoke. Because the sources of gasoline, its combustion products, and tobacco smoke emissions are well known, no specific action was recommended for these materials during the emissions inventory and source testing design stages of the present study. It was considered important, however to draw attention to the general public's exposure to these substances. Pesticides are listed for the same reason, though a detailed examination of pesticides was beyond the scope of this study. Many pesticides are widely used, and some of them are known to be carcinogenic.

Other Rejected Substances. Acrylonitrile and vinylidene chloride were placed in a "provisionally rejected" group because of the panel's suspicion that imports of these compounds to California from Japan may be appreciable, yet are hard to substantiate. Should such imports be verified in the future, these two compounds would take on greater importance. Formaldehyde was also provisionally rejected because the preponderance of evidence indicates that it is not carcinogenic and that bis-(chloromethyl)ether is not formed from formaldehyde in appreciable quantities in industrial environments.¹⁵ The occupationally controlled carcinogens ethyleneimine and beta-propiolactone were rejected in part because of their reactivity in air. At the time of this study, DBCP, a pesticide, was no longer being produced in California and was therefore rejected from further consideration.

Occupational Regulations and Community Exposure

A question of interest to the CARB was whether the regulation of acknowledged occupational carcinogens adversely affects the ambient air outside the workplace. Our general findings can be illustrated by the example of asbestos.

Asbestos is a very widely used material for which no ambient air standard exists. Concentrations in the workplace are limited to an eight-hour time-weighted average concentration of two fibers/cm³ of air and a ceiling concentration of ten fibers/cm³. In meeting this standard, exhausting air containing asbestos to the ambient air is not restricted, except by the USEPA's requirement that there shall be no visible emissions containing asbestos particles from such facilities, excluding brake shops.¹ Considering that, under certain conditions, 10³ asbestos fibers/cm³ could be emitted without being visible,¹⁶ this standard may allow considerable asbestos emissions. It is unlikely, however, that emissions would actually approach these levels. First, since the OSHA standard cannot generally be achieved

by ventilation alone, the generation of asbestos particles in the workplace must be greatly reduced. Second, the air is usually filtered to prevent recirculation of asbestos to a workplace. Asbestos waste must be disposed of in sealed impermeable bags or containers. Thus, under current occupational regulations, the ambient air generally appears to be afforded greater protection than it would without such regulations.¹⁶

Conclusion

The screening and ranking methodology presented in this paper proved to be a feasible approach to establishing a priority list of airborne carcinogens in California. We feel that it is an efficient means of focusing further efforts on emissions inventories, source testing, and ambient measurement, for it not only identifies all the carcinogens of potential concern, but it also permits the state regulatory agency to direct its research resources toward those substances of particular interest within its jurisdiction.

References

1. "National Emission Standards for Hazardous Air Pollutants: A Compilation as of April 1, 1978," PEDCO Environmental, Inc., for U.S. Environmental Protection Agency, EPA/340/1-78/008 (NTIS No.: PB 288 205), 1976.
2. S. Gray, New Jersey Department of Environmental Protection, Trenton, N.J., private communication, 1979.
3. H. E. Christensen, E. J. Fairchild, and R. J. Lewis, Sr., "Suspected Carcinogens: A Subfile of the NIOSH Registry of Toxic Effects of Chemical Substances," 2nd Ed., National Institute for Occupational Safety and Health, NIOSH 77-149.
4. B. B. Fuller, J. Hushon, M. Kornreich, R. Ouellette, L. Thomas, and P. Walker, "Scoring of organic air pollutants," for U.S. Environmental Protection Agency, Mitre Corporation Technical Report MTR-6248, 1976.
5. E. R. Lozano, "Toxicants Selected for Priority Environmental Assessment," correspondence with EPA Region VI Administrator, 1977.
6. "Survey of Vinyl Chloride Levels in the Vicinity of Keysor-Century, Saugus, California," U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver and San Francisco, EPA-330/2-77-017a, 1978.
7. D. Bardin, Testimony in "Hearings on Relationship Between Cancer and the Environment," U.S. House of Representatives, 94th Congress, 2nd Session, Committee on Interstate and Foreign Commerce, Serial No. 94-141, 1976, pp. 57-70.
8. T. H. Maugh, "Carcinogens in the workplace: where to start cleaning up," *Science* 197 (4310): 1268 (1977).
9. C. R. Warner, "Classification of the Exposure Hazard Presented by Thirty-Six Chemicals and Mixtures," Memorandum from Chemist, Office of the Associate Director for Carcinogenesis, Division of Cancer Cause and Prevention, to Supervisory GAO Auditor, General Accounting Office, 1975.
10. "Chemicals with Sufficient Evidence of Carcinogenicity in Experimental Ani-

mals," International Agency for Research on Cancer, IARC Working Group Report, Lyon, France, 1978.

