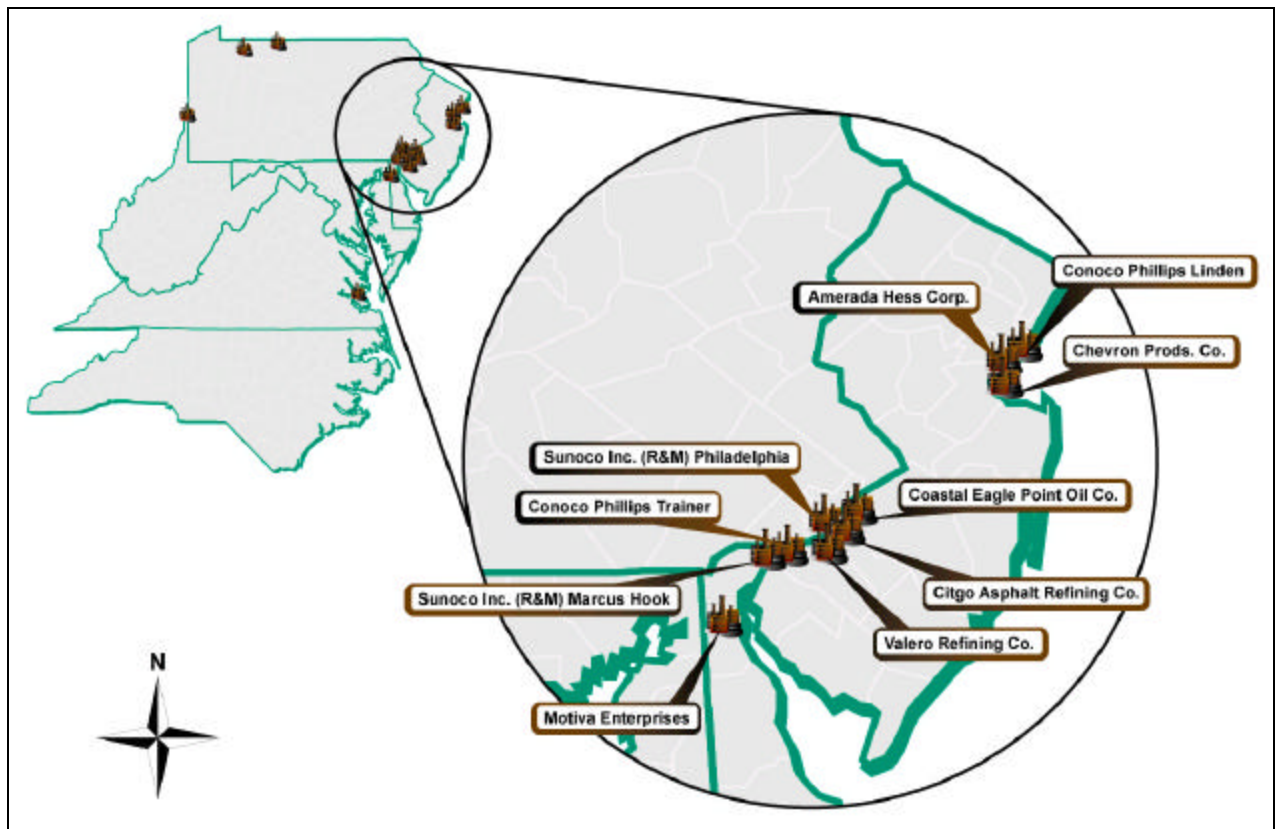


Evaluating Petroleum Industry VOC Emissions
in Delaware, New Jersey and Southeastern Pennsylvania
Final Report

October, 2003



Prepared by
MACTEC Federal Programs, Inc.

for the
Mid-Atlantic Regional Air Management Association

About MARAMA

The Mid-Atlantic Regional Air Management Association is a voluntary, non-profit association of ten state and local air pollution control agencies. MARAMA's mission is to strengthen the skills and capabilities of member agencies and to help them work together to prevent and reduce air pollution impacts in the Mid-Atlantic Region.

MARAMA provides cost-effective approaches to regional collaboration by pooling resources to develop and analyze data, share ideas, and train staff to implement common requirements.

The following State and Local governments are MARAMA members: Delaware, the District of Columbia, Maryland, New Jersey, North Carolina, Pennsylvania, Virginia, West Virginia, Philadelphia, and Allegheny County, Pennsylvania.

About MACTEC Federal Programs, Inc.

MACTEC, Inc. is a leader in the engineering, environmental and remedial construction industries. MACTEC provides premier management, technical, and professional services to help clients successfully manage complex businesses, projects, and facilities. Now operating with over 100 U.S. offices and 4,000 employees with specialists in over 50 scientific and engineering disciplines, MACTEC has the resources to perform virtually any scope of work, regardless of location, size or complexity.

MACTEC Federal Programs, Inc. is a division of MACTEC that provides these same services tailored to meet the unique needs of government agencies, including state/local agencies and federal agencies such as DoD, EPA, the National Park Service and others.

For copies of this report contact:

**MARAMA
Mid-Atlantic Regional Air Management Association
711 West 40th Street
Suite 312
Baltimore, MD 21211**

**phone 410.467.0170
fax 410.467.1737
<http://www.marama.org/>**

**Evaluating Petroleum Industry VOC Emissions
in Delaware, New Jersey and Southeastern Pennsylvania
Final Report**

Prepared by
MACTEC Federal Programs, Inc.
Edward Sabo
Senior Scientist

October, 2003

for the
Mid-Atlantic Regional Air Management Association
Dr. Serpil Kayin
Project Manager

ACKNOWLEDGEMENTS

MARAMA gratefully acknowledges the funding support provided by the United States Environmental Protection Agency. This project was funded by grants from the U.S. Environmental Protection Agency, Region II (X98236301-1) and Region III (X993674-05-02).

This report was produced for MARAMA by Edward Sabo of MACTEC Federal Programs, Inc. His dedication and professionalism were appreciated and made the final work products from this project successful.

MARAMA gratefully acknowledges the information provided by Dr. Larry Kleinman of Brookhaven National Laboratory. His research summarized in Appendix A provided the motivation for this study.

Numerous individuals provided directions guiding the project, reviewed the drafts of this report and gave insightful comments including:

George Fekete, New Jersey DEP
Wick Havens, Pennsylvania DEP
Ray Papalski, New Jersey DEP
Ravi Rangan, Delaware DNREC
Bruce Steltzer, Delaware DNREC
Gopal Sistla, New York DEC
Greg Tiernan, Philadelphia DPH
Brian Trowbridge, Pennsylvania DEP
Tom Weir, Philadelphia DPH

MARAMA's project manager was Dr. Serpil Kayin, with oversight from Susan S.G. Wierman, Executive Director of MARAMA.

TABLE OF CONTENTS

	<u>Page</u>
PROJECT OVERVIEW	1
CHARACTERIZATION OF THE REFINERY VOC EMISSION INVENTORY	1
EVALUTATION OF EMISSION ESTIMATION METHODS	3
FINDINGS	10
RECOMMENDATIONS.....	11

TABLES

	<u>Page</u>
Table 1. Capacity by Type of Process.....	4
Table 2. Comparison of Refinery VOC Emissions.....	5
Table 3. Comparison of VOC Emissions by Refinery and Process.....	6
Table 4. Comparison of Preferred VOC Emission Estimation Methods	
and the Methods Currently Used by Refineries in the Mid-Atlantic States	7

FIGURES

	<u>Page</u>
Figure 1. Location of Petroleum Refineries in the Mid-Atlantic States	2

APPENDICES

Appendix A. An Ozone Episode in the Philadelphia Metropolitan Area	
Appendix B. Memo #1: Final Work Plan – Comparison of Refinery VOC Emissions	
Appendix C. Memo #2: Identification of Petroleum Industry Facilities in the Mid-Atlantic States	
Appendix D. Memo #3: Identification of Petroleum Industry Emission Processes	
Appendix E. Memo #4: Potentially Missing Emission Processes	
Appendix F. Memo #5: Identification of Emission Estimation Methods	
Appendix G. Memo #6: Evaluation of Emission Estimation Methods	

(This page intentionally left blank)

PROJECT OVERVIEW

Recent ozone air quality investigations indicate the potential for underestimation of volatile organic compound (VOC) emissions from petroleum refineries. As part of the *Texas Air Quality Study 2000*, airplane measurements of ambient concentrations of VOC and highly photochemically reactive compounds were compared to the reported emission inventory estimates. The comparison indicated that VOC emissions may be significantly under-reported, specifically for industrial sources. Similar aircraft measurements in the Philadelphia area also found a substantial ozone plume downwind of the Delaware/Southeast Pennsylvania/New Jersey industrial area (See Appendix A). VOC emissions from petroleum refineries comprise a significant portion of the total industry related VOC emissions in this area. Finally, the Bay Area Air Quality Management District, the Texas Commission on Environmental Quality, and the U.S. Environmental Protection Agency have all acknowledged the potential for underestimation of VOC emissions from petroleum refineries.

The Mid-Atlantic Regional Air Management Association (MARAMA) recognizes that it is very important to have accurate emission estimates for use in photochemical modeling to analyze and assess the most appropriate control strategy to attain the National Ambient Air Quality Standard for ground-level ozone. In September 2002, MARAMA initiated a study of refinery VOC emissions in the multi-state Philadelphia metropolitan area. The following work products were developed and are attached as Appendices B-G:

- Memo #1 – Work Plan
- Memo #2 – Comparison of Facility Level Emissions from Existing Databases
- Memo #3 – Comparison of Process Level Emissions
- Memo #4 – Identification of Potentially Missing Emission Processes
- Memo #5 – Identification of Currently Used Emission Estimation Methodologies
- Memo #6 – Evaluation of Preferred Emission Estimation Methodologies

A technical workshop was held in May, 2003, to brief the MARAMA project team on interim results and to exchange information among the permitting, enforcement, inventory, and planning groups at each agency.

This Final Report is an executive summary of the important findings and recommendations for improving the inventory. First, we summarize the information available in existing petroleum refinery emission inventories. Next, we discuss the emission estimation methods currently used and the preferred emission estimation methods available for future inventory work. Finally, we summarize our findings and provide a series of recommendations to encourage both appropriate consistency among agencies and to promote the use of more accurate estimation methods.

CHARACTERIZATION OF THE REFINERY VOC EMISSION INVENTORY

Figure 1 shows the locations of the petroleum refineries in the MARAMA area. Seven petroleum refineries are clustered along the Delaware River in the Philadelphia metropolitan area. A second group of three refineries is located in New Jersey along the Arthur Kill River adjacent to New York City. There are two refineries in northwestern Pennsylvania, one refinery in tidewater Virginia, and one refinery in the West Virginia panhandle. Note that there are no petroleum refineries in the District of Columbia, Maryland, New York, or North Carolina.

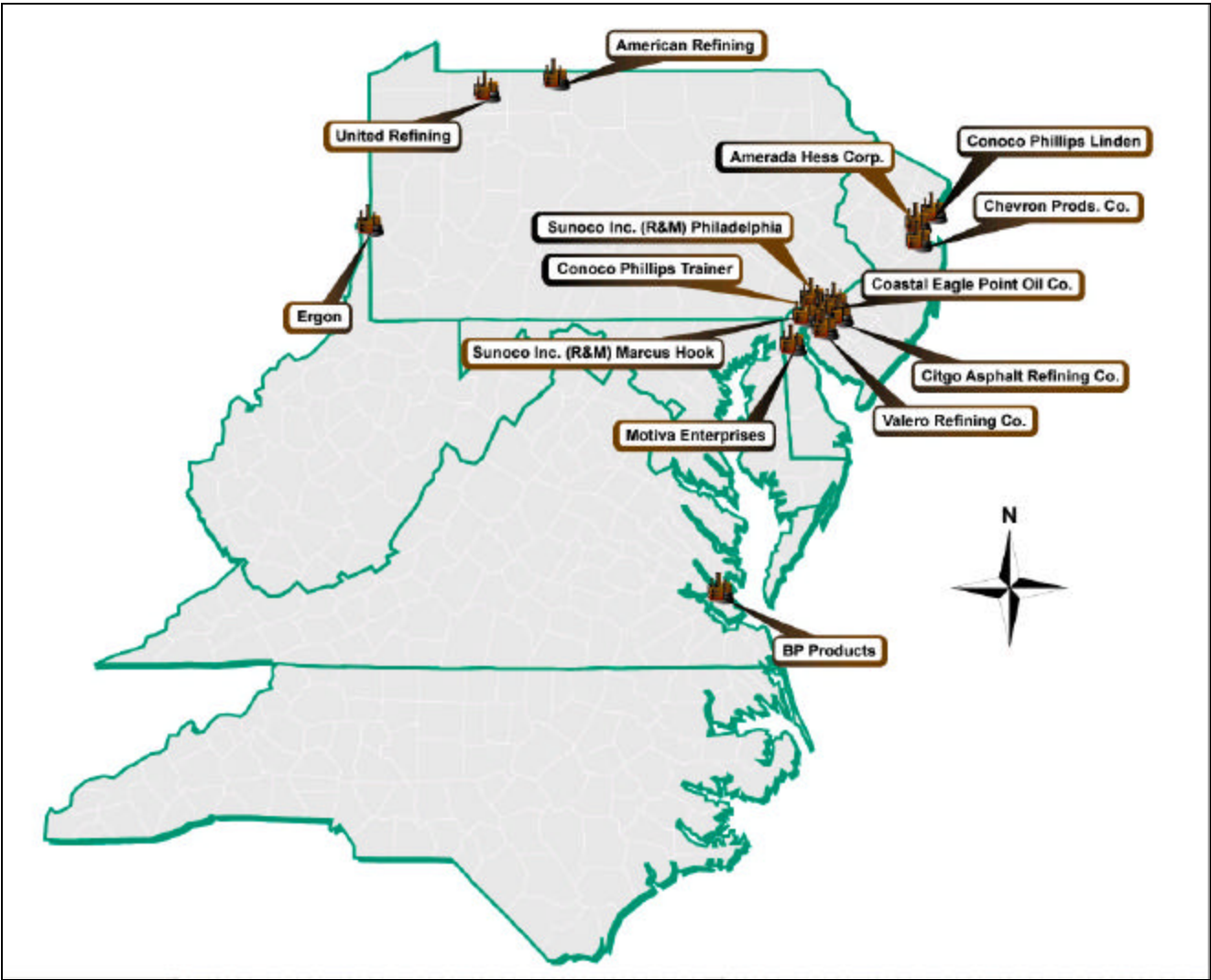


FIGURE 1

LOCATION OF PETROLEUM REFINERIES IN THE MID-ATLANTIC STATES

(Note: With the resources available for this project, the study focused on the 10 refineries located in the Delaware/Southeast Pennsylvania/New Jersey corridor. However, the recommendations of this study can be also used by other agencies to improve the emission inventories for petroleum refineries and other petroleum industry sources such as petroleum bulk stations, bulk terminals, and pipeline stations).

Table 1 shows refinery capacity data by type of process, based on information from the *Petroleum Supply Annual* published by the Energy Information Agency (EIA). Production data by individual refinery is not available from the EIA because of confidentiality issues. We looked at the emissions data for petroleum refineries that are contained in several recent emission inventories. Table 2 summarizes this information at the facility level, while Table 3 summarizes emissions at the process level. Important observations regarding the current VOC emission inventories include:

- There is considerable variation in emissions from refinery to refinery.
- There are large variations in emissions by refinery over time as reported in the different inventories (see Table 2).
- The relative contribution of each type of process varies noticeably by refinery.

These variations are not unexpected, as no two refineries are alike. Refineries differ in both size and by the type of separation, conversion, and treatment processes used. The emissions at a particular refinery are determined by the composition of the crude oil received and the chosen slate of commodities produced (i.e., gasoline, kerosene, fuel oil, chemical feed stock, etc.). The effectiveness of pollution control equipment is another variable. Refinery size alone does not explain the variations, as the facility-wide VOC emissions do not appear to be directly correlated with the refinery size shown in Table 1. For example, the Motiva Delaware City refinery and the Sunoco Philadelphia have roughly the same annual VOC emissions, yet the Sunoco refinery has twice the crude distillation capacity.

In addition to the physical differences in refineries, another explanation for the variability in refinery VOC emissions is differences in emission estimation methodologies. Emission estimation methodologies are discussed in the following section.

EVALUATION OF EMISSION ESTIMATION METHODS

To determine the emission estimation methods currently used, we first examined the estimation codes in each agency's electronic database. Agency files were reviewed to gather additional data since the codes in database usually don't provide enough detail regarding how emissions were calculated. For example, any available hard-copy or electronic emission statements and backup data submitted by the refineries were reviewed. As questions arose, we consulted with agency permit writers, inspectors, or inventory preparation personnel to obtain clarifications. MACTEC did not contact the refineries directly or visit the refineries to obtain additional information. Rather, the agencies contacted the refineries to obtain clarifications when appropriate.

We compared the emission estimation methods currently used to those that are considered the "preferred" methods (as derived primarily from these emission inventory guidance documents):

- EPA's *Compilation of Air Pollutant Emission Factors, AP-42, 5th Edition*;
- STAPPA/ALAPCO/EPA Emission Inventory Improvement Program (EIIP) guidance;
- *2002 Emissions Inventory Guidelines, Appendix A, Technical Supplement 1-5* published by the Texas Commission on Environmental Quality (TCEQ);
- *Compendium of Greenhouse Gas Emission Estimation Methodologies for the Oil and Gas Industry*, published by the American Petroleum Institute (API).

Table 4 compares the methods currently used to the preferred methods.

TABLE 1 – CAPACITY BY TYPE OF PROCESS^a
(Barrels per Stream Day)

State	Refinery/Location	Atmospheric Distillation	Vacuum Distillation	Thermal Cracking	Catalytic Cracking	Catalytic Hydrocracking	Catalytic Reforming	Catalytic Hydrotreating	Fuels Solvents Deasphalting
DE	Motiva Enterprises Delaware City	185,000 ^b	102,000	54,000 ^b	82,000 ^b	20,000	44,100 ^b	132,700	0
NJ	Amerada Hess Port Reading	0 ^c	0	0	62,500	0	0	0	0
NJ	Chevron Products Perth Amboy	83,000 ^d	47,000	0	0	0	0	0	0
NJ	Citgo Asphalt Refining Paulsboro	30,500 ^d	40,000	0	0	0	0	0	0
NJ	Coastal Eagle Point Oil Westville	146,000	49,000	0	55,000	0	30,000	59,000	0
NJ	ConocoPhillips Linden	263,000	65,000	0	145,000	0	29,000	160,000	21,000
NJ	Valero Refining Paulsboro	172,600	87,000	24,500	54,000	0	24,000	90,500	0
PA	ConocoPhillips Trainer	190,000	73,000	0	52,000	22,000	50,000	136,000	0
PA	Sunoco Inc. Marcus Hook	185,000	36,000	0	105,000	0	20,000	85,000	0
PA	Sunoco Inc. Philadelphia	355,000	160,000	0	118,500	0	86,000	191,000	0

- a) Source: The data in the table are based primarily on information from the *Petroleum Supply Annual* published by the Energy Information Agency (EIA).
- b) Capacity data provided by Bruce Steltzer, DNREC, based on Title V permit application.
- c) The Amerada Hess refinery was converted from a crude oil refinery and reopened in 1984 processing only refined intermediates.
- d) Distillation units were completely idle but not permanently shutdown.
- e) A “0” capacity indicates that the petroleum refinery does not use this particular process.

TABLE 2 – COMPARISON OF REFINERY VOC EMISSIONS

State	Refinery	1996 NET	1997 MARAMA	1999 NEI	2000/2001 State
DE	Motiva Enterprises Delaware City	1,484	1,342	1,521	690
NJ	Amerada Hess Port Reading	485	263	377	370
NJ	Chevron Products Perth Amboy	37	270	32	532
NJ	Citgo Asphalt Refining Paulsboro	0	231	0	40
NJ	Coastal Eagle Point Oil Westville	1,340	826	1,356	798
NJ	ConocoPhillips Linden	2,313	3,521	2,159	1,711
NJ	Valero Refining Paulsboro	1,341	654	1,229	829
PA	ConocoPhillips Trainer	232	241	258	290
PA	Sunoco Inc. Marcus Hook	828	862	393	376
PA	Sunoco Inc. Philadelphia	1,487	1,550	518	628
TOTAL		9,547	9,760	7,843	6,264

Data Sources:

1996 NET - EPA's 1996 National Emission Trends Inventory, data for this report were extracted from the October 2001 version of the NET database. Data for New Jersey appears to be 1990 estimates grown to 1996.

1997 MARAMA – Inventory developed regional ozone modeling in the Northeast. Based on the 1997 NET inventory supplemented with data supplied by MARAMA and NESCAUM states.

1999 NEI - EPA's 1999 National Emission Inventory, data for this report were extracted from Version 2 Final of the Criteria Pollutant inventory. Data for New Jersey appears to be 1990 estimates grown to 1999.

2000/2001 State – Recent inventories provided directly by the State and local agencies for this project. (DNREC – 2001, NJDEP – 2001; PADEP – 2000; PAMS – 2000).

TABLE 3 – COMPARISON OF VOC EMISSIONS (tons/year) BY REFINERY AND PROCESS

Refinery	Atmospheric Distillation Capacity (barrels/day)	Boilers and Process Heaters	Cokers, FCCs, and CO Boilers	Other Process Units	Process Equipment Leaks	Water Treatment	Cooling Towers	Flares	Storage	Unloading & Loading	Plant Total
Motiva Delaware City	185,000	35	219	1 ^a	37	260	4	1	123	9	690
Amerada Hess Port Reading	0 ^c	1	50	3	6	1	0 ^d	6	261	40	370
Chevron Perth Amboy	83,000	1	(b)	1	47	422	0 ^d	1	60	1	532
Citgo Asphalt Paulsboro	30,500	3	(b)	2	8	2	0 ^d	<1	25	<1	40 ^e
Coastal Eagle Point, Westville	146,000	88	41	1	31	111	0 ^d	315	205	6	798
ConocoPhillips Linden	263,000	37	13	1	1,132	111	0 ^d	28	368	21	1,711
Valero Refining Paulsboro	172,600	52	32	7	57	282	0 ^d	<1	399	<1	829
ConocoPhillips Trainer	190,000	43	<1	3	53	28	8	67	84	4	290
Sunoco Marcus Hook	185,000	34	<1	<1	100	46	25	3	140	30	376
Sunoco Philadelphia	355,000	67	50	<1	220	25	54	2	170	40	628
Totals	1,610,100	361	405	19	1,691	1,288	91	421	1,835	151	6,264

- a) The 1999 inventory included 149 tons/year from sulfur removal process. There were no emissions from this process in 2001.
- b) These two refineries do not have thermal or catalytic cracking units.
- c) The Amerada Hess refinery was converted from a crude oil refinery and reopened in 1984 processing only refined intermediates.
- d) Cooling tower emissions listed as an insignificant activity.
- e) VOC emissions from the Citgo Asphalt refinery are expected to be considerably lower than other refineries in the area. The refinery does not have any thermal or catalytic cracking capacity, and most of the product loading is of less volatile products such as #6 oil, asphalt, kerosene, and heating oil.

TABLE 4 – COMPARISON OF PREFERRED VOC EMISSION ESTIMATION METHODS AND THE METHODS CURRENTLY USED BY REFINERIES IN THE MID-ATLANTIC STATES

Source Category	Preferred Method	Methods Currently Used
Boilers, Heaters, Turbines, and IC Engines	Stack sampling is the preferred emission estimation methodology for VOC. There are currently no CEM methods for directly measuring VOC, so the use of short-term, site-specific stack test data is preferred over using industry average emission factors for a particular equipment/fuel type. If stack test data are not available, the use of AP-42 emission factors can be used.	Emissions are either based on source test data or calculated by multiplying an emission factor by the amount of fuel consumed. Some refineries appear to be using outdated or inappropriate emission factors.
Cracking Units/CO Boilers	Stack sampling is the preferred emission estimation methodology for VOC. Stack sampling provides a snapshot of emissions at the test conditions and does not address potential variability over time. Many refineries are required by NSPS Subpart J to have CEMs for opacity, CO, SO ₂ , and NO _x . There are currently no CEM methods for directly measuring VOC.	All but one the refineries base their emissions on source test data. The VOC emission rates obtained via source testing range from “not detected” to 9.45 lbs/hour (0 to 41 tons per year). VOC emissions from the Motiva Delaware City refinery are calculated using EPA emission factors, and are significantly higher than the emission estimates for the refineries that use stack test data to estimate emissions.
Process Vents	The MACT I rules require that process vent streams be controlled by reducing organic HAPs by 98% using incinerators, boilers, process heaters, or other devices. Some streams are not suitable for control by boilers/heaters, including those with varying flow rate and/or heating value, high volume/low heating value streams, and streams with corrosive compounds. Flares are often used to control these streams. The emissions from MACT I process vents are generally included under the boiler/heater and flare categories, and the emission estimation methods for those source categories should be used.	The 10 refineries in the Philadelphia/Delaware/New Jersey area reported very little VOC emissions from process vents. No refinery reported more than 5 tons per year from miscellaneous process vents. Typically, atmospheric vents should not have emissions except during upsets. Normally, the exhaust streams from these process vents are diverted to the refinery fuel gas system and combusted in boiler or process heaters to recover the fuel value while destroying the VOCs.
Flares	TCEQ recommends that emissions be based on the actual flow rate and the specific composition of the gas routed to the flare. The generally preferred method of obtaining pilot gas and flared gas flow rate and composition data is through continuous monitoring with quality assured instruments. TCEQ and API recommend vendor specific information as the preferred method for estimating flare efficiencies. In the absence of vendor information, the alternative approach is based on an estimated 98% combustion efficiency.	Most refineries use a simple AP-42 total hydrocarbon emission factor to calculate VOC emissions. This factor was developed in the early 1980’s and has not been updated by EPA since then. The emission factor does not take into consideration the flare efficiency or the composition of the material being flared. Most refineries monitor the pilot gas flow rate, while the methods used to determine waste gas flow rates and composition range accuracy from continuous monitoring to the use of historical/engineering estimates.

