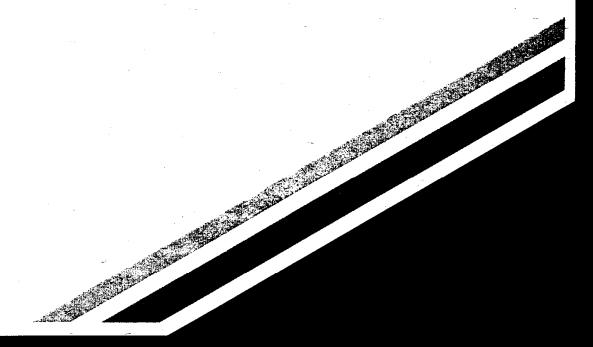




# Solvent Cleaning/Degreasing Source Category Emission Inventory



CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY



AIR RESOURCES BOARD Research Division

# SOLVENT CLEANING/DEGREASING SOURCE CATEGORY EMISSION INVENTORY

Final Report 93-341

#### **Prepared For:**

California Air Resources Board Research Division P.O. Box 2815 Sacramento, CA 95812

Prepared By:

Stephen M. Roe La Weeda Jones Patrick J. Costello

E.H. Pechan & Associates, Inc. 2880 Sunrise Blvd., Ste 220 Rancho Cordova, CA 95742

August 1996

,

#### **DISCLAIMER**

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

# **ACKNOWLEDGEMENTS**

This report was authored by Stephen Roe and Patrick Costello of E.H. Pechan & Associates, Inc. (Pechan) and La Weeda Jones of Regulatory Solutions International. The authors would like to thank Charles DiSogra of Freeman, Sullivan & Co. (FSC) and his staff for assisting in the end-user surveys conducted during this project. We also thank Charles for his contributions to the survey planning process and data reduction.

The authors thank Robert Grant, CARB's contract manager, for his assistance throughout the project. Other CARB staff who participated in the study were Richard Bode, Patricia Velasco, Krista Eley, and Larry Larsen.

This report was submitted in fulfillment of ARB Contract No. 93-341 "Solvent Cleaning/Degreasing Source Category Emission Study," by E.H. Pechan & Associates, Inc. under the sponsorship of the California Air Resources Board. Work was completed as of December 29, 1995.

#### **ABSTRACT**

The California Air Resources Board (CARB) is interested in improving its area source methodology for estimating emissions of total organic gases (TOG) and reactive organic gases (ROG) from the solvent cleaning and degreasing source category. In particular, CARB is interested in an inventory method that provides greater detail in both the types of solvents used and the type of equipment involved (e.g., vapor degreaser, cold cleaner). The current area source methods for this source category do not incorporate this level of detail, which limits regulatory analysis. CARB is also in need of a method to update the base year emission inventory developed during this project.

A comprehensive review of sources of data that could be used to develop base year emission estimates or inventory updates was conducted. These sources included government agencies, trade associations, and other industry sources. The results of this review showed that the only way to develop a base year inventory, with the level of detail desired by CARB, was to perform solvent surveys of the significant end-users. End-user surveys do not result in complete coverage of the source category, since only a predetermined end-user universe is sampled. Ideally, a comprehensive inventory would be developed through both end-user surveys and reliable solvent sales or production figures. Unfortunately, no sources of sales/production data were found for many of the solvents covered in this inventory. Further, for those solvents where sales data were available, reliable data for use in determining the fraction of solvent used for solvent cleaning purposes were often lacking.

To develop the base year inventory, an approach was developed that included two surveys: a comprehensive mail-out survey for facilities likely to use solvents during the cleaning of parts that are incorporated into products (manufacturing users); and a simpler telephone survey to gather information from facilities likely to use solvents during maintenance activities (maintenance users - e.g., auto repair facilities, maintenance users at manufacturing facilities).

Methods used to reduce and statistically analyze the data in order to develop an emissions model are discussed. There were 32 unique combinations of equipment and solvents identified during the end-user surveys that make up the model. These 32 combinations are characterized by three equipment or operation types: cold cleaners (e.g., batch-loaded cold cleaners, conveyorized cold cleaners, spray gun cleaners), vapor degreasers (e.g., batch and conveyorized vapor degreasers), and handwiping activities. The handwiping emissions presented in this study are the first to be reported for this source category by CARB. There are also 15 solvent categories that make up the 32 combinations of equipment and solvents, some of which are single solvents (e.g., 1,1,1-trichloroethane) and others being combinations (e.g., petroleum distillates).

The use of the model to develop county-, air district-, and state-level inventories is described, as well as methods that can be used to assess the uncertainty of the emission estimates. State-level emission estimates for the 1993 base year were 78,579 tons of

TOG. CARB's 1993 TOG estimate for this category was 58,400 tons. One significant difference in the two estimates is that, at the state level, the fraction of ROG in the revised estimates is over 70 percent compared to the value of 40 percent in CARB's 1993 inventory (CARB, 1995). The emissions model developed during this project will provide CARB with the ability to develop emission estimates and allocate emissions to counties and districts in a much more detailed and realistic fashion. In part, this is due to the allocation of emissions being based on employment population and not the general population.

Almost 80 percent of these emissions were estimated to occur within the South Coast and Bay Area districts. The previously unquantified handwiping operations contributed nearly 27 percent of the base year TOG emissions. From a solvents perspective, petroleum distillates were found to account for about half of the total base year TOG emissions.

A limited uncertainty assessment was performed for several equipment and solvent combinations. This assessment showed varying levels of uncertainty depending on the specific combination. For example, estimated annual 1993 TOG emissions in Los Angeles (L.A.) County for the trichloroethylene-batch-loaded vapor degreasing combination were shown to range from 60 tons (2.5<sup>th</sup> percentile) to 140 tons [97.5<sup>th</sup> percentile (mean = 99 tons)]. For cold cleaning using miscellaneous solvent blends, estimated annual L.A. County emissions ranged from 45 tons (2.5<sup>th</sup> percentile) to 2,928 [97<sup>th</sup> percentile (mean = 1,055)].

Since variability in activity and emission factors drives the uncertainty estimates, additional resolution of certain solvent-equipment pairings is needed to decrease the uncertainty. For example, additional data (e.g., surveys) for the miscellaneous blends-cold cleaning category is needed in order to further resolve the solvent usage patterns in this grouping. For example, the additional data may lead to disaggregation of the activity or emission factors for certain industry groups. Assuming that usage patterns are similar within industry groups, the newly formed industry-specific emission/activity factors will likely have lower variability. A similar argument could be made for disaggregation (increased resolution) for specific geographic regions.

Finally, while not representing the ideal source of inventory update data, information on industry employment was found to be the best data source for preparing inventory updates. Recommended methods for updating the base year estimates using the emissions model and employment data from the U.S. Bureau of Census are presented, along with recommendations for improving the emission estimates in future years.

## **CONTENTS**

	Pa	ge
DISCLA	AIMER	iii
ACKNO	OWLEDGEMENTS	iv
ABSTR.	ACT	v
TABLE	S AND FIGURES	ix
EXECU	TIVE SUMMARY	1
CHAPT INTRO A. B. C.	DUCTION  THE SOLVENT CLEANING AND DEGREASING SOURCE CATEGORY  1. Vapor Degreasing  2. Cold Cleaning  3. Wipe Cleaning Operations  4. Solvent Cleaning Compounds  KEY REGULATORY DEVELOPMENTS AFFECTING SOLVENT USE IN  CALIFORNIA  CURRENT AND FUTURE TRENDS OF SOLVENT DEGREASING IN  CALIFORNIA  1. 1,1,1-Trichloroethane (TCA)  2. Perchloroethylene (PERC)  3. Acetone  4. HCFC-141b  5. Alternatives  CURRENT CARB INVENTORY METHODS	9
	DDOLOGY FOR THE DEVELOPMENT OF A 1993 BASE YEAR ION INVENTORY TOP-DOWN VERSUS A BOTTOM-UP INVENTORY APPROACH 1. Problems Encountered in Developing a Top-Down Approach 2. Selected Inventory Approach END-USER SURVEYS 1. Survey Planning	21 23 26 26 26 32

# **CONTENTS** (continued)

-	Pa	age
CHAPT	ER III	37
1993 B	ER III ASE YEAR EMISSION INVENTORY RESULTS	37
Α.	MANITEACTURING USAGE	0,
	1. Data Reduction and Statistical Analysis	53
	2. 1993 Base Year Inventory	
В.	MAINTENANCE SOLVENT USAGE	58
	1. Data Reduction and Statistical Analysis	-
	2. 1993 Base Year Inventory	63
C.	TEMPORAL ALLOCATION	72
D.	BASE YEAR INVENTORY UNCERTAINTY	73
CHAP <sup>7</sup>	TER IV	70
INVEN	TORY UPDATE METHOD	70
A.	ASSESSMENT OF AVAILABLE DATA SOURCES	19
	1. Production Data	79
	2. Marketing Data	80
	3. Census Data	81
	4. Other Data	82
$\mathbf{B}$ .	RECOMMENDED UPDATE METHOD	82
С.	RECOMMENDATIONS FOR FUTURE INVENTORY EFFORTS	86
REFEI	RENCES	89
ABBRI	EVIATIONS & ACRONYMS	91
APPE	NDIX A: MANUFACTURING SOLVENT USER SURVEY PACKAGE	A-1
APPEI	NDIX B: EMISSION MODEL TABLES	B-1
	NDIX C. LINCERTAINTY MODELING RESULTS	

## **TABLES AND FIGURES**

Tables	Pa	age
ES-1	1993 Statewide Solvent Cleaning and Degreasing Emission Inventory	. 2
ES-2	1993 State TOG Emissions by ESP Combination	. 6
II-1	Assumed Universe of Solvent Cleaning End-Users	27
II-2	Equipment/Operation Types	28
II-3	Solvent List	29
II-4	Sample Frame	30
II-5	Minimum Sample Size	31
II-6	Manufacturing Survey Responses by MIG	33
III-1	Manufacturing Survey Distribution of Responding Facilities	37
III-2	Manufacturing Solvent Usage: Original 81 ESPs Reported	39
III-3	Solvent Combinations	40
III-4	ANOVA of Batch Versus Conveyorized Equipment Activity	41
III-5	Manufacturing Solvent Usage: Final 32 ESP Combinations	42
III-6	Pure Solvent Densities	44
III-7	Example 1: Distribution of Survey Records	45
III-8	Manufacturers Survey: Number of Facilities in Sample Frame	46
III-9	Example 1: Emission Model Table	47
III-10	Example 2: Distribution of Survey Records	48
III-11	Example 2: Comparison of Mean AFs by MIG	49
III-12	Example 2: Comparison of MIG 1,4,5,6 Mean AFs by Region	50
III-13	Example 2: Emission Model Table	50
III-14	Comparison of Employment Allocation Data Sets Using	
	VCAPCD Vapor Degreasing Data	52
III-15	Manufacturing Solvent Usage: Summary of Emission Model Variables	
	Statistics	54
III-16	Manufacturing Solvent Usage: MIGs 1-7 1993 State TOG Emissions	
	by ESP Combination	55
III-17	Manufacturing Solvent Usage: 1993 County-Level TOG Emissions	56
III-18	MIGs 1-7 Maintenance Solvent Usage: Final 25 ESP Combinations	59
III-19	MIGs 1-7 Maintenance Solvent Usage: Summary of Emission Model	
	Variable Statistics	61
III-20	Emissions Model Variables for Industry Group 8	62
III-21	Emissions Model Variables for Industry Group 9	64
III-22	Maintenance Solvent Usage: MIGs 1-7 1993 State TOG Emissions	
	by ESP Combination	64
III-23	MIGs 1-7 Maintenance Solvent Usage: 1993 Statewide TOG Emissions.	66
III-24	Industry Group 8: 1993 Statewide TOG Emissions	68
III-25	Industry Group 9: 1993 Statewide TOG Emissions	70
III-26	Temporal Activity for a Sample MIG	72
III-27	Results of the Uncertainty Analysis	77
IV-1	Appendix B Location of Emission Model Variables for Each	
	ESP Combination	84

# TABLES AND FIGURES (continued)

Figures	Pa	age
TT 1	Schematic of a Top-Down Inventory Approach	22
II-1	Ideal Solvent Commodity Flow	25
II-2	Ideal Solvent Commodity Flow	25
II-3	Typical Real-World Solvent Commodity Flow	20
···-	Distribution of AF for TCA-HWS in MIGs 2, 3, and 7	75
III-1	Distribution of Ar for Tea-trees in 1973 2, 9, and 7	75
III-2	Distribution of EF for TCA-HWS in MIGs 2, 3, and 7	10
	Monte Carlo Distribution of 1993 TOG Emissions for TCA-HWS	
III-3	Monte Carlo Discribution of 1000 100	76
	in L.A. County	10

#### **EXECUTIVE SUMMARY**

The primary objective of this study was to develop a comprehensive base year inventory of total organic gases (TOG) for the solvent cleaning source category. TOG emissions were developed at the county-, air district-, and state-levels. The inventory was broken down into equipment and operation types (e.g., vapor degreasers, cold cleaners, and handwiping) paired with specific solvents or solvent groups (e.g., 1,1,1-trichloroethane, petroleum distillates). A total of 32 pairings of equipment and solvents were identified during the inventory development process. The secondary objective of the study was to develop an update method for the base year inventory.

Comprehensive end-user surveys were performed to gather the necessary data for inventory development. An emissions model was developed from nearly 1,400 survey responses. The model consists of activity factors, emission factors, and solvent user fractions (emission model variables) and an emissions allocation data set. The emission allocation data set selected for this project is employment data from the 1993 County Business Patterns published by the U.S. Bureau of Census (BQC). The statewide 1993 base year inventory is presented in Table ES-1. Annual TOG emissions are presented by county and air district, and are broken out by manufacturing solvent usage and three categories of maintenance solvent usage.

A comprehensive review of sources of data that could be used to develop base year emission estimates or inventory updates was conducted. These sources included government agencies, trade associations, and other industry sources. The results of this review showed that the only way to develop a base year inventory, with the level of detail desired by CARB, was to perform solvent surveys of the significant end-users. End-user surveys do not result in complete coverage of the source category, since only a predetermined end-user universe is sampled. Ideally, a comprehensive inventory would be developed through both end-user surveys and reliable solvent sales or production figures. Unfortunately, no sources of sales or production data were found for many of the solvents covered in this inventory. Further, for those solvents where sales or production data were available, reliable data for use in determining the fraction of solvent used for solvent cleaning purposes were often lacking.

Manufacturing usage refers to any activity where a solvent is used to clean products during the manufacturing process, including final wipe prior to packaging and shipping. Manufacturing industry groups (MIGs) 1-7 represent the assumed universe of manufacturing solvent users in seven Standard Industrial Classification (SIC) code groupings: 1) Furniture and Fixtures (SICs 2514, 2519, 2522, 253x, 2542, 2599); 2) Fabricated Metal Products (SICs 34xx); 3) Industrial Machinery and Equipment (SICs 35xx); 4) Electronic and Other Electric Equipment (SICs 36xx); 5) Transportation Equipment (SICs 37xx); 6) Instruments and Related Products (SICs 38xx); and 7) Miscellaneous Manufacturing Industries (SICs 391x, 3949, 3965, 3993, 3999).

Table ES-1
1993 Statewide Solvent Cleaning and Degreasing Emission Inventory

		TOG (tons/year)					
Air District	County	Manufacturing Usage MiGs 1-7	MIGs 1-7	Group 8	Group 9	County/ District Totals	
Amador Co.	Amador	5.74	2.18	3.30	19.7	30.9	
Bay Area	Alameda	1,356	435	262	1,024	3,090	
,	Contra Costa	233	85.8	107	429	857	
	Marin	58.7	17.7	47.0	91.6	216	
	Napa	17.6	5.71	16.2	142	181	
	San Francisco	159	45.3	114	774	1,095	
	San Mateo	469	175	456	498	1,600	
	Santa Clara	6,195	2,255	223	1,401	10,105	
	Sonoma	276	130	51.8	248	707	
	Solano	115	29.5	45.9	118	310	
	Total	8,880	3,180	1,322	4,725	18,161	
Butte Co.	Butte	60.7	18.7	43.9	83.5	208	
Calaveras Co.	Calaveras	3.11	0.72	2.74	6.63	13.3	
Colusa Co.	Colusa	0.74	0.23	10.1	10.3	21.4	
El Dorado Co.	El Dorado	14,9	5.08	16.0	34.0	70.1	
Feather River	Sutter	12.0	3.65	43.7	35.1	94.5	
	Yuba	6.44	1.36	22.3	28.1	58.4	
	Total	18.4	5.01	66.0	63.2	153	
Glenn Co.	Glenn	0.45	0.14	4.23	23.2	28.0	
Great Basin Unified	Alpine	0.00	0.00	0.23	0.00	0.23	
	Inyo	0.13	0.04	3.49	5.50	9.16	
	Mono	0.93	0.19	1.56	0.75	3.45	
	Total	1.06	0.23	5.28	6.26	12.8	
Imperial Co.	Imperial	8.28	3.05	101	30.4	143	
Kern Co.	Kern¹	0.00	0.00	59.1	0.00	59.1	
Lake Co.	Lake	5.86	1.33	8.42	5.41	21.1	
Lassen Co.	Lassen	0.38	0.11	2.87	14.1	17.5	
Mariposa Co.	Mariposa	1.57	0.75	1.03	1.25	4.61	
Mendocino Co.	Mendocino	28.6	7.35	12.2	82.5	131	
Modoc Co.	Modoc	0.13	0.04	1.03	1.81	3.01	
Mojave Desert	Los Angeles <sup>2</sup>	0.00	0.00	51.7	0.00	51.7	
Mojaro Docon	Riverside <sup>2</sup>	0.00	0.00	80.5	0.00	80.5	
	San Bernardino <sup>2</sup>	0.00	0.00	51.6	0.00	51.6	
	Total	0.00	0.00	184	0.00	184	

## Table ES-1 (continued)

		TOG (tons/year)					
Air District							
	County	Manufacturing Usage MIGs 1-7	MIGs 1-7	Group 8	Group 9	County/ District Totals	
Monterey Bay	Monterey	76.3	27.1	201	125.3	430	
•	San Benito	11.6	3.16	20.8	23.9	59.6	
	Santa Cruz	121	44.1	41.6	241	449	
	Total	209	74.4	264	390	938	
North Coast Unified	Del Norte	1.67	0.46	1.40	10.5	14.0	
	Humboldt	12.4	4.23	<sup>*</sup> 15.5	142.1	174	
	Trinity	0.00	0.00	0.83	9.29	10.1	
	Total	14.1	4.69	17.7	161.9	198	
Northern Sierra	Nevada	57.5	19.8	8.63	19.2	105	
	Plumas	1.09	0.29	2.36	17.2	21.0	
	Sierra	0.00	0.00	0.19	4.14	4.33	
	Total	58.6	20.1	11.2	40.5	131	
Northern Sonoma	Sonoma <sup>3</sup>	0.00	0.00	7.75	0.00	7.75	
Placer Co.	Placer	151	51.4	36.7	76.0	315	
Sacramento Metro.	Sacramento	329	94.8	206	451	1,086	
San Diego Co.	San Diego	3,457	1,046	463	945	5,948	
San Joaquin Valley	Fresno	253	80.4	. 438	396	1,170	
	Kings	8.40	2.51	77.0	68.5	156	
	Kern	66.2	20.8	335	191	614	
	Madera	35.6	10.4	59.7	74.3	180	
	Merced	35.5	10.9	57.6	165	269	
	San Joaquin	247	70.5	178	405	903	
	Stanislaus	180	46.1	96.2	459	784	
	Tulare	112	29.6	359	234	736	
	Total	938	271 -	1,600	1,992	4,813	
San Luis Obispo Co.	San Luis Obispo	91.3	28.6	31.0	74.1	226	
Santa Barbara Co.	Santa Barbara	319	150	122	158	749	
Shasta Co.	Shasta	21.2	6.77	24.5	95.9	149	
Siskiyou Co.	Siskiyou	7.65	2.41	10.4	25.9	46.4	
South Coast	Los Angeles	14,681	4,005	1,672	8,755	29,304	
	Orange	5,418	1,642	449	2,168	9,726	
	Riverside	762	217	218	474	1,681	
	San Bernardino	1,225	303	173	756	2,474	
	Total	22,085	6,167	2,511	12,153	43,185	

## Table ES-1 (continued)

		TOG (tons/year)					
			Ma	intenance Us	age	County/	
Air District	Gounty	Manufacturing Usage MIGs 1-7	MiGs 1-7	Group 8	Group 9	District Totals	
Tehama Co.	Tehama	4.57	1.40	7.67	49.7	63.3	
		8,69	3,39	5.62	25.1	42.8	
Tuolumne Co.	Tuolumne				000	1,531	
Ventura Co.	Ventura	725	236	266	299		
	Solano <sup>3</sup>	0.00	0.00	18.8	0.00	18.8	
Yolo-Solano	1	66.1	17.6	47.4	124	256	
	Yolo Total	66.1	17.6	66.1	124	275	
State	Totals	37,516	11,400	7,492	22,171	78,579	

NOTES:

All emissions except those for group 8 allocated to SJVUAPCD.
 All emissions except those for group 8 allocated to SCAQMS.
 All emissions except those for group 8 allocated to BAAQMD.

Maintenance usage refers to any activity in which a solvent is used to clean machinery, tools, vehicle parts, or other equipment not incorporated into a product. The maintenance usage universe consists of all industries in MIGs 1-7 and two additional groups (industry groups 8 and 9). Industry group 8 includes service industries such as auto repair. Industry group 9 represents all manufacturing industries not included in MIGs 1-7. Both manufacturing and maintenance solvent usage occur in MIGs 1-7, whereas only maintenance solvent usage is assumed to occur in Groups 8 and 9.

The total 1993 TOG emissions estimate of 78,579 tons in Table ES-1 can be compared to CARB's current 1993 TOG emissions estimate for the solvent cleaning source category of 58,400 tons. The new inventory represents a significant improvement over CARB's current method which allows for speciation by about a half dozen solvent types, but not by any equipment types. The current method is also based primarily on 1983 production and end-user survey data. The new emissions data will allow for better resolution of the fraction of ROG for any given county. CARB's existing method uses defaults of 25 percent ROG for synthetic solvents and 100 percent for non-synthetic solvents (CARB, 1991). ROG was 40 percent of the statewide TOG in CARB's 1993 inventory, however, based on the data provided in Table ES-2, ROG was estimated to be closer to 70 percent from the results of this project.

Improvements to CARB's method include speciation by 15 solvent groups and three equipment groups as well as the use of actual 1993 end-user data. Table ES-2 presents the state inventory in terms of equipment-solvent pair (ESP) combinations. As shown, the previously uninventoried handwiping (HWS) category, accounted for nearly 27 percent (20,981 tons) of 1993 TOG emissions from solvent cleaning. Over 60 percent (47,456 tons) came from cold cleaning operations, including batch cold cleaners (BCC), conveyorized cold cleaners (CCC), or spray gun cleaning equipment (GCE). Vapor degreasing, including batch (BVD) or conveyorized vapor degreasers (CVD) accounted for the rest of the TOG emissions.

Petroleum distillates accounted for approximately 50 percent of the 1993 TOG emissions from solvent cleaning. The second largest solvent represented in the inventory is TCA, which accounted for almost 20 percent of the total TOG emissions. This considerable contribution from TCA is significant, given that the production of this solvent was phased out at the end of 1995. Ketones, such as acetone and methyl ethyl ketone (MEK), also represented a sizeable share (over 10 percent) of the total solvent cleaning TOG emissions.

Each of the 32 ESP combinations in Table ES-2 essentially represents a new area source category. It is recommended that CARB establish new Emission Inventory Codes (EICs) for each of these categories and delete the existing five categories for solvent cleaning. The attached report presents emission model variables for the ESP combinations and the equations used to geographically allocate TOG emissions.

As mentioned above, industry group employment data from BOC were used to allocate emissions for the 1993 base year inventory. It is recommended that BOC employment data be used for future inventory updates. It is further recommended that CARB work with the districts to set up new reporting criteria, such that solvent cleaning emissions data can be accurately categorized by the recommended equipment-solvent pairings (i.e.,

Table ES-2 1993 State TOG Emissions by ESP Combination

	Equipment /Operation Type					
Solvent Type	Vapor Cold Cleaning Degreasing (BCC/CCC/GCE) (BVD/CVD) Handwiping (HWS)			State Total		
CA	2,319	7,813	5,436	15,567		
CFC/CFC Blends	1,280	897	374	2,552		
HCFC	-	642	6.10	648		
(etones	3,803		4,268	8,071		
Alcohols/Alcohol Blends	2,689	-	· 1,285	3,974		
Methylene Chloride	32.8	-	1,607	1,640		
Petroleum Distillates	35,762	-	3,995	39,757		
Miscellaneous Pure Solvents	32.1	-	233	265		
PERC	-	430	15.2	446		
Foluene/Xylene	35.4	-	603	639		
TCE	-	249	68.2	317		
Glycol Ethers	66	-	354	420		
PFC Blends	-	100	y	100		
Terpenes	362	-	128	490		
Miscellaneous Blends	1,075	10.9	, 2,609	3,694		
State Equipment Total	47,456	10,142	20,981	78,579		

new EICs). This would negate the need to survey permitted facilities in the future. By doing this, resources would be freed up to further improve the quality of the solvent cleaning emissions inventory (e.g., more attention could be paid to the smaller sources, the assumed solvent user universe could be expanded).