11. "Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1977," American Conference of Governmental Industrial Hygienists, 1977.
12. M. B. Rogozen, D. F. Hausknecht and R. A. Ziskind, 1976, "A Methodology for Ranking Trace Elements in Fossil Fuels According to Their Potential Health Impact," by Science Applications, Inc. for Electric Power Research Institute, 1976.
13. L. Margler, R. Ziskind, M. Rogozen, and M. Axelrod, "An Inventory of Carcinogenic Substances Released into the Ambient Air of California, Vol. I, Final Report: Screening and Identification of Carcinogens of Greatest Concern," by Science Applications, Inc. for California Air Resources Board, 1979.
14. T. H. Maugh, "Estimating potency of carcinogens is an inexact science," *Science* 202 (4363): 38(1978).
15. C. C. Yao and G. C. Miller, "Research Study on Bis(Chloromethyl)Ether Formation and Detection in Selected Work Environments," by the Bendix Corporation for National Institute for Occupational Safety and Health, Cincinnati, Ohio, Contract No. 210-75-0056, 1979.
16. Occupational Cancer Control Unit, California Department of Industrial Relations, Los Angeles, California, private communications with staff members, 1979.

This paper was developed while Dr. Margler was a Staff Scientist in the Energy-Environment Systems Division of Science Applications, Inc. (SAI), 1801 Avenue of the Stars, Suite 1205, Los Angeles, CA 90067, and Mr. Reynolds was a Project Manager with the California Air Resources Board, Sacramento, CA 95812. Dr. Margler is currently employed as Director of Environmental Sciences for Winzler and Kelly Consulting Engineers, 633 Third Street, Eureka, CA 95501, and Mr. Reynolds is Air Pollution Control Director for the Lake County Air Pollution Control District, 255 N. Forbes Street, Lakeport, CA 95453. Dr. Rogozen is a Staff Scientist and Dr. Ziskind is Deputy Manager of the Energy-Environment Systems Division of SAI.

Appendix B
Disposition of Miscellaneous Sites

Gould, Inc., Vernon: Secondary Lead Smelter

The emissions of arsenic from the four large secondary lead smelters in California were estimated in the program. This estimate was based upon a uniform fugitive emission factor not well supported by measurement information. Therefore, source monitoring was recommended and Gould, Inc., Vernon, being the largest was singled out. It was however proposed to monitor both Gould and RSR Corp. (Quemetco) in the City of Industry since analysis of the plants revealed significant differences in plant equipment and engineering. The latter being more typical of a modern facility.

As a result of pre-test discussions and plant inspections we became aware that Gould was actively in the process of constructing a new facility which would completely replace the existing one. We have monitored progress on the new site and concluded it would be inappropriate to utilize program resources to conduct field tests at Gould. Emissions from the new Gould facility will be based upon test results from RSR.

PG & E - Pittsburg, PG & E - Salinas, and So. Cal Edison - Long Beach: Oil Fuel Power Plants

It was appropriate to consider the emission of arsenic from power plants during the initial study stages since trace quantities in the fuel oil are known to be emitted. Because of the population distribution in the vicinity of three plants and some unrealistically conservative estimates of emission factors, the facilities appeared among the top seventeen stationary sources of potential concern. However, as a result of a reexamination of emission data it was concluded that an error had been made in the material balance of arsenic - resulting in an emission factor equivalent of a 300% release. No literature was found to justify greater than a 30% transfer function. Thus we estimated, at the outside, the emission factor should be reduced from 0.13 lb per 1000 lb to approximately 0.013 lb and resulting arsenic emissions for the entire state were conservatively estimated to be 1,760 lbs (from 17,600) divided amongst all the state's power plants. Clearly then the four secondary lead smelters estimate of 59,400 lbs of arsenic

emissions per year makes consideration of power plant emissions of arsenic a very low priority.