TABLE 4 (continued)

Source Category	Preferred Method	Methods Currently Used
Process Equipment Leaks	<p>The EPA correlation equation approach is the preferred method when actual LDAR screening values are available. This approach involves entering each individual screening value into the correlation equation, which predicts the mass emission rate based on the screening value. Alternative methods include the use of unit specific correlation equations, “leak/no leak” emission factors, and industry average emission factors. There is considerable uncertainty associated with current methods to estimate process fugitive equipment leaks, as well as concern about the cost/difficulty of implementing LDAR programs. Another source of uncertainty is the effectiveness/timeliness of correcting leaks that are detected. As a result, current research is focusing on alternative methods. One area of research is to use optical imagers, such as open-path FTIR monitoring, to quantify emissions from leaking components.</p>	<p>All of the refineries use approved approaches from EPA’s <i>Protocol for Equipment Leak Emission Estimates</i>. Some refineries base their emissions on EPA’s preferred correlation equation approach that uses actual LDAR screening values to estimate emissions. Other refineries use the alternative “leak/no leak” method to calculate emissions. There are differences in how an individual refinery treats non-detects and components not monitored. VOC process equipment leak emissions vary widely from refinery to refinery due to differences in the size (number of equipment components monitored), liquid and gas streams processed, LDAR monitoring program requirements, and emission estimation methods used.</p>
Wastewater Treatment	<p>The WATER9 computer program is the preferred method. The model calculates average emission rates for each of the wastewater collection and treatment system components and applies these emission rates to each component at the refinery to determine the overall wastewater system emissions. The use of site-specific data (collection system layouts, wastewater flow data, wastewater composition data) is preferred, but in many cases the model will provide default values for many parameters.</p>	<p>Refineries use either an EPA -approved emission model (such as WATER8 or WATER9) or AP-42 emission factors. The use of an emission model is EPA’s preferred method. The AP-42 emission factors for oil/water separators are very dated and have not changed since the 1980 edition of AP-42. We could not accurately determine whether all wastewater treatment components (process drains, oil/water separators, refinery-specific treatment processes) are included in the inventory.</p>
Cooling Towers	<p>The preferred method uses the VOC concentration in the water coming to and leaving a cooling tower to calculate an emission rate. The TCEQ suggests that a test method developed by El Paso Products Company can be used to determine VOC emissions from a cooling tower. The difference in VOC between the inlet and outlet of the cooling water can be converted to a pounds per hour VOC mass emission rate for the cooling tower.</p>	<p>VOC emissions for cooling towers at the three Pennsylvania refineries are based on AP-42 emission factors, resulting in emission estimates from 8 to 54 tons per year. Emissions from the refineries in Delaware and New Jersey are either very small (< 5 tons per year) and listed as insignificant sources.</p>

TABLE 4 (continued)

Source Category	Preferred Method	Methods Currently Used
Storage Tanks	The current version of TANKS is Version 4.09b. A large amount of detail concerning tank configuration (seam length, fittings count) and material stored is required for accurate estimates for each tank. Using default data instead of actual plant specific data may lead to inaccuracies. The last major changes (from Version 3 to Version 4) occurred in September 1999. The emission calculations in TANKS Version 3 and Version 4 are virtually the same. The last major revision of loss factors and equations occurred between TANKS 2 and TANKS 3.0, with emissions more than doubling between Version 2 and Version 3.	All of the refineries use the TANKS program to estimate emissions, but very few are using the most current version. However, all of the refineries are using fairly recent versions of the model and differences in the version of TANKS used should not create drastic inconsistencies. Emissions from storage tanks appear to be reasonably consistent from refinery to refinery when one factors in the differences in refinery size, the number of tanks at the refinery, and the products stored.
Loading/Unloading Operations	The preferred approach is to use the loading loss mass balance equation from AP-42 Section 5.2 and product transfer rates, with source testing measurements to determine the control efficiency. Source tests can also be used to either directly determine the mass VOC emissions.	The refineries calculate their VOC emissions using an AP-42 material balance calculation and product transfer rates. Most of the operations are controlled, and the efficiency of the control device is frequently based on source testing. In some cases, the source tests are used to develop the VOC emission estimates.
Upsets and other Non-routine Emissions	Non-routine releases occur during maintenance/turn-around activities and during emergency/upset conditions. Non-routine emissions involve blowdown or venting emissions, either directly to the atmosphere, to the refineries fuel gas system, or to a flare. These emissions are generally episodic, occurring over a short period of time. Releases routed to the refinery fuel gas system or to a flare would be included with the combustion source or flare emission estimates. Direct release to the atmosphere can occur and the preferred approach for estimating VOC is through the use of a displacement equation. The displacement equation requires information on the amount of material and the composition of the material released directly to the atmosphere.	The refineries in the Philadelphia/Delaware/New Jersey area do not report emissions from non-routine activities in a consistent manner. Some refineries, such as Sunoco Marcus Hook, group emissions from purging/sampling activities with other fugitive releases. Other refineries, such as ConocoPhillips Trainer, report emissions from purging/sampling as a distinct emission point. Sunoco Philadelphia has an emission point for blowdown systems. Motiva Delaware City has an emission point for accidental releases. Some of the New Jersey refineries reported accidental releases, while others do not.

FINDINGS

1. In general, the refineries are properly applying “generally accepted” emission estimation methods consistent with the guidance contained in AP-42, the EIIP guidance, the TCEQ guidance, or the API guidance. Frequently, the refineries are using the “preferred” or most accurate method prescribed in the guidance, but in many cases the refineries use one of the simpler, alternative methods that are less resource intensive.
2. For some categories, such as boilers/heaters, the refineries are using outdated AP-42 factors. Also, we found a few instances where the emission factors in AP-42 differ from the emission factors in EPA’s FIRE emission factor database. MARAMA will be communicating the findings of this study to EPA.
3. Many of the AP-42 emission factors for petroleum refinery operations are very dated. The Petroleum Refining section of AP-42 (Section 5.1) was last updated in January 1995, but many of the emission factors listed in Section 5.1 have not changed since the early 1980’s. Similarly, the emission factor for flare operations in Section 13.5 of AP-42 is based on a study conducted in the early 1980’s. Some of the refineries still rely on these AP-42 emission factors. EPA has collected extensive data to support MACT standard development for numerous refinery processes and auxiliary operations. MARAMA will inquire whether EPA has any plans to update AP-42 sections with more recent data.
4. Emissions from three source categories (cooling towers, flares, and non-routine operations) are potentially missing or underestimated in the current inventory. Cooling tower emissions for the refineries in New Jersey and Delaware are very small compared to the emissions from the Pennsylvania refineries. Flaring emissions appear to be underestimated for some refineries, but there is generally not enough information available about flare flow rates and waste stream composition to accurately quantify emissions. Emissions from non-routine operations, such as upsets and maintenance activities, do not appear to be accurately accounted for in the inventory. Again, it is difficult to quantify non-routine emissions because of a lack of data for the events occurring.
5. Emissions from some categories are episodic and short-term in nature. These emissions, when accounted for, are generally averaged to develop the annual emission estimate. Obtaining better data on episodic emissions may be necessary for photochemical modeling of specific events or time periods.
6. The agencies are beginning to compile better inventories of speciated VOC emissions (primarily for HAPs). Obtaining better data on “highly reactive VOCs”, such as ethylene, may be necessary for an ozone modeling inventory.
7. It was beyond the scope of this project to determine the accuracy of the “preferred” emission estimation methodologies. For example, refineries use EPA’s TANKS program, the WATER9 model, and the correlation equation for estimating emissions from process equipment leaks. If the VOC emissions are significantly underestimated as indicated by the aircraft data, then an assessment of the uncertainty of the basic emission estimation methodologies may be needed.

RECOMMENDATIONS

There are opportunities to improve the quality and consistency of the inventory by promoting the use of the preferred emission estimation methods. We have developed the following recommendations for agency actions aimed at improving the emission estimation methodologies:

1. Request better documentation from refineries on emission estimation methods used (i.e., backup calculations, emission factors/models used, process rates, etc.) so that the agency can double check the completeness and accuracy of the emissions calculated by the refinery.
2. Conduct site visits to each refinery to review and verify the 2002 inventory data provided by the refineries and the emission estimation methods used. The 2002 inventory is particularly important because it will likely serve as the baseline for future planning activities such as the development of Reasonable Further Progress plans and attainment demonstrations.
3. Work collaboratively with refineries to promote the use of the most appropriate emission estimation methods (i.e., WATER model instead of *AP-42* factors, latest version of TANKS).
4. Work collaboratively with refineries to gain better understanding of flaring practices and promote better tracking of flare gas flow rates and composition.
5. Work collaboratively with refineries to promote better recordkeeping and reporting of emissions from upsets and non-routine releases.
6. Critically review equipment LDAR data and emission estimates (i.e., check for accurate component counts, leak fractions, and approaches for estimating LDAR effectiveness).
7. Critically review emission estimates to verify that the refineries are correctly reporting VOC emissions. In some cases, *AP-42* provides hydrocarbon emission factors in several forms, such as total hydrocarbons (THC), total organic gas (TOG), nonmethane hydrocarbons (NMHC), and volatile organic compounds (VOC).
8. Coordinate with air quality modelers to determine what additional information is needed to support air quality modeling and determine whether this information is available from each refinery. For example, it may be helpful to know if there were significant episodic releases during time periods selected for modeling or during the period when measurements were made aloft. It may also be helpful to gather information on “highly reactive VOCs” that are not routinely reported in the existing emission inventories.
9. Coordinate with TCEQ, BAAQMD, and SCAQMD regarding updated emission inventory guidance and on-going R&D work to improve estimation techniques.
10. Coordinate with EPA regarding *AP-42* issues/questions and any on-going R&D work to improve emission estimation methodologies.
11. Consider organizing and participating in a training workshop for DNREC, NJDEP, PADEP, PAMS personnel (inspectors, permit writers, inventory) regarding emission estimation methods for the refining industry. Consider inviting industry representatives to the workshop.
12. Consider organizing and participating in a session on refinery VOC emissions at the national annual emission inventory conference to exchange information among EPA, State/local agencies, and industry.

(This page intentionally left blank)

APPENDIX A

AN OZONE EPISODE IN THE PHILADELPHIA METROPOLITAN AREA

Adapted from "An Ozone Episode in the Philadelphia Metropolitan Area" Kleinman, L.I., W.F. Ryan, P.H. Daum, S.R. Springston, Y.-N., Lee, L.J. Nunnermacker, and J. Weinstein-Lloyd, manuscript prepared for Journal of geophysical Research.

In July and August of 1999, a Northeast Oxidant and Particle Study (NE-OPS) field campaign was conducted to determine causes for episodically high levels of O₃ and PM_{2.5}, focusing on the coupling of chemical and meteorological processes [Philbrick *et al.*, 2002]. The study was centered around the Philadelphia metropolitan area with regional coverage supplied by aircraft flights. Eight pollution episodes, with elevated concentrations of either O₃ or PM 2.5 or both, occurred within the 9 week field campaign [Ryan, www.atmos.umd.edu/~ryan/summary99.htm; Clark *et al.*, 2002].

The worst air quality occurred during the July 27-31 episode and in particular on the last day in which O₃ concentration at the Baxter site reached 165 ppb, the highest level observed in Philadelphia in the last 11 years [Clark *et al.*, 2002]. The episode started with the development of a broad ridge over the central U.S. and ended with the Northeast Corridor under the influence of an Appalachian lee trough with air flow in the along-corridor direction. For a portion of the morning of July 31, winds were nearly stagnant allowing local emissions to accumulate. Later in the day winds were from the SW at a calm 1-2 m s⁻¹. On the afternoon of July 31 there were high O₃ regions downwind of Baltimore and Philadelphia and near the Delaware –PA border. These regions were located in a narrow area that paralleled the Delaware River and I-95 Interstate highway.

As part of NE-OPS, the Department of Energy G-1 aircraft conducted 20 flights in the Philadelphia metropolitan area, measuring O₃, NO, NO_y, SO₂, CO, speciated hydrocarbons, HCHO and peroxides. There were aircraft flight on the morning and afternoon of July 31, giving us a picture of the accumulation of pollutants and consequent O₃ production. A persistent feature on most morning and afternoon flights was SO₂ and NO_x plumes encountered in a suburban/industrial area 30 km to the SW of downtown Philadelphia and 10 km NE of Wilmington, DE, along the Delaware-Pennsylvania border, near the Delaware River. High concentrations of CO, hydrocarbons, and aerosol particles were observed in the same area, but

with less regularity. On July 31 this region had the highest concentration of O₃ and other pollutants that we observed during the NE-OPS program.

Figure 1 shows NO_x emissions in the Philadelphia metropolitan area on a 4 by 4 km grid, from EPA's SMOKE model. Black grid squares have NO_x emissions greater than 10,000 ton/year. These are primarily from industrial sources and power plants located on or near the Delaware River. Also shown on this graph are 1) the locations of O₃ monitoring sites that recorded 1 hour average O₃ concentration on July 31 greater than 150 ppb and 2) the ground track of the G-1 aircraft on the morning of July 31. Note that under conditions of light SW winds, the high O₃ surface sites are located downwind of high emission rate regions on the Delaware River.

One of the O₃ hot spots (1 hour average = 162 ppb) was located in Chester, PA, just north of the DE-PA border. In contrast to the other high O₃ areas that were downwind of Baltimore or Philadelphia, the nearest upwind urban area to Chester is Wilmington, DE, a much smaller city. There is however evidence that there are significant impacts at Chester from nearby industrial and utility emission sources. The G-1 aircraft sampled just upwind of this site in the morning and again in the afternoon one hour before the surface O₃ maximum was recorded.

Figure 2 shows trace gas and aerosol measurements from the G-1 from the south side of the flight track shown in Fig. 1. The dominant feature in this figure is a plume, located near the Delaware River with peak concentrations given by: SO₂ > 66 ppb, CO = 790 ppb, NO_y > 121ppb, NO = 110 ppb, and PCASP = 5480 cm⁻³. Lower bounds are given for SO₂ and NO_y equal to the values where the data acquisition system went off-scale. Except for O₃, the concentrations of the trace gases shown in Fig. 2 were in each case the highest value recorded during the 20 NE-OPS G-1 flights. The concentration of ethene (6.5 ppb), propene (4.9 ppb), and several other hydrocarbons were likewise the highest that we observed during the field campaign. Ozone concentrations reach 100 ppb in the presence of 30 ppb of NO_x. O_x which is the sum of O₃ plus NO₂ and therefore accounts for titration has a maximum value of 136 ppb, indicating appreciable O₃ formation early in the morning.

Ratios of trace gasses through the plume suggest multiple types of emission sources. The extreme concentrations of ethene and propene are probably due to nearby chemical plants or refineries. The EPA point source inventory shows several close by plants including a cluster that was right underneath the aircraft ground track. We do not know if hydrocarbon concentrations are high because of high emission rates or because the sources are so close. On at least one other day, high hydrocarbons (although not as high as July 31) were found in the same place. NO_x , NO_y , and SO_2 could be from industry or power plants. CO is a puzzle. It is usually a tracer of urban emissions, but in our experience in several large cities we have never seen such high concentrations near 500 m altitude.

Figure 3 presents G-1 data for the July 31 afternoon flight, from the same region. In comparison to the morning observations, concentrations of primary pollutants are lower in the afternoon and the concentration of O_3 is significantly greater. The peak value of O_3 is 148 ppb, an increase of 63 ppb above the concentration in "background" air. At the point where the VOC sample was taken we calculate an O_3 production rate of 27 ppb h^{-1} . Thus we expect that significantly higher O_3 levels will occur downwind as was indeed observed at Chester, PA, later in the afternoon.

The July 31 episode shows that with light winds, areas outside of major cities can have very high O_3 due to local emissions. This episode, however, is not typical. It is more usual to have high O_3 concentrations under conditions with moderate wind speeds favoring inter-regional transport. The well-studied July 12-15, 1995 episode provides an excellent example of the more typical case [Ryan *et al.*, 1998; Zhang *et al.*, 1998; Seaman and Michelson, 2000].

References

Clark, R.D., C.R. Philbrick, W.F. Ryan, B.G. Doddridge, and J.W. Stehr, The effects of local and regional scale circulations on air pollutants during NARSTO-NE-OPS 1999-2001, *4th Conf. on Atmos. Chem.*, preprint vol. pp 125-134, Amer. Meteor. Soc., Orlando, FL, Jan., 2002.

Philbrick, C.R., et al., Overview of the NARSTO-NE-OPS program, *4th Conf. on Atmos. Chem.*, preprint vol. pp 107-114, Amer. Meteor. Soc., Orlando, FL, Jan., 2002.

Ryan, W.F., B.G. Doddridge, R.R. Dickerson, R.M. Morales, K.A. Hallock, P.T. Roberts, D.L. Blumenthal, J.A. Anderson, and K.L. Civerolo, Pollutant transport during a regional O₃ episode in the Mid-Atlantic states, *J. Air & Waste Manage. Assoc.*, **48**, 786-797, 1998.

Seaman, N.L., and S.A. Michelson, Microscale meteorological structure of a high-ozone episode during the 1995 NARSTO-Northeast Study, *J. Appl. Met.*, **39**, 384-398, 2000.

Zhang, J., S.T. Rao, and S.M. Daggupati, Meteorological processes and ozone exceedances in the Northeastern United States during the 12-16 July 1995 episode, *J. Appl. Met.*, **37**, 776-789, 1998.

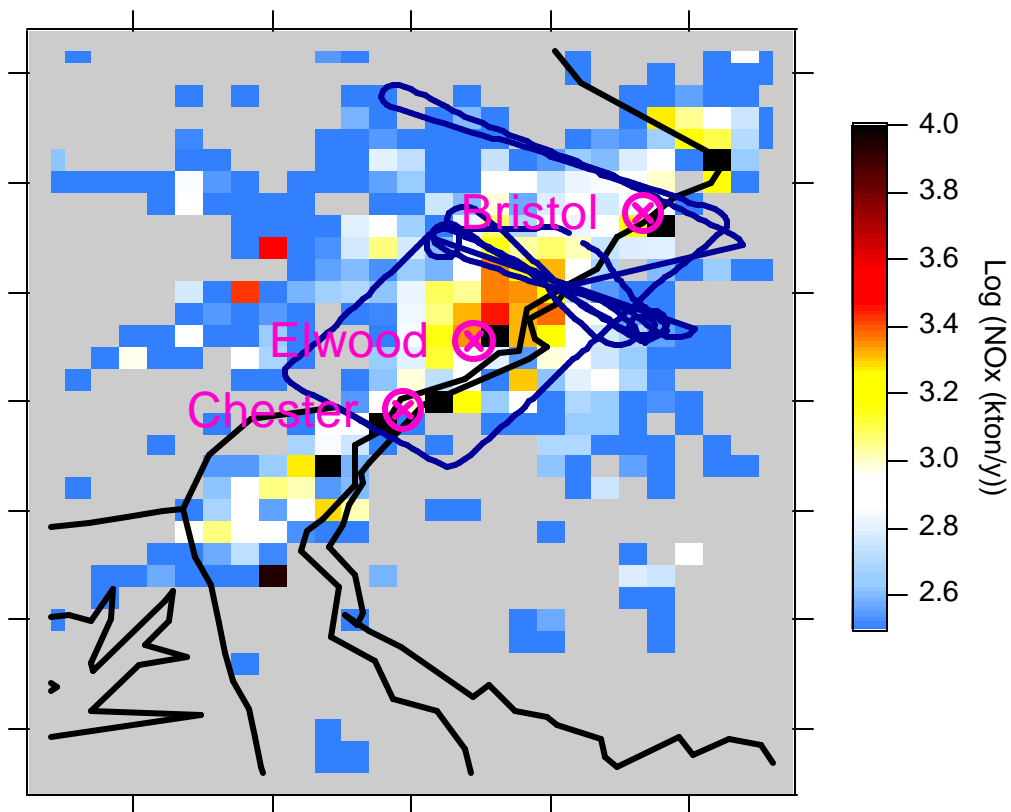


Figure 1. Map of Philadelphia metropolitan area. State outlines in black. Flight track of G-1 aircraft for the July 31 morning flight in dark blue. NO_x emission rates are from EPA's SMOKE model. Units are log (kton/year). Three O₃ monitoring sites within map boundaries had 1-hour average O₃ concentration greater than 150 ppb; Chester, PA (162 ppb), Elwood St., PA, 154 ppb, and Bristol, PA 151 ppb). High O₃ (154 ppb) was also observed at Aldino, MD, downwind of Baltimore, outside of this map region.

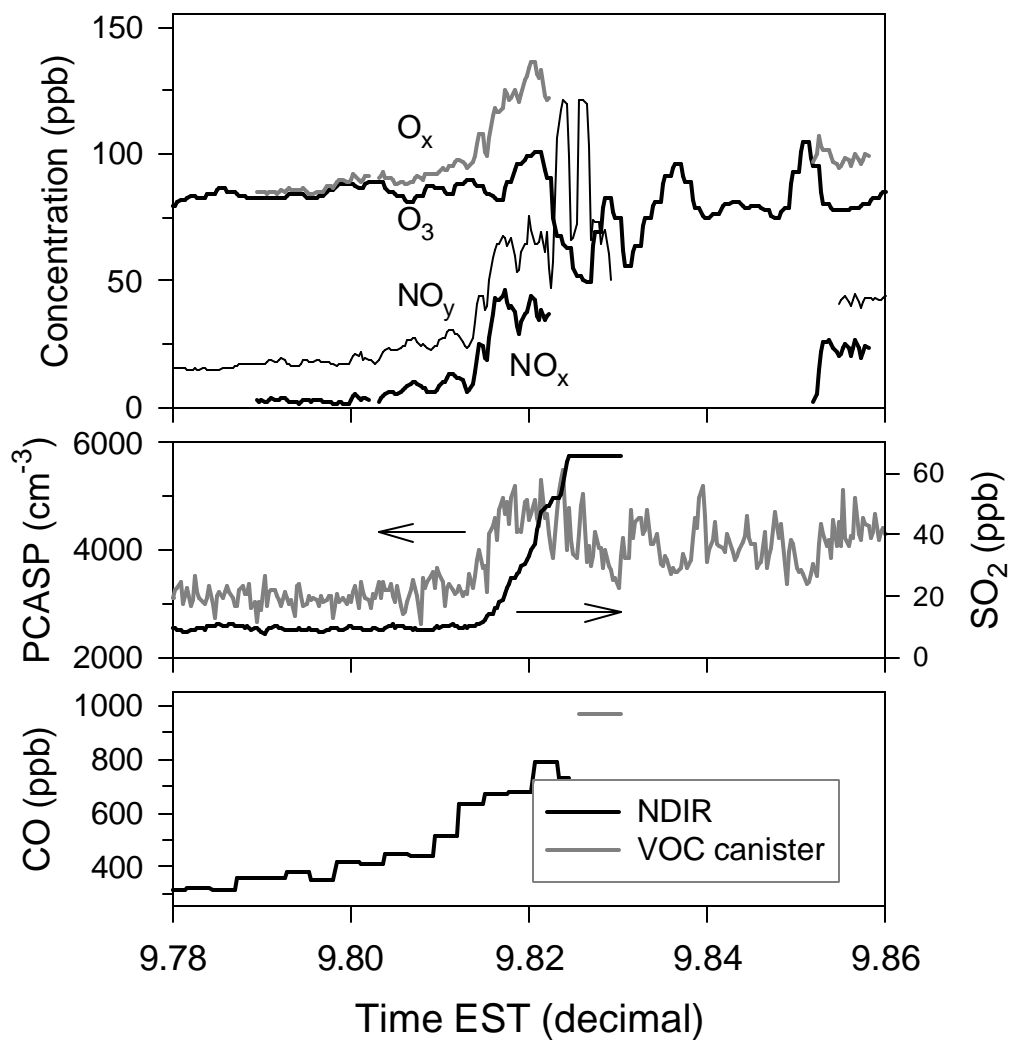


Figure 2. Trace gas and aerosol concentration from southern leg of morning G-1 flight, July 31, 1999. Altitude = 450 m. Top panel: $O_x = (O_3 + NO_2)$, O_3 , NO_y , and $NO_x = (NO + NO_2)$. Middle panel: Number concentration of accumulation mode aerosol particles (PCASP) and SO_2 . Bottom panel: CO continuous (NDIR) and grab sample (VOC canister). Periods of missing data are due to instruments in zero mode. Data acquisition system went off-scale for NO_y and SO_2 .