The end-user survey method employed to develop the base year estimates for this project does not provide comprehensive coverage of the source category, since the survey is based on a predetermined universe of significant solvent users. The actual solvent user universe consists of many more users who, individually, may have lower consumption patterns, but combined may add considerable volumes of usage. Ideally, the inventory method would involve both an end-user survey and an assessment of solvent production or sales data. Unfortunately, no sources of sales or production data were found for many of the solvents covered in this inventory. Further, for those solvents where sales/production data were available, reliable data for use in determining the fraction of solvent used for solvent cleaning purposes were often lacking.

Two maintenance groups, mining (e.g., oil/gas production services) and agricultural equipment were not included in the end-user survey. For these sources, emissions were extrapolated from parts washer data supplied by Safety-Kleen Corporation (SKC) and included in the group 8 maintenance totals (Kusz, 1995). Some overlap exists between the SKC and the survey data, and some small degree of double-counting is expected. The amount of double-counting and the uncertainty associated with these estimates can not be quantified. It is recommended that additional data be collected in future inventory efforts to better characterize these groups and possibly other user groups that were not surveyed (e.g., railroad maintenance).

The Federal government (e.g., military bases) was another group that was not surveyed. Data for the majority of these sources should be available from the point source inventories maintained by each air district. Therefore, emissions from CARB's Emission Data System (EDS) for military bases need to be added to the estimates provided in this report. All other point source solvent cleaning emission estimates for industry groups that fall within the user universe specified in this report should be subtracted out of the emission estimates to avoid double-counting.

A limited uncertainty assessment was performed for several equipment and solvent combinations. This assessment showed varying levels of uncertainty depending on the specific combination. For example, estimated annual 1993 TOG emissions in Los Angeles (L.A.) County for the trichloroethylene-batch-loaded vapor degreasing combination were shown to range from 60 tons (2.5<sup>th</sup> percentile) to 140 tons [97.5<sup>th</sup> percentile (mean = 99 tons)]. For cold cleaning using miscellaneous solvent blends, estimated annual L.A. County emissions ranged from 45 tons (2.5<sup>th</sup> percentile) to 2,928 [97.5<sup>th</sup> percentile (mean = 1,055)]. These two examples represent some of the most certain and uncertain estimates for the inventory, respectively. The variability in activity factors (which drives the uncertainty estimates) for the other solvent and equipment combinations were between those for the two examples given above.

From the limited uncertainty analysis, it becomes clear that additional data on some of the solvent-equipment pairings are needed. Additional data (e.g., surveys, more detailed district reporting data) will allow for further disaggregation of activity and

emission factors for these groupings. These more highly resolved activity/emission factors (i.e., factors that are industry- or geographic region-specific) will likely have much lower variability. This is clearly shown in the emission model results, which show that for those groupings with good industry/geographic region resolution, variability in emission/activity factors is relatively low.

# CHAPTER I

#### A. THE SOLVENT CLEANING AND DEGREASING SOURCE CATEGORY

Solvent cleaning and degreasing, hereafter referred to simply as solvent cleaning, represents one of the most ubiquitous sources of air pollutant emissions. From auto repair shops to large aerospace facilities, almost every commercial and industrial establishment that has a need to clean parts will utilize degreasing equipment or perform wipe cleaning with solvents.

Not only does solvent cleaning represent a ubiquitous and largely fugitive source of emissions, together with other sources of solvent use, it also represents a significant portion of the total stationary source volatile organic compound (VOC) emissions in California. According to the California Air Resources Board's (CARB's) 1993 Emission Inventory, solvent-use sources account for 46 percent of the total stationary source VOC emissions in California (CARB, 1995). Because there is uncertainty regarding what the individual contribution from the solvent cleaning and degreasing source category is, the need to develop an improved emission inventory for this source category is evident.

Solvent cleaning can be defined broadly as the mechanical act of cleaning parts. The various types of solvent cleaning and degreasing can be placed in the broad categories of vapor degreasing, cold solvent cleaning, and wipe cleaning. Likewise, solvent degreasing equipment can be placed in the broad categories of conveyorized degreasers (both cold and vapor), batch-loaded vapor degreasers, batch-loaded cold cleaners, and wipe cleaning stations. Although there are well over 30 solvents currently in use, solvent types can also be categorized broadly — as either halogenated [e.g., 1,1,1-trichloroethane (TCA), perchloroethylene (PERC), freon] or nonhalogenated (e.g., mineral spirits, xylene, acetone, water-based solvents).

#### 1. Vapor Degreasing

The basic design of an open-top vapor degreaser includes a tank for holding the solvent, and a heating system to heat and vaporize the liquid solvent. As the liquid vaporizes, a vapor layer is formed above the liquid solvent. The cleaning action is provided by the solvent vapor condensing on the cooler parts; contaminants are either dissolved or are flushed from the parts. The cleaning operation is complete when the temperature of the parts reaches that of the vapor, thereby, ending the condensation process. Because solvent vaporization is occurring, emission losses are high.

Halogenated solvents such as TCA and PERC are ideal for use in vapor degreasing because they can be heated without risk of explosion; their common chemical property is the absence of a "flash point." One definition of a flash point is the temperature at which a solvent will self-ignite upon heating. In order to utilize a solvent in a vapor degreaser,

one must heat the solvent to at least its boiling point. Hence, if a solvent reaches its flash point before it reaches its boiling point, self-ignition (or an explosion) will occur. Solvents that have flash points below their boiling points include acetone, isopropyl alcohol, Varnish Maker's and Painter's (VM & P) naphtha, xylene and toluene. Thus, these solvents are not found in vapor degreasing applications.

#### 2. Cold Cleaning

Cold cleaning, though typically thought of as including solvents used at or below room temperature, also include solvents which are heated to a temperature below their boiling points. Cold cleaning is becoming more common place, as the use of traditional vapor degreasing declines. New and sophisticated equipment have been recently designed for use in cold cleaning. To accomplish the same degree of cleaning, these equipment rely more on mechanical action (i.e., agitation, ultrasonics, flushing, etc.) and less on the solvency of the chemical. Cold cleaning equipment, as defined here, includes a wide range of equipment. Specific equipment belonging to this category include the following: batchloaded cold cleaners, remote reservoir cold cleaners, semi-aqueous cleaning equipment, film cleaning equipment, parts washers, gun cleaning equipment (GCE), and water cleaning equipment.

## Wipe Cleaning Operations

Wipe cleaning operations include solvent cleaning done by hand or without the use of equipment included in the categories of vapor degreasing or cold cleaning. Emissions from wipe cleaning operations are, by far, the most ubiquitous of any equipment group. For example, washing a truck or car by flushing with detergent or solvents, or cleaning a millimeter-wide electronic component with a Q-tip soaked in alcohol, are technically defined as wipe cleaning operations.

Despite the fact that wipe cleaning operations are believed to be so pervasive, emissions from this source category have not been previously estimated by state and local regulatory agencies. This is due, in part, to the fact that wipe cleaning sources are not required to have operating permits in most local air districts. Hence, no accounting is done of such sources.

## 4. Solvent Cleaning Compounds

As will be described in the following sections, significant changes in solvent use have been (and will be) occurring due to current and pending regulatory actions. Despite the fact that the production of TCA will be banned on December 31, 1995, according to the 1993 baseline inventory developed herein, TCA is still one of the predominant solvents used in solvent cleaning. TCA is stable in the lower atmosphere and does not participate in the photochemical reaction to create ground-level ozone. Traditionally, compounds that contribute to ground-level ozone have been stringently regulated at the federal, state and local levels. Air pollution regulations did not start to become stringent in California until the late 1960's. Then, TCA was considered an "exempt solvent" by many agencies and replaced trichloroethylene (TCE) in the late 1960's as the predominant solvent. This was due to the adoption of general solvent-use rules which classified TCE and other compounds as "photochemically reactive."

Other halogenated solvents widely used in vapor degreasing include PERC and 1,1,2-trichloro-1,2,3-trifluoroethane (CFC-113). The production of CFC-113, like TCA, was phased out on December 31, 1995. PERC, though considered a toxic air contaminant by state and local regulatory agencies, will likely remain in the coming years as a vapor degreasing solvent. TCE, though not widely used because of its photochemical activity and toxicity will also remain (in very limited quantities) as a vapor degreasing solvent. Likewise, the use of methylene chloride (METH), which is scarcely used today as a vapor degreasing solvent, will also remain in use in limited quantities.

Solvents used in cold cleaning equipment and wipe cleaning operations are varied. Such solvents range in complexity and properties from the use of plain soap and water to the use of halogenated solvents such as TCA or PERC.

Several traditional and many new alternative solvents and technologies will experience increased use in the near future. These solvents and alternatives include the following: 1) no-clean technology; 2) water cleaning formulations; 3) high-boiling point solvents (e.g., mineral spirits, terpenes, stoddards, etc.); 4) the hydrochlorofluorocarbon, HCFC 141-b; 5) perfluorinated compounds; 6) miscellaneous synthetic blends (e.g., monochlorotoluenes and chlorobenzotrifluorides); 7) volatile methyl siloxanes; 8) methylene bromide and/or brominated hydrocarbons; and 9) advanced technology cleaning (e.g., supercritical fluid cleaning, plasma cleaning and, UV-ozone cleaning).

# B. KEY REGULATORY DEVELOPMENTS AFFECTING SOLVENT USE IN CALIFORNIA

Solvent use in the United States has changed dramatically during the last six years and will continue to undergo additional significant changes in the coming years. The catalyst that fueled these changes was the adoption of the following ground-breaking regulatory acts:

The Montreal Protocol — The Montreal Protocol consisted of a unilateral agreement by major nations to ban the production of ozone-depleting substances;

Federal Clean Air Act Amendments of 1990 — On July 30, 1992, the U.S. Environmental Protection Agency (EPA) issued its final rule-implementing Section 604 of the Clean Air Act (CAA) Amendments of 1990. This section called for a phaseout of production and consumption of Class I substances [e.g., chlorofluorocarbons (CFCs) and TCA| by the year 2000. Consumption, as defined in that rule, equals production plus imports minus exports.

Accelerated Production Phaseout — On February 11, 1992, the United States, in response to recent scientific findings that the hole in the ozone layer over the Antarctic had increased, announced that it would accelerate the phaseout of production of CFCs, halons, carbon tetrachloride, and TCA to December 31, 1995.

Copenhagen Amendments to the Montreal Protocol — In November 1992, the Copenhagen amendments to the Montreal Protocol were adopted, which called for an accelerated production phaseout of CFCs by January 1, 1996. The parties to the Montreal

Protocol also agreed in Copenhagen to phase out the production and consumption of hydrochlorofluorocarbons (HCFCs) by the year 2030.

Federal Labeling Law — On February 11, 1993, EPA issued the final rule (effective 5/15/93) which mandates labeling of containers and products that contain or are manufactured with ozone-depleting compounds.

Final Phaseout Rule Adopted — On December 10, 1993, EPA issued its final rule (effective 1/1/94), implementing the accelerated phaseout of Class I substances and established Class II (e.g., HCFCs) phaseout schedules. This rule additionally accelerated phaseout dates of the more damaging HCFCs. Most notable on the schedule, is the phaseout date of January 1, 2003, established for HCFC- 141b, which has been increasingly used as an alternative for CFC-113 and TCA.

Significant New Alternatives Policy Adopted — On March 18, 1994, EPA promulgated its final rule establishing the Significant New Alternatives Policy (SNAP). This policy defines a process for continuing review of substitutes to ozone-depleting substances to determine their acceptability and provides a petition process to add and delete substances from published lists of acceptable and unacceptable substitutes. As of July 28, 1995, EPA's list of acceptable alternatives to TCA and CFC-113 in solvent cleaning include: aqueous cleaners, semi-aqueous cleaners (e.g., petroleum-based and water), perfluorocarbons (PFCs), organic solvents (e.g., esters, ketones, ethers), TCE, PERC, METH, supercritical fluids, plasma cleaning, and UV/Ozone cleaning. Pending substitutes include HCFC-122, HFC-4310, volatile methyl siloxanes, and perfluoropolyethers. Unacceptable alternatives include HCFC 141b and dibromomethane (i.e., methylene bromide).

Halogenated Solvent Cleaner NESHAP Adopted — In November 1994, EPA promulgated national emission standards for hazardous air pollutants (NESHAP) for halogenated solvent cleaners. These standards implement section 112 of the CAA setting maximum achievable control technology (MACT) standards for processes which emit chemicals identified in the Act list of 189 hazardous air pollutants (HAP). The Halogenated Solvent Cleaner NESHAP requires batch vapor solvent cleaning machines and in-line solvent cleaning machines to meet emission standards reflecting the application of MACT. Area source batch cold cleaning machines are required to achieve generally available control technology (GACT). The rule, which allows for a three year final compliance period ending in 1997, regulates emissions of the following HAP solvents: METH, PERC, TCE, TCA, carbon tetrachloride, and chloroform. Even though carbon tetrachloride and chloroform are rarely used in solvent cleaning, EPA added these chemicals to its original list to ensure the regulation of future use. The rule is significant in that it establishes no size level cutoff for compliance under the rule. Unlike local California district and CARB reasonably available control technologies (RACT) and best available retrofit control technologies (BARCT) requirements, all machines, regardless of size, will have to meet the requirements of the rule. In the absence of a state Air Toxic Control Measure (ATCM), federal NESHAPs become state NESHAPs. Thus, because CARB does not have an ATCM for solvent cleaning, the federal NESHAP is automatically adopted by reference. Some local districts are in the process of revising their current rules to become consistent with the federal NESHAP. For example, the Bay Area Air Quality Management District (BAAQMD) will leave intact provisions of their current rules that are in line with the federal NESHAP, but will propose exemptions for halogenated solvent cleaners that must otherwise comply with the NESHAP. BAAQMD staff indicated that rule promulgation is not expected until late summer or fall of 1996 (Bateman, 1995).

Phaseout Rule Amendments — On May 10, 1995, EPA issued the final rule implementing amendments to the accelerated phaseout schedule adopted on December 19, 1993. The final rule does the following: 1) changes the requirements for the post-phaseout period for transformation and destruction of ozone-depleting substances; 2) establishes the framework for the post-phaseout production of exempted essential uses; 3) revises the control for imports of controlled substances that are used or recycled; 4) eases the requirements for exporting substances to Article 5 countries; 5) changes the allowance requirements for exports of ozone-depleting substances; 6) clarifies the requirements for "heels" (solvent that remains in containers) that are returning to the U.S.; 7) provides a period of reconciliation in which allowance balances may be adjusted; and 8) simplifies the recordkeeping and reporting requirements. The changes made in this rule are intended to ease the economic burden on industry. What is significant, however, is the fact that the production phaseout date remained at December 31, 1995.

Final Rule Excluding Acetone as a VOC Adopted — On June 16, 1995, EPA issued the final rule revising the definition of VOC to specifically exclude the compound acetone. In the rulemaking background, EPA cited scientific evidence to assert that acetone displays negligible photochemical reactivity. The exemption of acetone as a VOC will pave the way for its increased use in key applications, most notably foam blowing. Local districts are expected to follow suit and exempt acetone from their definitions of a VOC.

# C. CURRENT AND FUTURE TRENDS OF SOLVENT DEGREASING IN CALIFORNIA

The solvent use industry will undergo pivotal and rapid changes during the next six to eight years. Significant solvent switching occurred within the past few years and will continue to occur in the coming years. Some new solvents arrived on the market (e.g., PFCs, HCFCs, semi-aqueous, etc.), while some old ones experience increased use (e.g., mineral spirits, perchloroethylene, glycol ethers, terpenes, etc.). In 1993, TCA and CFC's alone accounted for 40 percent of the total solvent used in manufacturing solvent usage. This, occurred despite the fact that the production of these chemicals was due to be phased out in two years. On December 31, 1995, production of TCA and CFC-113 was phased-out for all intents and purposes. Only production for essential uses (e.g., metered dose inhalers) and exportation to developing (Article 5) countries will be allowed. Users have responded to the imminent ban of ozone-depleting substances in one of four ways: 1) some users planned early and implemented environmentally benign alternatives (e.g., aqueous cleaning); 2) some users switched to alternatives that have other environmental problems (e.g., PFCs, HCFCs); 3) a number of users have switched to traditionally used alternatives (e.g., perchloroethylene); and 4) a number of users began stockpiling TCA and CFC-113 in order to delay the inevitable and ensure a sufficient supply for a number of years.

#### 1. 1,1,1-Trichloroethane (TCA)

Despite the fact that the mandated production phaseout of TCA has recently occurred, TCA is still one of the predominant solvents used in solvent degreasing today. Even in the absence of production and significant distribution, TCA use will continue in the coming years. Users will use stockpiled amounts and/or will purchase recycled or reconstituted TCA. Based on the researchers experience and knowledge of the industry, significant use can be expected to last for the next 2 to 10 years.

#### 2. Perchloroethylene (PERC)

Even though the South Coast Air Quality Management District (SCAQMD) data base indicates an overall decline in the number of degreasing equipment, the number of permitted PERC degreasers has recently increased (SCAQMD, 1995). The most probable explanation for this trend is that users are taking advantage of the fact that PERC remains unregulated as a toxic air contaminant (TAC). Users in desperate need of a substitute for TCA and CFC-113 are converting to PERC without having to undergo SCAQMD Rule 1401 review. For the last two years, SCAQMD was expected to amend Rule 1401 (New Source Review of Toxic Air Contaminants). That amendment would, in part, add PERC to the list of TACs to be reviewed for all new sources. Rule 1401 currently requires that acceptable risk levels be met before permits for new sources of TACs are granted. Because PERC has a high unit risk factor, if PERC is ever added to the Rule 1401 list of TACs, it will be difficult to obtain permits for conventional degreasers using PERC. Due to significant controversy surrounding the proposed Rule 1401 amendments, the rulemaking has been delayed significantly.

An interesting paradox is occurring with the current use and regulation of PERC. It has been known for years that PERC has negligible photochemical reactivity. Despite this fact, California has traditionally regulated PERC as an ozone precursor and VOC. In recent years, PERC's status as a toxic compound has been the subject of much debate. Due to it's suspected carcinogenicity, PERC was identified as a TAC by the State of California. As a result of this identification, there are source-specific rules that regulate PERC as a TAC (e.g., dry cleaning rules). As mentioned beforehand, for the past two years, SCAQMD has attempted to add PERC to the list of TACs regulated under Rule 1401. In part, because of the current pro-business/anti-regulatory climate, the addition of PERC to the Rule 1401 list has been an uphill battle for SCAQMD.

With the current stringent regulation of VOCs, and the pending phaseout of ozone-depleting substances, users are left with few solvents that are suitable for use in vapor degreasers. In light of this fact, several new alternatives have emerged (e.g., aqueous solvents, semi-aqueous solvents, citrus/pine solutions, etc.). Users, however, have been slow to adopt the new alternatives and have fought long and hard for the continued use of halogenated vapor degreasing solvents. Agencies have responded to this by allowing PERC to remain as a viable vapor degreasing solvent. Even though the Federal NESHAP for Solvent Cleaning stringently regulates PERC and other HAPS, EPA allows its use under the Significant New Alternatives Policy as an acceptable alternative to TCA and CFC-113 in solvent cleaning. Other evidence of the trend toward increased PERC use includes SCAQMD's proposal to exempt PERC as a regulated Regional Clean Air Incentives Market (RECLAIM) compound (based on the latest RECLAIM development

proposals). Thus, PERC would not be subject to declining emission levels as will be mandated for other VOCs under the RECLAIM program. There is also speculation that PERC may be eventually exempted by EPA as a VOC. Clearly, the evidence suggests that PERC's use as a cleaning solvent will continue to grow.

#### 3. Acetone

Another solvent that will likely see increased use in the future is acetone. As mentioned previously, acetone was recently exempted as a VOC by EPA. Many States and local districts can be expected to follow suit and exempt acetone as well. On November 17, 1995, SCAQMD exempted acetone from its definition of a VOC. In addition to acetone, SCAQMD also exempted ethane, volatile methyl siloxanes (VMS), and parachlorobenzotrifluoride (PCBTF). In addition to PERC and styrene, SCAQMD is also proposing to exempt acetone as a regulated RECLAIM compound. In the immediate future, many solvent users will begin to use acetone to comply with solvent-use regulations. Several coating manufacturers have already formulated compliant coatings with combinations of acetone, PCBTF, and VMS. Significant increases in the use of acetone are likely in key applications such as foam blowing and industrial coating use. Acetone is currently used in cold cleaning and handwiping operations. It's increased use in cold cleaning and handwiping is likely but is not expected to be as significant as other applications, due to the fact that the odor of acetone has traditionally been quite disagreeable to workers. Its use as a vapor degreasing solvent is infeasible due to the fact that its self-ignitability (flash point of 0°F) poses an extreme fire and explosion danger.

#### 4. HCFC-141b

As mentioned earlier, production of HCFC 141-b will be phased out on January 1, 2003 and EPA's Significantly New Alternatives Policy deems it an unacceptable substitute for TCA and CFC-113 in solvent cleaning applications. Despite this fact, HCFC 141-b use has increased in recent years. Because there is essentially no enforcement of the Significantly New Alternatives Policy, its increased use is likely for the near future. The suitability of HCFC 141-b as a vapor degreasing solvent is questionable. Besides being an extremely expensive solvent, HCFC 141-b boils at about 90°F. HCFC 141-b is thus much more volatile than most traditional vapor degreasing solvents and expensive degreasers with triple-coil condensers are typically custom-designed for its use to prevent excessive losses.

#### 5. Alternatives

Alternatives to vapor degreasing solvents have experienced increased use in recent years, but not as much as was anticipated. Alternatives to traditional vapor degreasing include the following:

- No-clean technology;
- Water cleaning formulations;
- High-boiling point solvents (e.g., petroleum-based, mineral spirits, terpenes, stoddards, etc,);
- Perfluorinated compounds;

- Miscellaneous synthetic blends (e.g., monochlorotoluenes and chlorobenzotrifluorides);
- Volatile methyl siloxanes;
- Methylene bromide and/or brominated hydrocarbons; and
- Advanced technology alternatives (e.g., supercritical fluid cleaning, plasma cleaning and, UV-ozone cleaning).

Most of the alternatives have companion problems. The perfluorinated compounds are not good cleaners and due to the fact that they have extremely high atmospheric lifetimes, they will likely be heavily regulated in the future as global warming compounds.

Several miscellaneous synthetic blends (e.g., monochlorotoluene and parachlorobenzotrifluoride) have recently appeared on the market. On November 17, 1995, SCAQMD exempted PCBTF from its definition of a VOC, therefore, it is expected that this compound should see increased use in the coming years. As of July 28, 1995, EPA is currently reviewing the acceptability of both monochlorotoluenes and chlorobenzotrifluorides under the SNAP program.

The volatile methyl siloxanes and the advanced technology alternatives will likely see some use in precision cleaning applications. As mentioned beforehand, along with acetone and PCBTF, SCAQMD also exempted volatile methyl siloxanes from the definition of a VOC.

The advanced technology alternatives will require the use of extremely expensive, specially-designed equipment and, therefore, few users are expected to adopt such an option. Some users can be expected to adopt no-clean technologies, involving process changes that totally eliminate the need for cleaning.

The use of high-boiling point solvents has increased somewhat in recent years. This may be due, in part, to the fact that most air district regulations do not require operating permits for equipment employing their use. Like high-boiling point solvents, equipment employing the use of water cleaning formulations also require no operating permits in most districts. However, the anticipated increase in the use of water cleaning alternatives has fallen significantly short of expectations.

#### **CURRENT CARB INVENTORY METHODS** D.

CARB currently prepares its statewide inventory with a methodology that provides an estimate of the overall source category emissions, which encompasses both point and area sources. The last comprehensive statewide inventory was prepared for base year 1993 (CARB, 1991). To report only area source emissions, CARB compiles local district estimates of point source emissions, which it subtracts from the overall emission inventory.

CARB uses two major area source categories for compiling estimates of solvent emissions from solvent cleaning: Industrial and Commercial. Within these two source categories, CARB defines two major categories of solvents as synthetic and non-synthetic. As defined by CARB, the synthetic category includes the halogenated solvents, PERC,

TCA, TCE, METH, and CFC-113, while the non-synthetic category includes petroleum solvents such as mineral spirits and stoddard solvent.

CARB further breaks down the two area source categories by the use of "Category of Emission Source" or CES numbers (these are currently being replaced by EICs). Sources in the industrial categories include manufacturing and maintenance industries (not auto repair shops) and are comprised of the following three CES numbers:

CES 46813 Manufacturing and Industrial. Degreasing. Non-synthetic-Evap.
CES 46821 Manufacturing and Industrial. Degreasing. Synthetic-Evap.
Manufacturing and Industrial. Maintenance Industries. Degreasing. Solvent-Evap.