In a literature review by SAI - Methodology for Ranking Trace Elements in Fossil Fuels According to their Potential Health Impact (Rogozen, 1976) - emissions estimates for 15 trace substances were researched for coal and fuel oil power plant conversion. Source content, combustion process transfer functions and control methodology were considered to develop emission factors. The output to input ratio computed and utilized in the study for arsenic was 0.02 to 0.3 (i.e. transfer function between 2 and 30%) reflecting the wide variety of fuels, processes and controls nationwide. The upper end reflecting both high arsenic coals and poor emission control devices. Clearly neither of those conditions accurately apply to the three sites and thus substantiate the decision not to perform emissions measurements.

Calaveras Asbestos Company - Copperopolis: Asbestos Mining and Milling

In the past (late sixties and early seventies) the Calaveras Asbestos Company came under heavy criticism after inspection measurements revealed serious problems. However significant reduction of emissions have occurred prompted by NESHAP regulation and occupational standards. SAI inspected the site in December 1979 under an EPA contract. An emissions inventory was published under that work (Ziskind, 1980) and the bottom line conclusion is that currently no significant emission are being released as a result of blasting which would reach the public. The open pit is some 900 feet deep with blasting at the bottom. Over 80 percent of emissions in the CARB Emission Inventory System were attributed to pit blasting. In fact at its current depth blasted material does not reach the mine surface with the explosive placement used. Additionally the site is more remote than might be realized. The situation is vastly different today than in the past and currently attention should be paid to the issues of occupational exposure and breakdown of ventilation system controls in the milling operations. We recommended that no further consideration be given to this site for the purposes of this program i.e. identification of significant releases which might be responsible for causing hot spots of population exposure.

Various Refineries

It was established early in the analysis program that benzene emissions from refinery operations could, in the aggregate, constitute a significant source. Since there are a large number of refineries in California (46 in Los Angeles County itself at the time of examination) with a wide variety of types, sizes, ages, etc., their evaluation could represent a monumental task. It was noted immediately that within the total scope of the study the design and conduct of a refinery testing program which would develop a complete benzene emissions inventory for one site was impractical let alone to characterize emissions from three i.e. those listed among the 17 most significant potential stationary source emitters.

The three refineries were singled out for special attention in the previous phase because they uniquely had components which process materials containing 10 or more percent by weight benzene. (46 FR 1165, Jan 5, 1981 pg. 1491) Estimates by EPA (Federal Register, 1981) indicate that 90 percent or more of the total benzene fugitive emissions arise from such components. Therefore attention is appropriately focused on the three benzene production/consumption refineries: Chevron (Richmond) Arco (Carson) and Chevron (El Segundo). SAI staff considered the possibility of a testing program at one of these refineries and concluded it would not be cost-effective for a number of reasons:

- California is a minor producer and consumer of benzene with approximately 1.5% of the 11.4 billion pounds produced and consumed nationally in 1977. This can be compared with the fact that California has approximately 10% of the nation's population. Benzene exposure to the general population has been partitioned among the various sources. Approximately 90% of exposure is estimated (SRI, 1978) to be caused by gasoline distribution activities and vehicle emissions in urban areas with nearly all of the balance by benzene handling operations (refineries and chemical plants). In the case of California this percentage will be even more disproportionate because of its greater share of the population and lesser share of the benzene handling. Furthermore since the three refinery sites are heavily urbanized no new rural population segment is being exposed.

- California's most heavily urbanized Air Quality Management Districts have already adopted benzene fugitive emission standards comparable and with some features more stringent than the proposed national emission standard. (46 FR 1165, Jan 5, 1981) Thus the conclusion derived above (i.e. refinery emissions are secondary cause of exposure to the urban population) is further reinforced since it is projected that releases from components in benzene service (>10% benzene) will be reduced by 73% by the proposed Federal Standards. The District rules (e.g. South Coast Air Quality Management District #466 and 466.1) are not restricted to benzene per se nor to only components in benzene service. The rules also include flanges in addition to the components called out in the propose national standard.

The EPA estimated that if the proposed emission standard were adopted the maximum annual benzene concentration for a plant would be 3.6 ppb at a distance of 0.1 kilometer away. Comparing this ground level concentration with the general urban background in California of 19 ppb shows the latter to dominate. In recognition of the secondary importance of these three sites it was decided to utilize program resources to develop field data at other sites where little emissions information was available.