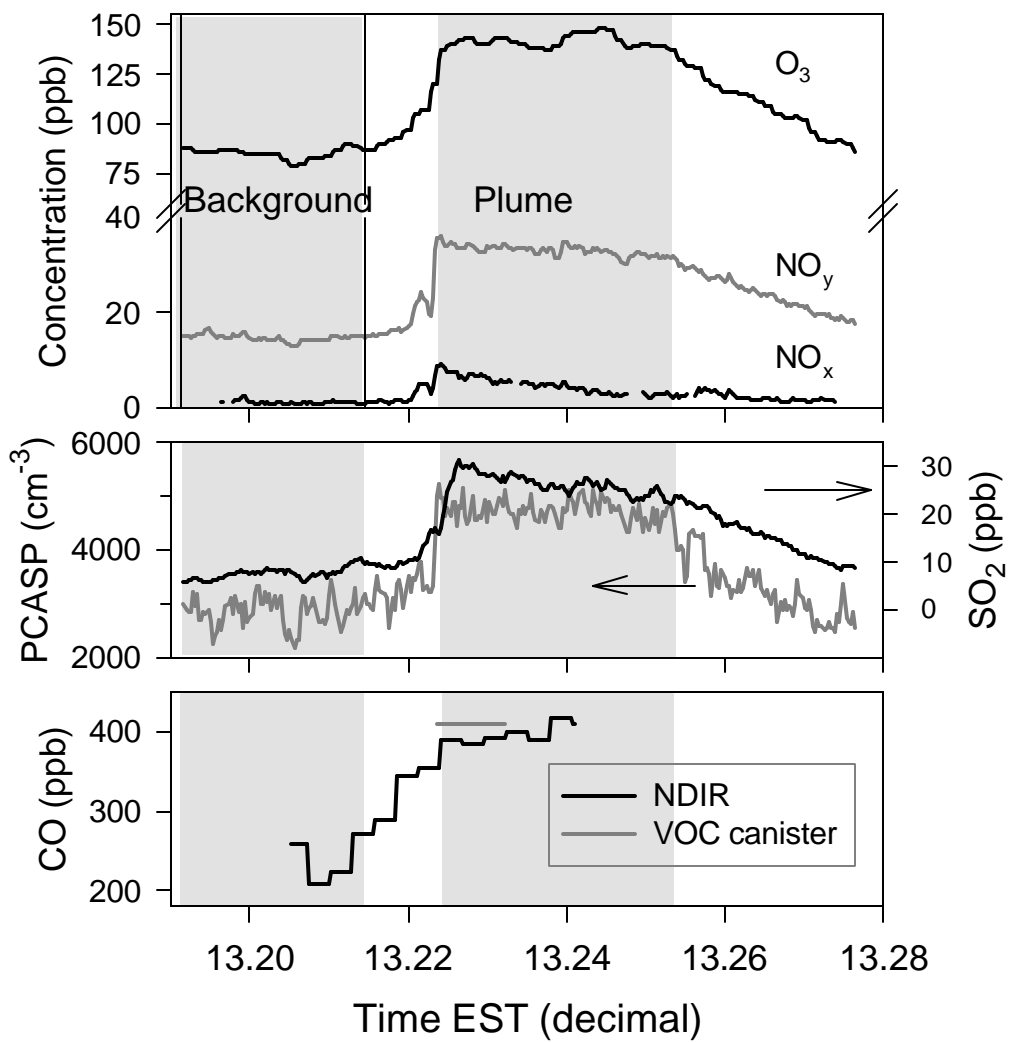


Figure 3 Trace gas and aerosol concentration from southern leg of afternoon G-1 flight, July 31, 1999. Altitude = 870 m. Top panel: O_3 , NO_y , and NO_x ($NO + NO_2$). Middle panel: Number concentration of accumulation mode aerosol particles (PCASP) and SO_2 . Bottom panel: CO continuous (NDIR) and grab sample (VOC canister).

APPENDIX B

**TECHNICAL MEMORANDUM #1
FINAL WORK PLAN**

COMPARISON OF REFINERY VOC EMISSIONS

**TECHNICAL MEMORANDUM #1
FINAL WORK PLAN**

COMPARISON OF REFINERY VOC EMISSIONS

Prepared for:

Susan S.G. Wierman, Executive Director
Mid-Atlantic Regional Air Management Association (MARAMA)
711 W. 40th Street
Suite 318
Baltimore, MD 21211-2109

November 12, 2002
5925.001

Submitted by

PES, a MACTEC Company
560 Herndon Parkway
Suite 200
Herndon, VA 20170
(703) 471-8383, FAX (703) 481-8296
EJSabo@mactec.com

TABLE OF CONTENTS

	Page
INTRODUCTION	1
SCHEDULE AND DELIVERABLES	1
TASK 1 – PROJECT MANAGEMENT	1
TASK 2 – IDENTIFY FACILITIES OF INTEREST	3
TASK 3 – IDENTIFY VOC SOURCES ACCOUNTED FOR IN INVENTORY .	4
TASK 4 – IDENTIFY UNACCOUNTED FOR SOURCES	6
TASK 5 – IDENTIFY VOC EMISSION ESTIMATION METHODS	8
TASK 6 – EVALUATE CALCULATION METHODS	10
TASK 7 – PREPARE FINAL REPORT	10
PROJECT ORGANIZATION AND KEY PERSONNEL	11

TABLES

	Page
Table 1. Summary of Deliverables and Schedule	2
Table 2. Typical Air Emission Sources in the Petroleum Industry.....	5
Table 3. File Review Protocol	7

INTRODUCTION

A recent MARAMA-sponsored investigation of VOC emissions and ambient monitoring data concluded the following:

1. Evidence indicates that ambient atmospheric VOC concentrations in the Philadelphia area are significantly higher than estimated by regional inventories,
2. Petroleum refineries are a significant source of VOC in the PA-NJ-DE-MD ozone non-attainment areas, and
3. VOC emissions estimates from petroleum refineries, and possibly other petroleum industry facilities, have a large potential to be underestimated.

The purpose of this project is to lay the groundwork for developing an improved regional emissions inventory for refinery VOC emissions. This project entails a detailed comparison of member states' refinery VOC source identification and VOC emissions estimation methods. The primary pollutants of interest are total VOCs and speciated VOCs.

SCHEDULE AND DELIVERABLES

Table 1 provides a summary of the tasks to be performed, deliverables produced, schedule, and requirements for inputs for state agencies. The details of our technical plan are presented in the following sections organized by task.

TASK 1 – PROJECT MANAGEMENT

A teleconference with PES, MARAMA and member states was held on Friday, September 20 to discuss the expectations for the project. Discussions held during the teleconference provided clarifying information that helped us prepare this detailed work plan.

We provided a draft work plan (Technical Memorandum #1) to MARAMA members for review and comment. A three-week comment period followed. After reviewing all comments, we are finalizing this work plan which will guide all future technical activities.

We will participate in periodic conference calls with project participants to discuss progress, resolve any issues or problems that arise, and plan future work. We will prepare summaries of the conference calls to identify any decisions made or issues that have not been resolved.

We will also participate in a technical meeting in the general Baltimore/Philadelphia area. We will prepare presentation slides for this meeting, make formal presentations as required, and participate in round-table discussions. We will prepare a summary of the meeting to identify any decisions made. The technical meeting is likely to be held in March/April of 2003.

Finally, we will monitor the project schedule and budget, and prepare monthly progress reports.

TABLE 1**SUMMARY OF DELIVERABLES AND SCHEDULE**

Task	Deliverable	Draft Deliverable Due Date	State Comments Due Date	Final Deliverable Due Date	Assistance Needed From MARAMA/States
1	Tech. Memo #1—Work Plan	Oct 2	Oct 21	Nov 12	Consensus on inventory(ies) to be used for baseline assessment. Agreements needed to gain access to state files
	Teleconference	Early October			Feedback on draft Work Plan
2	Tech. Memo #2 – List of Petroleum Industry Facilities	Nov 15	Dec 6	Dec 20	Electronic emission inventories (preferably in NEI format)
3	Tech. Memo #3 – List of Sources Contained in State Emission Inventories	Nov 22	Dec 13	Dec 27	Electronic emission inventories (preferably in NEI format)
	Teleconference or meeting	Early January			Discussion of draft Memos #1 and #2 Decision on whether to do Task 4a.
4	Tech. Memo. #4 – List of Unaccounted for Sources	Feb 17	Mar 10	Mar 24	Access to agency files, including emission statements, permits, inspection reports, and compliance monitoring reports
5	Technical Memorandum #5 – Description of Emission Estimation Methods	Feb 17	Mar 10	Mar 24	As needed access to agency inspectors, permit writers, and inventory personnel to clarify information contained in files or to answer questions regarding the facility
	Teleconference or meeting	Mid-March			Roundtable discussion of results to date and suggestions for improving the analysis
6	Tech. Memo.#6 – Evaluation of Calculation Methods	Apr 14	May 5	May 19	As needed access to agency inspectors or permit writers to clarify information contained in files or to answer questions regarding the facility
	Teleconference or meeting	Mid-May			Presentation and discussion of all Memos
7	Final Report in PDF, Word, and camera ready format	Jun 2	Jun 23	Jun 30	Feedback on draft final report

TASK 2 – IDENTIFY THE FACILITIES OF INTEREST

We will identify petroleum industry sources in the following geographic areas: the District of Columbia, Delaware, Maryland, New Jersey, Pennsylvania, Virginia, West Virginia, and New York. We will use the following North American Industry Classification System (NAICS) and corresponding Standard Industrial Classification (SIC) codes to identify facilities of interest:

<u>NAICS Code</u>	<u>SIC Code</u>	<u>Description</u>
32411	2911	Petroleum Refineries
32412	2951 and 2952	Asphalt Paving, Roofing, and Saturated Materials Manufacturing
324191	2992	Petroleum Lubricating Oil and Grease Manufacturing
42271	5171	Petroleum Bulk Stations, Terminals and Product Wholesalers
42272	5172	Petroleum Bulk Stations, Terminals and Product Wholesalers
48611	4612	Pipeline Transportation of Crude Oil
48691	4613	Pipeline Transportation of Refined Petroleum Products

We will query several national databases in an attempt to identify all facilities of concern. These data sources include:

- EPA's Toxic Release Inventory. Provides facility-level emissions as reported by industry, categorized as either stack or fugitive emissions for VOCs such as benzene, toluene, ethylbenzene, xylene, MTBE, n-hexane, and 1,2,4-trimethylbenzene.
- EPA's 1999 Criteria Pollutant National Emission Inventory. Provides emission unit level VOC emissions as reported by the States in their 1999 Periodic Emission Inventory. Also provides VOC emissions for area sources. According to EPA, Version 2 Final 1999 NEI for criteria pollutants should be on their ftp site by mid-October.
- EPA's 1999 Hazardous Air Pollutant National Emission Inventory. Provides emission unit level HAP emissions compiled from data reported by State agencies, EPA MACT databases, and the TRI. According to EPA, Version 3 Draft 1999 NEI for HAPs should be on their ftp site by October 7.
- 1996/1997 MARAMA Regional VOC Emission Inventory. Contains state agency emission inventories based on the 1996 Periodic Emission Inventory.
- Energy Information Administration's *Petroleum Supply Annual*. Contains information on the supply and disposition of crude oil and petroleum products by refinery.

These databases are publicly available via the Internet.

We will also obtain 2000 or 2001 data from the respective agencies for all facilities within the Philadelphia CMSA or Philadelphia Ozone Nonattainment Area. The Philadelphia-Wilmington-Trenton PA-NJ-DE-MD CMSA includes the following counties: Pennsylvania Portion: Bucks, Chester, Delaware, Montgomery, and Philadelphia; New Jersey Portion: Atlantic, Burlington, Camden, Cape May, Cumberland, Gloucester, and Salem; Delaware Portion: New Castle; Maryland Portion: Cecil. In addition to these counties, we will include two additional counties that are part of the Philadelphia Ozone Nonattainment Area - Mercer County, NJ, and Kent County, DE.

We have asked PADEP, NJDEP, Philadelphia AMS, and DNREC to investigate the availability of 2000/2001 calendar year inventories. PES has requested that the data be sent in NIF 2.0 format (see <http://www.epa.gov/ttn/chief/nif/index.html>). If data cannot be put in NIF 2.0 format, PES has asked that agencies supply documentation of available formats. Agencies have been asked to coordinate with Ed Sabo at PES regarding the transfer of data.

We will compare the results of these queries to aid in the identification of facilities potentially missing from the state's emission inventory databases. We will prepare a series of summary tables that compares the information available in the databases listed above. We will also develop and provide detailed electronic databases or spreadsheets with the raw data that we used. We will document the results of the searches in Technical Memorandum #2 detailing the list of facilities by name (and former name if recent change in ownership), location, brief process description, capacity by product, NAICS/SIC code, and facility-wide VOC and HAP emissions. We will distribute a draft version of Technical Memorandum #2 to project participants for review and comment. After addressing all comments, we will prepare a final Technical Memorandum #2.

TASK 3 – IDENTIFY VOC SOURCES ACCOUNTED FOR IN THE INVENTORIES

We will use the emission inventory databases provided by the states to identify the individual emission sources at each facility. For sources in the Philadelphia CMSA, we will prepare the emission unit-level summaries using the 2000/2001 data provided by the state/local agencies above. For other States, the 1999 NEI for criteria pollutants (Version 2) will be used.

For the facilities identified above, we will prepare emission summary reports at the process level to identify individual emission units. The summary report will contain the following information:

- Facility name and location
- NAICS/SIC code
- Emission point identification codes
- Source Classification Code (SCC) and generic SCC description
- State emission point description (if available in comment fields)
- VOC emissions – annual and ozone season daily
- VOC emissions estimation method code and description
- VOC emission control device and control efficiency
- VOC rule effectiveness and rule penetration

We will prepare emission summaries at the process level by type of source to summarize the VOC emissions attributable to each type of process. Table 2 shows the typical air emission sources found at petroleum industry facilities. We will also develop and provide detailed electronic databases or spreadsheets with the raw data that we used. We will document the results of the searches in Technical Memorandum #3. We will distribute a draft version of Technical Memorandum #3 to project participants for review and comment. After addressing all comments, we will prepare a final Technical Memorandum #3.

TASK 4 – IDENTIFY VOC SOURCES WITHIN THE FACILITIES NOT ACCOUNTED FOR IN THE INVENTORIES

We will need to examine state and local agency files to identify individual VOC sources that are not accounted for in the inventory. Our initial focus will be on petroleum refineries in the Philadelphia CMSA:

Jurisdiction	Company	Location
Philadelphia	Sunoco Inc. (R&M)	Philadelphia
SE Pennsylvania	Sunoco Inc.	Marcus Hook
	Phillips 66 Co.	Trainer
Delaware	Motiva Enterprises LLC (formerly Star Enterprise)	Delaware City
New Jersey	Phillips 66 Co.	Linden
	Valero Refining	Paulsboro
	Mobil Oil	Paulsboro
	Coastal Eagle Point Oil	Westville
	CITGO Asphalt Refining	Paulsboro

We will also review files for other important sources (such as bulk terminals) identified during Tasks 2 and 3. We will visit the appropriate state or local agency to review the files for each source. Our costs for this task are based on reviewing the files for 10 petroleum refineries and 10 additional sources. Facilities outside the Philadelphia CMSA will be included if resources permit in the following order: Pennsylvania, New Jersey, and Delaware; followed by New York and Virginia; and then Maryland, West Virginia, and DC.

Identifying unaccounted for sources will require a detailed review of each agency’s files. Table 3 outlines our procedures for reviewing agency files. The objectives of the reviews are:

- (a) verify that the computerized emission inventory matches other available information in hard copy Title V permits, emission statements, and other files.
- (b) gather data on emission estimation methods since the computer codes in database usually don’t provide enough details of how emissions were calculated. Agency files may provide information on leak detection calculation methods, emission factors, wastewater models, temperatures, and control device efficiencies used for calculating emissions.

TABLE 2

TYPICAL AIR EMISSION SOURCES IN THE PETROLEUM INDUSTRY

<p>External Combustion Sources Boilers Furnaces Process heaters</p> <p>Internal Combustion Sources Gas turbines Reciprocating engines</p> <p>MACT I Process Vents^a Alkylation units Blending units Catalytic hydrotreating Catalytic hydrocracking Chemical treatment units Crude distillation Lube oil production Hydrogen production Isomerization Polymerization Solvent extraction Vacuum distillation</p> <p>MACT II Process Vents^b Catalytic cracking unit (CCU) catalyst regeneration vent (fluid and thermal units) Catalytic reformer unit (CRU) catalyst regeneration vents Sulfur recovery unit</p>	<p>Process Equipment Leaks Pump seals Compressor seals Valves Pressure relief devices Flanges Open-ended lines Sampling connections</p> <p>Wastewater Treatment Process drains and collectors Oil-water separators Air flotation systems Surface impound basins and ponds Cooling water towers</p> <p>Storage Vessels Fixed roof External floating roof Internal floating roof</p> <p>Loading Operations Marine Vessels (tankers and barges) Rail tank cars Tank trucks</p> <p>Other Sources Flares</p>
---	---

- a) Miscellaneous process vents covered by 40CFR Part 63 Subpart CC - National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries (commonly referred to as MACT I Standard)
- b) Sources covered by 40CFR Part 63 Subpart UUU - National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries – Catalytic Cracking (fluid and Other) Units, Catalytic Reforming Units, and Sulfur Plants (referred to as MACT II Standard)

TABLE 3 - FILE REVIEW PROTOCOL

- 1. Review Information in Electronic Databases**
 - a) Agency's current inventory (2000 or 2001)
 - b) EPA's NEI (criteria and HAP)
 - c) EPA's TRI
 - d) EIA capacity and operating data

 - 2. Identify and Briefly Review Information in Agency Files**
 - a) Title V permit (including application and statement of basis)
 - b) Recent construction permits
 - c) Annual emission statements
 - d) Title V semi-annual monitoring reports and annual compliance certifications
 - e) NSPS/NESHAP/MACT monitoring reports
 - f) Agency inspection reports

 - 3. Perform Completeness Checks**
 - a) Check 2000/2001 inventory against Title V list of significant and insignificant emission units
 - b) Check 2000/2001 inventory against 2000/2001 emission statement
 - c) Check 2000/2001 inventory against prior year emission statements and inventories
 - d) Identify potentially missing sources
 - e) Provide explanation for any missing sources

 - 4. Gather Information About Emission Estimation Methods**
 - a) Identify how were emissions estimated (AP-42 emission factor, other emission factor emission model, CEM, stack test, etc.)
 - b) For equipment leaks, determine which approach was used (average emission factor, screening ranges, EPA correlation, unit-specific correlation). Compile available leak rate data from LDAR monitoring reports.
 - c) For wastewater treatment, determine which approach was used (manual calculations, emission models, measurement data, emission factors).
 - d) For storage tanks, determine which version of TANKS was used and compile available input parameters such as temperatures used in the calculations
 - e) Identify control devices and control efficiencies used
 - f) Determine adjustments made to calculate ozone season daily emissions
 - g) Determine how rule effectiveness and rule penetration were applied
 - h) Determine if any adjustments were made for excluding nonreactive VOCs
 - i) Determine if and how speciated VOCs or HAP emissions were derived

 - 5. Perform Accuracy Checks**
 - a) Check for mathematical errors in emission calculations
 - b) Check for units conversion errors
 - c) Verify correct transcription of data from paper submittals into the electronic database
-

(c) gather any available compliance data that may indicate that the inventory underestimates emissions (excess emission reports, notification of upsets, any non-compliance issues, frequency of leak detection monitoring – quarterly vs annual)

As questions arise, we may need to consult with agency permit writers, inspectors, or inventory preparation personnel to obtain clarifications regarding emission sources and emission estimation methods.

We do not think it's appropriate for site visits to plants. If the type of data listed above is not available in the files, we will prepare a note indicating the type of data we could not find the files. We would interact with agency permit writers, inspectors, or emission inventory specialists to add details or resolve questions. The agencies may want to request additional emission calculation details from the facilities to assist in our assessment.

We will use the information gathered during the file reviews to help identify potential missing sources. We will also use the information gathered in Tasks 5 and 6 to evaluate emission estimation methods. The results of this task will be documented in Technical Memorandum #4 detailing unaccounted for sources. We will distribute a draft version of Technical Memorandum #4 to project participants for review and comment. After addressing all comments, we will prepare a final version.

TASK 5 – IDENTIFY VOC EMISSION ESTIMATION METHODS

The computer databases will contain a generic description of the emission estimation method used for each process. The valid codes are:

<u>Code</u>	<u>Emission Estimation Method</u>
01	CEMS – CONTINUOUS EMISSION MONITORING SYSTEM
02	ENGINEERING JUDGEMENT
03	MATERIAL BALANCE
04	STACK TEST
05	EPA SPECIATION PROFILE
06	STATE/LOCAL SPECIATION PROFILE
07	MANUFACTURER SPECIFICATION
08	EPA EMISSION FACTOR
09	STATE/LOCAL EMISSION FACTOR
10	SITE-SPECIFIC EMISSION FACTOR
11	VENDOR EMISSION FACTOR
12	TRADE GROUP EMISSION FACTOR

These computer codes do not provide enough information to rigorously assess the methods used to calculate emissions. Information obtained during the file reviews will be used to supplement the emission estimation code used in the database. By reviewing the emission statements and other information in the files, we will attempt to provide a more detailed explanation of how

emissions were calculated for each source at the facility. We will attempt to identify source-specific methodologies used by individual refiners, the version of TANKS used to calculate storage tank emissions, and the source of emission factors used to calculate process emissions.

We will focus on the methods used for estimating fugitive emissions from equipment leaks. Fugitive emissions tend to be large and there is considerable variation in approaches for estimating emissions from these sources. According to the EIIP document entitled *Preferred and Alternative Methods for Estimating Fugitive Emissions from Equipment Leaks*, there are four basic approaches for estimating emissions from equipment leaks in a specific processing unit. The approaches, in order of increasing refinement, are:

- Average emission factor approach;
- Screening ranges approach;
- EPA correlation approach; and
- Unit-specific correlation approach.

The approaches increase in complexity and in the amount of data collection and analysis required. All the approaches require some data collection, data analysis and/or statistical evaluation. These approaches range from simply using accurate equipment counts with average emission factors to the more complex method of developing unit-specific correlations of mass emission rates and screening values. In general, the more refined approaches require more data and provide more accurate emission estimates for a process unit. Also, the more refined approaches, especially the unit-specific correlation approach that uses bag sampling data, require a larger budget to implement the program and develop the correlation equations. Our review of the agency's files will help us identify the specific methods used by the industry or state to estimate fugitive VOC emissions from leaking equipment.

EPA's National Enforcement Investigation Center has conducted studies that suggest that refineries sometime significantly underestimate VOC emissions from equipment leaks by not fully identifying all leaking components. It is unlikely that there will be sufficient information available in the agency's files to make an assessment as to whether refiners are accurately identifying leaking components. A separate rule effectiveness study would be needed to address this issue in detail.

We are not suggesting a rule effectiveness study at this time. However, this is something that MARAMA may want to consider after this project is completed. For this project, we will have no way to verify whether industry monitoring results are accurate or can be confirmed by independent monitoring. EPA did independent monitoring that suggests gross underreporting of emissions. For example, when EPA conducted leak monitoring at Motiva in Delaware, it found that 6.1% of the valves leaked compared to only 1.6% reported by the facility. We would include a simple sensitivity analysis as part of Task 5 to answer the question "What if the leak rate was underestimated by x percent- what is the potential range of emissions unaccounted for in the inventory?"

While we will focus on equipment leaks, we will also look at all typical air emission sources found in the industry, including those previously listed in Table 2. We will identify the specific methods used by the industry or state to estimate VOC emissions for all of these categories.

During the file reviews, we will collect available data on seasonal/diurnal production rates. We will attempt to determine the temperatures used in the emission calculations for fuel storage/transfer operations. We will also attempt to collect any information available on emissions from startup/shutdown or process upsets. We will provide examples of how emissions may be affected by these parameters, but do not envision performing extensive recalculation of emissions under this contract. We would include a simple sensitivity analysis as part of Task 5 to assess the relative importance of temporal variations on VOC emissions.

The deliverable for this task will be Technical Memorandum #5, detailing what methods have been employed to estimate total VOC emissions for each type of source and each unit operation. We will distribute a draft version of Technical Memorandum #5 to project participants for review and comment. After addressing all comments, we will prepare a final version.

TASK 6 - EVALUATE CALCULATION METHODS

We will develop and implement a methodology to evaluate the emission calculation methods identified in Task 5. Our approach will consider using or adapting EPA's Data Attribute Rating System (DARS) methodology to assist in evaluating data associated with emission inventories. The system disaggregates emission inventories into emission factors and activity data, then assigns a numerical score to each of these two components. Each score is based on what is known about the factor and activity parameters, such as the specificity to the source category and the measurement or estimation techniques employed. The resulting emission factor and activity data scores are combined to arrive at an overall confidence rating for the inventory. The DARS defines certain classifying attributes that are believed to influence the accuracy, appropriateness, and reliability of an emission factor or activity and derived emission estimates. This approach is semiquantitative in that it uses numeric scores; however, scoring is based on qualitative and often subjective assessments. The exact criteria and scoring factors will be developed in consultation with MARAMA. The deliverable for this task will be Technical Memorandum #6, detailing the ranking of methods and associated technical justification. We will distribute a draft version of Technical Memorandum #6, address all comments, and prepare a final version.