Sources in the Commercial categories include automotive repair facilities and are comprised of the following two CES numbers:

CES 46854 Commercial Degreasing. Synthetic Solvents CES 46847 Commercial Degreasing

To develop total organic gas (TOG) emission estimates for the Industrial Degreasing category, CARB used 1983 national production data from the Chemical Marketing Reporter, and an estimate of the California percentage of national use (abstracted from a 1985 CARB-sponsored study) to estimate "national availability for solvent cleaning" for five categories of halogenated solvents (TCA, TCE, PERC, METH, and CFC-113). The U.S. Bureau of Economic Analysis (BEA) economic index was used to grow the 1983 production data to 1993. County population estimates were then used to allocate statelevel emissions to counties. Base year emissions have been forecasted to future years by the use of growth factors.

TOG emission estimates for the Commercial Degreasing category are based on 1983 information from Safety-Kleen Corporation (SKC) and 1977 information from EPA. Emission estimates of non-SKC maintenance degreasers are based on an emission factor (EF) developed by EPA and activity data supplied by SKC. Emission estimates from SKC units are based on data supplied by SKC which included the number of SKC units, the amount of solvent consumed, the amount of solvent recycled, and the density of the solvent (CARB, 1991).

#### E. THE NEED FOR INVENTORY METHOD IMPROVEMENT

The latest CARB inventory for solvent cleaning was prepared for 1993 emissions. Emissions in CARB's 1993 inventory are based on 1983 production figures, and are grown with BEA data to 1993. The fact that significant solvent switching has occurred over the last several years raises a considerable amount of uncertainty in the use of 1983 production figures to estimate 1993 emissions.

CARB's current 1993 inventory provides coverage of approximately a half dozen solvent types and no differentiation by equipment type, rather than the wide range of solvent and equipment types that are actually present in the source category. The

production of two of the solvent types covered, TCA and CFC-113, will be phased out by the end of 1995. Only production for essential uses and developing countries will be allowed. Thus, national production estimates of those solvents will no longer apply to the actual use, and an update to the inventory based on production data could not be used.

The need to better understand emissions from solvent cleaning is evident. In addition to a better understanding of the overall emissions contributed by the source category, CARB desires to gain additional understanding of the specific solvent and equipment types employed. CARB is also interested in developing an accurate update method for solvent cleaning emissions.

CARB's current methodology for developing it's statewide emissions inventory for solvent cleaning has characteristics of a "top-down" approach. A top-down approach involves gathering information on the production, distribution, and solvent end-use patterns and distributing the resultant emissions to counties, air districts, and the state. CARB uses national availability data, estimates of the California percentage of such data, economic activity data, and population data to develop its statewide emissions inventory for solvent cleaning. Since CARB's estimate of the California percentage of national availability is based on 1982 end-user survey data that was scaled up to the State level, the method currently employed is not truly a top-down method. A list of the limitations of the current approach follows:

- To develop California percentages of national availability, an industry snapshot was developed through an end-user survey performed in 1982.
- National availability data are adjusted for growth using U.S. Bureau of Economic Analysis economic data.
- 3. A relationship is assumed to exist between national availability and California consumption.
- Only half dozen or so solvents are considered.
- It is assumed that solvents available for use in California for a particular year are actually used and emitted in that particular year.
- It is assumed that no stockpiling of solvents occur. All solvents purchased for use are used and emitted in the same year.

Each of the above assumptions leads to a considerable amount of unquantifiable uncertainty in the resulting inventory.

In response to several recent regulatory developments, a considerable amount of solvent switching and stockpiling continues to occur. In response to these developments, many distributors began putting their customers on allocations. Thus, distributors refused to sell their customers more than their allocation, even though more than their allocation would be available for use in a particular year. Distributors voluntarily affected the amount of solvent that was used in the same year in which it the solvent was

available. Switching, stockpiling, and allocations are not accounted for in the national availability of a solvent.

Due to the pending phaseout of TCA, many users have been using recycled and/or reconstituted TCA blends. Unless data were gathered from all TCA recyclers, the use of recycled solvent would not be reflected in the national availability figures, thus no accounting of its use would be done in a top-down approach.

## CHAPTER II METHODOLOGY FOR THE DEVELOPMENT OF A 1993 BASE YEAR EMISSION INVENTORY

## A. TOP-DOWN VERSUS A BOTTOM-UP INVENTORY APPROACH

To develop emission inventories of most area VOC sources, two general approaches are considered: a top-down approach and a bottom-up approach. A top-down approach, sometimes referred to as a market balance, involves gathering information on production, distribution, and solvent end-use patterns, and then building logical relationships between these stages. National emission estimates are made using the solvent production data as a starting point and algorithms are developed from distribution, end-use, and disposal data. The national emission estimates are then distributed to counties, air districts, and the state with the use of an allocation data set, such as census data. Top-down approaches have been used in previous inventory efforts for EPA (Pechan, 1993a; Pechan, 1993b).

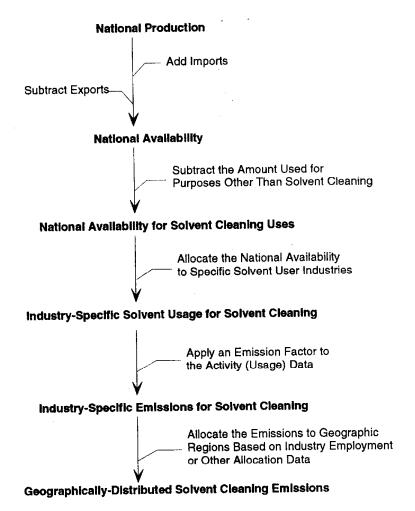
A bottom-up approach involves gathering information directly from solvent users and scaling up the emission estimates using census or other data to a geographic region of interest (e.g., counties, air districts, state). Valley Research Corporation (VRC) used this approach to estimate solvent cleaning emissions for the South Coast Air Basin (VRC, 1989).

The primary advantage to using a top-down approach is that since an estimate of the amount of solvent produced is obtained, then theoretically, the upper limit of solvent available is known (as mentioned in Chapter I, solvent production data does not include recycled solvent). A market balance model can then be developed with information on distribution and end-use. Since the estimate of solvent produced serves as an input to the market balance, a theoretical accounting is made of all of the estimated available solvent.

Figure II-1 shows a schematic of a top-down approach that could be used to estimate emissions for the source category. Information on the national production of a solvent is obtained from the U.S. Bureau of Commerce's International Trade Commission (ITC) or other source (e.g., marketing reports). Data on the import and export of the solvent are added and subtracted from the production estimate to develop an estimate of national availability (NA). Information is then gathered on the uses of the solvent (i.e., through an end-user survey) in order to develop a factor that when multiplied by NA will give an estimate of the national volume of solvent used for solvent cleaning purposes. The next step is to gather information from distributors or end-users on the fraction of use by each industry (and any regional differences in usage patterns).

**FINAL** 

# Figure II-1 Schematic of a Top-Down Inventory Approach



After the fractional industry use has been determined, it can be allocated to different geographic regions using information from the U.S. Bureau of Census (BOC), which is the only comprehensive (in terms of industry coverage) source available for this purpose.

As described in Chapter I, CARB currently uses an approach with some top-down characteristics to develop estimates of halogenated solvent emissions. The current method is not a true top-down approach, however. CARB uses a factor for California consumption developed from 1982 end-user survey data to determine the fraction of the nationally-available solvent that was used in California (SAIC, 1985; CARB, 1991). This method does not incorporate any information on solvent distribution. Therefore, some usage is over-allocated, since the end-user survey did not cover the entire universe of solvent users, only the assumed universe of the study's authors (SAIC, 1985).

#### 1. Problems Encountered in Developing a Top-Down Approach

At the request of CARB, researchers assessed the potential for gathering information on the production, distribution, and end-use of solvents, so that a true top-down model could be developed. Although a top-down approach seems logical and may be the best choice for some source categories, as illustrated below, several issues either reduce the utility of this method or add unquantifiable uncertainty to the emission estimates produced. The information gathered on production and distribution was also assessed for use in a combined top-down and bottom-up approach.

To estimate national availability as shown in Figure II-1, information is available from the ITC on the national production, import, and export for approximately a dozen solvents. Unfortunately, this represents less than half of the solvents currently in use within the source category and does not cover solvent blends. In addition, no information is available as to the precision of these estimates (i.e., national production is estimated by the ITC from surveys of solvent producers). Of the solvent types listed in Table ES-II, only data on TCA, PERC, TCE, ketones, alcohols, some glycol ethers, and toluene/xylenes are available from the ITC (ITC, 1994). This represents less than 40 percent of the estimated 1993 statewide emissions, which are dominated by petroleum distillates (see Table ES-II). Data on one species each of HCFCs and petroleum distillates are also available from the ITC, but it is not known how much of the solvent type each individual species represents.

Estimates on the production of some of the solvents not covered by the ITC are available from chemical marketing sources, such as the *Chemical Marketing Reporter*, Frost and Sullivan, or The Freedonia Group (Pitkin, 1995; Gangloff, 1994; and Santos, 1995). However, these estimates are based on limited surveys of solvent producers and no information on the precision of the estimates is available. Even with the marketing studies, information on the production of approximately half of the solvents and solvent blends is lacking. Manufacturer surveys were beyond the scope of this project and were not performed.

Other information sources investigated for solvent production include trade associations, such as the Chemical Manufacturers Association, the National Petroleum Refiners Association, and the Halogenated Solvents Industry Alliance. In addition government agencies, including EPA and the Department of Energy were consulted. Few

of these sources had information on solvent production and, for those that did, the data could always be traced back to the ITC.

The limited information on solvent sales and production that was identified could serve a purpose in performing market balance studies. For example, if data were available on all of the other uses for the solvent, as well as emissions data, the bottom-up data could be compared to the production or sales data.

In a top-down approach, after national availability for any given solvent is estimated, it is necessary to account for the fraction of national availability that is used for the purpose of solvent cleaning. Other uses for these chemicals include use as constituents within coating formulations or solvent blends and precursors in the production of other chemical commodities. Unfortunately, information pertaining to the amount of any given solvent that is used strictly for solvent cleaning purposes is limited.

Marketing resources, such as the *Chemical Marketing Reporter*, provide information on the end use of several solvents, however these surveys are not performed on a routine basis and, again, only address a limited number of the solvents currently in use. For example, the following solvents had data published in the indicated month/year (Santos, 1995): acetone (9/93); ethanol (2/94); fluorocarbons (3/92); isopropanol (8/93); methyl ethyl ketone (7/93); methyl isobutyl ketone (8/93); methylene chloride (3/92); o-xylene (8/92); perchloroethylene (1/92); 1,1,1-trichloroethylene (1/92); and trichloroethylene (2/92). In addition, the end-use estimates are not always specific to solvent cleaning. Sometimes an end-use as a "solvent" is listed, so that the fraction that is used for solvent cleaning cannot be extracted from other uses such as coating thinners (Pitkin, 1995). In addition, the uncertainty associated with these estimates cannot be quantified.

The only data sources available for allocating national availability to industry groups are previous user surveys, air district permit data bases, and CARB's EDS (SAIC, 1985; VRC, 1989). Previous user surveys are not considered to be a valid source for industry allocation purposes, due to the changes in solvent usage patterns that have occurred over the last five to ten years. Air district data bases contain information only on permitted facilities, and, therefore, do not provide data representative of the overall solvent user population. CARB's EDS is based largely on data received' from the district permitting programs, and, consequently, is also not a representative source of data.

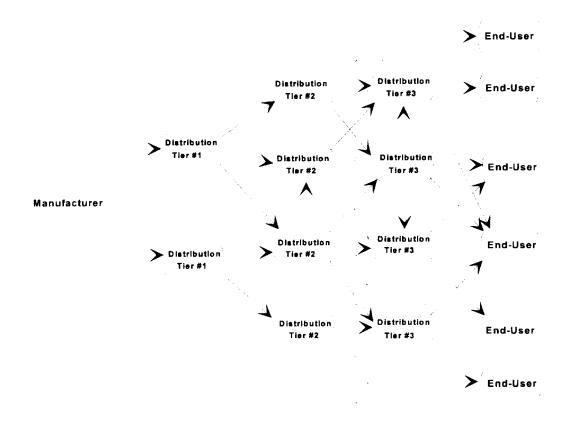
The researchers also assessed the possibility of obtaining information from solvent distributors, so that the same gap that exists in the current CARB method would not exist in the emissions model created during this project. Distributors contacted include Allied Signal, Dow Chemical, Dupont, 3M, Ashland Chemical, Alpha Metals Incorporated, Great Western Chemical, and Berje Incorporated. From this assessment, it was determined that solvent distribution patterns are extremely complex. Instead of the ideal situation shown in Figure II-2, where a single manufacturer sells product to a single distributor who may then sell to several end-users, a much more complex, ever-changing distribution web exists. A hypothetical example of this distribution web is shown in Figure II-3.

From viewing Figure II-2, it becomes apparent that gathering information to unravel the web and characterize solvent distribution would not be possible. For any given solvent, a single manufacturer will typically use more than one primary distributor who

# Figure II-2 Ideal Solvent Commodity Flow



Figure II-3
Typical Real-World Solvent Commodity Flow



will often repackage the bulk product and sell to a second tier of distributors or end-users. The second tier of distributors will often repackage the product to sell to a third tier of distributors or end-users. In addition, there can be movement of product within distribution tiers. Hence, a complete coverage of the many distributors involved, not a random survey, would be needed in order to adequately characterize solvent distribution. Obviously, with dozens of solvents, dozens of manufacturers, and hundreds, if not thousands, of distributors involved, any attempt to characterize distribution patterns through manufacturer and distributor contacts would fail. Finally, it is not clear that distributors maintain and would be willing to share information [e.g., Standard Industrial Classification (SIC) Codes] on the customers to whom they sell.

For this project, CARB wanted solvent emissions to be characterized by equipment types (e.g., vapor degreasers, cold cleaners, hand wiping). Information on the equipment types in use can only be obtained through end-user surveys. Surveys of equipment vendors will only result in information on equipment sold during a given year, which does not relate to the equipment used during a given year. A piece of equipment such as a vapor degreaser or cold cleaner may have a useful life of 15 years or more. Therefore, there is no way to relate the equipment sold during a given year to the equipment actually used. Since, the pairing of equipment and solvent types was a primary objective of CARB, an end-user survey was always a necessary component of the project, even if a top-down inventory approach was deemed viable.

#### 2. Selected Inventory Approach

The biggest problem associated with a bottom-up approach to inventory development is coverage of the entire source category. As mentioned above, this problem also exists with the top-down approach, since production data are only available for about half of the solvents and solvent blends currently in use. Since the primary data source in a bottom-up approach is a user survey, the sampling frame needs to be representative of the entire user universe. For an ubiquitous source category, such as solvent cleaning and degreasing, this is an impossible task (unless resources are unlimited). Another problem is the difficulty and expense associated with performing a user survey, especially given the technical nature of the survey data requirements.

Although significant problems are noted above with both approaches, a bottom-up approach that included a comprehensive end-user survey was selected as the primary data gathering method for this project. Although some coverage of the true user universe would be sacrificed using this approach, the remaining problems could be overcome. Sources of data currently available for the preparation of a top-down inventory were deemed inadequate for the development of the type of inventory desired by CARB.

#### **B. END-USER SURVEYS**

#### 1. Survey Planning

The first step was to develop a solvent user universe representing significant users that could be studied within the resources allocated for the project. A depiction of this assumed user universe is shown in Table II-1. The user universe is divided into two

primary groups: manufacturing processes and maintenance activities. Solvent use in manufacturing processes refers to any activity where a solvent is used to clean products during manufacturing, including cleaning prior to final packaging. Maintenance activities include the cleaning of machinery, tools, vehicle parts, or other equipment that are not incorporated into a product. The assumed user universe is similar to those assumed in earlier studies of this source category (Pechan, 1993; SAIC, 1985; VRC, 1989).

Table II-1
Assumed Universe of Solvent Cleaning End-Users

General Category	Group	Primary SIC	Description
Manufacturing Processes (and	1	2514, 2519, 2522, 253, 2542, 2599	Furniture and Fixtures (all except wood products manufacturing)
associated Maintenance	2	34	Fabricated Metals
Activities)	3	35	Industrial Machinery
	4	36	Electronic Equipment
	5	37	Transportation Equipment
	6	38	Instruments and Related Equipment
	7	391, 3949, 3965, 3993, 3999	Miscellaneous Manufacturing: jewelry, silverware and plated ware; sporting and athletic goods; fasteners, buttons, needles, and pins; signs and advertising specialties; manufacturing activities not elsewhere classified
Maintenance Activities	8	417, 423, 449, 45, 551, 554, 559, 753, 76	Bus Terminal Facilities; Truck Terminal Facilities Marine Transportation Services; Air Transportation Services; New and Used Car Dealers; Gasoline Service Stations; Automotive Dealers not elsewhere classified; Auto Repair Shops; Miscellaneous Repair Services
	9	2000 - 3999	Manufacturing Maintenance Activities (most all manufacturing except those identified above)

The user universe is also divided into nine industry groups, based largely on SIC code. Seven of the nine industry groups make up the manufacturing segment of the universe (these seven are referred to as manufacturing industry groups or MIGs). The eighth group includes service industries, such as vehicle repair. The final group encompasses all of the maintenance activities occurring in the manufacturing sector (i.e., SIC codes 2000-3999), except for those in MIGs 1-7. Since solvent cleaning is such a ubiquitous process, the establishment of the user universe (i.e., significant solvent users) involved balancing the list of potential end-users against the available project resources. Therefore, the assumed universe shown in Table II-1 should not be construed as all

inclusive. Other end-users span the most of the entire range of SIC codes. These include users involved in the maintenance of agricultural equipment, oil and gas producing equipment, and railroad equipment, among others.

A listing of the major equipment categories was then created. Table II-2 provides the equipment list. This listing is referred to as equipment/operation types, since handwiping may or may not involve equipment (e.g., a handwiping station). Equipment/operation codes are provided, and are used throughout the rest of this report to reference specific equipment/operation types.

Table II-2 Equipment/Operation Types

Equipment/Operation Type	Possible Synonym(s)	Code
Batch-Loaded Vapor Degreasers	Open-Top Vapor Degreasers, Enclosed Batch Design Vapor Degreasers, Advanced Vapor Degreasers	BVD
Conveyorized Vapor Degreasers	In-Line Vapor Degreasers	CVD
Gun Cleaning Equipment		GCE
Conveyorized Cold Cleaners	In-Line Cold Cleaners	CCC
Batch-Loaded Cold Cleaners	Remote Reservoir Cold Cleaners, Parts Washers, Water Cleaning Equipment, Semi-Aqueous Cleaning Equipment, Ultrasonic Cold Cleaners	BCC
Handwiping Stations, Handwiping - General	Wipe Cleaning, Solvent Flushing Operations, Coating Application Equipment Cleaning	HWS

The next step in survey planning was to develop a comprehensive list of the potential solvents that may be currently in use. Table II-3 provides this listing, including solvent codes that are used to reference solvents and solvent blends. In developing the lists of equipment/operation and solvent types, the researchers attempted to limit, where possible, the overall number of potential equipment-solvent pairings (ESPs) that might result. The reason for this is that as the number of potential ESPs increases, the number of survey responses for any particular ESP would decrease (for a set number of respondents). Therefore, equipment were combined into the six major equipment types and solvents were combined, in some cases, based on similar physical and chemical characteristics.

The research team selected two survey methods to gather data. For the manufacturing users, a mail-out survey package was selected, since the usage patterns were expected to be diverse in terms of the range of solvents and equipment types represented. For the maintenance user groups, a computer-assisted telephone interviewing (CATI) survey approach was selected as the best method, since the usage patterns were simpler (i.e., fewer solvent and equipment types would be encountered) and questions could be preprogrammed into a CATI system. The maintenance group was also primarily made up of facilities that are unregulated by air districts (or unfamiliar with environmental reporting requirements). Therefore, the likelihood of getting responses to a questionnaire via mail from this group seemed extremely low.

#### Table II-3 Solvent List

Solvent	Abbreviations, Synonyms, Comments	Code
	Pure Solvents	<u></u>
1,1.1-Trichloroethane	TCA, methyl chloroform	101
1,1,2-Trichloro-1,2,2-trifluoroethane	trichlorotrifluoroethane, CFC-113, Freon 113, FC-113	102
1,1-Dichloro-1-fluoroethane	HCFC-141b, dichlorofluoroethane	103
Acetone		104
Ethyl alcohol	ethanol	105
Isopropyl alcohol	IPA, isopropanol	106
Methyl ethyl ketone	MEK, 2-butanone, ethyl methyl ketone	107
Methyl isobutyl ketone	MIBK, hexone	108
Methylene chloride	METH, dichloromethane	109
Mineral spirits	petroleum spirits, lacquer spirits, mineral thinner, mineral turpentine, Painters naphtha, VM&P naphtha, solvent naphtha, white spirits, benzine	110
n-Hexane		111
n-Methyl -2-pyrrolidinone	NMP, M-pyrol	112
Perchloroethylene	PERC, tetrachloroethylene	113
Safety Kleen		114
Toluene	toluoi	115
Trichloroethylene	TCE, ethylene trichloride	116
Petroleum Distillates	naphtha, aromatic naphtha, aromatic solvent, benzin, petroleum ether, hi- flash naphthaethylene	117
Xylene	xylol, dimethylbenzene, o-xylene, m-xylene, p-xylene, xylene mixed isomers	118
UNLISTED PURE SOLVENT	any pure solvent system not listed above	199
	Solvent Blends	
Alcohol blends	blends of ethanol, propanol, etc.	201
Chlorofluorocarbon blends	CFCs, CFC blends	202
Dibasic ester solutions	DBE (combination of three dibasic esters): dimethyl gluterate; dimethyl adipate; dimethyl succinate	203
Glycol ethers and glycol ether acetates	ethylene glycol ethyl ether acetate, 2-ethoxy ethanol acetate, 2- ethoxyethyl acetate, ethylene glycol monobutyl ether (many others not listed)	204
Hydrochlorofluorocarbon blends	HCFCs, HCFC blends	205
Methylene bromide	often mixed with terpenes or other high boiling compounds	206
o-Dichlorobenzene	synthetic solvent mixture	207
Other halogenated blends	monochlorotoluene blend, chlorobenzotrifluoride blend, other halogenated (chlorinated, brominated, or fluorinated) blends	208
Perfluorocarbon blends	PFCs, PFC blends	209
Terpenes	citrus/pine derived solutions; d-limonene solutions	210
Water-based solutions	any water-based solution not listed above, excluding soaps/detergents	211
UNLISTED MIXTURE	any solvent mixture not appearing on the list above	299

For the mail-out survey, a survey package was developed that included: cover letters from the researchers and CARB, one page of instructions, a one page example, three tables (solvent list, equipment list, and control equipment list), and two survey forms (one for manufacturing uses, and one for maintenance uses). An example survey package is presented in Appendix A.

Respondents to the mail-out survey were requested to fill out a form in response to questions about solvent use. Each record in the form corresponded to an ESP that was used by the facility in 1993. The 1993 base year was selected for two reasons. First, 1993 was the most recent year for which allocation data (e.g., BOC census data) would be available. Second, since the survey was originally scheduled to begin late in 1994, the 1993 calendar year would be the most recent year for which respondents would have a full set of usage data. Even though the survey did not begin until the Spring of 1995, the 1993 census data were still the most recent allocation data available.

Control equipment was divided into three categories: carbon adsorption, incineration, and other. Respondents were prompted to write in the type of control, if "other" was selected. Overall, the survey was designed to be as simple and concise as possible, while still providing the minimum amount of data required to develop a 1993 base year inventory.

Sampling frames for both mail-out and CATI surveys were obtained from Dun & Bradstreet (D&B). Since solvent usage patterns may be influenced by geographic area (i.e., federal ozone attainment status) and facility size (e.g., differences between a small "mom and pop" plating shop versus a large modern facility), the frame was stratified by industry group, region, and facility size (<50 employees or  $\ge$  50 employees). Table II-4 provides the sampling frame used for the manufacturers (mail-out) survey. From the D&B data base, the sampling frame consisted of about 35,000 California businesses operating in 1995.

Table II-4
Sample Frame

		Numb	er of Facilities b	y Region/Facil	ity Size*	·	
MIG	1		2		3	}	Total
	<50	>=50	<50	>=50	<50	>=50	
1	467	76	202	12	17	2	776
2	3,561	402	1,657	163	194	10	5,987
3	6,871	426	3,596	312	402	7	11,614
4	2,715	568	1,779	425	102	5	5,594
5	1,483	259	595	62	104	2	2,505
6	1,788	321	1,208	201	97	7	3,622
7	2,984	147	1,517	24	242	0	4,914
tal	19,869	2,199	10,554	1,199	1,158	33	35,012

NOTE:

\*Regions: 1 = Severe and extreme ozone nonattainment areas; 2 = Moderate and serious ozone nonattainment areas; 3 = Attainment areas. Facility size = Number of total employees.