TASK 7 – PREPARE FINAL REPORT

We will prepare a draft final report that summarizes the results of the previous tasks. The draft final report will be based upon the six Technical Memoranda previously developed. We propose to present the results of the study at a regularly scheduled meeting of the MARAMA states. Prior to the meeting, we will distribute the draft final report for MARAMA and state agency review. We will incorporate comments on the draft report and prepare a final report. The final report will be prepared in both MS Word format and Adobe PDF format. The final report will also be submitted as a camera-ready hard copy along with 50 hard copies. Each of these components will be prepared for distribution and display on the MARAMA web site. Inventory files will be submitted in MS EXCEL format and the current NIF format unless otherwise specified by MARAMA.

PROJECT ORGANIZATION AND KEY PERSONNEL

Mr. Edward Sabo will serve as Program Manager. He is an experienced manager of emission inventory development and quality assurance programs. Mr. Sabo recently developed the MARAMA regional ozone precursor emission inventory by integrating State emissions data with the EPA's 1996 National Emissions Inventory. He has also been involved in a number of projects related to the petroleum refining industry and is knowledgeable of the industry's sources and techniques for estimating emissions. Mr. Sabo will direct and monitor technical and financial performance throughout the project and will serve as the primary contact with MARAMA on technical and project management issues.

Mr. John Chehaske will serve as Technical Director. He has participated in nearly 100 projects designed to characterize emissions, develop emission factors, evaluate innovative processes and control techniques, and determine compliance. He will provide guidance on interpretations of leak detection and stack testing data.

Mr. Douglas Toothman will coordinate QA/QC activities.

Dr. Kenneth Meardon will be responsible for evaluating leak detection and repair data and emissions from process sources, while Mr. Tracy Johnson will evaluate storage tanks and gasoline transportation/marketing sources. Other mid- and junior-level chemical engineers and environmental scientists will be assigned to help compile, summarize, and analyze data.

APPENDIX C

FINAL TECHNICAL MEMORANDUM #2

**IDENTIFICATION OF PETROLEUM INDUSTRY FACILITIES
IN THE MID-ATLANTIC STATES**

REVISED FINAL TECHNICAL MEMORANDUM #2

**IDENTIFICATION OF PETROLEUM INDUSTRY FACILITIES
IN THE MID-ATLANTIC STATES**

Prepared for:

Susan S.G. Wierman, Executive Director
Mid-Atlantic Regional Air Management Association (MARAMA)
711 W. 40th Street
Suite 318
Baltimore, MD 21211-2109

October 14, 2003
5925.002

Submitted by

Edward Sabo
MACTEC Federal Programs, Inc.
560 Herndon Parkway
Suite 200
Herndon, VA 20170
(703) 471-8383, FAX (703) 481-8296
EJSabo@mactec.com

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
IDENTIFICATION OF PETROLEUM REFINERIES	2
Refinery Locations	2
Refinery Capacity Data	2
Refinery Production Data.....	2
Refinery Emissions Data	8
IDENTIFICATION OF OTHER PETROLEUM INDUSTRY FACILITIES	12
REFERENCES	19

TABLES

	<u>Page</u>
Table 1. Petroleum Refineries in the Mid-Atlantic States	3
Table 2. Capacity by Type of Process as of January 1, 2002	5
Table 3. Trends in Refinery Production of Finished Petroleum Products	6
Table 4. Comparison of Refinery VOC Emissions.....	9
Table 5. HAP Emissions for Refineries as Reported in the 1999 NEI	10
Table 6. Comparison of 1997 and 2000 TRI Emissions for Refineries	11
Table 7. Summary of VOC Emission by SIC Code.....	13
Table 8. Facilities with >50 Tons/Year of VOC.....	15

FIGURES

	<u>Page</u>
Figure 1. Refineries in the Mid-Atlantic States	4
Figure 2. Trends in Refinery Production along the East Coast.....	7
Figure 3. Relative Importance of VOC Emissions by Petroleum Industry Category	14

INTRODUCTION

A recent MARAMA-sponsored investigation of VOC emissions and ambient monitoring data concluded that (1) petroleum refineries are a significant source of VOC in the PA-NJ-DE-MD ozone non-attainment areas, and (2) VOC emissions estimates from petroleum refineries, and possibly other petroleum industry facilities, have a large potential to be underestimated. The purpose of this project is to lay the groundwork for developing an improved regional emissions inventory for petroleum industry VOC emissions. This project entails a detailed comparison of member states' source identification and VOC emissions estimation methods.

In this Memorandum, we identify petroleum industry facilities in the MARAMA states (District of Columbia, Delaware, Maryland, New Jersey, North Carolina, Pennsylvania, Virginia, West Virginia), and New York. Petroleum industry facilities are defined using the following North American Industry Classification System (NAICS) and corresponding Standard Industrial Classification (SIC) codes to identify facilities of interest:

NAICS Code	SIC Code	Description
324110	2911	Petroleum Refineries
324121	2951	Asphalt Paving Mixture and Block Manufacturing
324122	2952	Asphalt Shingle and Coating Materials Manufacturing
324191	2992	Petroleum Lubricating Oil and Grease Manufacturing
324199	2999	All Other Petroleum and Coal Products
493190	4226	Special Warehousing and Storage (Petroleum Bulk Stations and Terminals for Hire)
488320	4491	Marine Cargo Handling
488390	4499	Water Transportation Services (Lighterage)
486110	4612	Pipeline Transportation of Crude Oil
486910	4613	Pipeline Transportation of Refined Petroleum Products
422710	5171	Petroleum Bulk Stations, Terminals and Product Wholesalers
422720	5172	Petroleum Product Wholesalers, except Bulk Stations and Terminals

We used the following databases to identify facilities of concern:

- Energy Information Administration reports and databases
- EPA's Toxic Release Inventory
- EPA's 1996 Criteria and 1999 Criteria and HAP National Emission Inventory
- 1997 MARAMA Regional VOC Emission Inventory
- State and local agency 2000/2001 Emission Inventories

The first part of this memorandum summarizes and analyzes available information about petroleum refineries. The second part discusses other petroleum industry sources.

IDENTIFICATION OF PETROLEUM REFINERIES

Table 1 identifies the petroleum refineries located in the mid-Atlantic region. The data in the table are based primarily on information from the *Petroleum Supply Annual*¹ published by the Energy Information Agency (EIA). According to the EIA, modest growth in product demand and volatile crude oil prices caused a wave of joint ventures, mergers, and restructuring of the U.S. petroleum industry during the latter part of the 1990's. To facilitate the identification of petroleum refineries, Table 1 lists both the current name of the refinery and recent name changes, refinery sales, shutdowns, and reactivations.

Refinery Locations

Figure 1 shows the locations of the petroleum refineries based on the latitude/longitude provided in EPA's 2000 Toxic Release Inventory². Seven petroleum refineries are clustered along the Delaware River in the Philadelphia metropolitan area. A second group of three refineries is located in New Jersey along the Arthur Kill River adjacent to New York City. There are two refineries in northwestern Pennsylvania, one refinery in tidewater Virginia, and one refinery in the West Virginia panhandle. Note that there are no petroleum refineries in the District of Columbia, Maryland, New York, and North Carolina.

Refinery Capacity Data

Table 2 shows refinery capacity data³ by type of process as of January 1, 2002. The data show that no two refineries are alike. They differ in size and by the type of separation, conversion, and treatment processes located at each refinery. The refining operations at a particular refinery are determined by the composition of the crude oil received and the chosen slate of commodities produced. EIA data (not presented here) also show that total production capacity has increased very little over the past few years.

Refinery Production Data

Refineries also differ in the type of end product produced. Production data by individual refinery is not available because of confidentiality issues. The EIA withholds production data for individual refineries to avoid disclosure of individual company data.

EIA does publish production data⁴ grouped by geographic region. Figure 2 and Table 3 summarize production data for the East Coast District, which includes all refineries in the MARAMA states listed in Table 1 plus two small refineries in Georgia. The EIA data shows that both the total production and the relative mix of commodities produced by East Coast refineries do not fluctuate greatly from year to year. However, two trends are apparent: (1) gasoline production has increased by about 19% from 1995 to 2001; and (2) production of low sulfur distillate oil has increased by 52% from 1995 to 2001, while higher sulfur distillate oil has decreased slightly.

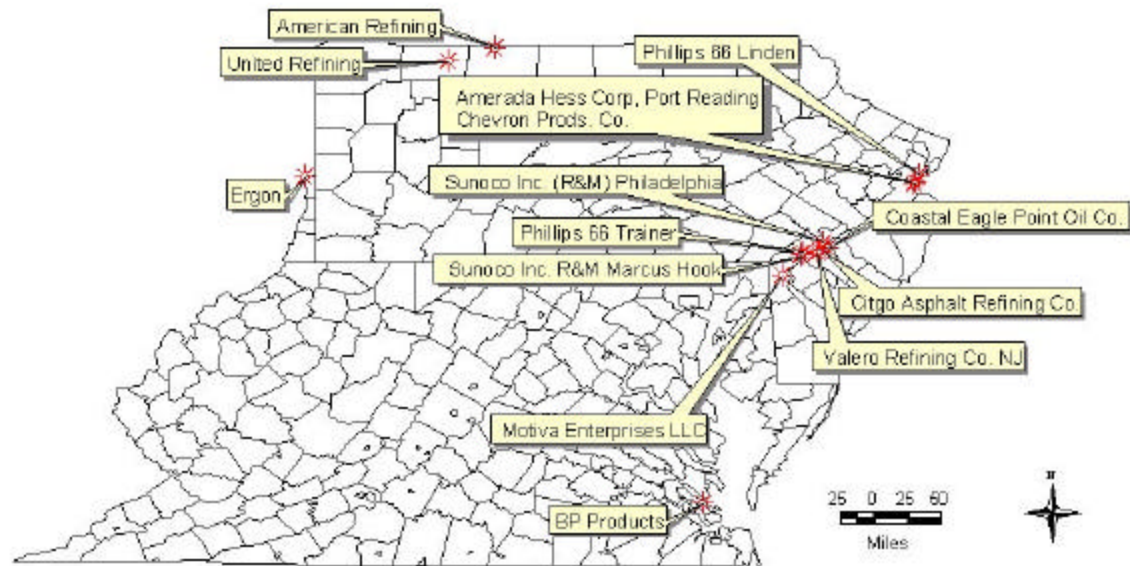
TABLE 1 - PETROLEUM REFINERIES IN THE MID-ATLANTIC STATES

State	County	Facility Name/Location	Refinery Sales, Shutdowns, Reactivations, and Name Changes
DE	New Castle	Motiva Enterprises LLC Delaware City	7/98 bought from Star Enterprise Formerly Texaco?
NJ	Middlesex	Amerada Hess Corp. Port Reading	
NJ	Middlesex	Chevron U.S.A. Inc. Perth Amboy	
NJ	Gloucester	Citgo Asphalt Refining Co. Paulsboro	
NJ	Gloucester	El Paso Corp/Coastal Eagle Point Oil Westville	1/01 bought from Coastal Corp.
NJ	Gloucester	Valero Refining Co. Paulsboro	10/98 bought from Mobil Oil Corp
NJ	Union	Conoco Phillips Linden (Bayway)	9/01 bought from Tosco Refining Co. Pre-1995 - Bayway Refining Corp Formerly Exxon?
PA	McKean	American Refining Group Inc. Bradford	4/97 bought from Witco Corp.
PA	Delaware	Phillips 66 Co. Trainer	9/01 bought from Tosco Refining Co (Bayway Refining). 1997 reactivated 2/96 bought from BP Oil and shutdown
PA	Delaware	Sunoco Inc. Marcus Hook	
PA	Philadelphia	Sunoco Inc. (R&M) Philadelphia	1994 bought adjacent refinery from Chevron and integrated two refineries into one facility 1988 bought from Atlantic Refining
PA	Warren	United Refining Co. Warren	
VA	York	BP Products North America, Inc. Yorktown	12/98 bought from Amoco Corp. USA
WV	Hancock	Ergon West Virginia Inc. Newell (Congo)	7/97 bought from Quaker State Corp.

Notes:

1. There are no refineries in New York, Maryland, North Carolina, and the District of Columbia.
2. EIA used to consider two additional facilities in Pennsylvania as refineries – Allied Signal in McKean County and Calumet Lubricants in Venango County. These facilities make specialty lubricants, waxes, and additives. PADEP does not consider these facilities to be refineries.

Figure 1. Refineries in the Mid-Atlantic



Source: 2000 Toxic Release Inventory

**TABLE 2 – CAPACITY BY TYPE OF PROCESS AS OF JANUARY 1, 2002
(Barrels per Stream Day)**

State	Refinery/Location	Atmospheric Distillation	Vacuum Distillation	Thermal Cracking	Catalytic Cracking	Catalytic Hydrocracking	Catalytic Reforming	Catalytic Hydrotreating	Fuels/Solvents Deasphalting
DE	Motiva Enterprises Delaware City	185,000 ^a	102,000	54,000 ^a	82,000 ^a	20,000	44,100 ^a	132,700	0
NJ	Amerada Hess Port Reading	0	0	0	62,500	0	0	0	0
NJ	Chevron Products Perth Amboy	83,000 ^b	47,000	0	0	0	0	0	0
NJ	Citgo Asphalt Refining Paulsboro	30,500 ^b	40,000	0	0	0	0	0	0
NJ	Coastal Eagle Point Oil Westville	146,000	49,000	0	55,000	0	30,000	59,000	0
NJ	Phillips 66 Linden	263,000	65,000	0	145,000	0	29,000	160,000	21,000
NJ	Valero Refining Paulsboro	172,600	87,000	24,500	54,000	0	24,000	90,500	0
PA	American Refining Bradford	10,500	0	0	0	0	1,800	3,330	0
PA	Calumet Lubricants ^c Rouseville	0	0	0	0	0	0	0	0
PA	Phillips 66 Trainer	190,000	73,000	0	52,000	22,000	50,000	136,000	0
PA	Sunoco Inc. Marcus Hook	185,000	36,000	0	105,000	0	20,000	85,000	0
PA	Sunoco Inc. Philadelphia	355,000	160,000	0	118,500	0	86,000	191,000	0
PA	United Refining Co. Warren	68,000	31,000	0	26,000	0	14,000	45,000	0
VA	BP Products Yorktown	61,800	37,300	19,000	30,200	0	12,100	30,860	0
WV	Ergon Newell	20,000	8,600	0	0	0	3,400	10,300	0

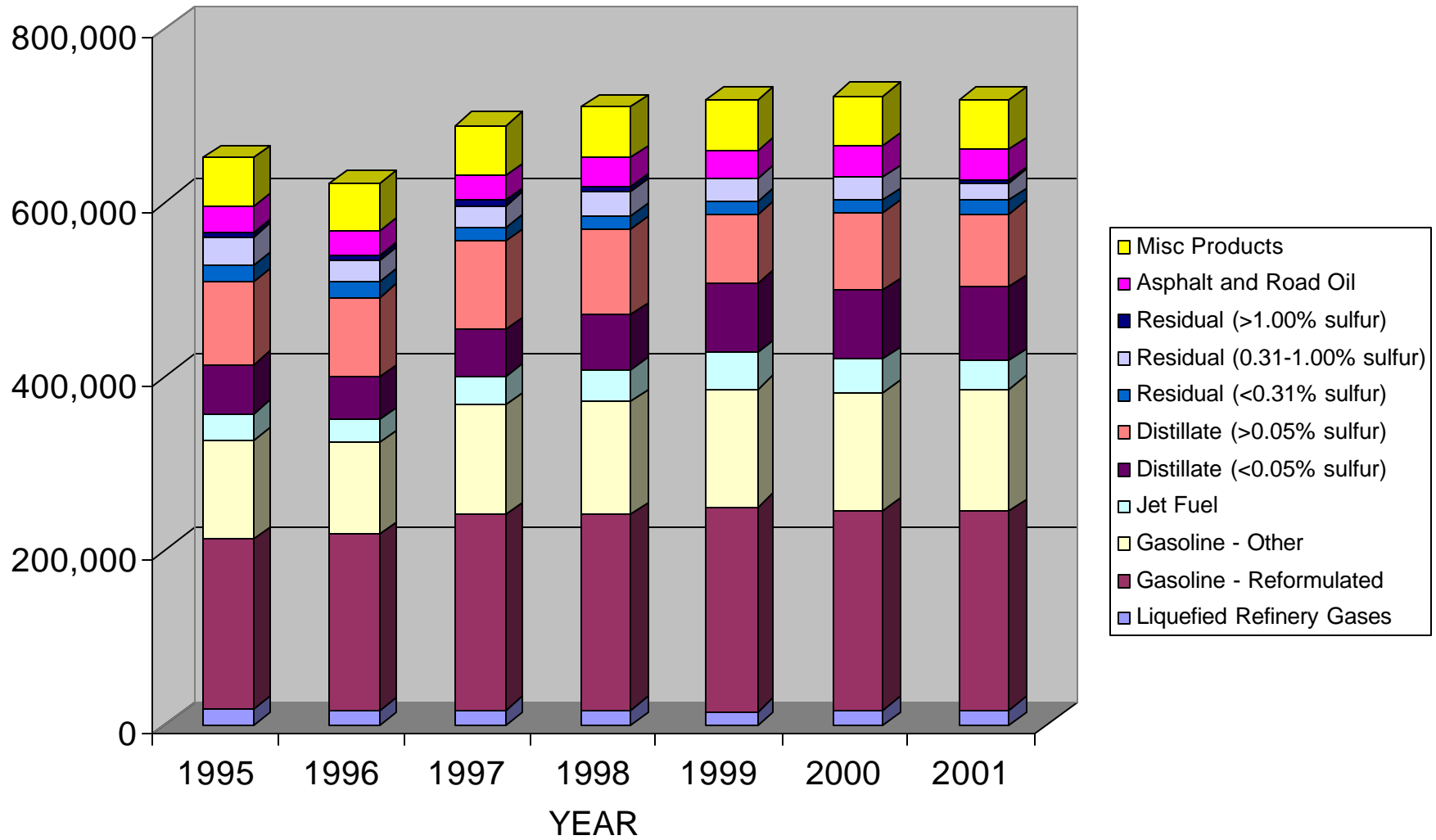
- a) Capacity data provided by Bruce Steltzer, DNREC, based on Title V permit application.
b) Distillation units were completely idle but not permanently shutdown.
c) Refinery operations shutdown beginning June 2000.
d) A "0" capacity indicates that the petroleum refinery does not use this particular process.

**TABLE 3 – TRENDS IN REFINERY PRODUCTION OF FINISHED PETROLEUM PRODUCTS
EAST COAST DISTRICT^a
(Thousand Barrels)**

Commodity	1995	1996	1997	1998	1999	2000	2001
Liquefied Refinery Gases (ethane, propane, butane, isobutane)	17,330	15,761	16,993	16,836	15,092	16,619	16,871
Gasoline – Reformulated	195,023	203,195	224,012	223,823	234,759	229,441	228,030
Gasoline – Oxygenated	1,727	-	8	2	356	-	722
Gasoline – Other	113,804	105,522	126,110	130,567	136,293	134,859	140,998
Jet Fuel	31,487	26,291	33,116	36,397	41,692	38,149	30,831
Distillate (<0.05% sulfur)	56,206	47,671	54,063	61,775	78,397	79,897	85,664
Distillate (>0.05% sulfur)	94,949	92,754	100,708	99,314	79,021	88,271	84,445
Residual (<0.31% sulfur)	19,300	17,532	16,794	15,100	15,504	15,117	15,350
Residual (0.31-1.00% sulfur)	31,890	23,749	25,134	27,927	26,245	25,999	20,570
Residual (>1.00% sulfur)	4,931	5,862	4,490	6,777	-2,663 ^b	-364 ^b	2,553
Asphalt and Road Oil	31,375	28,903	28,867	31,711	32,594	36,689	35,063
Misc Products (kerosene, petroleum coke, naphthas, lubricants, waxes)	54,048	54,962	57,837	59,085	58,170	56,998	57,266
Total	652,070	622,202	688,132	709,314	715,460	721,675	718,363

- a) The Energy Information Administration withholds production data for individual refineries to avoid disclosure of individual company data. Production data for the East Coast District includes all refineries in the MARAMA states listed in Table 1 plus two small refineries in Georgia.
- b) Negative production will occur when the amount of a product produced during the year is less than the amount of the same product that is reprocessed or reclassified to become another product during the same year.

**Figure 2. Trends in Refinery Production along the East Coast
(Thousand Barrels)**



Refinery Emission Data

Emissions data for petroleum refineries are available from several sources, including:

- Recent Agency Inventories⁵. Most recent inventory available and provided directly by the State and local agencies for this project (DNREC – 2001 for Motiva and Maritrans, 1999 for all other sources; NJDEP – 2001; PADEP – 2000; PAMS – 2000).
- 1997 MARAMA Regional VOC Emission Inventory⁶. Inventory developed for regional ozone modeling in the Northeast. Based on the 1997 NEI inventory supplemented with data supplied by MARAMA and NESCAUM states.
- EPA's 1996 Criteria⁷ and 1999 Criteria⁸ and HAP⁹ National Emission Inventory. Provides process emissions for VOC and individual HAPs.
- EPA's Toxic Release Inventory¹⁰. Provides facility-level emissions as reported by industry, categorized as either stack or fugitive emissions for toxic VOCs such as benzene, toluene, xylene, and MTBE. Not all VOC's are required to be reported. For example, pentanes and butanes make up a significant portion of gasoline vapors, but these compounds are not required to be reported under the TRI program.

Table 4 summarizes air emissions reported in the national, regional, and state/local VOC emission inventories. Important observations include

- There is considerable variation in emissions from refinery to refinery. These variations do not appear to be directly correlated with the refinery capacities shown in Table 1. For example, the BP refinery in Yorktown ranks relatively small in terms of capacity, but ranks relatively high in terms of VOC emissions.
- A few refineries show rather large changes in emissions. The BP Yorktown and Sunoco Philadelphia facilities show large emission decreases from 1996 to 1999, while the Ergon West Virginia facility shows a large increase.
- In New Jersey, the EPA 1996 and 1999 inventories appear to use older plant identifiers and emissions data (possibly grown from 1990 estimates). New Jersey provided updated information for the 1997 MARAMA inventory, including new plant identifiers and emissions that differ significantly from those reported in the EPA 1996 and 1999 NEI.

The reason(s) for these and other variations will be examined in later tasks.

Table 5 summarized HAP emissions from refineries as reported in the draft Version 3 of the 1999 NEI for HAPs. The NEI for HAPs contains a mixture of State-supplied data, data from EPA's MACT standard development files, and the TRI.

Table 6 summarizes air emissions as reported by the petroleum refineries. Two reporting years are shown – 1997 and 2000. Table 6 shows that the types and amounts of specific toxic VOC species vary from refinery to refinery and from year to year. For example, MTBE emissions at the Motiva refinery increased from 18 tons in 1997 to 136 tons in 2000. Another example is the Phillips 66 Linden refinery, where propylene emissions increased from 50 to 138 tons per year. The emissions reported by industry in the TRI in some cases differ significantly from the emissions in the EPA's NEI. For example, toluene emissions from Motiva are reported as 67.5 tons per year in the NEI, but only 3 tons per year in the TRI. Again, the reason for these and other variations will be examined in later tasks.

TABLE 4 – COMPARISON OF REFINERY VOC EMISSIONS

State	Current Name/Former Name(s)	PLANT ID	1996 NET	1997 MARAMA	1999 NEI	Recent State
DE	Motiva Enterprises, Delaware City Star Enterprise	10-003-0016	1,484	1,342	1,521	690
NJ	Amerada Hess, Port Reading	34-023-17996 34-023-15652	485	263	377	370
NJ	Chevron Prods, Perth Amboy	34-023-18058 34-023-15023	37	270	32	537
NJ	Citgo Asphalt Refining, Paulsboro	34-015-55831	0	231	0	42
NJ	Coastal Eagle Point Oil, Westville	34-015-55781 34-015-55004	1,340	826	1,356	801
NJ	Phillips 66, Linden Bayway Refining, Exxon	34-039-41805 34-039-40003	2,313	3,521	2,159	1,712
NJ	Valero Refining, Paulsboro Mobil Oil	34-015-55829 34-015-55006	1,341	654	1,229	846
PA	American Refining, Bradford Witco	42-083-0004 22-2318612-2	154	160	0 ^a	137
PA	Phillips 66, Trainer Bayway Refining	42-045-0030 06-1331906-1	232	241	258	290
PA	Sunoco Inc. R&M, Marcus Hook	42-045-0025 23-1743283-12	828	862	393	376
PA	Sunoco Inc R&M, Philadelphia	42-101-1501	1,487	1,550	518	629
PA	United Refining Co., Warren	42-123-0003 25-1411751-1	1,085	1,133	1,639	1,012
VA	BP Products, Yorktown	51-199-0004	2,012	2,092	1,180	1,180
WV	Ergon, Newell Quaker State	54-029-0008	19	492	247	247
Total for Petroleum Refineries			13,340	14,184	11,236	8,869

- a) VOC emissions for American Refining are missing from 1999 NEI; emission estimates are present for other pollutants.
- b) Not shown above are several facilities that were classified under SIC code 2911 in the EPA/MARAMA databases that are not refineries. They are either storage facilities or chemical plants. These facilities will be listed in the second part of this memorandum as “other petroleum industry” facilities.

Data Sources:

1996 NET - EPA’s 1996 National Emission Trends Inventory, data for this report were extracted from the October 2001 version of the NET database.

1997 MARAMA – Inventory developed regional ozone modeling in the Northeast. Based on the 1997 NET inventory supplemented with data supplied by MARAMA and NESCAUM states.

1999 NEI - EPA’s 1999 National Emission Inventory, data for this report were extracted from Version 2 Final of the Criteria Pollutant inventory.

Recent State – Recent inventories provided directly by the State and local agencies for this project.

(DNREC – 2001 for Motiva and Maritrans, 1999 for all other sources; NJDEP – 2001; PADEP – 2000; PAMS – 2000).

TABLE 5 – HAP EMISSIONS (tons/year) FOR REFINERIES AS REPORTED IN THE 1999 NEI

State	Refiner/ NTI Unique ID	1,3 Butadiene	2,2,4 Trimethyl pentane	Benzene	Ethyl Benzene	Hexane	MEK	MTBE	Toluene	Xylenes	Sum of 188
DE	Motiva Enterprises NTI26218	3.6	68.1	31.6	14.4	59.6	8.8	43.1	67.5	60.4	541
NJ	Amerada Hess, Port Reading NTI34872	0.0	10.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	21
NJ	Chevron Prods, Perth Amboy NTI34873	1.6	24.6	12.7	4.8	20.6	2.7	8.9	24.0	1.9	127
NJ	Citgo Asphalt Refining, Paulsboro NTI34863	1.6	24.6	12.6	4.8	20.9	2.9	9.0	24.0	19.9	127
NJ	Coastal Eagle Point Oil, Westville NTI34862	3.0	65.1	32.5	14.7	53.2	7.8	17.6	75.6	64.1	382
NJ	Phillips 66, Linden NTI6375	5.0	73.9	29.9	13.6	71.4	0.3	25.5	66.7	58.7	419
NJ	Valero Refining, Paulsboro NTI6403	3.1	56.0	0.0	0.0	0.0	7.7	0.0	0.0	0.0	95
PA	American Refining, Bradford NTI44764	0.2	18.7	5.5	3.3	11.6	0.4	3.0	14.2	13.0	82
PA	Phillips 66, Trainer NTI113	3.6	61.2	24.5	11.3	56.0	10.5	19.9	54.7	48.0	468
PA	Sunoco Inc. R&M, Marcus Hook NTI109	3.5	67.3	36.3	16.0	57.1	8.9	19.2	83.8	70.4	400
PA	Sunoco Inc R&M, Philadelphia NTI40723/NTI40724	0.4 6.6	1.8 107.7	14.9 47.3	6.2 22.0	4.5 98.8	0.0 18.4	6.5 33.3	9.1 110.4	6.1 95.8	78 591
PA	United Refining Co., Warren NTI40732	1.3	42.5	15.8	7.7	31.1	3.2	10.3	20.2	35.6	259
VA	BP Products, Yorktown NTI42309	1.2	38.9	14.8	7.1	29.1	3.4	10.0	33.0	28.9	191
WV	Ergon, Newell NTI46752	0.2	0.2	0.5	0.0	0.6	3.8	4.3	9.5	0.1	28

- a) Sum of 188 includes all HAPs, both organic and inorganic.
b) NTI lists the Sunoco Philadelphia refinery with two unique ID numbers.

TABLE 6 – COMPARISON OF 1997 AND 2000 TRI EMISSIONS (tons/year) FOR REFINERIES

State	Refiner/TRI ID	Toluene		Propylene		Xylene		MTBE		MEK		Benzene		Other Organics ^a		Total Organics ^b	
		1997	2000	1997	2000	1997	2000	1997	2000	1997	2000	1997	2000	1997	2000	1997	2000
DE	Motiva Enterprises 19706-TXCDL-2000W	4	3	3	1	3	3	18	136	-	-	3	5	12	23	42	170
NJ	Amerada Hess, Port Reading 07064-MRDHS-750CL and 07064-SCNDR-CLIFF	3	3	1	1	1	2	29	18	-	-	1	1	39	7	75	32
NJ	Chevron Prods, Perth Amboy 08861-CHVRN-1200S	3	7	-	-	3	7	-	-	-	-	3	4	10	27	18	45
NJ	Citgo Asphalt Refining, Paulsboro 08066-SVWLC-4PARA	-	<1	-	-	-	<1	-	-	-	-	<1	<1	-	<1	<1	1
NJ	Coastal Eagle Point Oil, Westville 08093-CSTLG-RTES1	28	12	2	1	22	12	52	23	-	-	15	12	39	35	158	94
NJ	Phillips 66, Linden 07036-XXN -1400P	-	35	50	138	-	36	37	59	-	-	-	16	32	84	119	367
NJ	Valero Refining, Paulsboro 08066-MBLLC-BILLI	15	8	1	<1	12	12	4	15	-	-	6	4	19	17	57	56
PA	American Refining, Bradford 16701-KNDLL-77NKE	13	30	-	-	3	3	<1	-	48	74	<1	<1	4	4	67	111
PA	Phillips 66, Trainer 19061-BPLCM-POSTR	7	3	<1	20	5	6	9	7	-	-	4	1	6	9	32	46
PA	Sunoco Inc. R&M, Marcus Hook 19061-SNRFN-GREEN	21	22	19	3	4	2	15	13	-	-	4	5	30	24	93	68
PA	Sunoco Inc R&M, Philadelphia 19145-TLNTC-3144P	16	14	5	4	17	14	28	12	-	-	23	20	50	40	139	104
PA	United Refining Co., Warren 16365-NTDRF-POBOX	5	3	26	14	2	1	1	1	-	-	5	3	34	27	74	48
VA	BP Products, Yorktown 23692-MCLCM-2201G	45	2	6	3	35	2	40	16	-	-	9	2	53	13	187	36
WV	Ergon, Newell 26050-RGNWS-STATE	9	13	-	-	1	<1	-	-	24	52	<1	1	1	2	36	69

a) Other organics include compounds such as methanol, hexane, ethylene, cyclohexane, ethylbenzene, and other compounds.

b) Total organics includes only those VOCs that are required to be reported to the TRI.

IDENTIFICATION OF OTHER PETROLEUM INDUSTRY SOURCES

In addition to petroleum refineries, there are several other types of industrial facilities associated with the petroleum industry. We identified other petroleum industry sources using the 1997 MARAMA Regional Inventory, the EPA's 1999 NEI for HAPs, the 1999 NEI for Criteria Pollutants, the 2000 Toxics Release Inventory, and recent State/local agency databases. Note that commercial establishments, such as gasoline service stations, are not included in this analysis.

We prepared Table 7 to summarize each segment of the industry in terms of the number of facilities and emissions. For each SIC grouping, Table 7 shows the number of facilities, total VOC emissions reported in the 1997 MARAMA inventory, and total VOC emissions reported in the 1999 NEI.

Figure 3 is a graphical representation of the data contained in Table 7. The figure shows the relative importance of each petroleum industry source category, which varies somewhat for the three inventories.

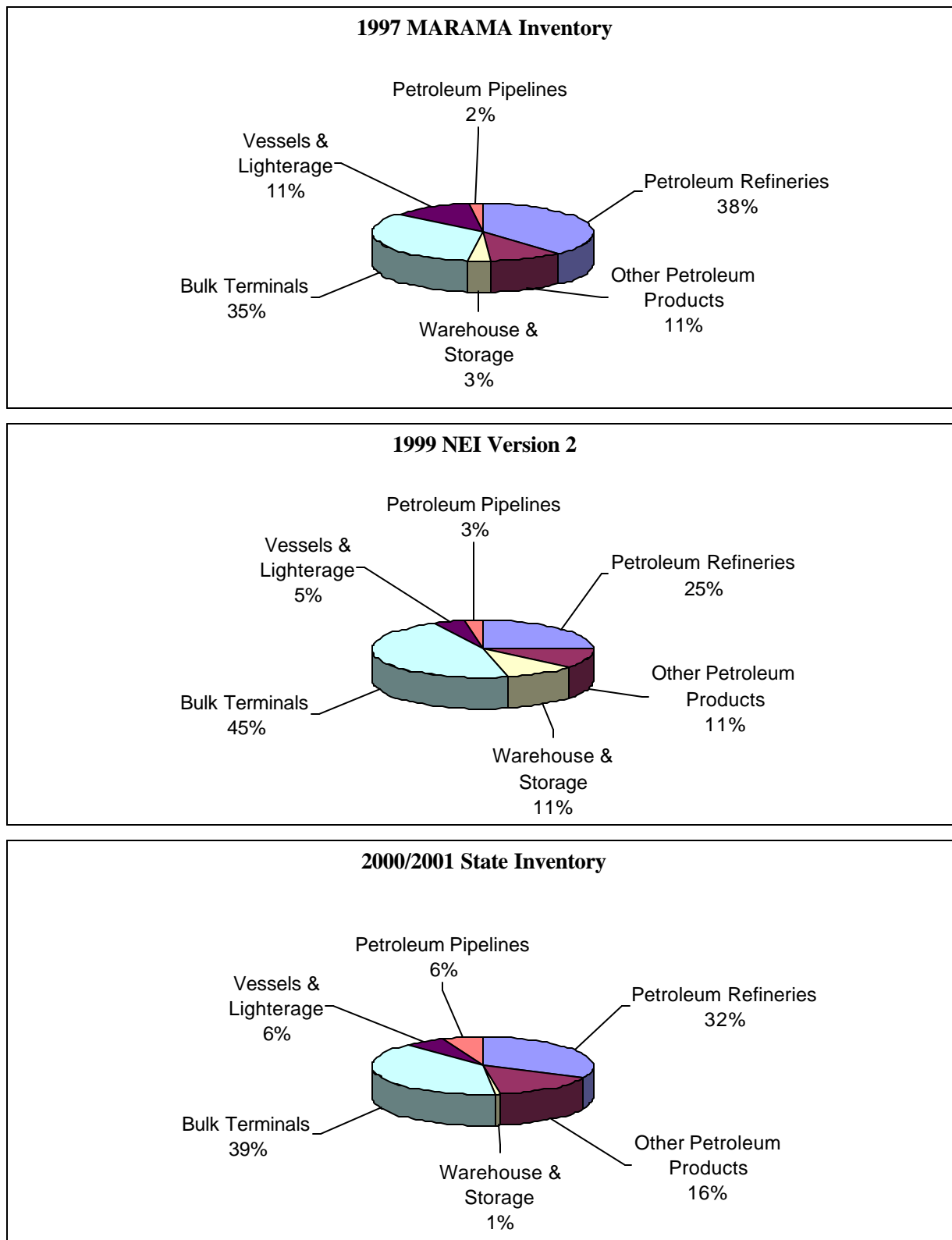
We prepared Table 8 to identify an initial list of facilities of potential interest for further study. Table 8 lists all facilities that have emissions greater than 40 tons per year, as reported in either the 1997 MARAMA inventory or 1999 NEI. Table 8 also provides an indication as to whether the facility is included in any of four databases: the 2000 TRI, the 1999 NEI for HAPS, the 1997 MARAMA inventory, and the 1999 NEI for Criteria Pollutants.

**TABLE 7 – SUMMARY OF VOC EMISSIONS (tons/year) BY SIC CODE
(FOR DC, DE, MD, NJ, NY, PA, VA, WV)**

NAICS	SIC	Description	Number of Facilities^a	1997 MARAMA	1999 NEI	Most Recent^a
324110	2911	Petroleum Refineries	14	14,184	11,236	8,869
		Facilities likely misclassified using SIC 2911 Refineries	6	795	298	281
324121	2951	Asphalt Paving Mixture and Block Manufacturing	259	535	1,132 ^b	497
324122	2952	Asphalt Shingle and Coating Materials Manufacturing	21	204	534	168
324191	2992	Petroleum Lubricating Oil and Grease Manufacturing	25	1,351 ^c	1,385 ^c	1,683
324199	2999	All Other Petroleum and Coal Products	24	1,824	1,999	1,981
	4226	Special Warehousing and Storage	24	1,196	4,910 ^d	169
488320	4491	Marine Cargo Handling	6	2,442 ^e	795	39
488390	4499	Water Transportation Services (Lighterage)	1	1,687	1,362	1,635
486110	4612	Pipeline Transportation of Crude Oil	3	23	41	44
486910	4613	Pipeline Transportation of Refined Petroleum Products	27	735	1,148	1,573
422710	5171	Petroleum Bulk Stations, Terminals and Wholesalers	389	12,738 ^f	20,676	10,941
422720	5172	Petroleum Wholesalers, except Bulk Stations/Terminals	11	108	346	165
		Totals	810	37,822	45,861	28,045

- a) Recent inventories provided directly by the State and local agencies for this project (DNREC – 2001 for Motiva and Maritrans, 1999 for all other sources; NJDEP – 2001; PADEP – 2000; PAMS – 2000). . All other States are based on 1999 NEI.
- b) Most of the difference between 1997 and 1999 is caused by two large sources in New Jersey (Desorte Associates 376 tpy in Camden County and Witco Chemical 283 tpy in Middlesex County) that are in the 1999 NEI but not in the 1997 MARAMA or 2001 NJDEP inventory.
- c) Over 90% of this total is from two facilities (Alox Corp, Niagara, NY and Calumet Lubricants, Rouseville, PA)
- d) Most of the difference between 1997 and 1999 is caused by a large source in New Jersey (Northville Linden Terminal 3,119 tpy in Union County) that is in the 1999 NEI but not in the 1997 MARAMA or 2001 NJDEP inventory.
- e) Over 90% of this total is from one facility (Marathon Ashland Petroleum 2,248 tpy in Wayne County, WV)
- f) Most of the difference between 1997 and 1999 is caused by three large sources in New Jersey (Sun 3,263 tpy in Essex County, IMTT Bayonne 3,476 tpy in Hudson County, and BP Oil 767 tpy in Union County) that is in the 1999 NEI but not in the 1997 MARAMA or 2001 NJ DEP inventory.

Figure 3. Relative Importance of VOC Emissions by Petroleum Industry Source Category



**TABLE 8 – FACILITIES WITH > 50 TONS/YEAR OF VOC AS REPORTED IN
THE 1997 MARAMA, 1999 NEI, AND RECENT STATE INVENTORY**

State	County	Facility Name	1997 VOC (TPY)	1999 VOC (TPY)	RECENT (TPY)
SIC 2911 – PETROLEUM REFINERIES					
DE	New Castle	MOTIVA ENTERPRISES, LLC	1,341.6	1,521.0	690.0
NJ	Gloucester	CITGO ASPHALT REFINING COMPANY	231.1		42.1
NJ	Gloucester	COASTAL EAGLE POINT OIL COMPANY	825.9	1,356.2	801.1
NJ	Gloucester	VALERO REFINING (MOBIL OIL CORP)	653.6	1,229.2	846.0
NJ	Middlesex	AMERADA HESS (PORT READING) CORPORATION	262.9	376.6	369.9
NJ	Middlesex	CHEVRON PRODUCTS COMPANY	270.2	32.4	536.8
NJ	Union	PHILLIPS 66 (BAYWAY REFINING, EXXON)	3,521.0	2,158.6	1712.0
PA	Delaware	PHILLIPS 66 (BAYWAY REFINING, TOSCO)	241.2	258.3	290.0
PA	Delaware	SUN CO INC (MARCUS HOOK REFINERY)	862.3	393.3	375.9
PA	McKean	AMERICAN REFINING (WITCO CHEM CORP)	160.4		137.0
PA	Philadelphia	SUN COMPANY, INC.	1,550.0	518.6	629.0
PA	Warren	UNITED REFINING CO	1,132.9	1,639.0	1,012.0
VA	York	AMOCO PETROLEUM PRODUCTS, REFINING BG	2,092.1	1,179.7	1,179.7
WV	Hancock	ERGON (QUAKER STATE CORP)	492.3	246.9	246.9
SIC 2911 – FACILITIES LIKELY MISCLASSIFIED					
NJ	Gloucester	MOBIL RESEARCH & DEVELOPMENT C		75.0	15.7
NJ	Gloucester	PETROLEUM RECYCLING, INC.		63.2	
WV	Pleasants	ST. MARYS REFINING COMPANY, INC.	119.9	144.7	144.7
WV	Wetzel	CNG - HASTINGS EXTRACTION PLANT	664.3		
SIC 2951 – ASPHALT PAVING MIXTURE AND BLOCK MANUFACTURING					
NJ	Camden	DESORTE, C. ASSOCIATES, INC.		375.7	
NJ	Middlesex	WITCO CHEMICAL CORPORATION		283.4	
WV	Harrison	CLARKSBURG ASPHALT	3.6	92.6	92.6
SIC 2952 – ASPHALT SHINGLE AND COATING MATERIALS MANUFACTURING					
NJ	Hudson	OWENS CORNING KEARNY ROOFING/ASPHALT	131.1		31.8
NJ	Hudson	TRUMBULL ASPHALT COMPANY		377.5	
SIC 2992 – PETROLEUM LUBRICATING OIL AND GREASE MANUFACTURING					
NJ	Gloucester	MOBIL OIL CORPORATION	2.0	75.0	49.7
NY	Niagara	ALOX CORP	1,310.8	1,282.0	1,282.0
PA	Venango	CALUMET LUBRICANTS (PENNZOIL PROD CO)	546.8	326.6	326.6
SIC 2999 – ALL OTHER PETROLEUM AND COAL PRODUCT MANUFACTURING					
NY	Onondaga	CITGO PETROLEUM SYRACUSE TERMINAL	133.4	124.1	124.1
NY	Onondaga	COASTAL OIL NEW YORK INC	93.5	87.1	87.1
NY	Onondaga	MOBIL OIL CORP - TERMINAL #31-009	80.5	75.0	75.0
NY	Oswego	AGWAY BREWERTON PETROLEUM TERMINAL	278.7	259.5	259.5
PA	Beaver	MARATHON ASHLAND PETROLEUM LLC	32.8	63.8	63.8
PA	Butler	PENRECO INC	528.1	271.1	271.1
PA	McKean	ALLIED SIGNAL (PETROWAX, HONEYWELL)	340.1	280.9	280.9
PA	Venango	PETROWAX PA INC	308.7	515.2	515.2
WV	Marshall	VENCO MOUNDSVILLE CALCINING PLANT	1.2	255.1	255.1

**TABLE 8 – FACILITIES WITH > 50 TONS/YEAR OF VOC AS REPORTED IN
THE 1997 MARAMA, 1999 NEI, AND RECENT STATE INVENTORY**

State	County	Facility Name	1997 VOC (TPY)	1999 VOC (TPY)	RECENT (TPY)
SIC 4226 – SPECIAL WAREHOUSING AND STORAGE					
NJ	Gloucester	GATX TERMINALS CORPORATION	234.6		
NJ	Hudson	IMTT-BAYONNE	232.1		
NJ	Hudson	POWELL DUFFRYN TERMINALS, INC	113.3	356.2	
NJ	Middlesex	GATX TERMINALS CORPORATION	397.7		
NJ	Middlesex	GATX TERMINALS CORPORATION		345.8	
NJ	Middlesex	MARCONA OCEAN INDUSTRIES, LTD.		896.5	
NJ	Middlesex	STOLTHAVEN PERTH AMBOY INC	133.3		
NJ	Union	NORTHVILLE LINDEN TERMINAL COR		3,119.1	
SIC 4491 – MARINE CARGO HANDLING					
NJ	Essex	STAR OIL		195.9	
NJ	Middlesex	ROYAL PETROLEUM		426.2	
PA	Delaware	SUNOCO INC (R&M)/HOG ISLAND TERMINAL	192.4	85.3	0.1
WV	Wayne	MARATHON ASHLAND PETROLEUM LLC	2,248.4	38.9	38.9
SIC 4499 – WATER TRANSPORTATION SERVICES (LIGHTERAGE)					
DE	Sussex	MARITRANS GP, INC.	1,686.9	1,361.8	1,635.0
SIC 4613 – PIPELINE TRANSPORTATION OF REFINED PETROLEUM PRODUCTS					
NJ	Gloucester	COLONIAL PIPELINE COMPANY	22.6	286.3	31.6
NJ	Union	BUCKEYE PIPE LINE COMPANY,L.P.	186.8	25.5	614.4
NY	Suffolk	EAST SETAUKET TERMINAL-TOSCO PIPELINECO	138.2	135.5	135.5
PA	Berks	SUN PIPE LINE CO	55.7	49.8	49.8
PA	Delaware	BUCKEYE PIPE LINE CO LP	143.1	63.7	103.4
PA	Lehigh	BUCKEYE PIPELINE CO	77.1	288.6	288.6
VA	Cumberland	COLONIAL PIPELINE CO-MITCHELL JUNCTION	22.7	76.7	76.7
SIC 5171 – PETROLEUM BULK STATIONS, TERMINALS, AND WHOLESALEERS					
MD	Baltimore City	AMERADA HESS TERMINAL	54.2	58.9	58.9
MD	Baltimore City	EXXON - TERMINAL	70.6		
MD	Baltimore City	MOTIVA TERMINAL	79.9	125.9	125.9
MD	Baltimore City	TOSCO/BAYWAY - BALTIMORE TERMINAL	70.8	17.3	17.3
MD	Wicomico	CATO - MARINE ROAD SEE 22-99	100.0		
NJ	Bergen	AMERADA HESS CORPORATION	15.2	440.3	1.3
NJ	Camden	AMERADA HESS CORPORATION	78.1	38.1	56.6
NJ	Camden	CITGO PETROLEUM CORPORATION	13.1	122.5	6.5
NJ	Essex	AMERADA HESS CORPORATION	15.7	641.8	16.1
NJ	Essex	BP MARINE AMERICAS	7.3		89.6
NJ	Essex	GETTY TERTMINALS CORPS.	30.0	310.6	
NJ	Essex	STAR ENTERPRISE	68.7	37.8	172.0
NJ	Essex	SUN COMPANY INC. (R&M)	70.2	3,263.1	36.2
NJ	Gloucester	B.P. OIL, INC.	15.3	99.9	
NJ	Gloucester	CUMBERLAND FARMS INC.		247.6	
NJ	Gloucester	GATX TERMINALS CORPORATION		273.4	
NJ	Gloucester	MOBIL OIL CORPORATION	52.9	112.5	
NJ	Hudson	IMTT-BAYONNE		3,476.8	
NJ	Middlesex	AMERADA HESS CORP	143.2		

**TABLE 8 – FACILITIES WITH > 50 TONS/YEAR OF VOC AS REPORTED IN
THE 1997 MARAMA, 1999 NEI, AND RECENT STATE INVENTORY**

State	County	Facility Name	1997 VOC (TPY)	1999 VOC (TPY)	RECENT (TPY)
SIC 5171 – PETROLEUM BULK STATIONS, TERMINALS, AND WHOLESALERS					
NJ	Middlesex	AMERADA HESS CORP	82.2	0.2	69.7
NJ	Middlesex	AMOCO OIL COMPANY	69.1		101.3
NJ	Middlesex	SHELL OIL PRODUCTS COMPANY	255.5	156.1	
NJ	Middlesex	SUN COMPANY, INC. (R&M)	44.2	78.8	17.1
NJ	Monmouth	GLOBE PETROLEUM INC.		62.9	
NJ	Union	B.P. OIL, INC.		766.8	
NJ	Union	CITGO PETROLEUM CORPORATION	143.3	444.1	135.2
NJ	Union	GULF OIL LIMITED PARTNERSHIP	50.1		25.3
NJ	Union	MOBIL OIL CORPORATION	77.2		68.4
NJ	Union	MOBIL OIL CORPORATION		186.7	
NJ	Union	NORTHVILLE INDUSTRIES CORP.	99.1		
NY	Albany	AGWAY ENERGY ALBANY TERMINAL	168.4	164.1	164.1
NY	Albany	CITGO PETROLEUM GLENMONT TERMINAL	231.5	225.7	225.7
NY	Albany	MOBIL OIL ALBANY TERMINAL #31-001	100.6	98.1	98.1
NY	Broome	AGWAY VESTAL TERMINAL	179.6	184.3	184.3
NY	Broome	AMERADA HESS VESTAL TERMINAL	67.8	69.5	69.5
NY	Chemung	GRIFFITH OIL CO INC- BIG FLATS TERMINAL	69.5	67.7	67.7
NY	Erie	NOCO ENERGY CORP	118.1	114.8	114.8
NY	Erie	SUN CO. TONAWANDA TERMINAL	168.6	164.3	164.3
NY	Kings	DITMAS TERMINAL - 364 MASPETH AVENUE	83.3	84.9	84.9
NY	Kings	METRO TERM -498 KINGSLAND AVE	112.2	113.2	113.2
NY	Kings	TEXACO NY CITY SALES TERMINAL	123.6	125.6	125.6
NY	Monroe	MOBIL OIL CORP ROCHESTER TERMINAL	72.7	72.6	72.6
NY	Monroe	SUN COMPANY ROCHESTER TERMINAL	76.1	76.0	76.0
NY	Nassau	CARBO-CONCORD OIL	339.6	331.7	331.7
NY	Nassau	COMMANDER OIL TERMINAL	62.4	88.1	88.1
NY	Nassau	GULF OIL OCEANSIDE TERMINAL	54.6	52.9	52.9
NY	Nassau	MOBIL OIL INWOOD TERMINAL	50.6	49.0	49.0
NY	Nassau	MOTIVA ENTERPRISES LLC, INWOOD MARKET	772.5	748.5	748.5
NY	Nassau	SUN OIL OCEANSIDE MARKETING TERMINAL	58.8	57.5	57.5
NY	Oneida	AGWAY PETROLEUM TERM - MARCY	254.7	248.3	248.3
NY	Onondaga	MOBIL TED PARK TERMINAL	88.4	90.7	90.7
NY	Onondaga	SUN COMPANY INC (R&M) - SYRACUSE	55.9	54.4	54.4
NY	Orange	COASTAL OIL NEWBURGH FACILITY	368.6	357.1	357.1
NY	Orange	WAREX TERMINALS CORP - SOUTH TERMINAL	91.8	86.6	86.6
NY	Rensselaer	AMERADA HESS RENSSELAER TERMINAL	181.4	174.4	174.4
NY	Rensselaer	GULF OIL RENSSELAER TERMINAL	76.3	72.5	72.5
NY	Rensselaer	PETROLEUM FUEL & TERMINAL RENSSELAER	98.4	95.9	95.9
NY	Rensselaer	TRANSMONTAIGNE-RENSSELAER TERMINAL	171.0	166.8	166.8
NY	Richmond	MOBIL OIL-4101 ARTHUR KILL RD	54.5	52.7	52.7
NY	Suffolk	HOLTSVILLE TERMINAL- TOSCO PIPELINE CO	1,668.9	1,616.7	1,616.7
PA	Allegheny	EXXON NEVILLE ISLAND MARKETING TERMINAL	63.7		
PA	Allegheny	EXXON NEVILLE ISLAND MARKETING TERM		68.4	68.4