For the maintenance users CATI survey, two non-stratified samples were obtained from D&B. One sample covered the service industries (e.g., auto repair) and the other covered maintenance users within the manufacturing sector (SIC codes 2000-3999, minus those being surveyed with the mail-out questionnaire). The research team did not believe that stratification was necessary for the maintenance users, since solvent usage patterns were not likely to be strongly affected by geographic area or facility size (e.g., these sources are typically not regulated by district rules due to the size of the equipment and solvents used, and the type of equipment/solvent is generally the same regardless of facility size).

For the manufacturers survey, a sample of 6,055 was obtained from D&B [Freeman, Sullivan & Co. (FSC), 1995]. The sample size was arrived at by first determining the minimum sample size required. Since there were no pre-existing data on the variability of solvent use, a calculation for proportional sampling was used. Because some proportions, such as the proportion of users employing a specific ESP, were to be estimated from the survey data, this was not an unreasonable sample size calculation method (FSC, 1995). Also, this method generally computes sample sizes larger than a method incorporating a known variance, unless the variance is very large. The formula assumes a variance of 0.25 and uses a 95 percent confidence level with a given precision. To calculate a sample size ( $\eta$ ) the following formula was used:

$$\eta = \frac{(\sigma z^2)}{e^2} \tag{1}$$

where the variance  $(\sigma)$  is equal to p(1-p) and p=0.5 (i.e., a 50 percent probability of a yes or no answer). The confidence level (z) is the value 1.96 and  $\varepsilon$  is the predetermined level of precision for the estimated proportion (FSC, 1995).

Table II-5 shows the derivation of the minimum sample size. The minimum sample was designed to achieve a 15 percent within cell precision and a 7 to 8 percent precision at the MIG level. The total minimum sample size required was 1,262 (achieving an overall 3 percent level of precision). The required sample size of over 6,000 was derived by assuming a 20 percent response rate to the survey (i.e., 1,262/0.20).

Table II-5
Minimum Sample Size

		Nun	ber of Facilitie	s by Region/Fa	cility Size*			
MIG		1		2	, .	3	Total	Precision
	<50	>=50	<50	>=50	<50	>=50		
1	39	27	35	9	12	2	124	0.08
2	42	39	42	34	35	8	200	0.07
3	42	39	42	38	39	6	206	0.07
4	42	40	42	39	30	4	197	0.07
5	41	37	40	25	30	2	175	0.07
6	42	38	41	35	30	6	192	0.07
7	42	33	42	15	36	-	168	0.07
Total	290	253	284	195	212	28	1,262	0.03
precision	0.06	0.06	0.06	0.06	0.06	0.07		

NOTE: Regions: 1 = Severe and extreme ozone nonattainment areas; 2 = Moderate and serious ozone nonattainment areas; 3 = Attainment areas. Facility size = Number of total employees.

For the maintenance users survey, a minimum sample size of 200 for each group 8 and 9 were calculated. These sample sizes would achieve the same 7 percent precision level as the manufacturing groups shown in Table II-5.

#### 2. Survey Execution

#### a. Manufacturers Survey

Trained telephone interviewers successfully contacted and recruited 2,874 firms (48 percent) to take part in the study. As part of this contact, the interviewers located and spoke with the person within the company who was knowledgeable of the firm's solvent use and recruited them to agree to receive and complete a printed survey questionnaire. As for the balance of the original sample, 11 percent refused to participate, another 14 percent claimed that their firm used no solvents at all, 12 percent could never be reached (four attempts were made), and 15 percent of the sample numbers were found to be disconnected.

The name, title, address, and telephone numbers of all participants were confirmed and it was explained that a questionnaire would be mailed to them. The contact information was entered into a data base for mailing and tracking purposes. Questionnaires were mailed within five business days of the original contact. Approximately two weeks after the mailing, if a completed questionnaire was not received, a follow-up telephone call was made to remind participants to complete their questionnaires. A total of 1,825 reminder calls were attempted (64 percent of the recruited sample) and reminders successfully left for 75 percent of these.

The research team operated a toll-free hot-line during the course of the survey (May through July of 1995) to answer questions and assist respondents in completing their survey forms. Most of the calls received were from small businesses who did not have an environmental specialist on staff or did not have experience in environmental regulatory compliance. Calls from larger firms tended to be related to the nature of the survey itself. For example, many of these calls questioned the need to perform such a survey, since much of the information requested was submitted annually to the local district. In these cases, it was explained that the information submitted to the districts was not at the same level of detail necessary for this inventory effort (this was also explained in the survey package).

After about one-third of the targeted responses had been received, the researchers analyzed the responses to make sure that certain industry groups, geographic areas, or facility sizes would not be under-represented in the final results. The analysis showed that the response rate was uniform across MIGs, regions, and facility sizes. These results suggested that no adjustments to the survey approach were needed.

However, additional analysis of the completed surveys by MIG and number of unique ESPs was performed. This analysis showed that MIGs 4, 5, and 6 reported use of a high percentage of the total potential ESPs (67 possibilities, at that point) compared to the other groups. In other words, these MIGs had the highest variability in ESPs used. Therefore, if the survey had continued on without making any adjustments (and the data

received had come back with the same uniformity), the data for each ESP for these MIGs would have been relatively dilute compared to the other MIGs (1 through 3, and 7).

A call-back procedure to place more emphasis on MIGs 4 through 6 was implemented to obtain a higher percentage of responses from these groups. The call-back procedure was changed for these MIGs to allow for two call-backs, instead of the single reminder that had been planned for the entire sample. The results of this adaptation to the survey procedure were mixed. The percentage of total responses for MIG 4 increased while those for MIGs 5 and 6 did not. However, after all of the reported ESPs had been combined into the final 32 ESP combinations (discussed in Chapter III), MIGs 2 through 6 showed the highest number of reported ESP combinations (23 to 28 of a possible 32). This is shown in Table II-6. Of the highly variable industry groups, MIG 5 was the least represented at 13.2 percent of the total responses.

Table II-6
Manufacturing Survey Responses by MIG

MIG	Responses <sup>1</sup>	Percentage of Total Responses	Number of ESP Combinations Reported <sup>2</sup>
1	55	5.6	. 12
2	193	19.5	26
3	175	17.7	25
4	171	17.3	27
5	130	13.2	23
6	169	17.1	28
7	95	9.6	. 14
Total	988	100	32 possible ESP combination

NOTES:

<sup>1</sup>Final number of valid responses following quality assurance checks.

A total of 1,102 responses were received for the manufacturers survey. Of these, 988 were considered acceptable responses, after all quality assurance checks had been performed. Hence, the overall acceptable response rate was 16.3 percent (988/6,055). Of the 988 acceptable responses, 354 indicated no manufacturing solvent use while 654 had manufacturing solvent usage for at least one ESP. Over half of the responses, 496, showed no maintenance solvent usage while 492 reported maintenance usage for at least one ESP.

<sup>&</sup>lt;sup>2</sup>The combining of ESPs is discussed in Chapter III.

#### b. Maintenance Survey

The CATI survey of maintenance users was begun after the recruitment of manufacturers was completed. Respondents were asked a series of questions regarding the type of solvents used and whether or not the activity included a parts washer (i.e., batch-loaded cold cleaning - BCC) or if handwiping was performed. Data on the quantity of solvent either used for handwiping or added back to parts washers over the course of a week, month, or year were also gathered. In addition, information on the number of parts washers used and the number of employees at the facility was obtained.

Industry groups 8 and 9 were sampled until the minimum sample target (200 complete responses for each group) was reached. A total of 1,527 telephone numbers were dialed to obtain the necessary responses [response rate of over 26 percent; (FSC, 1995)].

#### c. Quality Assurance/Quality Control

During the CATI survey of maintenance users, interviewers were monitored by supervisors to assure that data were being accurately gathered. Following the survey, data were down-loaded from the CATI system into a statistical software package. Data checks were performed to identify any missing data. Information contained on interviewer data correction sheets was also added at this time to the data base.

Quality assurance efforts in the mail-out survey of manufacturing facilities were more extensive due to the complexity of the requested data. When completed questionnaires were received, each was checked for missing or technically invalid data. In cases where corrections or additional data were needed, the facility was re-contacted by telephone. Typical data validations and corrections obtained during these call-backs are listed below:

- Verification of facility SIC code and primary business;
- · Addition of missing personnel totals;
- Gathering of missing TOG content or Material Safety Data Sheet (MSDS) for blends or unlisted solvents;
- Clarification of appropriate solvent and equipment usage when duplicate data were entered on manufacturing and maintenance use questionnaires;
- Correction of technically invalid or unlikely solvent-equipment pairings (e.g., mineral spirits-vapor degreasing); and
- Validation of the existence of an exhaust control when the unlisted exhaust control code was entered.

For the manufacturers survey, manufacturing usage data and maintenance usage data were entered into separate data bases. Visual rechecks of the computer entries and original questionnaire entries were conducted to correct data entry errors. Also, each data base was systematically checked by field for technically invalid entries. This search revealed, for example, several records of GCE use in the manufacturing use data base. Because this equipment is by definition maintenance equipment (cleaning of coating spray guns), these records were transferred to the maintenance usage data base.

Throughout the data gathering phase, an attempt was made to exclude all records with non-solvent cleaning and degreasing usage to avoid inventory overlap with other

CARB solvent-related source categories. painting, adhesives, photoresist/stripping survey, they were eliminated from the d	When solvent uses such as architectural g, and aerosol spray cans were encountered in the ata base.
Survey, they were eliminated nom the a	•
	· ·
	4
	i .
•	,
	,
	,
	EINAL

# CHAPTER III 1993 BASE YEAR EMISSION INVENTORY RESULTS

Developing the 1993 base year emission inventory for the solvent cleaning source category required quality assurance of survey responses, data consolidation, statistical analyses, selection of an emissions allocation method, and final allocation of emissions to counties. These efforts are discussed in this chapter and the emission inventory results for both manufacturing and maintenance solvent usage are presented.

#### A. MANUFACTURING USAGE

Manufacturing solvent usage refers to any activity where a solvent is used to clean products during the manufacturing process, including cleaning prior to final packaging. Cleaning of machinery, tools, or other support equipment that are not incorporated into a product is considered maintenance and is excluded from this manufacturing solvent usage category. As discussed earlier, a mail-out survey was used to gather data on manufacturing solvent usage in the assumed universe of MIGs 1-7. Valid survey forms were received from 988 facilities. Table III-1 shows the distribution of these responding facilities across the survey strata - MIG, region, and facility size (i.e., <50 and ≥50 total employees).

Table III-1

Manufacturing Survey Distribution of Responding Facilities

		Number o	f Facilities by	Region and Fa	cility Size		
MIC		1		2		3	Total
MIG	<50	>=50	<50	>=50	<50	>=50	7014
1	15	6	23	5	6	0	55
2	33	38	55	55	. 7	5	193
3	31	26	73	38	5	2	175
4	27	37	43	59	3	2	171
5	27	30	46	20	′ 7	0	130
6	40	25	60	37	4	3	169
7	22	26	40	5	. 2	0	95
Total	195	188	340	219	34	12	988

As expected, based on the sample frame and survey design, the bulk of responding facilities fell within MIGs 2-6 and regions 1 and 2. These two regions include 1993 ozone nonattainment areas in the South Coast and the Bay Area, where most of the state's manufacturing occurs. Few responding facilities came from region 3, counties which were

in attainment in 1993. These less-populated areas have relatively little manufacturing and very few large facilities with more than 50 employees.

Extensive quality assurance procedures were used to arrive at these final 988 facility responses and to verify the accuracy of their submitted data. The mail survey actually drew a total of 1,102 facility responses; however, 114 were considered invalid for one of the following reasons:

- Facility refused to provide or could not provide necessary data;
- Facility SIC code outside MIGs 1-7;
- Facility not in business in 1993 base year; and
- Response arrived too late for inclusion in data analysis.

#### Data Reduction and Statistical Analysis

#### a. Data Consolidation/Quality Assurance

As discussed in Chapter II, the mail survey had facilities select among 31 solvent categories and 5 equipment types (excluding GCE) to characterize their manufacturing solvent cleaning usage. Out of this large number of potential ESPs, 81 ESPs were initially reported from the 988 responding facilities. These are presented in Table III-2.

The research team decided to reduce the number of ESPs to the smallest amount that made sense technically. An emissions model and base year inventory developed using this large number of ESPs would be extremely cumbersome and complex. Also, 19 of the ESPs had only one record of use reported in the survey. Emissions estimates scaled up from just one response would carry a high and unknown level of uncertainty and could not be technically justified. For these reasons, it became necessary to combine some data and reduce the number of ESPs to a more manageable level.

Prior to combining any data, several of the original 81 ESPs were eliminated through further QA checks and call-backs to respondents. For example, many records of vapor degreasing (BVD, CVD) were discovered to actually be cold cleaning (BCC, CCC) in which the solvent was heated but not vaporized. This effort, combined with the initial QA checks, eliminated incorrect vapor degreasing ESPs for acetone, ethanol, isopropanol, MEK, mineral spirits, Safety Kleen, petroleum distillates, unlisted pure solvents, alcohol blends, glycol ethers, and terpenes. Other incorrect records were deleted through efforts to exclude non-solvent cleaning usage from this inventory. When solvent uses such as architectural painting, adhesives, photoresist/stripping, and aerosol spray cans were encountered, they were eliminated from the data base to avoid inventory overlap with other CARB solvent-related source categories. Several of the halogenated solvent records were determined to be aerosol cans. Deleting these eliminated all HCFC blends and some of the other halogenated ESPs.

After all quality assurance was completed, the first level of data consolidation involved combining solvents into groups. Many of the solvents with similar density, evaporative characteristics, and chemical family could be grouped together for emissions analysis without sacrificing data quality. Table III-3 shows the original solvent list reduced to 15 solvent groups.

Table III-2

Manufacturing Solvent Usage: Original 81 ESPs Reported

Solvent	Code		Number o	f Records by E	quipment Typ	oe .
20146111		BVD	CVD	BCC	CCC	HWS
TCA	101	58	3	17	-	47
CFC	102	23	1	8	2	18
HCFC	103	10	1	•	-	5
Acetone	104	2	-	18	-	177
Ethanol	105	1	-	2	1	27
Isopropanol	106	3	· -	22	1	174
MEK	107	3	-	5	-	59
MIBK	108	-	-	-	•	1
Methylene Chloride	109	-	-	4	-	21
Mineral Spirits	110	1	-	33	3	113
Hexane	111	-	-	-	-	3
NMP	112	-	-	1	-	-
PERC	113	6	1	1	-	3
Safety Kleen	114	6	-	43	-	16
Toluene	115	-	-	. 2	-	19
TCE	116	5	-	-	-	6
Petroleum Distillates	117	1	1	` 11	-	23
Xylene	118	-	-	3	-	11
Unlisted Pure Solvents	199	-	1	, 7	•	26
Alcohol Blends	201	1		e 4	2	17
CFC Blends	202	2	-		•	3
DBE	203	-	-	-	-	1
Glycol Ethers	204	2	-	8	5	29
HCFC Blends	205	1	-	٠.	•	3
Other Halogenated	208	-	•		-	2
PFCs	209	2	-	-	-	1
Terpenes	210	1	-	. 5	1	8
Water-Based	211	-	-	. 4	-	6
Unlisted Mixtures	299	4	-	20	2	62

# Table III-3 Solvent Combinations

Solvent Group	Includes Original Survey Solvents (Codes)
TCA	TCA (101)
CFC/CFC Blends	CFC (102), CFC Blends (202)
HCFC	HCFC (103)
Ketones	Acetone (104), MEK (107), MIBK (108)
Alcohols/Alcohol Blends	Ethanol (105), IPA (106), Alcohol Blends (201), other unlisted (e.g., Methanol)
Methylene Chloride	Methylene Chloride (109)
Petroleum Distillates	Mineral Spirits (110), Safety Kleen (114), Petroleum Distillates (117), other unlisted (e.g., Kerosene)
Miscellaneous Pure Solvents	Unlisted Pure Solvents (199), n-Hexane (111), NMP (112)
PERC	PERC (113)
Toluene/Xylene	Toluene (115), Xylene (118)
TCE	TCE (116)
Glycol Ethers	Glycol Ethers (204), Water-Based Solutions (211)
PFC Blends	PFCs (209)
Terpenes	Terpenes (210)
Miscellaneous Blends	Unlisted Solvent Mixtures (299)

Halogenated solvents such as TCA and METH were not grouped, since they were well represented in the survey data and traditionally make up a large share of the solvents used in degreasing equipment. On the other hand, forming ketones, alcohols, and petroleum distillates groups was logical and justified based on the individual solvents' chemical and physical similarities (e.g., ethanol and IPA in alcohols/alcohol blends group). During this solvent grouping process, records of unlisted pure solvents (survey code 199) and unlisted mixtures (299) were examined to see if any could be combined into other solvent categories. Available MSDSs and other details on returned questionnaires showed that 11 of these unlisted responses could be placed in the alcohols/alcohol blends group. Most were methanol. Another 13 unlisted responses were placed in the petroleum distillates group. Most were kerosene or predominantly petroleum hydrocarbon mixtures. Examination of available MSDSs for water-based solutions (211) showed these to be glycol ether solutions. Their records were grouped with the glycol ethers (204). Note that the following original survey solvent codes did not appear in any valid responses for this source category and are not included in the emissions inventory:

- DBE (203);
- HCFC Blends (205);
- Methylene Bromide (206);
- o-Dichlorobenzene (207); and
- Other Halogenated (208).

The combining of solvents into 15 groups brought the number of unique ESP combinations down to 42. Analysis of survey records at this stage showed that another useful data consolidation could be made. Each ESP combination with conveyorized equipment, either CVD or CCC, contained less than five records. Four of the ten conveyorized ESP combinations had just one record of use. To reduce the uncertainty of emission estimates scaled up from these rarely used equipment, records for each solvent group used in CVD and CCC were combined with records for the corresponding batch equipment, BVD or BCC. While statistically significant differences may exist in the activity factors (AFs) of conveyorized versus batch equipment on a gallons solvent loss per parts cleaned basis, significant differences were not generally observed on a per employee basis (AF used in this study). Analysis of Variance (ANOVA) was used to test for differences between batch and conveyorized mean AFs. All records from solvent groups using both equipment types were included. Results in Table III-4 clearly indicate no significant difference (F<F<sub>critical</sub>).

Table III-4
ANOVA of Batch Versus Conveyorized Equipment Activity

Analysis		ANOVA Statis AF (gallons/em	
	P-value	F	F-critica
BVD vs CVD	0.377	0.788	3.931
BCC vs CCC	0.857	0.032	3.831

With all solvent and equipment grouping completed, the number of unique ESP combinations was reduced to 32. It is this final set of 32, described in Table III-5, which was used to develop the emissions inventory for the manufacturing solvent usage category. Each ESP combination in the table contains one data record for each user facility. Of course, many facilities had usage records for more than one ESP combination. Also, due to the consolidations discussed earlier, facilities with multiple solvent or equipment use within one ESP combination (e.g., the alcohols ethanol and IPA; equipment BCC and CCC) required a composite record. For these records, gallon-weighted total organic gas contents (lb TOG/gal solvent) were calculated and usage volumes were summed. Because many of the final 32 ESP combinations included multiple solvents, equipment types, or the composite facility records just discussed, an estimated breakdown of emissions by individual solvents and equipment types is provided with each ESP combination's emission model table in Appendix B. Extreme caution should be exercised in the use of these solvent and equipment breakdowns since many were developed with very few survey responses (e.g., one or two responses for conveyorized equipment).

#### b. Emission Model Development

The ESP combinations in Table III-5 characterize the 1993 manufacturing solvent usage by 654 of the 988 responding facilities. Recall that 354 facilities reported no manufacturing solvent use. The table shows that TCA, CFC, and HCFC were the most commonly used solvents for vapor degreasing. Petroleum distillates, which include Safety-Kleen parts-washing solvent, were the predominant cold cleaning solvent group.

Another clear observation from the table is the extent to which handwiping is employed in manufacturing solvent degreasing. All solvent groups except PFC blends were used in HWS, with ketones, alcohols, and petroleum distillates the most widely employed. Nearly one-third of the 654 user facilities reported handwiping with ketones, mostly acetone.

Table III-5

Manufacturing Solvent Usage: Final 32 ESP Combinations

	Number o	f Records by Equip	ment Type
Solvent Group	BCC/CCC	BVD/CVD	HWS
TCA	15	63	47
CFC/CFC Blends	10	26	22
HCFC		.11	5
Ketones	25	•	215
Alcohols/Alcohol Blends	34		208
Methylene Chloride	4	-	19
Petroleum Distillates	102	•	143
Miscellaneous Pure Solvents	7	-	17
PERC	-	6	4
Toluene/Xylene	5	-	25
TCE	•	5	6
Glycol Ethers	10	-	26
PFC Blends	-	2	-
Terpenes	8	-	8
Miscellaneous Blends	13	2	41

All data records were sorted by ESP combination and converted to a Microsoft Excel 4.0 spreadsheet for the remainder of the analyses. All solvent volumes were converted to gallons, and densities to pounds per gallon. The next step in preparing these data for emission model development was the calculation of the key variables, AF and EF, for each record in each ESP combination. The AF is the gallons of solvent loss (evaporation) per employee per year. It is calculated with the use of Equation 2:

In the survey, manufacturing facilities reported both total number of employees and the number of employees engaged in production (excluding administrative personnel). An AF can be calculated using either total or production employees. As will be discussed later, the two versions of the AF were compared to determine the best emissions allocation method.

The numerator of the AF represents the net gallons lost (evaporated) in the solvent cleaning process. It was assumed that disposed solvent that was not thermally destroyed

would eventually result in emissions from landfills or publicly-owned treatment works (POTWs). Emissions overlap with these other sources was avoided by excluding the disposal fraction from the solvent cleaning inventory. Annual gallons of solvent used in 1993 were taken directly from the survey responses. Facilities also supplied disposed and recycled solvent volumes; however, some assumptions were made to improve the quality of these data. Because of the nature of handwiping activities, all HWS records were assumed to have no disposed or recycled fractions. In these cases, the AF numerator, gallons solvent lost, becomes simply gallons solvent used. For the cold cleaning and vapor degreasing equipment categories, some facilities indicated that all solvent used was eventually disposed or recycled. Because 100 percent recycle/disposal is not technically possible, appropriate average disposed or recycled fractions were substituted in these records. These averages, calculated from the fractions for similar solvent families and equipment types in the survey, are shown below:

- Halogenated solvent groups, BVD/CVD = 0.48;
- Halogenated solvent groups, BCC/CCC = 0.53;
- Petroleum Distillates, BCC/CCC = 0.62; and
- Other solvent groups, BCC/CCC = 0.59.

The second key variable to be calculated for each record, EF, is the pounds of TOG emissions per gallon of solvent loss. The EF is calculated with the use of Equation 3:

EF = solvent density · TOG content · [1-(collection efficiency · control efficiency)]

where:

solvent density = lb/gal;

TOG content = lb TOG/lb solvent

For pure organic compounds (e.g., TCA, acetone) with no exhaust controls, EFs are simply solvent densities obtained from literature and MSDSs. Table III-6 lists the densities which were used for all pure solvents appearing in the manufacturing survey. For solvent blends (e.g., glycol ethers, terpenes), solvent densities and TOG contents were obtained from survey response forms or attached MSDSs. In six cases, solvent densities and TOG contents could not be provided by respondents. For these cases, average solvent density x TOG content products were used which were calculated from all other responses with the same solvent blend code. For example, a value of 5.58 lb TOG/gal solvent was used for an alcohol blend (survey code 201) with no density or TOG data. This was the arithmetic average of all other alcohol blend (201) responses.

A few facilities employed exhaust controls in their manufacturing solvent usage. Of all records in the final set of 32 ESP combinations, 6 included catalytic or non-catalytic incinerators, 13 included carbon adsorbers, and 7 included unlisted control equipment such as air scrubbers or filters. For all records with exhaust control, a collection efficiency of 80 percent (0.80) was assumed in Equation 3. The following control efficiencies were assumed based on CARB data (CARB, 1989):

- Catalytic/Non-Catalytic Incinerator = 94 percent (0.94 in Equation 3);
- Carbon Adsorber = 85 percent (0.85 in Equation 3); and

• Other Unlisted Control = 70 percent (0.70 in Equation 3).

Table III-6
Pure Solvent Densities

Solvent	Code	Density, lb/gal
TCA	101	11.1
CFC	102	13.1
HCFC	103	10.1
Acetone	104	6.6
Ethanol	105	6.5
IPA	106	6.5
MEK	107	6.7
MIBK	108	6.6
Methylene Chloride	109	11.1
Mineral Spirits	110	6.5
n-Hexane	111	5.5
NMP	112	8.6
PERC	113	13.5
Safety Kleen	114	6.6
Toluene	115	7.2
TCE	116	12.2
Petroleum Distillates	117	5.5
Xylene	118	7.1
Unlisted Pure Solvents	199	MSDS

With AF and EF for each record calculated, the development of the emission model for the manufacturing solvent usage category was begun. The emission model consists of tables, one for each of the 32 ESP combinations, which contain values of AF, EF, and user fraction (UF) used to calculate annual TOG emissions per employee according to Equation 4:

$$AF \cdot EF \cdot UF = lb \cdot TOG/employee$$
 (4)

where:

AF = gal solvent loss/employee/year

EF = lb TOG/gal solvent

UF = ESP combination user employees/survey employees

Because AF is based only on the employees at facilities which use that particular ESP combination, but emissions allocations will be made based on user and non-user employees, UF is needed to appropriately scale the data. With no prior universe

employment data by ESP available, the best UFs are obtained from the survey data itself. UF can be in terms of total or production employees, but must always match the employee type used to develop AF. AF could have been developed using all survey responses (including non-users) which would have precluded the need for UF. However, in this case, the AF data would have been significantly skewed (negative) making statistical manipulations more difficult.

Developing an emission model table for an ESP combination required calculation of the most appropriate average AF and EF values, and using the appropriate UF scaling. The procedure is best explained through two examples, an ESP combination requiring simple analyses and a more complex ESP combination involving different AFs among the survey strata. Each case is based on total, rather than production, employees.

**Example 1: Simple Case** — The Miscellaneous Blends-BCC/CCC ESP combination included 13 records. Distribution of these records across MIGs, regions, and facility size classes is presented in Table III-7. With no survey responses in MIGs 1 and 7, it was assumed that there is no usage of this ESP combination in those industries and no emissions were allocated to them. However, it was assumed that usage occurs in region 3 despite the lack of responses. This was done because the odds of the survey capturing many region 3 facilities were inherently low due to the small amount of manufacturing in these mostly rural counties. The shaded area in Table III-7 represents the cells across which AF, EF, and UF were developed and emissions were allocated.

Table III-7
Example 1: Distribution of Survey Records

		Facility	Responses by	Region and Fa	cility Size		
MIG		1		2	3		
	<50	>=50	<50	>=50	<50	>=50	
1							
2				2			
3	1	2	:				
4				1			
5		3		1 ′			
6			2	1			
7				,			

It is important to remember that the manufacturing survey was stratified by MIG, region, and facility size. Therefore, AF and EF values within each cell must be weighted to account for differences between the group of ESP combination respondents and the sample frame. In this example, prior to averaging AF or EF across the shaded group of cells, the cell's sample weight,  $\mathbf{w}_i$ , was applied to each response in cell i. The derivation of  $\mathbf{w}_i$  is shown in Equation 5:

$$w_{i} = \frac{\left(\begin{array}{c} \text{number of facilities within cell i of sample frame} \\ \text{number of facilities within MIGs 2-6 of sample frame} \right)}{\left(\begin{array}{c} \text{number of facility records within cell i of ESP combination} \\ \text{number of facility records within MIGs 2-6 of ESP combination} \end{array}\right)}$$
(5)

Cell weighting factors act as frequencies, forcing all responses to be in the same proportions as in the sample frame. A weighted mean AF was calculated by Equation 6 for all of the combined cells (Burington and May, 1970):

Mean 
$$AF = \left(\frac{1}{\eta}\right) \sum w \cdot AF$$
 (6)

where: 
$$\eta = \sum w$$

Mean EFs were calculated in the same manner. Table III-8 shows the sample frame facility data used for weighting factor calculations. These were obtained from the 1993 County Business Patterns CD-ROM issued by the Bureau of Census (BOC, 1995). In this Miscellaneous Blends-BCC/CCC example, the weighting factor for the two records in cell MIG  $2/\text{region } 2/\geq 50$  employees is shown here: w = (153/18,597)/(2/13) = 0.053

Table III-8

Manufacturers Survey: Number of Facilities in Sample Frame

		Facil	ities by Region	and Facility Siz	.e*		
MIG	1		2		3		Total
	<50	>=50	<50	>=50	<50	>=50	
<del>_</del>	290	72	99	16	10	0	487
2	2,647	452	1,202	153	97	9	4,560
3	3,923	303	2,046	204	218	10	6,704
4	1,586	496	1,084	394	55	8	3,623
5	877	236	359	42	49	1	1,564
6	973	288	640	183	54	8	2,146
7	1,000	106	473	17	78	1	1,675
Total	11,296	1,953	5,903	1,009	561	37	20,759

NOTE: \*Sample frame based on 1993 BOC census data which are different than the 1995 D&B data used to develop the sampling requirements in Chapter II.

If this ESP combination contained enough records, a test for significant differences between mean AFs among strata would be performed to see if different AF values should be used in the emission model for different MIGs/regions. Following discussions with

CARB staff, a nominal minimum of 10 records per strata (e.g., MIG) was selected to justify this more complex statistical analysis. As seen earlier in Table III-7, the Miscellaneous Blends-BCC/CCC ESP combination contained no more than four records in any one MIG, the first level of stratification. Therefore, for this ESP combination, single overall AF and EF means were calculated across all record-containing cells in MIGs 2-6 using Equation 6. The results were as follows:

Mean AF = 2.39 gal solvent loss/employee/year Mean EF = 7.73 lb TOG/gal solvent

UF was derived by dividing the total employees in facilities with records in this ESP combination by the total employees in all MIG 2-6 facilities which responded to the survey. This yielded a value of 0.104, meaning an estimated 10 percent of MIG 2-6 employees work at facilities which use miscellaneous solvent blends in cold cleaning equipment. The completed emission model table for this ESP combination is shown in Table III-9. In this case, the same AF, EF, and UF were applied across all strata to which emissions will be allocated. The AFxEFxUF product can be simply multiplied by a county's 1993 total MIG 2-6 employment to yield estimated mass TOG emissions from this ESP combination.

Table III-9
Example 1: Emission Model Table

				Region/F	acility Size		
M	IIG 📙		1		2		3
	ļ	<50	>=50	<50	>=50	<50	>=50
1							
2	AF			2	.39		
	EF			. 7	7.73		
	UF			0	).10		
3	AF			2	2.39		
	EF			7	7.73		
	UF			0	).10		
4	AF	2.39					
	EF			7	7.73		
	UF			C	).10		
5	AF			2	2.39		
	EF			7	7.73		
	UF			C	).10		
6	AF			2	2.39		
-	EF			7	7.73		
	UF			(	).10		
7	<del>                                     </del>						

NOTES:

AF = Activity Factor in gal solvent loss/employee/year.

 $\mathsf{EF} = \mathsf{Emission} \; \mathsf{Factor} \; \mathsf{in} \; \mathsf{lb} \; \mathsf{TOG/gal} \; \mathsf{solvent}.$ 

UF = User Fraction in (User total employees/total MIG 2-6 survey employees)

**Example 2: Complex Case** — The TCA-HWS ESP combination contained 47 records distributed across cells as shown in Table III-10. The entire grid is shaded, indicating that usage was assumed and emissions were allocated across all strata.

Two of the MIGs contained more than 10 records, justifying a statistical comparison of mean AFs among strata as discussed earlier. This analysis began with selection of the appropriate MIGs or MIG groups for comparison. Mean AFs for MIG 4 and MIG 6 were calculated, since each MIG had more than 10 records. Examination of their unweighted raw AFs suggested that the 15 records in MIGs 2, 3, and 7 should be combined to calculate a mean AF. These MIGs had generally higher gallons solvent loss per employee compared to the other MIGs. A mean AF for MIG 5 was also calculated. Although it was under the nominal minimum of 10, the eight AF values in MIG 5 appeared distinctly lower than those in MIGs 2, 3, and 7. The one record in MIG 1 was withheld from any grouping until the other mean AFs were compared.

Table III-10
Example 2: Distribution of Survey Records

		Facility R	lesponses by F	Region and Fac	ility Size	
MIG		1	- 7	!		3
	<50	>=50	<50	>=50	<50	>=50
1	1					Ę
2	2	4	2	1.		
3				3		
4	1	5	1	2	1	1
5	ļ	4		4		
6	1	2	3	5		1
7		3				

Mean AFs were calculated according to Equation 6. The weighting factor was always based on the cells/strata over which the mean was being calculated. For example, in the mean AF for MIG 4, the weighting factors were obtained from Equation 7:

$$w_{i} = \frac{\left(\frac{number\ of\ facilities\ within\ cell\ i\ of\ MIG\ 4\ of\ sample\ frame}{number\ of\ facilities\ within\ MIG\ 4\ of\ ESP\ combination}\right)}{\left(\frac{number\ of\ facility\ records\ within\ cell\ i\ of\ MIG\ 4\ of\ ESP\ combination}{number\ of\ facility\ records\ within\ MIG\ 4\ of\ ESP\ combination}\right)}$$

Once calculated, the mean AFs were examined for significant differences using their variability data. The standard deviations, s, were obtained using Equation 8 (Burington and May, 1970):

$$s - \sqrt{\left(\frac{1}{\eta}\right)\sum w \cdot (AF - Mean \ AF)^2}$$
 (8)

where:

$$\eta = \sum w$$

Approximate 95 percent confidence intervals for the mean AFs were then determined using Equation 9 (Hoel, 1960):

95% Confidence Interval - Mean AF 
$$\pm 2 \cdot \frac{s}{\sqrt{\eta}}$$
 (9)

where:

$$\eta = \sum w$$

A comparison of the mean AFs in Table III-11 revealed a high degree of overlap for the MIG 4, 5, and 6 confidence intervals, with their mean AFs all around 2 to 3 gallons per employee. The mean AF for the MIG 2, 3, and 7 group was judged to be significantly higher due to the lack of overlap in confidence interval with the other MIGs. Because their AFs were not significantly different from each other, MIG 4, 5, and 6 data were now grouped. The MIG 1 record was also added to this grouping due to its similar AF (2.5 gal/employee). As shown in Table III-11, two distinct groupings were formed based on AF. For this ESP combination, TCA-HWS, industries in MIGs 2, 3, and 7 were found to have significantly higher AFs than industries in MIGs 1, 4, 5, and 6.

Table III-11
Example 2: Comparison of Mean AFs by MIG

MIG(s)	Number of Records	Mean AF, gal/employee/yr	95% Confidence Interval of Mean AF
2, 3, 7	15	14.3	4.0 to 24.6
4	11	2.77	1.2 to 4.3
5	8	1.82	0.0 to 3.7
6	12	2.69	1.4 to 4.0
1, 4, 5, 6	32	2.69	1.8 to 3.6

NOTE: 95% confidence intervals determined using equation 9.

Once significantly different AFs were established at the MIG level, a test for AF differences between regions within a MIG or MIG group would be performed if enough data were available. In this example, no region in the MIG 2, 3, and 7 group contained 10 or more records. Hence, this group's AF analysis is complete at the MIG level. However, the MIG 1, 4, 5, and 6 group contained enough records to justify analyzing AF by region.

 $\Lambda_{\mathrm{S}}$  shown in Table III-12, the mean AF for region 1, the severe and extreme nonattainment counties, was significantly higher than the mean AF for regions 2 and 3. This MIG group had reached the best level of resolution for AF. Data within each region were not compared by facility size class, the third level of stratification.

Table III-12 Example 2: Comparison of MIG 1,4,5,6 Mean AFs by Region

MIG Group	Region(s)	Number of Records	Mean AF, gal/employee/yr	95% Confidence Interval of Mean AF
	1	14	4.17	3.1 to 5.2
1, 4, 5, 6 1, 4, 5, 6	2, 3	18	0.32	0.1 to 0.6

NOTE: 95% confidence intervals determined using equation 9.

The emission model for this ESP combination was completed by calculating UFs and mean EFs for the same combinations of MIGs/regions used for the AF. The final model is presented in Table III-13.

Table III-13 **Example 2: Emission Model Table** 

	T			Region/Fa	acility Size		
M	ig 📙		1		2		3
	· -	<50	>=50	<50	>=50	<50	>=50
1	AF	4	.17			0.32	
,	EF	1	1.1			11.1	
	UF	0	.25			0.15	
2	AF				4.3		
_	EF				0.9		
	UF				.08		
3	AF				4.3		
	EF				0.9		
	UF			0	.08		
4	AF	4	.17			0.32	
	EF	1	1.1	1		11.1	
	UF	C	).25			0.15	
5	AF	4	1.17			0.32	
	EF	1	11.1	ĺ		11.1	
	UF	(	).25			0.15	
6	AF		1.17			0.32	
•	EF	1	11.1			11.1	
	UF	(	).25	•		0.15	
7	AF				14.3		
	EF				10.9		
	UF			(	0.08		

NOTES:

AF = Activity Factor in gal solvent loss/employee/year.

EF = Emission Factor in lb TOG/gal solvent.

UF = User Fraction in (User MIG & region group total employees/survey MIG & region group total employees).

For all ESP combinations with enough data, this same general procedure was used to determine the most appropriate emission model variables. First, mean AFs were resolved to the MIG or MIG group level, if significant differences were found. This part of the analysis was based on comparison of 95 percent confidence intervals and examination of the unweighted AF records. When enough data were available, mean AFs were then resolved to the region level for each MIG or MIG group, if there were significant statistical differences. Mean EFs were then calculated for the same combination of strata determined by the AF analysis. In all cases, weighting factors were based on the same cells/strata over which the means were calculated. Finally, UFs were calculated based on these same strata and the emission model was complete. Of the 32 ESP combinations in the manufacturing usage survey, 10 were analyzed using this complex procedure. Seven of these were resolved to the MIG or region level because of significant AF differences. Three did not have significant AF differences at the MIG level. Emission models for these three, along with the remaining 22, were developed like the simple case (Example 1) discussed earlier.

#### c. Selection of Allocation Data Set

Prior to completing the emission model tables for the entire set of 32 ESP combinations, analyses were conducted to determine which employment data set was the best for emissions allocation. Recall that the AFxEFxUF product could be calculated based on either total employees or production employees. If solvent emissions from a facility correlate well with the amount of production, perhaps allocation based on production employees only would be the more accurate way to establish the 1993 manufacturing solvent usage inventory. It was necessary to compare emissions allocations by both employment types to quantitatively judge the best allocation data set.

Specific 1993 TOG emission estimates for solvent cleaning equipment were obtained from CARB's Emission Data System (EDS). Files were available with 1993 actual TOG emission totals from permitted sources within the following Air Pollution Control Districts (APCDs) and Air Quality Management Districts (AQMDs):

- Ventura County APCD (VCAPCD);
- BAAQMD;
- Santa Barbara APCD; and
- San Joaquin Valley Unified APCD (SJVUAPCD).

Data in the EDS for 1993 SCAQMD emissions were determined to be 1990 emissions that had not been updated by the district.

From these files, data were extracted for vapor degreasing equipment (BVD/CVD) by MIG for several counties. Vapor degreasing TOG emissions were selected because the permit data would be more likely to contain the bulk of actual real world emissions (i.e., a much higher percentage of vapor degreasers are permitted versus cold cleaning equipment, and the amount of unpermitted vapor degreasing equipment would be very small and would create a small amount of emissions).

Emission estimates for the same set of counties, MIGs, and equipment were derived from the emissions model. First, AF, EF, and UF emission model variables were

determined for all seven BVD/CVD ESP combinations in the manufacturing survey (BVD/CVD emissions from maintenance solvent usage were assumed negligible and were not included in this analysis). Variables were calculated on both total and production employee bases. TOG emission estimates were calculated with the following general equation:

TOG (tons/year) - AF · EF · UF · 
$$\left(\frac{1}{2,000}\right)$$
 x Number of Employees (10)

where:

gal solvent loss/employee/year AF =

lb TOG/gal solvent EF =

ESP combination user employees/survey employees UF =

1/2,000 converts lbs to tons

Total employment data for 1993 were obtained from the 1993 County Business Patterns for California CD-ROM issued by the Bureau of Census (BOC, 1995). For production employment, advance data from the 1992 Annual Survey of Manufactures were obtained from the Bureau of Census (Hait, 1995). Production employment data from this source are available every five years. Employment data for 1992 were used as surrogate for 1993 in this analysis.

Simple linear regression of all the permitted TOG data against the model's TOG estimates revealed a slightly higher correlation coefficient, R2, when total employees were used  $(R^2=0.32)$  versus using production employee allocation  $(R^2=0.24)$ . Correlations were somewhat poor due to the use of many county and MIG permit data points which may not have completely captured all vapor degreasing emissions. For this reason, another set of regression analyses were performed using only MIG 4 TOG data. It was judged that vapor degreasing emissions from this industry group, electronic and other electric equipment, would be more completely captured by district permit data. In this case, total and production employment allocation methods yielded the same R2 of 0.94. Finally, regressions were performed using only Ventura County data. VCAPCD has no de minimus limit for vapor degreasing permits, so nearly all TOG emissions from this equipment should be captured. As shown in Table III-14, total employment gave a slightly better correlation with Ventura data compared with production employment.

Table III-14 Comparison of Employment Allocation Data Sets Using **VCAPCD Vapor Degreasing Data** 

		1993 TOG Emissions (tons p	er year)
MIG	Emission Model En	nployment Allocation	VCAPCD
	Total	Production	Permit Data
	48.3	46.9	48.1
4	30.3	22.3	32.5
4		25.5	12.2
5	27.0 21.8	14.1	6.3

Correlation Coefficient: R2 Total employment = 0.87; R2 Production employment = 0.73; (vs. Permit Data). NOTES:

Based on its equivalent or better correlations with actual data, the total employment allocation method was chosen over the production employment method for preparing the 1993 base year solvent cleaning and degreasing emission inventory. AF, EF, and UF emission model variables for all manufacturing and maintenance ESP combinations were calculated using total employees. All TOG emissions allocations to counties, districts, and the state were made using 1993 total employment data from the BOC County Business Patterns.

Once total employees were established as the best allocation method, the emission model tables for the 32 manufacturing usage ESP combinations were completed. AF/EF/UF tables are presented in Appendix B-1. Since none of the model variables could be resolved to the facility size level (due to insufficient responses), the facility size cut-offs were omitted from the Appendix B tables. Summary statistics for these variables are shown in Table III-15.

#### 2. 1993 Base Year Inventory

Table III-16 depicts the 1993 Base Year Inventory for Manufacturing MIGs 1-7, broken down by both equipment and solvent type. Total statewide 1993 TOG emissions from this category were estimated to be 37,516 tons. According to Table III-16, TCA accounted for approximately 34 percent of the 1993 TOG emissions from manufacturing industries, the largest of any one solvent group. This large representation by TCA is significant in that production of this solvent was phased out by the end of 1995. CFCs, which are also scheduled to be phased out, account for nearly 7 percent of the emissions, and combined with TCA account for approximately 40 percent of the 1993 TOG emissions from manufacturing industries. Thus, users will likely continue to use TCA and CFCs even after the production ban is implemented.

Handwiping solvents account for 42 percent of the 1993 TOG emissions from manufacturing industries, the largest representation of any one equipment type. Handwiping solvents are not inventoried in CARB's current 1993 inventory, thus its inclusion represents one of the single most significant improvements to the inventory.

Other previously uninventoried solvents include HCFCs, toluene/xylene, terpenes, and petroleum distillates (only Stoddard solvent was previously inventoried). As shown in Table III-16, these solvents represent 1.7 percent, 1.5 percent, 0.9 percent, and 21.3 percent, respectively of the 1993 TOG emissions from manufacturing usage. The large representation by petroleum distillates is significant because it was previously thought that the use of such solvents were confined primarily to the maintenance categories. The inclusion of HCFCs, petroleum distillates, glycol ethers, PFC blends, and terpenes is significant in that these solvents represent alternatives to TCA and CFCs and are expected to experience increased use in coming years.

Table III-17 depicts the 1993 TOG emissions from manufacturing usage broken down by county and air district. As expected, counties belonging to the South Coast, Bay Area, and San Diego County air districts account for over 90 percent of the statewide TOG emissions.

Table III-15

Manufacturing Solvent Usage: Summary of Emission Model Variables Statistics

	Τ				Emission Model Variables						
	Al	location To	):			AF			EF		UF
ESP Combination	MIG	Region	Facility Size	п	Mean	S	CV	Mean	S	CV	
CA - BCC	1-6	All	Ail	15	2.82	3.73	1.32	11.1			0.0
	1,3,4,6,7	Ali	All	30	3.07	3.63	1.18	11.1	•	-	0.1
CA - BVD/CVD	2	Ali	All	15	21.8	11.2	0.52	11.1	-	•	0.
	5	All	All	18	6.95	8.87	1.28	11.1	•		0.4
	1,4,5,6	1	Alt	14	4.17	1.74	0.42	11.1	•	•	0.
CA - HWS	1,4,5,6	2,3	All	18	0.32	0.47	1.45	11.1	•	- ]	0.
	2,3,7	All	All	15	14.3	12.1	0.84	10.9	1.27	0.12	0.
	3 - 6	All	All	10	2.64	12.4	4.69	13.1	-	-	0.
CFC/CFC Blends - BCC/CCC	2-6	Ail	All	26	l.	0.91	0.98	13.1	0.47	0.04	0
CFC/CFC Blends - BVD/CVD	3 - 7	Ali	All	22		0.82	1.58	12.6	1.37	0.11	0
CFC/CFC Blends - HWS	\	All	All	11		3.62	0.94	10.1		- }	0
HCFC - BVD/CVD	2,3,4.6	All	Alf	5	1	0.47	0.75	10.1		-	0
HCFC - HWS	2-7	All	All	25	1	1.62	1.25	6.63	0.05	0.01	0
Ketones - BCC		All	All	96	<b>↓</b>	. 2.31	2.51	6.46	0.83	0.13	0
Ketones - HWS	1,4,6	All	All	119	1	13.3	2.79	6.62	0.21	0.03	C
	2,3,5,7	All	All	11	<u> </u>	10.33	1.30	6.31	0.28	0.04	C
Alcohols/Alcohol Blends - BCC/CCC	2,3,5,6	All	All	1		1.55			0.49	0.08	(
	4		All	9		5,15		6.35	0.75	0.12	(
Alcohols/Alcohol Blends - HWS	1,2,4,7	All All	All	11					0.26	0.04	(
	3,5,6		All		4 1.31			11.1	<del></del>		
Methylene Chloride - BCC	3,4,6	All	All	'				1		-	(
Methylene Chloride - HWS	All	All		+;				<b>_</b>	0.36	0.06	_
Petroleum Distillates - BCC/CCC	2,3	1	All	4					0.54	0.08	,
	2,3	2,3	All	- 1	4 15.0			L	0.65	0.10	١,
	4,5	All	Ali		3 3.20				0.18	0.03	1
	6.7	All	All		<u> </u>			<del>                                     </del>		0.04	Η,
Petroleum Distillates - HWS	1,3	1	All	- i				1		0.06	i i
	1,3	2,3	All		1 4.84 28 21.7			1		0.09	1
	2,5,7	1	All	1	6.06		_			0.05	
	2.5.7	2,3 All	All All		23 1.10			1			l l
	4,6		All	+	7 0.50					0.20	+-
Miscellaneous Pure Solvents - BCC	2,4	All	All	1.	17 1.9	-		1			1
Miscellaneous Pure Solvents - HWS	All	All			6 7.4		-				
PERC - BVD/CVD	2,5,7	Ali	All	ļ	4 0.6			1			
PERC - HWS	2,4,5	All	All	-	1					0.01	
Toluene/Xylene - BCC	2,3,4,6	All	All		5 1.4						
Toluene/Xylene - HWS	2 - 6	All	All	1	25 1.3			1			
TCE - BVD	2,5,6	Ali	All		5 9.7					0.27	,
TCE - HWS	1,2,6	All	All		6 1.0			i			1
Glycol Ethers - BCC/CCC	2,3,4,6	All	Ali	i i	10 0.7			1			1
Glycol Ethers - HWS	All	Ali	All		26 0.6	7 0.9	1.	5.04	7 3.20	, 0.0	1

E.H. PECHAN & ASSOCIATES, INC. Doc. # 95.12.004/517

Table III-15 (continued)

						Emi	ssion M	odel Varia	bles		
ESP Combination		Allocation To	<b>)</b> :	$\Box$		AF			EF		
Edi domentation	MIG	Region	Facility Size	n	Mean	S	CV	Mean	5	CV	CV UF
PFC Blends - BVD	3	All	All	2	0.36	0.24	0.65	14.2	-		0.23
Terpenes - BCC/CCC	2 · 6	All	All	8	2.00	6.74	3.37	4.43	2.49	0.56	0.09
Terpenes - HWS	1 - 6	All	All	8	0.11	0.23	2.19	6.39	1.38	0.22	0.01
Miscellaneous Blends - BCC/CCC	2 - 6	All	All	13	2.39	14.7	6.17	7.73	1.48	0.19	0.10
Miscellaneous Blends - BVD	4,6	All	AŧI	2	0.81	0.55	0.68	8.18	1.21	0.15	0.01
Miscellaneous Blends - HWS	All	All	Ali	41	3.11	4.21	1.35	6.46	1.62	0.25	0.24

NOTES:

n= number of records averaged

s = standard deviation

CV = coefficient of variation = s/mean

UF = user fraction

Table III-16
Manufacturing Solvent Usage: MIGs 1-7
1993 State TOG Emissions by ESP Combination

		Tons TOG/yea	r	
	Cold Cleaning (BCC/CCC)	Vapor Degrèasinģ (BVD/CVD)	HWS	State Solvent Total
TCA	561	7,750	4,360	12,670
CFC/CFC blends	1278	874	367	2,519
HCFC	-	642	4.55	646
Ketones	66.9	-	3,113	3,180
Alcohols/alcohol blends	2,623	-	978	3,601
Methylene chloride	32.8	-	1,584	1,616
Petroleum distillates	5,871	-	2,118	7,989
Miscellaneous pure solvents	30.7	-	212	242
PERC	-	430	15.2	446
Toluene/xylene	19.2	-	535	554
TCE	-	249	66.9	316
Glycol ethers	21.9	-	183	204
PFC blends	-	100	-	100
Terpenes	343	-	2.59	346
Miscellaneous blends	852	10.9	2,223	3,086
State equipment total	11,700	10,056	15,761	37,516

Table III-17

Manufacturing Solvent Usage: 1993 County-Level TOG Emissions

Air District	County	TOG (tons/year)
Amador Co.	Amador	5.74
	Alameda	1,356
Bay Area	Contra Costa	233
	Marin	58.7
	Napa	17.6
	San Francisco	159
	San Mateo	469
	Santa Clara	6,195
	Sonoma <sup>1</sup>	276
	Solano¹	115
	Total	8,880
Butte Co.	Butte	60.7
Calaveras Co.	Calaveras	3.11
Colusa Co.	Colusa	0.74
El Dorado Co.	El Dorado	14.9
Feather River	Sutter	12.0
	Yuba	6.44
	Total	18.4
Glenn Co.	Glenn	0.45
Great Basin Unified	Alpine	0.00
	Inyo	0.13
	Mono	0.93
	Total	1.06
Imperial Co.	Imperial	8.28
Lake Co.	Lake	5.86
Lassen Co.	Lassen	/ 0.38
Mariposa Co.	Mariposa	1.57
Mendocino Co.	Mendocino	28.6
Modoc Co.	Modoc	0.13
Monterey Bay	Monterey	76.3
	San Benito	11.6
	Santa Cruz	121
	Total	209
North Coast Unified	Del Norte	1.67
	Humboldt	12.4
	Trinity	0.00
	Total	14.1

## Table III-17 (continued)

Air District	County	TOG (tons/year)
Northern Sierra	Nevada	57.5
	Plumas	1.09
	Sierra	0.00
	Total	58.6
Placer Co.	Placer	151
Sacramento Metro.	Sacramento	329
San Diego Co.	San Diego	3,457
San Joaquin Valley	Fresno	253
	Kings	8.40
	Kern <sup>2</sup>	66.2
	Madera	35.6
	Merced	35.5
	San Joaquin	247
	Stanislaus	180
	Tulare	112
	Total	938
San Luis Obispo Co.	San Luis Obispo	91.3
Santa Barbara Co.	Santa Barbara	319
Shasta Co.	Shasta	21.2
Siskiyou Co.	Siskiyou	7.65
South Coast	Los Angeles <sup>3</sup>	14,681
	Orange	5,418
	Riverside <sup>3</sup>	762
	San Bernardino <sup>3</sup>	1,225
	Total	22,085
Tehama Co.	Tehama	4.57
Tuolumne Co.	Tuolumne	8.69
Ventura Co.	Ventura	725
Yolo-Solano	Yolo	66.1
	Total	66.1
Statewide N	Manufacturing Usage Total	37,516

NOTES:

All county emissions allocated to BAAQMD.
 All county emissions allocated to SJVUAPCD.
 All county emissions allocated to SCAQMD.