**TABLE 8 – FACILITIES WITH > 50 TONS/YEAR OF VOC AS REPORTED IN
THE 1997 MARAMA, 1999 NEI, AND RECENT STATE INVENTORY**

State	County	Facility Name	1997 VOC (TPY)	1999 VOC (TPY)	RECENT (TPY)
SIC 5171 – PETROLEUM BULK STATIONS, TERMINALS, AND WHOLESALERS					
PA	Berks	ATLANTIC REF & MKT CORP	50.9	16.2	16.2
PA	Blair	ELDORADO PROP CORP	51.7	35.9	35.9
PA	Chester	MOBIL OIL CORP	51.6	36.9	36.1
PA	Chester	SUN CO INC	54.1	48.3	46.3
PA	Delaware	SUN CO INC (#2 TANK FARM)	54.5	47.9	60.8
PA	Delaware	SUN CO INC (TWIN OAKS)	185.0	40.2	42.7
PA	Philadelphia	AMERADA HESS	42.8	18.6	123.6
PA	Philadelphia	EXXON COMPANY, U. S. A.	271.3	69.5	66.73
PA	Philadelphia	SUN CO, INC (R & M) - BELMONT TERMINAL	152.2	75.0	75.78
PA	Philadelphia	SUN COMPANY SCHUYLKILL RIVER TANK FARM	307.8	169.7	111.86
VA	Bedford	CHEVRON PRODUCTS CO	59.3	46.0	46.0
VA	Chesapeake	AMERADA HESS CORP	50.5	8.9	8.9
VA	Fairfax	CITGO PETROLEUM CORP	78.9	30.9	30.9
VA	Fairfax	EXXON COMPANY USA	95.8	115.0	115.0
VA	Fairfax	OLD DOMINION TERMINAL LLC	70.5	28.5	28.5
VA	Fairfax	SHELL OIL CO	53.8	44.8	44.8
VA	Fairfax	STAR ENTERPRISE	82.3	33.9	33.9
VA	Prince William	MOBIL OIL CO	61.6	47.1	47.1
VA	Richmond City	CITGO PETROLEUM CORP	50.5	52.6	52.6
VA	Richmond City	EXXON USA	59.6	67.1	67.1
VA	Richmond City	KOCH REFINING CO.,L.P.	53.7	25.1	25.1
VA	Richmond City	PRIMARY CORPORATION (KINDER MORGAN)	52.2	18.9	18.9
VA	Roanoke	EXXON CO USA	71.9	82.8	82.8
WV	Kanawha	GO-MART, INC. AMANDAVILLE TERMINAL	18.2	308.4	308.4
SIC 5172 – PETROLEUM WHOLESALERS, EXCEPT BULK STATIONS AND TERMINALS					
MD	Carroll	COLONIAL PIPELINE COMPANY	67.2	165.3	165.3
NJ	Atlantic	CRESCENZO, WM., INC.		164.6	

REFERENCES

1. U.S. Department of Energy, Energy Information Administration. *Petroleum Supply Annual*. Yearly publications from 1995-2001 available at:
http://www.eia.doe.gov/oil_gas/petroleum/data_publications/petroleum_supply_annual/psa_volume1/psa_volume1.html
2. U.S. Environmental Protection Agency. Toxic Release Inventory databases for available at:
<http://www.epa.gov/tri/tridata/>
3. U.S. Department of Energy, Energy Information Administration. Data from Table 38 of 2001 *Petroleum Supply Annual*. See:
http://www.eia.doe.gov/pub/oil_gas/petroleum/data_publications/petroleum_supply_annual/psa_volume1/current/pdf/table_38.pdf
4. Refinery net production of finished products is summarized in Table 17 of the *Petroleum Supply Annual*.
5. Recent inventories provided directly by the State and local agencies for this project. (DNREC – 2001 for Motiva and Maritrans, 1999 for all other sources; NJDEP – 2001; PADEP – 2000; PAMS – 2000).
6. Mid-Atlantic Regional Air Management Agency. The 1997 inventory data is available at:
<http://www.marama.org/rtc/ozone/>
7. U.S. Environmental Protection Agency. The **AirData** Web site provides access to the 1996 emission inventory for the entire United States. See:
<http://www.epa.gov/air/data/reports.html>
8. U.S. Environmental Protection Agency. Final Version 2 National Emission Inventory for Criteria Pollutants (November 2002). See:
<ftp://ftp.epa.gov/pub/EmisInventory/finalnei99ver2/criteria/readmecritv2.pdf>
9. U.S. Environmental Protection Agency. Draft Version 3 National Emission Inventory for Hazardous Air Pollutants (September 2002). See:
ftp://ftp.epa.gov/EmisInventory/draftnei99ver3/haps/documentation/readme99ntiver3_sept2002.pdf
10. U.S. Environmental Protection Agency. Toxic Release Inventory databases for available at:
<http://www.epa.gov/tri/tridata/>

APPENDIX D

FINAL TECHNICAL MEMORANDUM #3

**IDENTIFICATION OF PETROLEUM INDUSTRY
EMISSION PROCESSES
IN DELAWARE, NEW JERSEY, AND SOUTHEASTERN PENNSYLVANIA**

REVISED FINAL TECHNICAL MEMORANDUM #3

**IDENTIFICATION OF PETROLEUM INDUSTRY
EMISSION PROCESSES
IN DELAWARE, NEW JERSEY, AND SOUTHEASTERN PENNSYLVANIA**

Prepared for:

Susan S.G. Wierman, Executive Director
Mid-Atlantic Regional Air Management Association (MARAMA)
711 W. 40th Street
Suite 318
Baltimore, MD 21211-2109

October 14, 2003
5925.003

Submitted by

Edward Sabo
MACTEC Federal Programs, Inc.
560 Herndon Parkway
Suite 200
Herndon, VA 20170
(703) 471-8383, FAX (703) 481-8296
EJSabo@mactec.com

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
PETROLEUM REFINERY EMISSION PROCESSES	1
NON-REFINERY PETROLEUM INDUSTRY EMISSION PROCESSES	15
REFERENCES	17

TABLES

	<u>Page</u>
Table 1. Comparison of VOC Emission by Refinery and Process	2
Table 2. Emission Processes for Motiva Enterprises, Delaware City.....	5
Table 3. Emission Processes for Sunoco, Marcus Hook	6
Table 4. Emission Processes for BP Oil, Trainer.....	7
Table 5. Emission Processes for Sunoco, Philadelphia	8
Table 6. Emission Processes for Citgo Asphalt, Paulsboro	9
Table 7. Emission Processes for Coastal Eagle Point, Westville	10
Table 8. Emission Processes for Valero Refining, Paulsboro	11
Table 9. Emission Processes for Amerada Hess, Port Reading	12
Table 10. Emission Processes for Chevron, Perth Amboy.....	13
Table 11. Emission Processes for Conoco Phillips, Linden	14
Table 12. Petroleum Industry Emission Processes	16

FIGURES

	<u>Page</u>
Figure 1. Comparison of VOC Emission by Refinery and Process.....	3

INTRODUCTION

A recent MARAMA-sponsored investigation of VOC emissions and ambient monitoring data concluded that (1) petroleum refineries are a significant source of VOC in the PA-NJ-DE-MD ozone non-attainment areas, and (2) VOC emissions estimates from petroleum refineries, and possibly other petroleum industry facilities, have a large potential to be underestimated. The purpose of this project is to lay the groundwork for developing an improved regional emissions inventory for petroleum industry VOC emissions. This project entails a detailed comparison of member states' source identification and VOC emissions estimation methods. In Technical Memorandum #2, we identify all petroleum industry facilities in the MARAMA states (District of Columbia, Delaware, Maryland, New Jersey, North Carolina, Pennsylvania, Virginia, West Virginia), and New York.

This report (Technical Memorandum #3) focuses on individual emission processes at the 10 refineries located in Delaware, New Jersey, and southeastern Pennsylvania. This report also summarizes the emission processes at other petroleum industry facilities in Delaware, New Jersey, and southeastern Pennsylvania (Bucks, Chester, Delaware, Montgomery, and Philadelphia counties). These data are based on recent agency inventories¹ provided directly by the State and local agencies for this project (DNREC – 2001 data for Motiva and Maritrans, 1999 data for all other sources; NJDEP – 2001 data; PADEP – 2000 data; PAMS – 2000 data).

PETROLEUM REFINERY EMISSION PROCESSES

Emission processes for each refinery are listed in this section. Table 1 compares VOC emission estimates for the 10 refineries located in Delaware, New Jersey, and southeastern Pennsylvania. The emissions are grouped into nine categories² of sources:

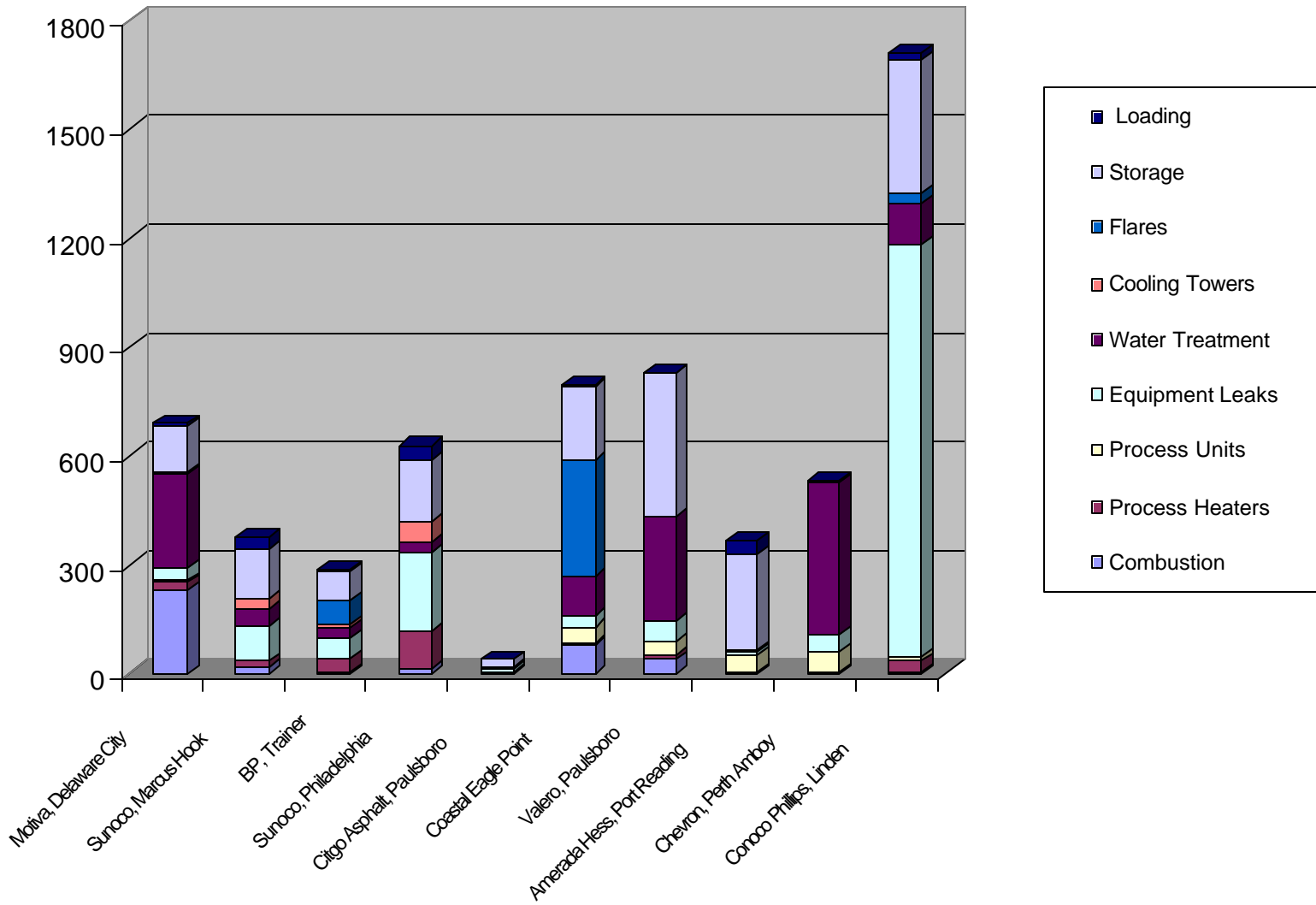
- **Combustion Sources.** Boilers are used to produce steam and to raise the temperature of feed materials to meet reaction or distillation requirements. Refinery fuels are typically residual oil, distillate oil, refinery gas, or natural gas. In addition to the typical refinery fuels, CO-rich regenerator flue gas also may be used as a fuel. Reciprocating engines are used to drive gas compressors and are usually fueled by natural gas or refinery gas. Gas turbines can fire a variety of fuels and are used as cogeneration units that produce electricity and steam for process needs.
- **Process Heaters.** Furnaces and process heaters are used throughout refineries to produce steam and to raise the temperature of feed materials to meet reaction or distillation requirements.
- **Process Units.** There are numerous separation, conversion, and treating processes that convert crude oil into end-products such as gasoline, fuel oils, and feedstocks for the petrochemical industry.
- **Process Equipment Leaks.** Emissions occur from process equipment whenever components in the liquid or gas stream leak. Components such as pumps, valves, pressure relief valves, and flanges are potential sources that can leak due to seal failure.

TABLE 1 – COMPARISON OF VOC EMISSIONS (tons/year) BY REFINERY AND PROCESS

Refinery	Combustion	Process Heaters	Process Units	Process Equipment Leaks	Water Treatment	Cooling Towers	Flares	Storage	Unloading & Loading	Plant Total
Motiva Delaware City	230	24	1 ^a	37	260	4	1	123	9	690
Sunoco Marcus Hook	16	18	<1	100	46	25	1	140	30	376
BP Trainer	3	40	3	53	28	8	67	84	4	290
Sunoco Philadelphia	14	103	<1	220	25	54	2	170	40	628
Citgo Asphalt Paulsboro	1	2	2	8	2	0 ^f	<1	25	<1	40 ^g
Coastal Eagle Point, Westville	81	7	42 ^b	31	111	0 ^f	315	205	6	798
Valero Paulsboro	40	12	39 ^c	57	282	0 ^f	<1	399	<1	829
Amerada Hess Port Reading	1	<1	53 ^d	6	1	0 ^f	6	261	40	370
Chevron Perth Amboy	1	<1	60 ^e	47	422	0 ^f	1	1	1	532
Conoco Phillips Linden	3	34	14	1,132	111	0 ^f	28	368	21	1,711
Totals	390	240	214	1,691	1,288	91	421	1,776	151	6,264

- a) The 1999 inventory included 149 tons/year from sulfur removal process. There were no emissions from this process in 2001.
- b) Includes 41 tons/year from FCCU catalyst regeneration process.
- c) Includes 32 tons/year from FCCU catalyst regeneration process.
- d) Includes 50 tons/year from FCCU catalyst regeneration process.
- e) Includes 60 tons/year from crude unit.
- f) Cooling tower emissions listed as an insignificant activity.
- g) VOC emissions from the Citgo Asphalt refinery are expected to be considerably lower than other refineries in the area. The Citgo refinery does not have any thermal or catalytic cracking capacity, and most of the product loading is of less volatile products such as #6 oil, kerosene, and heating oil.

Figure 1. Comparison of VOC Emissions (tons/year) by Refinery and Process



- **Wastewater Treatment.** All refineries employ some form of wastewater treatment prior to discharge to the environment or reuse in the refinery. Many of these collection and treatment system units are open to the atmosphere and allow organic-containing water to contact ambient air. Emission sources from wastewater collection and treatment systems include process drains and collectors, oil-water separators, air flotation systems, and surface impound basins and ponds.
- **Cooling Water Towers.** Refineries use large quantities of water for cooling throughout the refining process. Cooling towers are used to transfer heat from the cooling water to the atmosphere. Water that enters the tower may contain hydrocarbons from leaking equipment.
- **Flares.** Flares are commonly used for the disposal of waste gases during process upsets (e.g., start-up, shutdown) and emergencies.
- **Storage Vessels.** Storage vessels are used throughout the refining process to store crude oil and intermediate process feeds for cooling and further processing. Finished petroleum products are also kept in storage tanks before transport off-site. Tanks are equipped with either a fixed roof, an external floating roof, or an internal floating roof.
- **Loading Operations.** Crude oil is transported from production operations to a refinery by marine vessels (tankers and barges), rail tank cars, tank trucks, and pipelines. Refined petroleum products are conveyed to fuel marketing terminals and petrochemical industries by these same modes. Loading losses occur as organic vapors in empty cargo tanks are displaced to the atmosphere by the liquid being loaded into the tanks.

As shown in Table 1, emissions from process equipment leaks, wastewater treatment, and product storage tend to be the largest emitting source categories at each refinery. Within each source category, there is considerable variation in the magnitude of emissions from refinery to refinery. Also, the relative importance of each source category at a given refinery varies considerably from refinery to refinery. The reason(s) for these and other variations will be examined in later tasks.

Tables 2 through 11 list the individual emission processes that emit at least five tons per year of VOC for each refinery. For the Delaware and Pennsylvania refineries, there are literally hundreds of emission processes, most of which emit less than 5 tons per year. NJDEP appears to group several processes into a single emission unit, so there are much fewer emission units reported in the database for New Jersey refineries. Also, NJDEP did not provide Source Classification Codes.

TABLE 2
REFINERY PROCESSES WITH VOC EMISSIONS > 5 TONS/YEAR
MOTIVA ENTERPRISES, DELAWARE CITY, DELAWARE
(DNREC AND EPA NEI SITE ID: 10-003-0016)

Emission Unit ID	Process ID	SCC	VOC Emissions (tpy)	Emission Process Description	Emission Estimation Method^a
050	6	30600503	256	CPI&API SEPARATOR, TANKS	STATE/LOCAL EMISSION FACTOR
002	1	10201402	108	FLUID COKER CO BOLER 22H3	EPA EMISSION FACTOR
012	1	10201402	107	CRACKER CO BOILER	EPA EMISSION FACTOR
083	9	30600802	20	VALVE MAINTENANCE	STACK TEST
966	1	40301009	11	INTER. TANK #66	EPA EMISSION FACTOR
083	2	30688801	8	VALVE MAINTENANCE	STACK TEST
945	2	40301099	7	INTER. TANK #45	EPA EMISSION FACTOR
081	2	40600240	7	BARGE LOADING	STATE/LOCAL EMISSION FACTOR
067	1	10100401	6	BOILER 4	EPA EMISSION FACTOR
072	1	30600104	5	METHANOL PLT HTR 41-H-1	EPA EMISSION FACTOR
			155	379 additional emission processes, each less than 5.0 tons/year	
			690	Total Refinery VOC Emissions	

a) Note: this is the emission estimation method identified in the agency's computer database)

TABLE 3
REFINERY PROCESSES WITH VOC EMISSIONS > 5 TONS/YEAR
SUNOCO, MARCUS HOOK, PENNSYLVANIA
(PADEP ID: 42-045-0025; EPA NEI SITE ID: 23-1743283-12)

Emission Unit ID	Process ID	SCC	VOC Emissions (tpy)	Emission Process Description	Emission Estimation Method^a
110	1	30600805	57	PURGING, SAMPLING, ETC.	COMPANY SCC EMISSION FACTOR
112	1	30600504	46	PROCESS DRAINS	COMPANY SCC EMISSION FACTOR
114	1	30600806	34	FACILITY-WIDE FUGITIVES (PETROL. GA SES)	CONTINUOUS EMISSION MONITOR
111	1	30600702	25	COOLING TOWERS	COMPANY SCC EMISSION FACTOR
203	1	40301099	16	TANK 12 FIXED ROOF 54 MBBL	COMPANY SCC EMISSION FACTOR
614	1	40600240	16	NAPHTHA-MARINE VESSEL	COMPANY SCC EMISSION FACTOR
138	1	40301141	13	TANK 252 EXT FLOAT 81.3 MBBL	COMPANY SCC EMISSION FACTOR
135	1	40301141	12	TANK 249 EXT FLOAT 54.4 MBBL	COMPANY SCC EMISSION FACTOR
402	1	30600807	9	BLIND CHANGING	COMPANY SCC EMISSION FACTOR
116	1	40600253	7	MARINE VESSEL BALLASTING	COMPANY SCC EMISSION FACTOR
128	1	40301151	7	TANK 234 INT FLOAT 70.1 MBBL	COMPANY SCC EMISSION FACTOR
099	2	30600106	6	NEW 12-3 CRUDE HTR.H3006	COMPANY SCC EMISSION FACTOR
610	1	40899999	5	TRUCK LOADING-TOLUENE	COMPANY SCC EMISSION FACTOR
060	2	30600106	5	15-1 NEW CRUDE HEATER	COMPANY SCC EMISSION FACTOR
092	1	10200701	5	15-BH 9 BOILER	COMPANY SCC EMISSION FACTOR
			114	90 Additional emission processes, each less than 5.0 tons/year	
			376	Total Refinery VOC Emissions	

a) Note: this is the emission estimation method identified in the agency's computer database)

TABLE 4
REFINERY PROCESSES WITH VOC EMISSIONS > 5 TONS/YEAR
CONOCO PHILLIPS (BP OIL), TRAINER, PENNSYLVANIA
(PADEP ID: 42-045-0030; EPA NEI SITE ID: 06-1331906-1)

Emission Unit ID	Process ID	SCC	VOC Emissions (tpy)	Emission Process Description	Emission Estimation Method^a
103	1	30600904	67	MAIN FLARE	COMPANY SCC EMISSION FACTOR
108	1	30600801	38	PIPELINE VALVES & FLANGES	COMPANY SCC EMISSION FACTOR
106	1	30600504	28	PROCESS DRAINS & H2O SEP.	COMPANY SCC EMISSION FACTOR
116	1	30600807	10	BLIND CHANGING	COMPANY SCC EMISSION FACTOR
127	1	40301142	9	#96 EXT.FLOAT 59M BBLs	COMPANY SCC EMISSION FACTOR
111	1	30600701	8	COOLING TOWERS	COMPANY SCC EMISSION FACTOR
126	1	40301142	8	#95 EXT.FLOAT 59M BBLs	COMPANY SCC EMISSION FACTOR
738	1	30600104	8	PLATFORMER FEED HEATER	COMPANY SCC EMISSION FACTOR
738	2	30600104	8	PLATFORMER FEED HEATER	COMPANY SCC EMISSION FACTOR
744	1	30600104	6	ACD 543 CRUDE HEATER	COMPANY SCC EMISSION FACTOR
745	1	30600104	6	ACD 544 CRUDE HEATER	COMPANY SCC EMISSION FACTOR
			94	61 Additional emission processes, each less than 5.0 tons/year	
			290	Total Refinery VOC Emissions	

a) Note: this is the emission estimation method identified in the agency's computer database)

TABLE 5
REFINERY PROCESSES WITH VOC EMISSIONS > 5 TONS/YEAR
SUNOCO, PHILADELPHIA, PENNSYLVANIA
(PAMS AND EPA NEI SITE ID: 42-101-1501)