### B. MAINTENANCE SOLVENT USAGE

Maintenance solvent usage refers to any activity in which a solvent is used to clean machinery, tools, vehicle parts, or other equipment that are not incorporated into a product. The maintenance portion of the 1993 base year emission inventory was developed primarily from three data sources:

- MIGs 1-7 mail-out survey;
- Industry Group 8 CATI survey; and
- Industry Group 9 CATI survey.

In the mail-out survey of MIGs 1-7, maintenance solvent usage data were obtained along with the manufacturing solvent usage data discussed in the previous section. Industry Group 8 includes maintenance and service industries such as automotive repair. Industry Group 9 consists of all manufacturing industries excluding MIGs 1-7. In addition to the three primary data sources above, data on SKC parts washers were used to develop emission estimates for two Group 8 service industries that were not included in the user surveys (agricultural and oil/gas production equipment maintenance). The SKC data and methods used to estimate emissions are detailed below.

## 1. Data Reduction and Statistical Analysis

#### a. Industry Groups 1-7

Maintenance usage data were provided by the same 988 facilities involved in the manufacturing usage inventory. Quality assurance procedures, data consolidation, and statistical analyses used to prepare the maintenance emission model tables were largely the same as for the manufacturing data discussed earlier. Unless differences are highlighted in this section, it can be assumed the same basic procedures were used.

In the mail survey, the facilities selected among 31 solvent categories and 6 equipment types, including GCE, to characterize their maintenance solvent degreasing usage. To minimize the number of ESP combinations to be analyzed, solvents were consolidated into groups as in the manufacturing analysis (Table III-3). During this grouping process, several records of unlisted pure solvents (survey code 199) and unlisted mixtures (299) were able to be combined into other groups. Five methanol and n-propanol records were placed with the alcohols/alcohol blends. Seven kerosene and petroleum hydrocarbon records were placed in the petroleum distillates group. Note that the following solvents did not occur in the MIGs 1-7 maintenance usage survey and are not included in this portion of the emissions inventory:

- n-hexane (111);
- PERC (113);
- CFC blends (202);
- DBE (203);
- HCFC blends (205);
- Methylene bromide (206);
- o-dichlorobenzene (207);

- Other halogenated (208); and
- PFC blends (209).

Equipment was consolidated into three groups - cold cleaning, vapor degreasing, and handwiping — as in the manufacturing usage survey. GCE was included with BCC/CCC in the cold cleaning group. Because solvent is not vaporized in gun cleaning operations, GCE AFs in gallons solvent loss per employee should be more similar to BCC/CCC than BVD/CVD operations. The equipment and solvent consolidations were necessary to reduce the number of ESP combinations to 25. These 25 ESP combinations, described in Table III-18, were used to develop the MIGs 1-7 portion of the maintenance solvent usage inventory.

Table III-18
MIGs 1-7 Maintenance Solvent Usage: Final 25 ESP Combinations

Solvent	Number of Records by Equipment Type			
Group	BCC/CCC/GCE	BVD/CVD	HWS	
TCA	7	. 5	20	
CFC/CFC blends	2	3	5	
HCFC	•	-	3	
Ketones	28	- •	97	
Alcohols/alcohol blends	9	-	97	
Methylene chloride	-	-	4	
Petroleum distillates	128	• -	168	
Miscellaneous pure solvents	2	-	9	
Toluene/Xylene	10	-	10	
TCE	-	-	2	
Glycol ethers	10	-	16	
Terpenes	5	-	9	
Miscellaneous blends	18	-	24	

Each ESP combination in the table contains one data record for each user facility. Many facilities have usage records for more than one ESP combination. Also, due to the consolidations just discussed, facilities with multiple solvent or equipment use within one ESP combination (e.g., the alcohols ethanol and IPA; equipment BCC, CCC, and GCE) required a composite record. For these records, gallon-weighted total organic gas contents (lb TOG/gal solvent) were calculated and usage volumes were summed. Because many of these final 25 ESP combinations include multiple solvents, equipment types, or the composite facility records just discussed, an estimated breakdown of emissions by individual solvents and equipment types is provided with each ESP combination's emission model table in Appendix B-2. As mentioned with the manufacturing usage inventory, extreme caution should be used when using these breakdowns, since many were developed from very few survey responses.

The ESP combinations in Table III-18 characterize 1993 maintenance solvent usage by 492 of the 988 MIG 1-7 facilities. Over half of the facilities surveyed, 496, reported no maintenance solvent usage. As with MIGs 1-7 manufacturing usage, the table shows a diverse range of solvent and equipment types. Not surprisingly, petroleum distillates were the most commonly used solvent in cold cleaning and handwiping maintenance operations.

To develop the emissions model, all data were sorted by ESP combination and converted to a Microsoft Excel 4.0 spreadsheet for the remainder of the analyses. All solvent volumes were converted to gallons, densities to pounds per gallon. As with the manufacturing usage, several assumptions were made prior to calculating the emission model variables. These included assuming no disposed or recycled fractions for HWS records, and substituting the following average disposed or recycled fractions in records which indicated technically invalid 100 percent recycle/disposal (average fractions developed from survey data):

- Halogenated solvent groups, BVD/CVD = 0.35;
- Halogenated solvent groups, BCC/CCC/GCE = 0.34;
- Petroleum distillates, BCC/CCC = 0.37; and
- Other solvent groups, BCC/CCC = 0.31.

Solvent densities for pure compounds were listed previously in Table III-6. Densities for solvent blends were obtained through the survey. As in the manufacturing usage analysis, records where no density was provided were assigned an average calculated from all other responses for that solvent code. For records with an exhaust control, the same collection and control efficiency assumptions were used as in the manufacturing analysis (see section III.A.1.b).

The emission model variables, AF, EF, and UF, were calculated for each of the 25 ESP combinations using the simple case method described in the manufacturing usage section. It was not anticipated that MIG or regional differences would significantly affect maintenance solvent usage patterns, so one overall weighted mean AF was calculated for each ESP combination. Weighting procedures were the same as described in the manufacturing usage section. All variables were in terms of total employees. Summary statistics for the variables are presented in Table III-19. As noted in the table, due to sewerely skewed AF data, two of the ESP combinations were assigned a median AF in the emission model. Emission model tables are provided in Appendix B-2.

#### b. Industry Group 8

Industry group 8 consists primarily of auto repair and related facilities. Data gathered during the CATI survey were used to develop estimates of AF and UF. The EFs are assumed to equal the density of the solvent and were taken from published sources (e.g., Sax and Lewis, 1987; MSDSs). Since the equipment/operations used in this group are limited to batch-loaded cold cleaning and handwiping and no exhaust controls are used, this assumption regarding EF is justified.

CATI responses were combined into the same ESP combinations as those from the manufacturers mail-out survey. In group 8, the only equipment-related ESP combination

Table III-19 MIGs 1-7 Maintenance Solvent Usage: Summary of Emission Model Variable Statistics

	Allocation To:					Emi	ssion M	odel Vari	ables¹		
FOR Ourthornian	Al	location T	o:			AF			EF		UF
ESP Combination	MIG	Region	Facility Size	n	Mean	S	cv	Mean	s	СУ	
TCA - BCC/GCE	1,5,6	All	All	7	2.90	6.99	2.41	11.1	•	-	0.28
TCA - BVD	2,3,6	ΑII	All	5	4.16	80.8	1.94	11.1	-		0.01
TCA - HWS	1 - 6	All	All	20	1.05	1.16	1.10	11.1	-	-	0.05
CFC/CFC Blends - BCC	4,6	All	All	2	0.14	0.10	0.70	13.1	•	-	0.01
CFC/CFC Blends - BVD	3,4,6	All	All	3	0.27	0.30	1.11	13.1	-	-	0.02
CFC/CFC Blends - HWS	4 - 6	All	All	5	0.08	0.12	1.53	13.1	0.06	0.004	0.03
HCFC - HWS	4,6,7	All	All	3	0.09	0.06	0.67	10.1	-	-	0.01
Ketones - BCC/GCE	2 - 6	All	ΑI	28	24.8	93.4	3.77	6.60	0.29	0.04	0.05
Ketones - HWS	All	Αll	All	97	1.91	6.39	3.34	6.60	0.18	0.03	0.18
Aicohols/Alcohol Blends - BCC/GCE	1,2,3,4,7	All	All	9	0.62	0.35	0.56	6.50		•	0.02
Alcohols/Alcohol Blends - HWS	Alí	Ali	- All	97	0.47	1.32	2.80	6.40	0.61	0.10	0.19
Methylene Chloride - HWS	3,5	All	ΑII	4	0.22	0.20	0.90	6.93	3.75	0.54	0.08
Petroleum Distillates - BCC/CCC/GCE	All	Αll	All	128	3.35	5.32	1.59	6.49	0.31	0.05	0.2
Petroleum Distillates - HWS	All	All	All	168	3.17	6.39	2.02	6.43	0.4	0.05	0.13
Miscellaneous Pure Solvents - BCC/GCE	2,4	All	All	2	0.09	0.003	0.04	7.58	1.07	0.14	0.0
Miscellaneous Pure Solvents - HWS	1-5	All	All	9	14.7 <sup>2</sup>	38.0	2.58	7.11	0.99	0.14	0.0
Toluene/Xylene - BCC/GCE	1,2,3,4,7	All	All	10	0.57	0,76	1.34	7.10	0.02	0.002	0.0
Toluene/Xylene - HWS	1 - 5	All	All	10	1.31	1.10	0.84	6.65	1.55	0.23	0.0
TCE - HWS	1,5	All	Ali	2	0.77	0.81	1.05	12.2	-	-	0.00
Glycol Ethers - BCC/CCC/GCE	1,2,3,5	All	All	10	2.42	2.86	1.18	4.62	2.10	0.46	0.0
Glycol Ethers - HWS	2,3,4,5,7	ΑII	All	16	0.84	1.99	2.36	5.60	3.71	0.66	0.1
Terpenes - BCC	2 - 5	All	All	5	0.44	0.42	0.95	3.32	2.27	0.68	0.0
Terpenes - HWS	2,4,5,7	All	All	9	1.53	1.62	1.06	6.08	1.96	0.32	0.0
Miscellaneous Blends - BCC/GCE	All	All	All	18	0.37	0.97	2.63	6.90	0.23	0.03	0.1
Miscellaneous Blends - HWS	1,2,3,4,5, 7	All	All	24	34.6³	62.3	1.80	6.91	1.00	0.14	0.2

NOTES:

'n = number of records averaged; s = standard deviation; CV = coefficient of variation = s/mean; UF = user fraction

<sup>&</sup>lt;sup>2</sup>Due to severely skewed data, median AF of 0.10 used in emission model. <sup>3</sup>Due to severely skewed data, median AF of 0.70 used in emission model.

observed was batch-loaded cold cleaning using petroleum distillates. Four handwiping ESP combinations were observed with the following solvents: petroleum distillates, ketones, TCA, and alcohols. Table III-20 provides the emission model variables. Based on the UF estimates, petroleum distillate cold cleaning and handwiping contribute the bulk of emissions for industry group 8.

Table III-20 Emissions Model Variables for Industry Group 8<sup>1</sup>

ESP Combination	AF (gal/emplyr)	EF (Ib TOG/gal)	UF (user empl./total empl.)
Petroleum Distillates-BCC	5.00 <sup>2</sup>	6.60	0.68
Petroleum Distillates-HWS	2.00 <sup>2</sup>	6.60	0.27
Ketones-HWS	1.00 <sup>2</sup>	6.60	0.01
TCA-HWS	3.27	11.1	0.01
Alcohols-HWS	0.23 <sup>2</sup>	6.50	0.01

NOTES:

For all ESP combinations in Table III-20 except TCA-HWS, the median value for AF was selected for use in the emissions model. This was due to the fact that usage data for the other ESP combinations were positively skewed. In these instances, the median is a better descriptor of central tendency than the mean.

For the petroleum distillates-BCC combination, over 80 percent of the annual usage (and hence, emissions) was SKC solvent. Precise estimates of the SKC fraction could not be made, since a large number of respondents did not know the amount of solvent added back to their parts washers by SKC. Mineral spirits made up about 7 percent of the annual usage and petroleum distillates made up another 5 percent.

Some respondents reported unlisted (i.e., not on the CATI interviewer's list) solvents. In these instances, the trade name of the product was entered into the CATI system. The unlisted products most often reported were detergents and water-based cleaning products (FSC, 1995). In some cases, the trade name of a known petroleum distillate product was given, and these records were added into the statistical analysis of model variables.

The ketones-HWS combination was almost entirely made up of acetone usage (over 99 percent by volume). For the alcohols-HWS combination, all of the usage was IPA. The petroleum distillates-HWS combination was dominated by mineral spirits use (almost 60 percent), although this fraction was heavily influenced by one large user. Another 5 percent of the usage for this combination was attributed to petroleum distillates and the balance to SKC.

<sup>&#</sup>x27;These variables do not apply to agricultural equipment maintenance and oil/gas production. Emissions for these groups were estimated separately with SKC data.

<sup>&</sup>lt;sup>2</sup> Median value reported.

The presence of SKC in the HWS combination above may indicate the potential for double-counting SKC usage, since, presumably, the solvent would have to be taken out of the parts washer to be used in handwiping activities. Since, respondents were questioned separately regarding usage in parts washers (BCC) versus HWS, it is assumed that any double-counting in SKC usage is not significant.

SKC (Kusz, 1995) provided a limited amount of data that was used to develop emission estimates for two groups outside of the assumed solvent users universe (see Table II-1). The two groups are agricultural equipment maintenance and mining/trades equipment maintenance. SKC data on the number of parts washers, typical annual losses from the most popular parts washer models, and estimates of market share were used to develop annual statewide TOG emission estimates. For agricultural maintenance, an estimate of 2,040 tons of TOG per year was developed. Emissions were allocated to the district and county level using BOC employment data for SIC codes 0710 and 0720. For mining/trades, an estimate of 412 tons of TOG per year was derived. For the purposes of allocation, it was assumed that all of the users in this group are involved in oil/gas field services (SIC codes 138x). Other mining operations are not likely to use SKC services due to their typically remote locations.

It should be noted that this use of SKC data does not include all of the potential solvent use, since it only refers to those facilities that might use SKC products. In addition, users in these industries may use other solvents to perform parts cleaning. All of the estimates derived from SKC data were added to the petroleum distillates-BCC ESP combination. It should also be noted that some degree of overlap exists between the survey data and the SKC data described above. For example, some repair services in the 76xx series of SIC codes, including agricultural and refrigeration equipment repair services, were covered in both sets of data. However, it was not possible to break out SKC usage data down to the SIC level. Therefore, some double-counting of emissions does occur in the base year inventory. This double-counting is, however believed to be small.

#### c. Industry Group 9

Industry group 9 consists of all manufacturing SIC codes (2000-3999) that are not represented in MIGs 1-7. As with industry group 8 above, CATI survey results were grouped into the appropriate ESP combinations. Seven ESP combinations were observed. The emissions model variables are presented in Table III-21 below. As seen from the UF estimates, cold cleaning emissions of petroleum distillates will dominate the emission estimates produced for industry group 9. For the alcohol ESP combinations, all usage reported was IPA. For ketones, 33 percent of the handwiping usage was MEK, and the rest was made up of acetone. For ketone-BCC, acetone made up over 98 percent of the usage (remainder MEK).

#### 2. 1993 Base Year Inventory

Table III-22 depicts the 1993 base year inventory for maintenance MIGs 1-7, broken down by both equipment and solvent type. Total 1993 TOG emissions from this category were estimated to be 11,400 tons. According to Table III-22, ketones, petroleum distillates and TCA accounted for approximately 40 percent, 29 percent, and 18 percent respectively of the 1993 TOG emissions from maintenance use of solvents in

manufacturing industries (MIGs 1-7). The entire category was previously unspeciated in CARB's current 1993 inventory (in terms of equipment or solvents), thus its inclusion as part of this inventory represents a significant improvement over the current inventory. As expected, very little vapor degreasing (<1 percent) is performed for maintenance purposes based on emission estimates. As shown in Table III-22, the bulk of the emissions (68 percent) are due to the equipment grouping BCC/CCC/GCE with the second largest contribution (31 percent) coming from HWS. As mentioned before, the inclusion of the previously uninventoried solvents, HCFCs, glycol ethers, PFC blends, and terpenes is significant in that they all represent alternatives to TCA and CFCs and are expected to experience increased use in coming years.

Table III-21
Emissions Model Variables for Industry Group 9

	AF (gal/emplyr)	EF (ib TOG/gal)	UF (user empl./total empl.)
ESP Combination	11.2	6.60	0.61
Petroleum distillates-BCC	2.00*	6.60	0.01
Petroleum distillates-HWS	<del>-</del>	6.60	0.02
Ketones-BCC	4.80*		0.02
Ketones-HWS	1.00*	6.60	0.005
Alcohols-BCC	3.00	6.50	
	1.03*	6.50	0.01
Alcohols-HWS TCA-HWS	7.66	11.1	0.02

NOTES:

Table III-22
Maintenance Solvent Usage: MIGs 1-7
1993 State TOG Emissions by ESP Combination

		Tons/	year	
	BCC/CCC/GCE	BVD/CVD	HWS	State Solvent Total
701	1,758	62.9	265	2,086
TCA	1,78	23:2	7.49	<b>32</b> .5
CFC/CFC blends		-	1.55	1.55
HCFC	3,482	-	1,084	4,567
Ketones	20.3	_	269	289
Alcohols/alcohol blends	20.0	_	23.7	23.7
Methylene chloride			1,136	3,323
Petroleum distillates	2,188	_	21.1	22.5
Miscellaneous pure solvents	1.37			84.7
Toluene/Xylene	16.2	-	1.35	1.35
TCE	-	-	172	216
Glycol ethers	44.2	-	125	145
Terpenes	19.5	-		608
Miscellaneous blends	223		385	
State equipment total	7,754	86.1	3,560	11,400

Median value reported.

Table III-23 depicts the 1993 TOG emissions from maintenance MIGs 1-7, broken down by county and air district. Counties belonging to the South Coast, Bay Area, and San Diego County, air districts account for over 90 percent of the statewide TOG emissions.

Table III-24 depicts the 1993 TOG emissions inventory for Maintenance Group 8 (Service Industries) broken down by ESPs and by county and air district. Total 1993 TOG emissions from this category were estimated to be 7,492 tons. As shown in the table, only five ESPs were identified in this industry group. As expected, the largest contribution is due to the ESP, petroleum distillates-BCC, accounting for almost 90 percent of the total. The petroleum distillate-BCC ESP is the category that was previously inventoried by CARB with the use of sales data from SKC. What is significant, however is the capturing of an additional 10 percent made up of the following ESPs: petroleum distillates-HWS; ketones-HWS; TCA-HWS; and alcohols-HWS. Also depicted in Table III-24, is a breakdown by county and air district. The South Coast, San Joaquin Valley Unified, and Bay Area districts account for over 70 percent of the total statewide emissions.

Emissions in the San Joaquin Valley are driven by contributions from agricultural and oil production equipment maintenance. As described in Section III.B.1.b above, these are categories that were not included in the end-user survey universe, but were added by using data from SKC (Kusz, 1995).

Table III-25 depicts the 1993 TOG emissions inventory for Maintenance Group 9, which includes manufacturing industries outside of MIGs 1-7. Total 1993 TOG emissions from this category were estimated to be 22,171 tons. Emissions are broken down by ESPs and by county and air district. Seven ESPs were observed in this category: petroleum distillates-BCC; petroleum distillates-HWS; ketones-BCC; ketones-HWS; alcohols-BCC, alcohols-HWS; and TCA-HWS. As was the case with Maintenance Group 8, the ESP petroleum distillates-BCC accounts for the largest contribution to the total inventory, nearly 95 percent. The breakdown by air districts shows 85 percent of the emissions coming from only three air districts: South Coast, Bay Area, and San Joaquin Valley Unified.

A comparison was made between 1993 emission estimates from petroleum distillates-BCC obtained through the use of the emissions model versus 1994 estimates made with the use of data provided by SKC (i.e., SKC data that fell within the user universe of Table II-1). Based on SKC estimates of market share, the number of SKC parts washers in the assumed universe of Table II-1, and typical losses from the most popular parts washer models, a 1994 annual statewide TOG estimate for all petroleum distillates-BCC of 11,089 tons was made (includes maintenance and manufacturing usage). From Table ES-2, the emissions model predicted more than three times this amount in 1993. The discrepancy is likely not due to differing economic conditions between the two years, but to SKC market share estimates which apply only to that fraction of the parts washer universe that is maintained by solvent reclaimers, such as SKC, Laidlaw Environmental Services, and others (Kusz, 1995).

# Table III-23 MIGs 1-7 Maintenance Solvent Usage: 1993 Statewide TOG Emissions

Air District	County	TOG (tons/yr)
Amador Co.	Amador	2.18
Bay Area	Alameda	435
Day Alca	Contra Costa	85.8
	Marin	17.7
	Napa	5.71
	San Francisco	45.3
	San Mateo	. 175
	Santa Clara	2,255
	Sonoma <sup>1</sup>	130
	Solano1	29.5
	Total	3,180
Butte Co.	Butte	18.7
Calaveras Co.	Calaveras	0.72
Colusa Co.	Colusa	0.23
El Dorado Co.	El Dorado	5.08
Feather River	Sutter	3.65
	Yuba	1.36
	Total	5.01
Glenn Co.	Glenn	0.14
Great Basin Unified	Alpine	0.00
Ciour Duoin Cime	Inyo	0.04
	Mono	0.19
	Total	0.23
Imperial Co.	Imperial	3.05
Lake Co.	Lake	1.33
Lassen Co.	Lassen	0.11
Mariposa Co.	Mariposa	0.75
Mendocino Co.	Mendocino	7.35
Modoc Co.	Modoc	0.04
Monterey Bay	Monterey	27.1
montory buy	San Benito	3.16
	Santa Cruz	44.1
	Total	74.4
North Coast Unified	Del Norte	0.46
	Humboldt	4.23
	Trinity	. 0.00
	Total	4.69

#### Table III-23 (continued)

Air District	County	TOG (tons/yr)
Northern Sierra	Nevada	19.8
	Plumas	0.29
	Sierra	0.00
	Total	20.1
Placer Co.	Placer	51.4
Sacramento Metro.	Sacramento	94.8
San Diego Co.	San Diego	1,046
San Joaquin Valley	Fresno	80.4
	Kings	2.51
	Kern <sup>2</sup>	20.8
	Madera	10.4
	Merced	10.9
	San Joaquin	70.5
	Stanislaus	46.1
	Tulare	29.6
	Total	271
San Luis Obispo Co.	San Luis Obispo	28.6
Santa Barbara Co.	Santa Barbara	150
Shasta Co.	Shasta	6.77
Siskiyou Co.	Siskiyou	2.41
South Coast	Los Angeles <sup>3</sup>	4,005
	Orange	1,642
	Riverside <sup>3</sup>	217
	San Bernardino <sup>3</sup>	303
	Total	6,167
Tehama Co.	Tehama	1.40
Tuolumne Co.	Tuolumne	3.39
Ventura Co.	Ventura	236
Yolo-Solano	Yolo	17.6
·	Total	17.6
Mainte	enance MIG 1-7 Total	11,400

NOTES:

All county emissions allocated to BAAQMD.
 All county emissions allocated to SJVUAPCD.
 All county emissions allocated to SCAQMD.

Table III-24
Industry Group 8: 1993 Statewide TOG Emissions

		T	OG Emissions by E	SP Combina	ation (tons	s/year)	
Air District	County*	Petroleum Distillates-BCC	Petroleum Distillates-HWS	Ketones- HWS	TCA- HWS	Alcohols- HWS	Totals
	Amador	2.85	0.39	0.01	0.05	0.00	3.30
Amador Co.	Alameda	224	33.2	0.55	4.36	0.14	262
Bay Area	Contra Costa	91.6	13.6	0.23	1.79	0.06	107
	Marin	40.7	5.55	0.09	0.73	0.02	47.0
	Napa	13.9	2.04	0.03	0.27	0.01	16.2
	San Francisco	96.8	14.5	0.24	1.90	0.06	114
	San Mateo	387	59.9	0.99	7.87	0.25	456
	Santa Clara	190	28.8	0.48	3.78	0.12	223
	Sonoma	44.4	6.44	0.11	0.85	0.03	51.8
	Solano	41.0	4.25	0.07	0.56	0.02	45.9
	Total	1,129	168	2.8	22.1	0.7	1,322
	Butte	40.4	3.05	0.05	0.40	0.01	43.9
Butte Co:		2.36	0.33	0.01	0.04	0.00	2.74
Calaveras Co.	Calaveras	9.73	0.29	.0.00	0.04	0.00	10.1
Colusa Co.	Colusa	13.7	2.01	0.03	0.26	0.01	16.0
El Dorado Co.	El Dorado	42.6	0.89	0.01	0.12	0.00	43.7
Feather River	Sutter	21.3	0.89	0.01	0.12	0.00	22.3
	Yuba	63.9	1.77	0.03	0.23	0.01	66.0
	Total		0.20	0.00	0.03	0.00	4.23
Glenn Co.	Glenn	4.00	0.20	0.00	0.00	0.00	0.23
Great Basin Unified	Alpine	0.19	1	0.00	0.06	0.00	3.49
	Inyo	2.95	0.47	0.00	0.03	0.00	1.5
	Mono	1.32	0.21	0.00	0.09	0.00	5.2
	Total	4.46	0.71		0.03	0.01	10
Imperial Co.	Imperial	98.9	1.65	0.03	<del></del>	0.01	59.
Kern Co.	Kern	57.2	1.65	0.03	0.22		
Lake Co.	Lake	7.63	0.69	0.01	0.09	0.00	8.4
Lassen Co.	Lassen	2.49	0.33	0.01	0.04	0.00	2.8
Mariposa Co.	Mariposa	0.89	0.12	0.00	0.02	0.00	1.0
Mendocino Co.	Mendocino	10.7	1.34	0.02	0.18	0.01	12.
Modoc Co.	Modoc	0.87	0.14	0.00	0.02	0.00	1.0
Mojave Desert	Los Angeles	44.3	6	0.11	0.8	1	51
Mojavo Dodon	Riverside	74.4	5.22	0.09	0.69	0.02	80
	San Bernardino	44.1	6.54	0.11	0.86	0.03	51
	Total	163	18.2	0.30	2.39	0.08	18
Monterey Bay	Monterey	195	5.52	0.09	0.73	0.02	20
Wichterey Day	San Benito	20.3	0.50	0.01	0.07	0.00	20
	Santa Cruz	37.3	3.71	0.06	0.49	0.02	41
	Total	252	9.72	0.16	1.28	0.04	26

#### Table III-24 (continued)

	T	TOG Emissions by ESP Combination (tons/year)								
Air District	County*	Petroleum Distillates-BCC	Petroleum Distillates-HWS	Ketones- HWS	TCA- HWS	Alcohols- HWS	Totals			
North Coast Unified	Del Norte	1.18	0.19	0.00	0.02	0.00	1.40			
North South States	Humboldt	13.1	2.08	0.03	0.27	0.01	15.5			
	Trinity	0.70	0.11	0.00	0.01	0.00	0.83			
	Total	15.0	2.38	0.04	0.31	0.01	17.7			
Northern Sierra	Nevada	7.34	1.12	0.02	0.15	0.00	8.63			
	Plumas	1.99	0.32	0.01	0.04	0.00	2.36			
	Sierra	0.16	0.03	0.00	0.00	0.00	0.19			
	Total	9.49	1.46	0.02	0.19	0.01	11.2			
Northern Sonoma	Sonoma	6.64	0.96	0.02	0.13	0.00	7.75			
Placer Co.	Placer	31.5	4.52	0.07	0.59	0.02	36.7			
Sacramento Metro.	Sacramento	177	24.7	0.41	3.25	0.10	206			
San Diego Co.	San Diego	404	51.2	0.85	6.73	0.21	463			
San Joaquin Valley	Fresno	421	14.7	0.24	1.93	0.06	438			
	Kings	75.7	1.13	0.02	0.15	0.00	77.0			
	Kern	324	9.35	` 015	1.23	0.04	335			
	Madera	58.3	1.18	0.02	0.15	0.00	59.7			
	Merced	54.8	2.39	0.04	0.31	0.01	57.6			
	San Joaquin	169	8.12	0.13	1.07	0.03	178			
	Stanislaus	88.7	6.50	0.11	0.85	0.03	96.2			
	Tulare	354	4.32	0.07	0.57	0.02	359			
	Total	1,545	47.7	0.79	6.3	0.20	1,600			
San Luis Obispo Co.	San Luis Obispo	26.4	3.99	0.07	0.52	0.02	31.0			
Santa Barbara Co.	Santa Barbara	112	8.49	0.14	1.12	0.04	122			
Shasta Co.	Shasta	20.8	3.25	0.05	0.43	0.01	24.5			
Siskiyou Co.	Siskiyou	9.62	0.69	0.01	0.09	0.00	10.4			
South Coast	Los Angeles	1,432	208	3.44	27.4	0.87	1,672			
	Orange	382	57.5	0.95	7.56	0.24	449			
	Riverside	201	14.1	0.23	1.86	0.06	218			
	San Bernardino	148	21.9	0.36	2.88	0.09	173			
	Total	2,163	302	4.99	39.7	1.26	2,511			
Tehama Co.	Tehama	6.57	0.95	0.02	0.13	· 0.00	7.67			
Tuolumne Co.	Tuolumne	4.79	0.72	0.01	0.09	0.00	5.62			
Ventura Co.	Ventura	253	11.1	0.18	1.45	0.05	266			
Yolo-Solano	Solano	16.8	1.74	0.03	0.23	0.01	18.8			
	Yolo	44.1	2.87	0.05	0.38	0.01	47.4			
	Total	60.8	4.61	0.08	0.61	0.02	66.1			
Group 8 Totals		6,710	679	11.2	89.3	2.83	7,492			

\*NOTE: Emissions for the following counties were divided between the appropriate air districts using census data: Kern, Los Angeles, Riverside, San Bernardino, Solano, and Sonoma (Asregadoo, 1995).

Table III-25
Industry Group 9: 1993 Statewide TOG Emissions

		Γ	TOG E	TOG Emissions by ESP Combination (tons/year)								
ir District	County	Petroleum Distillates- BCC	Petroleum Distillates- HWS	Ketones- BCC	Ketones- HWS	Alcohols- BCC	Alcohols- HWS	TCA- HWS	40.7			
1 0	Amador	18.6	0.06	0.23	0.05	0.04	0.03	0.64	19.7			
mador Co.	Alameda	970	2.9	11.7	2.73	2.12	1.60	33.3	1,024			
lay Area		406	1.2	4.9	1.14	0.89	0.67	14.0	429			
	Contra Costa	86.8	0.26	1.05	0.24	0.19	0.14	2.98	91.6			
	Marin	1,34.2	0.40	1.62	0.38	0.29	0.22	4.62	142			
	Napa San Francisco	733.1	2.2	8.9	2.06	1.61	1.21	25.2	774			
	San Mateo	471	1.4	5.7	1.33	1.03	0.78	16.2	498			
	Santa Clara	1,326	3.9	16.0	3.74	2.90	2.19	45.6	1,401			
		235	0.70	2.84	0.66	0.51	0.39	8.07	248			
	Sonoma' Solano'	111	0.33	1.35	0.31	0.24	0.18	3.83	118			
	Totai	4,474	13.3	54.1	12.6	9.8	7.4	154	4,725			
		79.0	0.23	0.96	0.22	0.17	0.13	2.72	83.5			
Butte Co.	Butte Calaveras	6.28	0.02	0.08	0.02	0.01	0.01	0.22	6.63			
Calaveras Co.	<del></del>	9.80	0.03	0.12	0.03	0.02	0.02	0.34	10.3			
Colusa Co.	Colusa	32.2	0.10	0.39	0.09	0.07	0.05	1.11	34.0			
El Dorado Co.	El Dorado			0.40	0.09	0.07	0.05	1.14	35.09			
Feather River	Sutter	33.2	0.10	0.32	0.08	0.06	0.04	0.92	28.15			
	Yuba	26.7	0.08	0.72	0.17	0.13	0.10	2.06	63.2			
	Total	59.9		0.27	0.06	0.05	0.04	0.76	23.2			
Glenn Co.	Glenn	21.98	0.07		0.00	0.00	0.00	0.00	0.00			
Great Basin Unified	Alpine	0.00	0.00	0.00	0.00	0.01	0.01	0.18	5.50			
	Inyo	5.21	0.02	0.06	0.00	0.00	0.00	0.02	0.75			
	Mono	0.71	0.00	0.01	0.00	0.01	0.01	0.20	6.26			
	Total	5.92	0.02		0.02	0.06	0.05	0.99	30.4			
Imperial Co.	Imperial	28.7	0.09	0.35			0.01	0.18	5.41			
Lake Co.	Lake	5.12	0.02	0.06	0.01	0.01	0.01	0.46	14.1			
Lassen Co.	Lassen	13.4	0.04	0.16	0.04	0.03		0.04	1.25			
Mariposa Co.	Mariposa	1.18	0.00	0.01	0.00	0.00	0.00		82.5			
Mendocino Co.	Mendocino	78.2	0.23	0.95	0.22	0.17	0.13	2.69	<del></del>			
Modoc Co.	Modoc	1.71	0.01	0.02	0.00	0.00	0.00	0.06	1.81			
Monterey Bay	Monterey	119	0.35	1.43	0.33	0.26	0.20	4.08	125.3			
	San Benito	22.6	0.07	0.27	0.06	0.05	0.04	0.78	23.9			
	Santa Cruz	228	0.68	2.76	0.64	0.50	0.38	7.85	241			
	Total	370	1.10	4.47	1.04	0.81	0.61	12.7	390			
North Coast Unified	Del Norte	9.93	0.03	0.12	0.03	0.02	0.02	0.34	10.5			
	Humboldt	135	0.40	1.63	0.38		0.22	4.63	142			
	Trinity	8.80	0.03	0.11	0.02	1	0.01	0.30	9.29			
	Total	153	0.45	1.85	0.43	0.34	0.25	5.3	162			

### Table III-25 (continued)

	Τ		TOG E	missions by E	SP Combina	tion (tons/ye	ar)		Takala
Air District	County	Petroleum Distillates- BCC	Petroleum Distillates- HWS	Ketones- BCC	Ketones- HWS	Alcohols- BCC	Alcohols- HWS	TCA- HWS	Totals
Northern Sierra	Nevada	18.1	0.05	0.22	0.05	0.04	0.03	0.62	19.2
	Plumas	16.3	0.05	0.20	0.05	0.04	0.03	0.56	17.2
	Sierra	3.92	0.01	0.05	0.01	0.01	0.01	0.13	4.14
	Total	38.4	0.11	0.46	0.11	0.08	0.06	1.32	40.5
Placer Co.	Placer	72.0	0.21	0.87	0.20	0.16	0.12	2.47	76.0
Sacramento Metro.	Sacramento	427	1.27	5.17	1.20	0.94	0.71	14.7	451
San Diego Co.	San Diego	895	2.7	10.8	2.52	1.96	1.48	30.8	945
San Joaquin Valley	Fresno	375	1.11	4.54	1.06	0.82	0.62	12.9	396
, ,	Kings	64.8	0.19	0.78	0.18	0.14	0.11	2.23	68.5
	Kern <sup>2</sup>	181	0.54	2.19	0.51	0.40	0.30	6.23	191
	Madera	70.3	0.21	0.85	0.20	0.15	0.12	2.42	74.3
	Merced	156	0.46	1.89	0.44	0.34	0.26	5.37	165
	San Joaquin	383	1.14	4.63	1.08	0.84	0.63	13.2	405
	Stanislaus	434	1.29	5.25	1.22	0.95	0.72	14.9	459
	Tulare	221	0.66	2.68	0.62	0.48	0.37	7.61	234
	Total	1,887	5.59	22.8	5.31	4.13	3.12	64.9	1,992
San Luis Obispo Co.	San Luis Obispo	70.1	0.21	0.85	0.20	0.15	0.12	2.41	74.1
Santa Barbara Co.	Santa Barbara	149	0.44	1.80	0.42	0.33	0.25	5.13	158
Shasta Co.	Shasta	90.8	0.27	1.10	0.26	0.20	0.15	3.12	95.9
Siskiyou Co.	Siskiyou	24.5	0.07	0.30	0.07	0.05	0.04	0.84	25.9
South Coast	Los Angeles <sup>3</sup>	8,290	25	100	23.3	18.2	13.7	285	8,755
	Orange	2,053	6.1	24.8	5.78	4.49	3.39	70.6	2,168
	Riverside <sup>3</sup>	449	1.3	5.4	1.26	0.98	0.74	15.4	474
	San Bernardino <sup>3</sup>	716	2.1	8.7	2.02	1.57	1.18	24.6	756
	Total	11,508	34.1	139	32.4	25.2	19.0	396	12,153
Tehama Co.	Tehama	47.0	0.14	0.57	0.13	0.10	0.08	1.62	49.7
Tuolumne Co.	Tuolumne	23.7	0.07	0.29	0.07	0.05	0.04	0.82	25.1
Ventura Co.	Ventura	284	0.84	3.4	0.80	0.62	0.47	9.75	299
Yolo-Solano	Yolo	118	0.35	1.42	0.33	0.26	0.19	4.04	124
	Total	118	0.35	1.42	0.33	0.26	0.19	4.04	124
Group 9 Totals	•	20,993	62.2	254	59.1	46.0	34.7	722	22,171

NOTES:

¹ All county emissions allocated to BAAQMD. ² All county emissions allocated to SJVUAPCD. ¹ All county emissions allocated to SCAQMD.

#### C. TEMPORAL ALLOCATION

A detailed analysis of temporal allocation factors was beyond the scope of this project. During the early planning stages, the researchers had planned on gathering temporal activity data from the survey respondents. However, after reviewing the additional burden this placed on the respondents, the research team felt that any non-essential data requirements, including temporal activity data should be left out of the surveys. Additional respondent burden would only serve to decrease the response rate.

An assessment was made of the temporal activity of solvent cleaning equipment in the data submitted by the districts to CARB. During the assessment of solvent cleaning temporal activity by industry group was analyzed. The results of this analysis showed very little variation in temporal activity between industry groups. Table III-26 shows typical results for monthly (August), weekly, and daily temporal activity for each industry group. Similarly, weekly and daily temporal activity showed little variation between MIGs.

Table III-26
Temporal Activity for a Sample MIG

	August Mont (monthly fra	August Monthly Activity (monthly fraction/yr) <sup>1,2</sup>		August Monthly Activity (monthly fraction/yr) <sup>1,2</sup> Weekly Activity (days/wk) <sup>1,2</sup>		Daily Activity (hours/day) <sup>1,2</sup>		
MIG	mean (median)	std. dev.	mean (median)	std. dev.	mean (median)	std. dev		
1	0.083 (0.083)	0	5.0 (5)	0	8.0 (8)	0		
2	0.083 (0.083)	0.004	5.8 (5)	6.2	8.7 (8)	4.2		
3	0.082 (0.083)	0.009	8.6 (5)	15	8.7 (8)	4.6		
4	0.083 (0.083)	0.004	5.3 (5)	0.64	11.4 (8)	5.9		
5	0.085 (0.083)	. 0.009	7.8 (5)	13 .	11.2 (8)	5.3		
6	0.083 (0.083)	0	5.2 (5)	0.44	9.1 (8)	3.4		
7	0.083 (0.083)	0	8.4 (5)	11	10.8 (8)	8		
8	0.083 (0.083)	0.003	5.1 (5)	0.42	9.2 (8)	3.6		
9	0.085 (0.083)	0.003	5.4 (5)	2.5	10.2 (8)	5.2		

NOTES:

Does not include idle or inactive equipment.

<sup>&</sup>lt;sup>2</sup> Statistics based on uncorrected data.

From Table III-26, it is clear that a temporal allocation of emissions for all industry groups should reflect equal monthly activity (i.e., 1/12 of the annual activity) and weekday operation during business hours (8 hours/day). As stated in Table III-26, the statistics are based on uncorrected data. In some cases, erroneous data points (e.g., 45 days/week) caused the mean to be placed outside the data limits and far from the median. Unpermitted facilities (i.e., those not included in CARB's data base) are assumed to have similar temporal activity patterns.

#### D. BASE YEAR INVENTORY UNCERTAINTY

A comprehensive assessment of the base year emissions inventory uncertainty was beyond the scope of this project. However, an assessment of the range of uncertainty associated with a few ESP emission estimates, which were derived from a range of variability in AFs and EFs, can provide a good qualitative sense of the overall inventory uncertainty. For example, a higher level of certainty is obtained from an ESP with low variability in AF and EF. The coefficient of variation (standard deviation divided by the mean) is a good statistic to use in identifying those ESPs with relatively high or low uncertainty. Sources of uncertainty for solvent cleaning emissions for each ESP include the following:

- variability in solvent usage (AF);
- variability in emission factor (EF);
- error in the estimation of solvent user population (UF); and
- error in overall population estimates used to allocate emissions (e.g., BOC).

The variability in the emission estimation parameters, AF and EF, can be assessed with the descriptive statistics for each ESP, such as the weighted mean and standard deviation (see Table III-15). For the purposes of this uncertainty analysis, the error associated with the solvent user fraction, UF, is assumed to be represented by the sampling error of the manufacturers survey. This survey achieved a sampling error of  $\pm$  7 to 8 percent for each MIG. Since the ESPs are generally weighted across industry groups, the sampling error by industry group should provide a reasonable estimation of the error in the user fraction estimate.

BOC population estimates are derived from a combination of data received from the Internal Revenue Service and BOC surveys (Hanczyrik, 1995). No information was available from BOC as to the error associated with their population estimates. Therefore, an error of  $\pm$  10 percent was assumed for the BOC data.

Monte Carlo simulations were performed on the emission estimation equations (i.e., AF x EF x UF x Population) using a commercial software called Crystal Ball. Distributions for AF were assumed to be normal with a mean and standard deviation equal to those derived from the survey data (see Table III-15). The assumption for normal distributions for AF followed the performance of a test for normality on the weighted survey data. These normality tests showed that although the unweighted survey data often showed significant skewness, the weighted data were not significantly skewed.

The distributions for EFs were also assumed to be normally distributed with a maximum value equivalent to the solvent density (the EF, expressed in lb/gal, can not be larger than its density). In some cases, there is no variability in EF, since the survey did not identify any users who used control equipment (e.g., carbon adsorbers) that would lower the EF. Uniform distributions were used for both UF and the BOC population estimate with the accompanying level of error (i.e.,  $\pm$  7 percent for UF and  $\pm$  10 percent for the BOC data).

The coefficients of variation of AF and EF for each of the 32 ESPs are provided in Table III-15. From this table, three ESPs were selected to represent the range of uncertainty for the base year inventory. The first ESP, TCE batch-loaded vapor degreasing, shows the lowest amount of variability in AF and no variability in EF (i.e., no controls were reported, see preceding paragraph). Hence, the emission estimates obtained through the use of these values will have the lowest amount of uncertainty. TCA handwiping was selected as an ESP that would also have a relatively low amount of uncertainty, especially for MIGs 1, 4, 5, and 6. The final ESP assessed was miscellaneous blends batch-loaded cold cleaning. This ESP showed the highest degree of variability in AF with additional variability in EF.

Figures III-1 and III-2 below show examples of the distributions used for AF and EF for TCA-HWS. Figure III-1 represents the distribution of AF for MIGs 2, 3, 7. The distribution is normal with a mean of 14.3 gal/emp-yr and a standard deviation of 12.1. A minimum value of 0 is selected, since AF can not take on negative values. Figure III-2 shows the distribution for EF in lbs/gal. The distribution is again normal with a mean of 10.9 and a standard deviation of 1.27. A maximum value of 11.11 was selected, since EF can not be larger than the density of TCA.

Figure III-3 shows the Monte Carlo distribution of base year TOG emissions for TCA-HWS in L.A. County.

Uncertainty ranges at the 95 percent confidence level and the forecasted mean are presented in Table III-27. Model output, including all of the input assumptions, is presented in Appendix C.

As shown in Table III-27, a relatively high level of certainty exists for the estimates made for TCE batch-loaded vapor degreasing as compared to the estimates made for cold cleaning with miscellaneous blends. At a confidence level of 95 percent, the range of TOG emissions estimated for TCE-BVD is only 189 tons per year at the State level. This compares to a range of almost 8,600 tons per year estimated for Misc. Blends-BCC. The mean standard errors for the two Monte Carlo distributions are 0.20 for TCE-BVD versus 7.83 for Misc. Blends-BCC (see Appendix C).

The uncertainty estimates for TCA-HWS and Misc. Blends-BCC show the effects of uncertainty in UF and BOC population estimates. As the geographic regions are expanded and the industry populations increase, uncertainty in UF and population estimates leads to potentially larger and larger errors in emission estimates. For TCA-HWS, the Monte Carlo distributions show a mean standard error of 6.77 at the L.A. County level and 14.29 at the State level.

Figure III-1
Distribution of AF for TCA-HWS in MIGs 2, 3, and 7

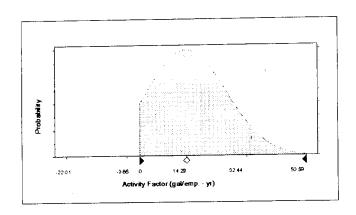


Figure III-2
Distribution of EF for TCA-HWS in MIGs 2, 3, and 7

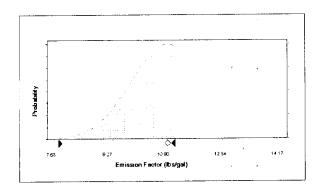


Figure III-3

Monte Carlo Distribution of 1993 TOG Emissions for TCA-HWS in L.A. County

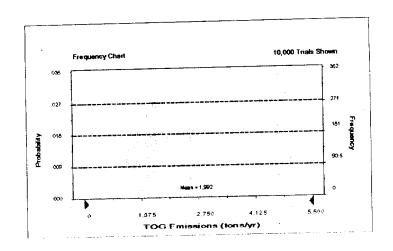


Table III-27
Results of the Uncertainty Analysis

ESP		Emission Fo	precast (tons TOG/y	i/yr)		
(MIGs)	Region	Mean	2.5th Percentile	97.5th Percentile		
TCE-BVD (all MIGs)	L.A. County	99	60	140		
,	SCAQMD	147	90	209		
	California	237	145	334		
TCA-HWS (MIGs 1,4,5,6)	L.A. County	1,241	289	2,274		
TCA-HWS (all MIGs)	L.A. County	1,992	758	3,370		
·	SCAQMD	3,104	1,154	5,310		
	California	3,643	1,301	6,738		
Misc. Blends-BCC (all MIGs)	L.A. County	1,055	45	2,928		
	SCAQMD	1,649	69	4,630		
	California	3,152	133	8,730		

The 95 percent confidence intervals given in Table III-27 above should give the reader a good sense of the uncertainty associated with the other base year emission estimates. Similar confidence intervals would be produced for ESPs with similar coefficients of variation (see Table III-15).