Emission Unit ID	Process ID	SCC	VOC Emissions (tpy)	Emission Process Description	Emission Estimation Method^a
550	1	30688801	86	PB FUGITIVE EMISS	EPA EMISSION FACTOR
019	3	30600106	50	1232 CO BOILER	EPA EMISSION FACTOR
905	1	30688801	50	GP PROCESS DRAINS	EPA EMISSION FACTOR
049	5	40899997	37	WHARF BARGE LOADING	EPA EMISSION FACTOR
025	1	30688801	29	1332 CRU FUGITIVES	STATE/LOCAL EMISSION FACTOR
556	1	30600503	25	WASTEWATER OPERATIONS	EPA EMISSION FACTOR
523	1	30600106	17	FLARES	EPA EMISSION FACTOR
044	1	30600701	13	490 COOLING TOWER	EPA EMISSION FACTOR
001	1	30688801	12	137 AVU FUGITIVE	STATE/LOCAL EMISSION FACTOR
904	1	30688801	10	GP BLIND CHANGING	EPA EMISSION FACTOR
035	1	30688801	10	1733 CU FUGITIVES	EPA EMISSION FACTOR
045	1	30600701	9	1232 COOLING TOWER	EPA EMISSION FACTOR
555	1	30600701	8	COMPLEX COOLING TOWER	EPA EMISSION FACTOR
712	1	40301103	8	PB TK 32	EPA EMISSION FACTOR
767	1	40301143	7	PB TK 190	EPA EMISSION FACTOR
042	1	30600701	7	137 COOLING TOWER	EPA EMISSION FACTOR
043	1	30600701	6	433 COOLING TOWER	EPA EMISSION FACTOR
034	1	30688801	6	1732 UDEX FUGITIVES	EPA EMISSION FACTOR
015	1	30688801	6	1232 FCCU FUGITIVES	STATE/LOCAL EMISSION FACTOR
723	1	40301019	5	PB TK 37	EPA EMISSION FACTOR
			229	644 Additional emission processes, each less than 5.0 tons/year	
			628	Total Refinery VOC Emissions	

a) Note: this is the emission estimation method identified in the agency's computer database)

TABLE 6
REFINERY PROCESSES WITH VOC EMISSIONS > 5 TONS/YEAR
CITGO ASPHALT, PAULSBORO, NEW JERSEY
(NJ DEP ID: 34-015-55831)

Emission Unit ID	VOC Emissions (tpy)	Emission Process Description	Emission Estimation Method^a
17	17	Storage Tanks #201, #101, #102, #103, #104, #105 and #106	AP-42
FG0	8	Fugitives	No Method Provided
8	5	Storage Tanks #9, #10, #11, #12, #13, #14, #20, #22 and #23	EPA Computer Program
	10	Additional Sources	
	40	Total Refinery VOC Emissions	

a) Note: this is the emission estimation method identified in the agency's computer database)

TABLE 7
REFINERY PROCESSES WITH VOC EMISSIONS > 5 TONS/YEAR
COASTAL EAGLE POINT, WESTVILLE, NEW JERSEY
(NJ DEP ID: 34-015-55781; EPA NEI SITEID: 34-015-55004)

Emission Unit ID	VOC Emissions (tpy)	Emission Process Description	Emission Estimation Method^a
52	315	Refinery plant flare system to control relief gas releases	Manufacturer's Estimate or Data
78	94	Storage tanks with primary service as gasoline storage	Material Balance
53	57	API separator and thickener to separate oil from water	Material Balance
55	53	Treat waste water to remove impurities	Material Balance
14	43	Fluid Catalytic Unit compressor internal combustion engines	Source Test or Other Measurements
9	41	Catalyst regeneration process of the FCCU and removes catalyst fines	Source Test or Other Measurements
99	37	4 power house boilers and 2 cogeneration units	AP-42
FG0	31	Fugitives	No Method Provided
74	28	Storage tanks with primary service as crude oil storage	Material Balance
84	19	Storage tanks with primary service as naphtha storage	Material Balance
85	14	Storage tanks with primary service as No 2 fuel oil storage	Material Balance
31	9	Holding vessel for slop oils from dewaxing	Material Balance
83	9	Storage tanks with primary service as Methyl tert Butyl Ether storage	Material Balance
81	5	Storage tanks with primary service as kerosene storage	Material Balance
87	5	Storage tanks with primary service as raffinate storage	Material Balance
	41	Additional processes	
	798	Total Refinery VOC Emissions	

a) Note: this is the emission estimation method identified in the agency's computer database)

TABLE 8
REFINERY PROCESSES WITH VOC EMISSIONS > 5 TONS/YEAR
VALERO REFINING, PAULSBORO, NEW JERSEY
(NJ DEP ID: 34-015-55829; EPA NEI SITEID: 34-015-55006)

Emission Unit ID	VOC Emissions (tpy)	Emission Process Description	Emission Estimation Method^a
53	282	WWTP	EPA Computer Program
30	233	Gasol. Tks.	AP-42
FG0	57	Fugitives	No Method Provided
29	49	Dist. Tks.	AP-42
20	38	UtilityPlant	Manufacturer's Estimate or Data
1	32	FCC Regen	Source Test or Other Measurements
31	30	MJA/Kero Tks	AP-42
28	20	Crude Tks.	AP-42
36	15	Resid Oil Tk	AP-42
33	15	MTBE Tankage	AP-42
45	15	Caustic Tks	AP-42
39	13	Slop Tanks	AP-42
34	11	Lube Tankage	AP-42
32	7	Naphtha Tks.	AP-42
	56	Additional processes	
	846	Total Refinery VOC Emissions	

a) Note: this is the emission estimation method identified in the agency's computer database)

TABLE 9
REFINERY PROCESSES WITH VOC EMISSIONS > 5 TONS/YEAR
AMERADA HESS, PORT READING, NEW JERSEY
(NJ DEP ID: 34-023-17996; EPA NEI SITEID: 34-023-15652)

Emission Unit ID	VOC Emissions (tpy)	Emission Process Description	Emission Estimation Method^a
8	261	Storage Tanks for petroleum hydrocarbon liquids	AP-42
1	50	Fluid Catalytic Cracking Unit – Process for cracking heavy petroleum oils using heat, pressure, and catalyst to produce lighter petroleum products	Continuous Emission Monitor
16	28	Marine Loading Operations	State or Local Agency Emission Factor
5	12	Truck Loading Rack	State or Local Agency Emission Factor
FG0	6	Fugitives	No Method Provided
9	6	The refinery flare is a safety device for combusting emergency releases from process operating equipment	AP-42
	5	Additional Sources	
370		Total Refinery VOC Emissions	

a) Note: this is the emission estimation method identified in the agency's computer database)

TABLE 10
REFINERY PROCESSES WITH VOC EMISSIONS > 5 TONS/YEAR
CHEVRON, PERTH AMBOY, NEW JERSEY
(NJ DEP ID: 34-023-18058; EPA NEI SITEID: 34-023-15023)

Emission Unit ID	VOC Emissions (tpy)	Emission Process Description	Emission Estimation Method^a
201	422	Emission from Surge Pond	Source Test or Other Measurements
3	60	Crude Unit	Source Test or Other Measurements
FG0	47	Fugitives	No Method Provided
	3	Additional Sources	
532		Total Refinery VOC Emissions	

a) Note: this is the emission estimation method identified in the agency's computer database)

TABLE 11
REFINERY PROCESSES WITH VOC EMISSIONS > 5 TONS/YEAR
CONOCO PHILLIPS, LINDEN, NEW JERSEY
(NJ DEP ID: 34-039-41805; EPA NEI SITEID: 34-039-40003)

Emission Unit ID	VOC Emissions (tpy)	Emission Process Description	Emission Estimation Method^a
FG0	1,132	Fugitives	AP-42
1	368	Storage Tanks	AP-42
10	111	Wastewater Treatment Plant	EPA Computer Program
3	34	Sulfur Bubble Heaters	AP-42
9	28	Emergency Flares	Best Engineering Judgment
8	13	Marine Loading	AP-42 and Source Test
4	13	FCBW	Source Test or Other Measurements
7	8	Truck Loading	AP-42 and Source Test
2	3	NSPS Heaters	AP-42
5	1	Sulfur Recovery Units	Best Engineering Judgment
1,711		Total Refinery VOC Emissions	

a) Note: this is the emission estimation method identified in the agency's computer database)

NON REFINERY EMISSION PROCESSES

Emission processes for all other non-refinery petroleum industry facilities are summarized in this section. Table 12 compares VOC emission estimates for all petroleum industry facilities located in Delaware, New Jersey, and southeastern Pennsylvania. The emissions are grouped by the same nine categories of sources that were used for refineries. The table shows that most of the VOC from non-refinery facilities are emitted from product storage and unloading/loading processes.

There are a few large VOC emitting non-refinery sources in the Delaware, New Jersey, and southeastern Pennsylvania area. The following non-refinery facilities emit more than 100 tons of VOC per year:

- Maritrans, Delaware (1,635 tpy, SIC = 4499)
- Buckeye Pipeline Co. Linden Station, New Jersey (614 tpy, SIC = 4613)
- Shell Oil Products Sewaren Plant, New Jersey (282 tpy, SIC = 5171)
- Motiva Enterprises, New Jersey (172 tpy, SIC = 5171)
- Citgo Petroleum Linden Terminal, New Jersey (135 tpy, SIC = 5171)
- Sunoco Schuylkill River Tank Farm, Philadelphia (112 tpy, SIC = 5171)
- Buckeye Pipeline Co. Boothwyn, Pennsylvania (103 tpy, SIC = 4613)
- BP Products Carteret Terminal, New Jersey (101 tpy, SIC = 5171)

In addition, there are 24 facilities that emit between 25 and 100 tons of VOC per year.

**TABLE 12 – COMPARISON OF VOC EMISSIONS (tons/year) FOR NON-REFINERY PROCESSES
FOR DELAWARE, NEW JERSEY, AND SOUTHEASTERN PENNSYLVANIA**

SIC Code	Combustion	Process Heaters	Process Units	Process Equipment Leaks	Water Treatment	Cooling Towers	Flares	Storage	Unloading & Loading	SIC Total
2911 – Petroleum Refineries	390	240	214	1,691	1,288	91	421	1,776	151	6,264
2951 – Asphalt Paving Mixtures	4	0	57	0	0	0	0	0	0	61
2952- Asphalt Shingles and Coatings	0	1	44	2	0	12	0	7	5	71
2992 – Lubricating Oil and Grease	1	0	7	1	2	1	0	14	35	61
2999 – Other Petroleum Products	1	0	11	0	0	0	0	1	1	14
4226 – Special Warehousing and Storage	0	0	0	11	0	0	0	31	19	61
4499 – Water Transportation (Lighterage)	0	0	0	0	0	0	0	0	1,635 ^a	1,635 ^a
4612 – Crude Oil Pipeline	0	0	0	0	10	0	0	31	0	41
4613 – Refined Petroleum Product Pipeline	0	0	11	31	0	0	0	867 ^b	0	908 ^b
5171 – Petroleum Bulk Stations	2	0	51	25	0	0	0	1,010	556	1,643
Totals	398	241	395	1,761	1,300	104	421	3,737	2,402	10,759

a) All of these emissions are from the Maritrans facility in Delaware

b) 70% of this total is from one facility – Buckeye Pipe Line Co. Linden Station in New Jersey

REFERENCES

1. Recent inventories provided directly by the State and local agencies for this project. (DNREC – 2001 data for Motiva and Maritrans, 1999 data for all other sources; NJDEP – 2001 data; PADEP – 2000 data; PAMS – 2000 data).
2. Source: *Air Pollution Engineering Manual*, edited by Anthony J. Buonicore and Wayne T. Davis, published by the Air and Waste Management Association, 1992.

APPENDIX E

FINAL TECHNICAL MEMORANDUM #4

**POTENTIALLY MISSING EMISSION PROCESSES FOR
FOR PETROLEUM REFINERIES
IN DELAWARE, NEW JERSEY, AND SOUTHEASTERN PENNSYLVANIA**

**TECHNICAL MEMORANDUM #4
FINAL**

**POTENTIALLY MISSING EMISSION PROCESSES FOR
FOR PETROLEUM REFINERIES
IN DELAWARE, NEW JERSEY, AND SOUTHEASTERN PENNSYLVANIA**

Prepared for:

Susan S.G. Wierman, Executive Director
Mid-Atlantic Regional Air Management Association (MARAMA)
711 W. 40th Street
Suite 318
Baltimore, MD 21211-2109

October 13, 2003
5925.004

Submitted by

Edward Sabo
MACTEC Federal Programs, Inc.
560 Herndon Parkway
Suite 200
Herndon, VA 20170
(703) 471-8383, FAX (703) 481-8296
EJSabo@mctec.com

TABLE OF CONTENTS

	Page
INTRODUCTION	1
METHODOLOGY	1
MOTIVA ENTERPRISES LLC, DELAWARE CITY, DE.....	2
SUNOCO INC. (R&M), MARCUS HOOK, PA.....	4
CONOCO PHILLIPS, TRAINER, PA.....	6
SUNOCO, PHILADELPHIA, PA.....	8
CITGO ASPHALT, PAULSBORO, NJ.....	10
COASTAL EAGLE POINT, WESTVILLE, NJ	11
VALERO REFINING, PAULSBORO, NJ	12
AMERADA HESS, PORT READING, NJ.....	13
CHEVRON PRODUCTS, PERTH AMBOY, NJ	14
CONOCO PHILLIPS, LINDEN (BAYWAY), NJ.....	15

TABLES

	Page
Table 1. Motiva Enterprises, Delaware City, DE	3
Table 2. Sunoco, Marcus Hook, PA	5
Table 3. Conoco Phillips, Trainer, PA.....	7
Table 4. Sunoco, Philadelphia, PA	9
Table 5. Citgo Asphalt, Paulsboro, NJ.....	10
Table 6. Coastal Eagle Point, Westville, NJ	11
Table 7. Valero Refining, Paulsboro, NJ	12
Table 8. Amerada Hess, Port Reading, NJ.....	13
Table 9. Chevron, Perth Amboy, NJ.....	14
Table 10. Conoco Phillips, Linden (Bayway), NJ.....	15

INTRODUCTION

Recent ozone air quality investigations indicate the potential for underestimation of volatile organic compound (VOC) emissions from petroleum refineries. As part of the *Texas Air Quality Study 2000*, airplane measurements of ambient concentrations of VOC and highly photochemically reactive compounds were compared to the reported emission inventory estimates. The comparison indicated that VOC emissions may be significantly under-reported, specifically for industrial sources. Similar aircraft measurements in the Philadelphia area also found a substantial ozone plume downwind of the Delaware/Southeast Pennsylvania/New Jersey industrial area. VOC emissions from petroleum refineries comprise a significant portion of the total industry related VOC emissions in this area. Finally, the Bay Area Air Quality Management District, the Texas Commission on Environmental Quality, and the U.S. Environmental Protection Agency have all acknowledged the potential for underestimation of VOC emissions from petroleum refineries.

In Technical Memorandum #2, we identify all petroleum industry facilities in the MARAMA states (District of Columbia, Delaware, Maryland, New Jersey, North Carolina, Pennsylvania, Virginia, West Virginia), and New York. Technical Memorandum #3 focused on identifying individual emission processes at the 10 refineries and other petroleum industry facilities located in Delaware, New Jersey, and southeastern Pennsylvania. This report, Technical Memorandum #4, attempts to identify individual VOC sources that are potentially not accounted for in the existing emission inventories.

METHODOLOGY

The methodology to identify potentially missing sources involved comparing the data in the electronic emission inventory databases to other information available in the State/local agency files. Specific follow-up questions were prepared for the refineries when agency files did not contain sufficient information about emission estimation methods or where clarifying information was needed. The objectives of the file reviews were to:

- verify that the computerized emission inventory matches other available information in Title V permits, emission statements, and other agency files;
- gather data on emission estimation methods since the computer codes in database usually don't provide enough details of how emissions were calculated; review agency files to gather information on leak detection calculation methods, emission factors, wastewater models, temperatures, and control device efficiencies used for calculating emissions;
- gather any available compliance data that may indicate that the inventory underestimates emissions (excess emission reports, notification of upsets, any non-compliance issues, frequency of leak detection monitoring – quarterly vs. annual).

This memorandum summarizes the results of the file reviews for each facility. Three comparisons were made to identify potentially missing sources:

- compare current (2000 or 2001) inventory to past inventories;
- compare current (2000 or 2001) inventory to sources listed in the Title V permit;
- compare current (2000 or 2001) inventory to sources typically found at other refineries.

This memorandum summarizes the results of these comparisons for each facility.

MOTIVA ENTERPRISES LLC, DELAWARE CITY, DE

The Delaware City refinery began production in 1957 as part of the Tidewater Oil Company's refining system. Located 15 miles from Wilmington, it has a capacity of 185,000 barrels a day. In 1967, Tidewater merged into the Getty Oil Company. The plant then became an important part of Texaco's domestic system when Texaco acquired Getty in 1984. The Delaware City refinery was part of Star Enterprise, a joint venture company between Texaco and Saudi Aramco from 1989 until 1998, when it became one of Motiva Enterprises' four refineries.

Table 1 compares the VOC emission inventories for 1996, 1999, and 2001. The refinery-wide VOC emissions in 2001 were roughly one-half of the reported emissions in 1996 and 1999. The primary reasons for the emission decrease are as follows:

- Emission points 027 and 028 (Sulfur recovery units #1 and #2) both had significant emission reductions due to a change in emission estimation methodology. For the 1996 and 1999 inventories, VOC emissions were based on an EPA emission factor. Testing by the company was done on the SRUs in 2001, and the VOC emissions data from this testing was used to calculate VOC emissions in 2001.
- Emission point 050 (CPI&API Separator, Tanks) had a 132 tpy reduction, which according to the company was the result of Benzene NESHAP work.
- Emission point 051 (Wastewater treatment plant) had a reduction from 209 tpy to 4 tpy, which according to the company was the result of Benzene NESHAP work.
- Emission point 052 (Oil recovery system) did not operate in 2001, and the 38 tpy reported in previous inventories was the permitted emission rate, not the actual rate. For the years 2001 onward, emissions will be based on actual operating time.
- Emission point 081 (Barge loading) had a reduction from 150 tpy to 9 tpy due to changes in the operation of the Marine Vapor Recovery (MVR) system. In 1996, the MVR system was operational for a part of the year for gasoline loading. In 1999, the MVR system was used for gasoline loading but was not required for methanol loading. In 2001, the MVR system was used for both gasoline and methanol loading.
- Emission point 083 (Process fugitives) had a reduction from 143 tpy to 37 tpy. The company uses a computer program that uses the EPA's correlation equations contained in the *Protocol for Equipment Leak Emission Estimates*. Presumably the emission reduction was due to a decrease in the number of components that were found to be leaking.
- Emission point 110 (Cracker Regen Bypass) had emissions of 68 tpy in 1999, but 0 tpy in both 1996 and 2001. According to the company, the number of days that the coker and FCCU operate without the CO boilers is provided as part of the emission inventory. VOC emissions are calculated for these periods and are included in the inventory.

There do not appear to be any other sources missing from the 2001 inventory that were previously included in either the 1996 or 1999 inventory.

VOC emissions from the Coker and Cracker CO Boilers (Emission points 002 and 012) are significantly higher than the emissions reported for similar sized units at other refineries in the study area. VOC emissions from the Motiva refinery are calculated using emission factors from

TABLE 1**MOTIVA ENTERPRISES, DELAWARE CITY, DE**

Emission Source	VOC Emissions (tons per year)		
	1996	1999	2001
001 – Coker without CO Boiler with Incinerator	2	1	<1
002 – Fluid Coker CO Boiler 22H3	105	130	108
011 – Cracker without CO Boiler	10	<1	<1
012 – Cracker CO Boiler	101	101	107
027 – Sulfur Recovery Unit 1	72	66	<1
028 – Sulfur Recovery Unit 2	78	84	<1
050 – CPI&API Separator, Tanks	388	388	256
051 – Wastewater Treatment Plant	209	4	4
052 – Oil Recovery System	38	38	0
067-070 Boilers 1-4	19	19	9
080, 520, 530, 532 – Flare Systems	0	1	1
081 – Barge Loading	150	74	9
083 – Fugitives (process equipment leaks)	143	74	37
110 – Cracker Regen Bypass	0	68	0
521, 523 – Cooling Towers	0	0	4
Product Storage Tanks	115	121	123
All other sources	20	45	43
Refinery Total	1,342	1,213	690

EPA's FIRE database for three SCCs: 1-02-014-02 (process gas), 1-02-014-04 (residual oil), and 1-02-014-02 (natural gas). In the 2001 inventory, Motiva reported 110 tons per year of VOC from coker off-gas combustion and 109 tons per year of VOC from the cracker CO boiler. The other refineries base their estimates on source test data, and the VOC emission rates obtained via source testing range from "not detected" to 9.45 lbs/hour (0 to 41 tons per year). If Motiva does not have stack test data for the CO boilers, then DNREC may want to investigate alternative emission estimation approaches, such as those suggested in the TNRCC *Technical Guidance Package for Chemical Sources: Fluid Catalytic Cracking Units* (Draft RG-110), February 2001.

The emission factor used for flaring emissions (Emission points 080, 520, 530, 532) appear to be questionable. The factor of 5.6 lbs/mmft³ was obtained from EPA's FIRE database. The quality of this factor is "U", meaning unknown quality. There is no documentation in FIRE as to the origin of the 5.6 lbs/mmft³ emission factor. DNREC may want to consider using the emission factor found in Table 13.5-1 of AP-42 (0.14 lbs/10⁶ Btu). If this factor is used with the estimated annual usage of 108 mmft³ (roughly 110,160 10⁶ Btu), then the VOC emissions from flaring would be 7.7 tpy instead of 0.3 tpy.

SUNOCO INC. (R&M), MARCUS HOOK, PA

The Marcus Hook refinery began operations in 1902. It can process 185,000 barrels a day of low sulfur, sweet crude oil into a wide range of petroleum and petrochemical products – including gasoline, aviation fuel, kerosene, heating oil, residual fuel, propane butane, and petrochemicals. The major petrochemicals are benzene, toluene, xylene, cyclohexane, propylene, ethylene, and ethylene oxide; these are sold to chemical companies, which use them to make plastics, antifreeze, carpets, pillows, detergents, carbonated beverages and dry ice, among other products. The crude oil is obtained primarily from the North Sea and West Africa. Recent improvements at the refinery include: (1) a major cogeneration plant was completed in 1987; (2) a major environmental effort (known as the Middle Creek Project) to improve the system for collecting and transporting refinery waste-water prior to treatment was completed in 1994; (3) construction of a polypropylene splitter that provides feedstock for petrochemical partnerships was completed in 1996; (4) an upgrade to the FCCU in 2000 that added approximately 20,000 bbl/d capacity; and (5) construction began on a 750 megawatt cogeneration plant in 2001.

Table 2 compares the VOC emission inventories for 1994, 1997, and 2000. The refinery-wide VOC emissions in 2000 were roughly 20% of the reported emissions in 1994 and 70% of the reported emissions in 1997. The primary reasons for the emission decreases are as follows:

- Emission point 112 (Process drains/wastewater) had VOC emissions of 396 tpy in the 1994 inventory but only about 50 tpy in 1997 and 2000 inventory. The emission reductions are presumably related to a change from using an uncontrolled EPA AP-42 emission factor to the controlled AP-42 emission factor as a result of changes in the wastewater processing system.
- Emission point 115 (Marine vessel loading) had VOC emissions of 212 tpy in the 1994 inventory, 53 tpy in 1997, and 0 tpy in 2000. This emission point is for gasoline loading, which did not operate in 2000-2002 but may resume in the future.
- Emission point 116 (Marine vessel ballasting) had VOC emissions of 69 tpy in the 1994 inventory, 60 tpy in the 1997 inventory, and 7 tpy in the 2000 inventory. Beginning in 1994, the refinery started using segregated tankers (separate tanks for product and ballast), which minimized VOC emissions.
- Emission point 500 (Middle Creek conveyance) had VOC emissions of 350 tpy in 1994, but zero emissions in 1997 and 2000. This source was an open-air wastewater stream that was enclosed and still exists. Zero emissions are questionable, but they are thought to be small.
- Emission points 608-614 (Product loading) are emission points for loading gasoline and other organic chemicals into trucks and marine vessels. VOC emissions were 324 tpy 1994 inventory but only 31 tpy in the 1997 inventory and 16 tpy in the 2000 inventory. PADEP has indicated that the refinery is not loading as much product into trucks and vessels as it had done earlier.

There do not appear to be any sources missing from the 2000 inventory that were previously included in either the 1994 or 1997 inventory.

TABLE 2
SUNOCO, MARCUS HOOK, PA

Emission Source	VOC Emissions (tons per year)		
	1994	1997	2000
101 – FCC Unit and CO Boiler	<1	0	0
104, 105 – Plant Flares	52	3	3
110 – Fugitives (purging/sampling)	75	63	57
111 – Cooling Towers	31	30	25
112 – Process Drains/Wastewater	396	49	46
114 – Facility-wide Fugitives	3	9	34
115 – Marine Vessel Loading	212	53	0
116 – Marine Vessel Ballasting	69	60	7
117 – Gasoline Loading Rack	0	1	1
500 – Middle Creek Conveyance	350	0	0
608-614 – Product Loading	370	38	23
Product Storage Tanks	192	183	140
All Other Sources	34	44	40
Refinery Total	1,784	533	376

Emissions from the FCC Unit CO boiler are very low compared to other refineries. The company reported that a stack test was performed in February 2001 showing 0.83 lbs/hour of VOC. For the 2002 inventory, the company is reporting 10.7 tpy.