## CHAPTER IV INVENTORY UPDATE METHOD

Four types of data were assessed to find a source of information that could be used by CARB to develop reliable annual updates to the inventory. For the most part, these data sources have been previously introduced in Chapter II during the discussion of base year inventory development. The data source types are as follows:

**Production Data** — information on solvent production at the national level, such as that published by the ITC;

Marketing Data — information on solvent production and end use published by such sources as The Freedonia Group, SRI, and Frost and Sullivan;

Census Data — data on employment by SIC code such as that maintained by BOC; and

Other Data — data from government agencies and industry sources, such as trade associations and solvent reclaimers (e.g., SKC).

The following sections provide detailed discussions of the strengths and weaknesses of using each of the three data source types. A discussion then follows as to the recommended data source and methods to be used for inventory updates. The research team also provide suggestions for actions that could be taken to continually improve upon the quality of the inventory in future years, while keeping research costs down.

#### A. ASSESSMENT OF AVAILABLE DATA SOURCES

#### 1. Production Data

As discussed in Chapter II, nearly all estimates of solvent production currently available are those published by the ITC. The only other sources of production data are those published by marketing sources which are discussed below. The same advantages and disadvantages exist for using this data to update an inventory as for preparing a base year inventory.

The primary advantage to using production data is that it is available for little or no cost. The data is also easy to manipulate. If one assumes that an increase in production over the base year means an increase in solvent cleaning use, then the update is as simple as multiplying the base year inventory estimate by the ratio of update year solvent production to base year solvent production. However, as previously discussed, national production figures may provide poor indicators of solvent cleaning use due to other uses of the chemical commodity. One slight disadvantage of this data source, as with any data

obtained from the Department of Commerce, is that the data has a lag time of two to three years. Hence, a 1995 update to the 1993 base year inventory can not be made until 1997 or 1998.

The primary disadvantage in using production data to update the inventory is that only partial coverage of the source category can be made. As discussed in Chapter II, data on solvent production, import, and export are only available for about half of the solvents identified during the user surveys. This issue, plus the lack of a known relationship between national production and solvent cleaning use, limits production data to, at best, a partial role for inventory updating.

Good examples of where the use of production data falls apart as an inventory update method, are any of the ESP combinations involving TCA. The 1993 base year inventory shows TCA as a popular solvent in many industries for both vapor degreasing and handwiping activities (see Chapter III). As discussed in Chapter I, the production of TCA will be phased out in 1996. If one were to use production data to update the inventory to 1996, the ITC data would show that no TCA was produced in 1996. Obviously, one would not assume that all solvent cleaning activities involving TCA had ceased in 1996. Therefore, for all of the 1993 TCA users, assumptions would need to be made as to whether solvent cleaning was still occurring in 1995. If it was assumed that solvent cleaning was still occurring, the type of solvent used in 1996, the equipment used in 1996, and the amount of solvent used in 1996 would all require assumptions.

#### 2. Marketing Data

As with production data, information gathered and published by marketing firms can only fulfill a partial role in updating an inventory. These reports will offer estimates of solvent end usage, such as the market fraction of a chemical commodity used as a solvent. These end usage estimates are often based on a limited number of manufacturer surveys. By multiplying the end user fraction by the national production estimate from the ITC, one could obtain an estimate of national usage of a chemical as a solvent. Again, multiplying a ratio of the update year national solvent usage to the base year national usage by the base year emission estimate would provide an update estimate.

Some of the problems in carrying out an inventory update as described above have been mentioned during the discussion of base year inventory preparation. These problems include:

- The fact that marketing reports on solvents are published in three to five year intervals. These reports can be thought of as compilations of studies on individual solvents that were performed since the last solvent publication. Hence, the individual solvent studies can be either brand new or up to five years old. If one were to attempt to use the information in one of these reports to update the inventory, information might be available for some solvents for the update year, but not for others;
- Market end use estimates are not always specific to solvent cleaning. In some cases, end use estimates may be categorized very broadly, such that it is not

possible to differentiate the fraction of a chemical commodity used for solvent cleaning from the fraction used as a component in coating mixtures;

- The lack of source category coverage. Even if marketing data is combined with the production data discussed above, many of the solvents in the base year inventory would not be covered; and
- Solvent marketing reports are not published on any specific schedule. The
  reports typically come out at three to five year intervals, however there is no
  guarantee that a solvent report would be available at the time when CARB
  desired to perform an update.

Any single issue described above may not be overly detrimental to the reliability of the update inventory estimates. However, when all of the issues are collectively examined, it should be apparent that numerous assumptions are involved, many with no scientific backing. Hence, no sense of the update inventory reliability can be gathered.

#### 3. Census Data

While being far from an ideal data source for inventory updates, census data has been used in previous inventory efforts (Pechan, 1993a; Pechan, 1993b). Previous inventory efforts, as well as this one, have attempted to locate a source of update data that is tied to production. No data were found that covered the wide range of manufacturing activities covered by this source category. In addition, service industries are included. Census data have the advantage of covering the entire source category, as well as the following advantages:

- The data is readily obtainable and easily manipulated;
- The data, while not being intimately tied to production or service activity, provide
  and indication of activity through the growth or decline of employment in the
  various industry and service groups. This requires the assumption that an
  increase in employment is related to an increase in activity and employment
  decreases lead to declines in activity;
- Census data not only provide an indication of activity growth or decline, but also the movement of industry between geographic regions (i.e., as industrial activity declines in one area and employment decreases or as industry becomes established in new areas).

As with solvent production data, a two to three year lag time exists from the year in which the information is gathered to when it is made available by BOC. Other disadvantages include the fact that growth factors developed from census data can not describe changes in the types of solvents or equipment made by industry since the base year. However, none of the other sources of data, with the possible exception of marketing data in limited instances, have the capability to make adjustments for usage trends.

#### 4. Other Data

Other data sources include information from government agencies and trade associations. These sources have also been previously discussed in Chapter II. As previously mentioned, data provided by most of these sources can usually be traced back to ITC production data. Therefore, the same problems exist with the use of this data in an update method as described above under production data.

One source of information identified not related to production was sales data from solvent reclaimers, such as SKC. SKC was contacted early in the project and a request was made for information on sales and recycle volumes, the number and type of equipment (e.g., parts washer sizes or gun cleaners), and the SIC code of the industrial entity. SKC provided limited data on the total number of parts washers and gun cleaners at the state level and by major industrial category (e.g., mining/trades, manufacturing). SKC also provided some estimated market shares and annual solvent loss statistics for parts washers by equipment size (Kusz, 1995).

Unfortunately, the researchers were not able to obtain SKC information necessary to perform updates to the portions of the inventory involving SKC products. This information includes sales and recycle volumes by industry group. After several unsuccessful attempts were made to gather this information, the researchers concluded that it would not be a reliable source of update information for CARB. In addition, the information would be of limited value, since it would only cover a limited portion of the overall inventory. The only exception to this is some parts washer data by broad-based industry groups. These data were used to develop base year estimates for agricultural and oil production equipment maintenance (see discussion Section III.B.2). Since these categories were not covered in the user survey, this SKC data may be useful to estimate emissions for the above two industry groups.

#### B. RECOMMENDED UPDATE METHOD

After assessing the strengths and weaknesses of the above data sources, the research team selected census data as the best data source for inventory updates. Emission estimates can be updated with BOC census data for the update year (BOC County Business Patterns - California), the emission model variables in Appendix B, and equation 10:

TOG (tons/year) - AF · EF · UF · 
$$\left(\frac{1}{2,000}\right)$$
 x Number of Employees

Each of the 32 ESP combinations introduced in this report represents a new area source category. It is recommended that CARB provide EIC numbers for each of these categories and delete the existing 5 categories (CARB, 1991).

Since, in many cases, the emission estimation variables may be specific to geographic region or industry group, updating the inventory will require more work than the application of a simple growth factor. Simply applying an update year to base year

employment ratio to the summarized emission estimates in Chapter III will result in erroneous estimates. This is due to the fact that for some ESP combinations emissions may be driven by increases/declines in specific industries and not by industry group employment as a whole (e.g., employment in MIGs 1-7)

For any one of the 32 new source categories, one to four sets of equations may be involved in inventory updates depending on whether the ESP combination is observed in manufacturing activities (groups 1-7), manufacturing maintenance activities (groups 1-7), service related maintenance activities (group 8), or manufacturing maintenance activities (group 9). The number of equations per set depends on the number of unique model variable sets. Table IV-1 shows the breakdown of where ESP combinations were observed, and hence, the number of equation sets involved. The table also provides the Appendix B page number where the model variables are located.

As an example, TCA handwiping occurs in both manufacturing and maintenance usage categories of groups 1-7. From the model tables in Appendix B-1 (page B1-3), the manufacturing model table shows three unique sets of input variables, so three separate equations are needed along with the appropriate employment estimates (for a statewide estimate). In addition, from the table for the maintenance usage in Appendix B-2 (page B2-3), three more unique sets of model variables are presented. Therefore, a summation of six equations will be needed for a 1995 statewide update estimate:

Emissions (tons/yr) =  $\Sigma$ AF x EF x UF x 1995 MIG/Region employment x 1/2000 =

```
(4.17 x 11.1 x 0.25 x 1995 CA employment in MIGs 1,4,5,6 for Region 1 x 1/2000) +
```

It should be noted that if an update estimate only for L.A. county was desired, the second equation in the summation above (which adds emissions for Regions 2 and 3) would not be needed, and the employment data for L.A. county would be used instead of state employment.

For most of the 32 ESP combinations, information is supplied in Appendix B on speciation of equipment combinations (e.g., percentage of BCC, CCC, and GCE for cold cleaning combinations) and solvent combinations (e.g., acetone and MEK for the ketones combination). These data are provided primarily for informational purposes and should be used with extreme caution, since they are often based on a limited number of survey responses.

For the two group 8 maintenance user groups, oil/gas production and agricultural equipment maintenance, the statewide emission estimates should also be updated with the use of BOC employment data, until better base year data are developed.

<sup>(0.32</sup> x 11.1 x 0.15 x 1995 CA employment in MIGs 1,4,5,6 for Regions 2, 3 x 1/2000) +

 $<sup>(14.3 \</sup>times 10.9 \times 0.08 \times 1995 \text{ CA employment in MIGs } 2,3,7 \text{ for all Regions } \times 1/2000) +$ 

<sup>(1.05</sup> x 11.1 x 0.05 x 1995 CA employment in MIGs 1 - 6 for all Regions x 1/2000) +

 $<sup>(3.27 \</sup>times 11.1 \times 0.01 \times 1995 \text{ CA employment in group 8 for all Regions x 1/2000}) +$ 

<sup>(7.66</sup> x 11.1 x 0.02 x 1995 CA employment in group 9 for all Regions x 1/2000)

Table IV-1

Appendix B Location of Emission Model Variables for Each ESP Combination

		Appendix B Page Number by Usage Category				
ESP Combination <sup>1</sup>		Manufacturing Usage (Groups 1-7)	Maintenance Usage (Groups 1-7)	Maintenance Usage (Group 8) <sup>2</sup>	Maintenance Usage (Group 9)	
,	TCA - Cold Cleaning	B1-1	B2-1	-		
2	TCA - Vapor Degreasing	B1-2	B2-2	·	-	
3	TCA - Handwiping	B1-3	B2-3	B2-3	B2-3	
4	CFC/CFC Blends - Cold Cleaning	B1-4	B2-4	-		
5	CFC/CFC - Vapor Degreasing	B1-5	B2-5	-	-	
6	CFC/CFC Blends - Handwiping	B1-6	B2-6	-	-	
7	HCFC - Vapor Degreasing	B1-7		-	-	
8	HCFC - Handwiping	B1-8	B2-7	-	-	
9	Ketones - Cold Cleaning	B1-9	B2-8	-	B2-8	
10	Ketones - Handwiping	B1-10	B2-9	B2-9	B2-9	
11	Alcohols/Alc. Blends - Cold Cleaning	B1-11	B2-10	-	B2-10	
12	Alcohols/Alc. Blends - Handwiping	B1-12	B2-11	B2-11	B2-11	
13	Methylene Chloride - Cold Cleaning	B1-13	-	-		
14	Methylene Chloride - Handwiping	B1-14	B2-12	·	-	
15	Petroleum Distillates - Cold Cleaning	B1-15	B2-13	B2-13	B2-13	
16	Petroleum Distillates - Handwiping	B1-16	B2-14	B2-14	B2-14	
17	Misc. Pure Solvents - Cold Cleaning	B1-17	B2-15	-	-	
18	Misc. Pure Solvents - Handwiping	B1-18	B2-16	-		
19	PERC - Vapor Degreasing	B1-19	•			
20	PERC - Handwiping	B1-20	-		-	
21	Toluene/Xylene - Cold Cleaning	B1-21	B2-17	-	•	

#### Table IV-1 (continued)

		Appendix B Page Number by Usage Category				
	ESP Combination <sup>1</sup>	Manufacturing Usage (Groups 1-7)	Maintenance Usage (Groups 1-7)	Maintenance Usage (Group 8) <sup>2</sup>	Maintenance Usage (Group 9)	
22	Toluene/Xylene - Handwiping	B1-22	B2-18	-	-	
23	TCE - Vapor Degreasing	B1-23	•	-	-	
24	TCE - Handwiping	B1-24	B2-19	-	-	
25	Glycol Ethers - Cold Cleaning	B1-25	B2-20	-	-	
26	Glycol Ethers - Handwiping	B1-26	B2-21	•	-	
27	PFC Blends - Vapor Degreasing	B1-27	-	-	-	
28	Terpenes - Cold Cleaning	B1-28	B2-22	•	-	
29	Terpenes - Handwiping	B1-29	B2-23	-	-	
30	Misc. Blends - Cold Cleaning	B1-30	B2-24	-	-	
31	Misc. Blends - Vapor Degreasing	B1-31		-	-	
32	Misc. Blends - Handwiping	B1-32	B2-25	-	-	

NOTE:

<sup>1</sup> Cold cleaning includes BCC, CCC, and GCE equipment. Vapor degreasing includes BVD and CVD equipment. <sup>2</sup>Emissions for the agricultural equipment maintenance and oil/gas production services groups are calculated separately using data from SKC.

## C. RECOMMENDATIONS FOR FUTURE INVENTORY EFFORTS

Over the course of this project, the researchers identified three primary obstacles in developing base year inventories from end-user surveys and inventory updates for the solvent cleaning source category:

- the expense of developing accurate base year inventories and the reporting burden to the responding industry. When considered with district reporting requirements, survey responses were, in some cases, somewhat duplicative in nature;
- the difficulty in developing base year inventories and inventory updates with adequate coverage of a complex and ubiquitous source category; and
- the nonavailability of update data that addresses changes in solvent usage patterns.

The research team feels that if CARB were to work with the districts to establish industry reporting requirements that are consistent with the new CES codes, then a valuable information source could be tapped. The incremental burden to industry to report emissions by CES code (or some descriptor of the ESP combination involved) would be insignificant. The reporting of this information would serve to decrease the overall reporting burden, since randomly-selected permitted facilities would no longer be required every so often to fill out long survey questionnaires. For this project, surveying permitted facilities was necessary for three reasons. First, data collected by the districts is not reported at the same level of detail desired by CARB (i.e., by both equipment and solvent type). Second, in order to develop a statistically-sound survey, the entire universe of users (i.e., both permitted and unpermitted facilities) had to be combined into the sampling frame in order to draw a random sample. Finally, it is extremely difficult, if not possible with existing sources of data, to screen permitted facilities out of a procured mailing list.

An additional benefit to gathering this data from district reporting is that resources, such as those that have been spent in the past to gather base year data from permitted facilities could be spent on expanding the solvent user universe or better characterizing unpermitted sources. Additional smaller users could be added to the universe, and the information gathered would provide better source category coverage. Alternatively, resources could be saved using the existing universe, since the survey requirements (a major factor in base year inventory development) would be smaller.

On the issue of inventory updates, the research team feels that there will always be a need to periodically develop new base year inventories. Available sources of update data have significant short-comings:

 they do not provide the necessary source category coverage (i.e., the number of solvents involved);

- they can not be used to assess changes in solvent usage patterns (i.e., a blanket increase or decrease in solvent consumption would have to be applied across the user industries); and
- for those solvents or industries that are covered, the data is either of unknown quality or requires an assumed relationship (e.g., data from limited marketing surveys).

Accordingly, the 1993 base year inventory (source category snap shot) quality will begin to fade with each succeeding update that is performed. The research team believes that updates to the base year inventory, using the data and methods referenced above, will provide reasonably reliable emissions data for the next three to five years (i.e., until the 1996 to 1998 inventory years). After that time, significant changes will have again occurred in the source category (as described in Chapter I), such that emission estimates will be highly uncertain. The research team believes that if the recommendations supplied above are implemented, more comprehensive, accurate, and cost-effective inventory information can be gathered in the future.

The limited uncertainty analysis performed as part of this project showed that considerable uncertainties exist for certain ESP combinations (i.e., the ESPs with model variables with high variability). Table III-27 shows that emission estimates for ESP combinations that are relatively well characterized (e.g., TCE-BVD) could still, in reality, vary by 60 to 70 percent (the 2.5<sup>th</sup> percentile divided by the mean or the mean divided by 97.5<sup>th</sup> percentile). Conversely, for ESPs that are characterized relatively poorly (Misc. Blends-BCC/CCC), estimates could vary by several times to over an order of magnitude (NOTE: this ESP combination is characterized with, by far, the most uncertain emission estimates. The range of uncertainty for all of the other ESP combinations should be closer to the first two examples in Table III-27, based on the coefficients of variation shown in Tables III-15 and III-19).

The only way to reduce the uncertainty in the emission estimates is to better characterize the usage patterns for those ESP combinations of interest. This has to be done through further disaggregation of the emission model variables, and possibly, the ESP combinations themselves. Additional data for these ESP combinations would be needed in order to perform this work. In the future, additional surveys and the use of more detailed district reporting data could be used to fill these data needs. With the additional data, the emission model variables (e.g., activity factor) could be further disaggregated by industry group or geographic region, which would likely lead to model variables with lower variability, and hence, less uncertainty.

#### **REFERENCES**

- Asregadoo, 1995: R. Asregadoo, California Air Resources Board, personal communication with S. Roe, E.H. Pechan & Associates, Inc., December 19, 1995
- BOC, 1995: U.S. Department of Commerce, Bureau of Census, "County Business Patterns 1992 & 1993," CD-CBP-92/93, September 1995.
- Bateman, 1995: B. Bateman, Bay Area Air Quality Management District, personal communication with L. Jones, Regulatory Solutions International, November 20, 1995.
- Burington and May, 1970: R.S. Burington and D.C. May, "Handbook of Probability and Statistics with Tables," Second Edition, 1970.
- CARB, 1989: California Air Resources Board, "Technical Guidance Document for the Emission Inventory Criteria and Guidelines Regulation for AB 2588," Technical Support Division, August 1989.
- CARB, 1991: California Air Resources Board, "Methods for Assessing Area Source Emissions in California," Emission Inventory Branch, Technical Support Division, September 1991.
- CARB, 1995: California Air Resources Board, "Emission Inventory 1993," Emission Inventory Branch, Technical Support Division, June 1995.
- FR, 1995: Federal Register, "Protection of Stratospheric Ozone; Acceptable Substitutes for the Significant New Alternatives Policy (SNAP) Program," July 28, 1995.
- FSC, 1995: Freeman, Sullivan & Co., "Manufacturing and Maintenance Solvent Usage Survey," prepared for E.H. Pechan & Associates, Inc., June 1995.
- Gangloff, 1994: C. Gangloff, The Fredonia Group, Inc., personal communication with R. Coad, E.H. Pechan & Associates, Inc., November 9, 1994.
- Hait, 1995: A. Hait, Bureau of Census, U.S. Department of Commerce, personal communication with P.J. Costello, E.H. Pechan & Associates, Inc., October 3, 1995.
- Hanczyrik, 1995: P. Hanczyrik, Bureau of Census, U.S. Department of Commerce, personal communication with S. Roe, E.H. Pechan & Associates, Inc., October 18, 1995.
- Hoel, 1960: P.G. Hoel, "Elementary Statistics," John Wiley & Sons, Inc., December 1960.
- ITC, 1994: United States International Trade Commission, "Synthetic Organic Chemicals", United States Production and Sales, 1993, USITC Publication No. 2810, November 1994.

### **REFERENCES** (continued)

- Kusz, 1995: J. Kusz, Safety-Kleen Corporation, written correspondence to S. Roe, E.H. Pechan & Associates, Inc., March 8 and May 24, 1995.
- Pechan, 1993a: E.H. Pechan & Associates, Inc., "Development of an Interim 1990 Emission Inventory," prepared for the U.S. Environmental Protection Agency, Source Receptor Analysis Branch, February 1993.
- Pechan 1993b: E.H. Pechan & Associates, Inc., "Regional Interim Emission Inventories (1987-1991) Volume 1: Development Methodologies," prepared for the U.S. Environmental Protection Agency, Source Receptor Analysis Branch, February 1993.
- Pitkin, 1995: J. Pitkin, Frost & Sullivan, personal communication with S. Roe, E.H. Pechan & Associates, Inc., November 8, 1995.
- SAIC, 1985: Science Applications International Corporation, "Development and Improvement of Organic Compound Emission Inventories for California," Final Report, prepared for the California Air Resources Board, January 1985.
- Santos, 1995: B. Santos, Chemical Marketing Reporter, personal communication with L. Jones, Regulatory Solutions International, January 23, 1995.
- Sax and Lewis, 1987: I. Sax, and R. Lewis, "Hazardous Chemicals Desk Reference," Van Nostrand Reinhold Company, Inc., 1987.
- SCAQMD, 1995: South Coast Air Quality Management District, "Permitting Data Base 1993-1995," 1995.
- VRC, 1989: Valley Research Corporation, "Inventory of Solvent Use and Emissions from Degreasing and Non-Architectural Surface Coating in the South Coast Air Basin," prepared for the California Air Resources Board, June 1989.

#### ABBREVIATIONS AND ACRONYMS

AFs activity factors
ANOVA analysis of variance

AQMD Air Quality Management District
ATCM Air Toxic Control Measure

BAAQMD Bay Area Air Quality Management District BARCT best available retrofit control technologies

BCC batch- loaded cold cleaning

BEA U.S. Bureau of Economic Analysis

BOC U.S. Bureau of Census BVD batch-loaded vapor degreaser

CAA Clean Air Act

CARB California Air Resources Board

CATI computer-assisted telephone interviewing

CCC conveyorized cold cleaner
CES Category of Emission Source
CFC-113 trichlorotrifluoroethane
CFC chlorofluorocarbon(s)
D&B Dun & Bradstreet
EDS Emission Data System
EF emission factor(s)

EPA U.S. Environmental Protection Agency

ESP equipment-solvent pairing(s)

GACT generally available control technology

GCE gun cleaning equipment
HAP hazardous air pollutants
HCFC hydrochlorofluorocarbon(s)
HWS hand-wiping solvent

ITC U.S. Bureau of Commerce International Trade Commission

MACT maximum achievable control technology

MEK methylethyl ketone METH methylene chloride

MIG manufacturing industry group(s)
MSDS Material Safety Data Sheet

NA national availability

NESHAP national emission standards for hazardous air pollutants

PCBTF parachlorobenzotrifluoride

PERC perchloroethylene PFC perfluorocarbon(s)

POTWs publicly-owned treatment works

RACT reasonably available control technologies
RECLAIM reasonably available control technologies
Regional Clean Air Incentives Market

SCAQMD South Coast Air Quality Management District

SIC Standard Industrial Classification

SJVUAPCD San Joaquin Valley Unified Air Pollution Control District

SKC Safety-Kleen Corporation

## ABBREVIATIONS AND ACRONYMS (continued)

SNAP	Significant New Alternatives Policy
TAC	toxic air contaminant
TCA	1,1,1-trichloroethane
TCE	trichloroethylene
TOG	total organic gas
UF	user fraction
VCAPCD	Ventura County Air Pollution Control District
VM&P	Varnish Maker's and Painters
VOC	volatile organic compound
VMS	volatile methyl siloxanes