Although the VOC emissions from flares appears low compared to other refineries, this is explainable since the refinery's primary flare is the ethylene complex flare located in the Delaware portion of the refinery. Emissions from this flare should be in the Delaware emission inventory.

CONOCO PHILLIPS, TRAINER, PA

The Trainer refinery began operations in the early 1900's. The Trainer refinery can process 190,000 barrels a day of crude oil into a wide range of petroleum fuel products – including gasoline, diesel, jet fuel, heating oil, residual fuel, and propane. The crude oil is obtained primarily from the North Sea and West Africa. In 1996 Tosco acquired the Trainer refinery from BP Oil. Phillips Petroleum purchased Tosco in 2001, and merged with Conoco, Inc., later in 2001 to create Conoco Phillips.

Table 3 compares the VOC emission inventories for 1994, 1997, and 2000. The refinery-wide VOC emissions in 2000 were roughly 15% of the reported emissions in 1994 and 36% of the reported emissions in 1997. The primary reasons for the emission decreases are as follows:

- Emission point 105 (Marine vessel loading) had VOC emissions of 501 tpy in the 1994 inventory, but <1 tpy in 1997 and 2000. The change in emissions reflects the operation of a marine vapor recovery unit as required by PADEP regulations. The refinery could not confirm the 1994 emission rate since the refinery was owned and operated by BP Oil at the time.
- Emission point 106 (Process drains and H₂O separator) had emissions of 311 tpy in 1997 and 28 tpy in 2000. The refinery indicated that they changed emission estimation methodologies in 1998. The 1997 VOC emissions were calculated using EPA emission factors, while the 2000 VOC emissions were estimated using the EPA wastewater treatment model WATER8. The refinery could not confirm the 1994 emission rate since the refinery was owned and operated by BP Oil at the time.
- Emission point 108 (Pipeline valves and flanges) had VOC emissions of 530 tpy in the 1994 inventory but only 22 tpy in 1997 and 38 tpy in 2000. For the 1997 and 2000 inventories, the refinery used a computer program that uses screening values and the EPA's correlation equations contained in the *Protocol for Equipment Leak Emission Estimates*. The refinery could not confirm the 1994 emission rate since the refinery was owned and operated by BP Oil at the time.
- Emission point 112 (Purging and sampling) had VOC emissions of 295 tpy in 1994 but only 7 tpy in 1997 and 5 tpy in 2000. For the 1997 and 2000 inventories, the refinery used average emission factors contained in the *Protocol for Equipment Leak Emission Estimates*. The refinery could not confirm the 1994 emission rate since the refinery was owned and operated by BP Oil at the time. The VOC emission estimates for this source have been reduced since 1997 due to the use of closed loop sampling systems.

There do not appear to be any sources missing from the 2000 inventory that were previously included in either the 1994 or 1997 inventory.

TABLE 3**CONOCO PHILLIPS, TRAINER, PA**

Emission Source	VOC Emissions (tons per year)		
	1994	1997	2000
101 – FCC Unit and CO Boiler	3	2	3
103 – Main Flare	162	349	67
104 – Marine Vessel Ballasting	64	0	0
105 – Marine Vessel Loading	501	<1	<1
106 – Process Drains and H2O Separator	208	311	28
108 – Pipeline Valves and Flanges	530	22	38
111 – Cooling Towers	8	5	8
112 – Purging and Sampling	295	7	5
116 – Blind Changing	9	6	10
Product Storage Tanks	80	88	84
All Other Sources	16	24	47
Refinery Total	1,876	814	290

SUNOCO, PHILADELPHIA, PA

The Sunoco Philadelphia refinery is the combination of two (2) completely independent and previously self-sufficient refineries. In 1988, Sunoco acquired the Point Breeze refinery in South Philadelphia as part of its purchase of Atlantic Refining and Marketing Company. In 1994, Sunoco purchased the adjacent Girard Point refinery owned by Chevron (and prior to that, owned by Gulf Oil) Integrating the two refineries into one facility with two operating areas, Sunoco created the Philadelphia Refinery, the oldest continuously operating petroleum facility in the world with origins dating back to the 1860's when the petroleum industry was in its infancy.

The Philadelphia Refinery can process 355,000 barrels a day of crude oil into fuels – including gasoline, aviation fuel, kerosene, heating oil, residual fuel, propane and butane for sale throughout the Northeast region to retail, wholesale and commercial customers. In addition, this facility produces petrochemical feedstocks – primarily cumene, which is shipped to Sunoco's Frankford Chemicals plant to make phenol, used in the manufacture of plastics and synthetics.

Table 4 compares the VOC emission inventories for 1996, 1998, and 2000. The refinery-wide VOC emissions in 2000 were roughly 42% of the reported emissions in 1996. VOC emissions reported in the 1998 and 2000 inventories were reasonably similar. The primary reasons for the emission decreases from 1996 to 2000 are as follows:

- Most of the difference in emissions at the Girard Point area is due to a change in process fugitive emissions – from 289 tpy in 1996 to 74 tpy in 2000. There is no information currently available to determine the reason for this emission reduction.
- Emissions from the blowdown system (Emission Point 050) at Girard Point decreased from 26 tpy in 1996 to 2.8 tpy in 2000. Sunoco's backup calculation spreadsheet has multiplies the AP-42 controlled emission factor by an unexplained 0.1 factor that results in the emissions being an order of magnitude lower in 2000.
- Most of the difference in emissions at the Point Breeze area is due to a change in process fugitive emissions – from 397 tpy in 1996 to 86 tpy in 2000. There is no information currently available to determine the reason for this emission reduction.
- Product storage emissions at the Point Breeze area decreased from 257 tpy in 1996 to 144 tpy in 2000. There is no information currently available to determine the reason for this emission reduction.

There appears to be an error in the oil/water separator emission calculations at Girard Point. VOC emissions in 1998 were about 22 tpy, but were 0 in the 2000 inventory. This difference appears to be caused by an error in Sunoco's emission calculation spreadsheet where the annual water flow to the oil/water separators appears to be incorrectly calculated. It appears that the emissions calculated for this source would be about 31 tpy when the correction to the spreadsheet is made.

VOC emissions from unmonitored process drains at Point Breeze appear to be missing from 2000 inventory. These emissions are included under process fugitive emissions. Sunoco's backup calculation spreadsheet showed 38.4 tpy from process drains in 1999, but were 0 tpy in the 2000 inventory.

TABLE 4
SUNOCO, PHILADELPHIA, PA

Emission Source	VOC Emissions (tons per year)		
	1996	1998	2000
Girard Point			
010, 014, 016 Flares	5	19	2
019 1232 FCCU CO Boiler	98	30	50
042-045 Cooling Towers	35	35	35
046 Wastewater Separator 2b	11	9	<1
047 Wastewater Separator 4	17	13	<1
049 Wharf Barge Loading	79	11	39
050 Blowdown System	26	3	3
Process Fugitives	289	70	74
905 Process Drains	0	0	50
Product Storage	79	39	26
Other Processes	19	14	25
Girard Point Total	658	233	312
Point Breeze			
523 Flares	47	40	17
547 Loading Operations	50	20	1
550 Fugitives	397	112	86
552-555 Cooling Towers	19	19	19
556 Wastewater Operations	24	24	25
Product Storage	257	120	144
Other Processes	27	36	24
Point Breeze Total	821	371	316
Refinery Total	1,479	604	628

VOC emissions from the Unit 868 FCC at Point Breeze are reported as zero in the PAMS database, and Sunoco's backup calculations report the VOC emissions from Unit 868 FCC as "not detected". VOC emissions at FCC units at other refineries in the area are in the 10 to 100 tpy range, and there appears that VOC emissions from the Unit 868 FCC may be underreported. A review of the stack test is needed to verify whether VOC emissions are truly zero from this source.

CITGO ASPHALT, PAULSBORO, NJ

Citgo Asphalt and Refining Company is the largest asphalt refiner on the East Coast. The company owns and operates two asphalt refineries, located in Paulsboro, New Jersey and Savannah, Georgia. The Citgo Paulsboro asphalt refinery can process 30,500 barrels of crude oil per day into asphalt used in the construction and resurfacing of roadways. Other applications include specialty asphalts for the roofing industry and emulsions products.

Table 5 compares the VOC emission inventories for 1999, 2000, and 2001. The refinery-wide VOC emissions were similar in each of the three inventories. There do not appear to be any sources missing from the 2001 inventory that were previously included in either the 1999 or 2000 inventory.

For several reasons, the VOC emissions from the Citgo Asphalt refinery are expected to be considerably lower than other refineries in the area. The refinery does not have any thermal or catalytic cracking capacity. The number of fugitive emission components are much less than the other refineries. There are no cooling towers at Citgo – cooling is performed using a closed looped ethylene glycol fan system. Most of the product loading is of less volatile products such as #6 oil, asphalt, kerosene, and heating oil.

TABLE 5

CITGO ASPHALT, PAULSBORO, NJ

Emission Source	VOC Emissions (tons per year)		
	1999	2000	2001
U8 Storage Tanks #9, #10, #11, #12, #13, #14, #20, #22, #23	5.4	4.5	5.2
U9 Wastewater Treatment	2.1	1.9	2.0
Boilers and Process Heaters	9.4	7.6	3.0
U17 Storage Tanks #201, #101, #102, #103, #104, #105 and #106	13.5	16.1	17.1
FG0 Fugitives	7.9	8.9	8.3
ISO Insignificant Sources	0	6.2	3.5
All Other Sources	4.7	5.6	3.0
Refinery Total	43.0	51.1	42.1

COASTAL EAGLE POINT, WESTVILLE, NJ

The Coastal Eagle Point refinery was built by Texaco in 1949 and acquired by Coastal in 1985. It has a refining capacity of 146,000 barrels per day of crude oil, which is obtained primarily from the North Sea. The refinery produces large volumes of gasoline and diesel, as well as paraffin for aviation fuel and other applications. That part of the gas oil not used to make diesel ends up as domestic heating oil and fuel oil for such customers as power stations.

Table 6 compares the VOC emission inventories for 1999, 2000, and 2001. The refinery-wide VOC emissions were similar in each of the three inventories. There do not appear to be any sources missing from the 2001 inventory that were previously included in either the 1999 or 2000 inventory.

The Coastal Eagle Point refinery has extremely high VOC emissions from flares compared to other refineries. There is little documentation in RADIUS to determine how these emission estimates were calculated. NJDEP should review these estimates and contact the refinery to determine whether they are correct.

TABLE 6

COASTAL EAGLE POINT, WESTVILLE, NJ

Emission Source	VOC Emissions (tons per year)		
	1999	2000	2001
U9 FCCU	42	40	41
U10 FCCU compressor IC engines	44	42	43
U52 Refinery plant flare system	281	382	315
U53 API separator and thickener	67	60	57
U55 Wastewater treatment	61	55	53
FG0 Fugitives	74	66	31
Boilers/heaters/IC engines	48	45	45
Product loading	8	7	6
Product storage	263	202	196
All other sources	18	15	14
Refinery Total	906	914	801

VALERO REFINING, PAULSBORO, NJ

The Paulsboro refinery, which began operations in 1917, was originally designed to manufacture lubricating oil. Today, the refinery has a total feedstock throughput capacity of approximately 195,000 barrels per day and processes crude oil into a variety of products, including gasoline, lube oil base stocks, mid-distillate products, asphalt, petroleum coke, liquefied propane gas, fuel oil and molten sulfur. In addition, the refinery produces significant volumes of asphalt that are marketed to paving and roofing contractors. It also produces a variety of lube oil base stocks that are sold to the adjacent finished lube blending and packaging plant. The Paulsboro refinery receives a variety of feedstocks, including sour crudes such as Arab Light, Arab Heavy, Oriente and Kirkuk. Valero acquired the Paulsboro refinery from Mobil in 1998.

Table 7 compares the VOC emission inventories for 2000 and 2001 (the 1999 emission inventory was not available). The refinery-wide VOC emissions were similar in 2000 and 2001 inventories. There do not appear to be any sources missing from the 2001 inventory that were previously included in 2000 inventory.

Emissions from cooling towers, flares, and product loading are all less than 1 tpy. These appear low compared to other refineries. NJDEP should obtain supporting documentation from Valero to verify whether these estimates are accurate.

TABLE 7

VALERO REFINING, PAULSBORO, NJ

Emission Source	VOC Emissions (tons per year)		
	1999	2000	2001
U1 FCCU	na	31	31
U2-U19 Boilers/heaters/IC engines	na	14	14
U20 Utility plant	na	38	38
U21-U25 Refinery plant flare system	na	<1	<1
U53 Wastewater treatment	na	298	282
FG0 Fugitives	na	59	57
Product loading	na	<1	<1
Product storage	na	424	413
All other sources	na	16	11
Refinery Total	na	880	846

na – not available

AMERADA HESS, PORT READING, NJ

The Port Reading Refinery produces gasoline and other fuel products by processing intermediates in a fluid catalytic cracking unit. The refinery is able to operate its fluid catalytic cracking unit at rates of up to 62,000 barrels per day using refined intermediates. Originally built 1958, the refinery was converted from a crude oil refinery and reopened in 1984. The refinery makes gasoline for the East Coast market and can deliver jet fuel to all three major New York airports via pipeline.

Table 8 compares the VOC emission inventories for 1999, 2000, and 2001. The refinery-wide VOC emissions in 2001 were higher than the reported emissions in 1999 and 2000. The primary reasons for the emission increase are as follows:

- Emission point U8 (Storage tanks) had a VOC emission increase from 137 tpy in 1999 to 261 tpy in 2001.
- Emission point U16 (Marine loading operations) had a VOC emission increase from 0 tpy in 1999 to 28 tpy in 2001.

There do not appear to be any sources missing from the 2001 inventory that were previously included in either the 1999 or 2000 inventory.

TABLE 8

AMERADA HESS, PORT READING, NJ

Emission Source	VOC Emissions (tons per year)		
	1999	2000	2001
U1 FCCU	49	46	50
U4, U10, U11, U12 Boilers/heaters	<1	<1	<1
U5 Truck loading rack	0	0	12
U6 Wastewater treatment	2	2	1
U8 Storage tanks	137	146	261
U9 Refinery flare	6	8	6
U16 Marine loading operations	0	0	28
FG0 Fugitives	11	9	6
All other sources	4	4	6
Refinery Total	209	215	370

CHEVRON PRODUCTS, PERTH AMBOY, NJ

The Chevron Products Co. Perth Amboy site has been used for petroleum refining since 1920. In 1983, Chevron reduced its operations at the site to just asphalt production and the storage and transfer of petroleum products. It can process 83,000 barrels a day of crude oil.

Comparison with Previous Inventories

Table 9 compares the VOC emission inventories for 2000 and 2001 (the 1999 emission inventory was not available). The refinery-wide VOC emissions in 2001 were higher than the reported emissions in 2000. The primary reason for the emission increase is as follows:

- Emission point U10 (Effluent treatment plant) had a VOC emission increase from 245 tpy in 1999 to 422 tpy in 2001.

There do not appear to be any sources missing from the 2001 inventory that were previously included in the 2000 inventory.

TABLE 9

CHEVRON PRODUCTS, PERTH AMBOY, NJ

Emission Source	VOC Emissions (tons per year)		
	1999	2000	2001
U2 Storage tanks	na	64	60
U6 Power plant	na	<1	<1
U10 Effluent treatment plant	na	245	422
U7 Flares	na	<1	1
FG0 Fugitives	na	45	47
All other sources	na	5	6
Refinery Total	na	361	537

na – not available

CONOCO PHILLIPS, LINDEN (BAYWAY), NJ

The Linden (Bayway) refinery began operations in the early 1900's. It can process 190,000 barrels a day of crude oil and features the largest fluid catalytic cracking unit in the world. The refinery receives crude oil via tanker primarily from fields in the Atlantic Basin. The refinery produces a wide range of petroleum fuel and petrochemical products – gasoline, low-sulfur diesel, home heating oil, jet fuel, propane, asphalt, polypropylene, and other chemical feedstocks. The Linden (Bayway) refinery has been owned by a number of companies - the Bayway Refining Company, Exxon, and Tosco. Phillips Petroleum purchased Tosco in 2001, and merged with Conoco, Inc., in later in 2001 to create Conoco Phillips.

Table 10 compares the VOC emission inventories for 1999, 2000, and 2001. The refinery-wide VOC emissions in 1999 and 2001 were similar, but the emissions in 2000 were considerably higher due to higher emissions from process fugitives. No reason for the increased emissions was provided by the refinery. Wastewater treatment plant emissions rose from 44 tpy in 2000 to 111 tpy in 2001, possible because of due to increased skimming facility outages in 2001.

VOC emissions from the Conoco Phillips Linden refinery are much higher than the other refineries in the study area. There are several reasons that make these emission estimates appear to be reasonable. First, it is a large refinery, having the largest catalytic cracking capacity in the region. As a result of its size, it has a large number of fugitive emission components and the method used to estimate fugitive emissions appears to include some conservative assumptions. Third, the emission statement includes emissions from two adjacent marketing terminals (Linden Marketing Terminal and Tremley Point Terminal). Adjacent marketing terminals are usually included as separate facilities in the emission inventory. For example, Sunoco's Schuylkill River Tank Farm is treated as a separate facility and its emissions are tabulated separately from the Sunoco Philadelphia refinery.

TABLE 10
CONOCO PHILLIPS, LINDEN, NJ

Emission Source	VOC Emissions (tons per year)		
	1999	2000	2001
U1 Storage tanks	548	490	368
U2 and U3 Heaters	13	15	34
U4 FCBW (Fluid catalytic cracking unit)	12	13	13
U7 Truck loading	8	9	8
U8 Marine loading	4	4	13
U9 Emergency flares	1	1	28
U10 Wastewater treatment plant	54	44	111
FG0 Fugitives	1,177	1,882	1,132
All other sources	1	1	4
Refinery Total	1,816	2,458	1,712

APPENDIX F

FINAL TECHNICAL MEMORANDUM #5

**IDENTIFICATION OF EMISSION ESTIMATION METHODS FOR
PETROLEUM REFINERIES
IN DELAWARE, NEW JERSEY, AND SOUTHEASTERN PENNSYLVANIA**

**TECHNICAL MEMORANDUM #5
FINAL**

**IDENTIFICATION OF EMISSION ESTIMATION METHODS FOR
PETROLEUM REFINERIES
IN DELAWARE, NEW JERSEY, AND SOUTHEASTERN PENNSYLVANIA**

Prepared for:

Susan S.G. Wierman, Executive Director
Mid-Atlantic Regional Air Management Association (MARAMA)
711 W. 40th Street
Suite 318
Baltimore, MD 21211-2109

October 13, 2003
5925.005

Submitted by

Edward Sabo
MACTEC Federal Programs, Inc.
560 Herndon Parkway
Suite 200
Herndon, VA 20170
(703) 471-8383, FAX (703) 481-8296
EJSabo@mactec.com

TABLE OF CONTENTS

	Page
EXECUTIVE SUMMARY	1
METHODOLOGY	2
COMBUSTION SOURCES	4
FCC UNITS, COKERS, AND CARBON MONOXIDE BOILERS	7
FLARES	10
PROCESS EQUIPMENT LEAKS	13
WASTEWATER TREATMENT	17
COOLING TOWERS	22
STORAGE TANKS.....	24
UNLOADING AND LOADING OPERATIONS.....	25
REFERENCES	30

TABLES

	Page
Table 1. Comparison of VOC Emission by Refinery and Process	3
Table 2. Emission Factors for Natural Gas and Process Gas Boilers/Heaters	5
Table 3. Emission Factors Used by Refineries for Natural Gas and Process Gas Boilers/Heaters	5
Table 4. Emission Factors for Oil-Fired Boilers/Heaters	6
Table 5. Emission Factors Used by Refineries for Oil-Fired Boilers/Heaters.....	6
Table 6. VOC Estimation Methods for Cokers/FCC Units and CO Boilers	8
Table 7. VOC Emissions and Estimation Methods for Flares	12
Table 8. VOC Emissions and Estimation Methods for Process Equipment Leaks	15
Table 9. VOC Emissions and Estimation Methods for Wastewater Treatment	20
Table 10. VOC Emissions and Estimation Methods for Cooling Towers.....	23
Table 11. VOC Emissions and Estimation Methods for Storage Tanks.....	26
Table 12. VOC Emissions and Estimation Methods for Truck and Railcar Loading Operations.....	28
Table 13. VOC Emissions and Estimation Methods for Marine Vessel Loading Operations.....	29

EXECUTIVE SUMMARY

Recent ozone air quality investigations indicate the potential for underestimation of volatile organic compound (VOC) emissions from petroleum refineries. As part of the *Texas Air Quality Study 2000*, airplane measurements of ambient concentrations of VOC and highly photochemically reactive compounds were compared to the reported emission inventory estimates. The comparison indicated that VOC emissions may be significantly under-reported, specifically for industrial sources. Similar aircraft measurements in the Philadelphia area also found a substantial ozone plume downwind of the Delaware/Southeast Pennsylvania/New Jersey industrial area. VOC emissions from petroleum refineries comprise a significant portion of the total industry related VOC emissions in this area. Finally, the Bay Area Air Quality Management District, the Texas Commission on Environmental Quality, and the U.S. Environmental Protection Agency have all acknowledged the potential for underestimation of VOC emissions from petroleum refineries.

In Technical Memorandum #2, we identified petroleum industry facilities in the MARAMA states (District of Columbia, Delaware, Maryland, New Jersey, North Carolina, Pennsylvania, Virginia, West Virginia), and New York. Technical Memorandum #3 focused on identifying individual emission processes at the 10 refineries and other petroleum industry facilities located in Delaware, New Jersey, and southeastern Pennsylvania. Technical Memorandum #4 identified individual VOC sources that are potentially not accounted for in the existing emission inventories. This report, Technical Memorandum #5, describes the VOC emission estimation methods used for each source category within the refineries.

In general, the refineries are using emission estimation methods consistent with the Emission Inventory Improvement Program's (EIIP) preferred and alternative methods. In some, but not all cases, they use the preferred or most accurate method. Otherwise, they use one of the simpler, alternative methods based upon available data. The following paragraphs summarize the emission estimation methods for each source category:

- Boilers and Process Heaters. VOC emissions from boilers and heaters fired with either natural gas or refinery (process) gas are usually calculated by multiplying an emission factor by the amount of gas consumed. In some cases, source test data is available. Emission factors change over time as new and better source test data becomes available. Some refineries appear to be using outdated or inappropriate emission factors. There is an opportunity to increase the consistency in the emission factors used.
- Cracking Units/CO Boilers. All but one the refineries base their emissions on source test data. The VOC emission rates obtained via source testing range from "not detected" to 9.45 lbs/hour (0 to 41 tons per year). VOC emissions from the Motiva Delaware City refinery are calculated using EPA emission factors, and are significantly higher than the emission estimates for the refineries that use stack test data to estimate emissions.
- Flares. Most refineries use a simple AP-42 total hydrocarbon emission factor to calculate VOC emissions. This factor was developed in the early 1980's and has not been updated by EPA since then. The emission factor does not take into consideration the flare efficiency or the composition of the material being flared. To calculate emissions, the emission factor is multiplied by the amount of pilot gas and waste material sent to the flare. Most refineries monitor the pilot gas flow rate. Waste gas flow rates and

composition are determined using several different approaches, ranging in accuracy from continuous monitoring to the use of historical estimates and engineering assumptions. There is an opportunity to increase the consistency in methods used to determine the amount of material sent to the flare systems.

- **Process Equipment Leaks.** All of the refineries use approved approaches from EPA's *Protocol for Equipment Leak Emission Estimates*. Some refineries base their emissions on EPA's preferred correlation equation approach that uses actual LDAR screening values to estimate emissions. Other refineries use the alternative "leak/no leak" method to calculate emissions. There are differences in how an individual refinery treats non-detects and components not monitored. VOC process equipment leak emissions vary widely from refinery to refinery due to differences in the size (number of equipment components monitored), liquid and gas streams processed, LDAR monitoring program requirements, and emission estimation methods used.
- **Wastewater Treatment.** Refineries use either an EPA-approved emission model (such as WATER8 or WATER9) or AP-42 emission factors. The use of an emission model is EPA's preferred method. The AP-42 emission factors for oil/water separators are very dated and have not changed since the 1980 edition of AP-42. Further information is needed to ensure that all wastewater treatment components (process drains, oil/water separators, refinery-specific treatment processes) are included in the inventory.
- **Cooling Towers.** VOC emissions for cooling towers at the three Pennsylvania refineries are based on AP-42 emission factors, resulting in emission estimates from 8 to 54 tons per year. Emissions from the refineries in Delaware and New Jersey are either very small (< 5 tons per year) or listed as insignificant sources.
- **Storage Tanks.** All of the refineries use the TANKS program to estimate emissions, but very few are using the most current version. However, all of the refineries are using fairly recent versions of the model and differences in the version of TANKS used should not create drastic inconsistencies. Emissions from storage tanks appear to be reasonably consistent from refinery to refinery when one factors in the differences in refinery size, the number of tanks at the refinery, and the products stored.
- **Loading Operations.** The refineries calculate their VOC emissions using an AP-42 material balance calculation and product transfer rates. Most of the operations are controlled, and the efficiency of the control device is frequently based on source testing. In some cases, the source tests are used to develop the VOC emission estimates.

METHODOLOGY

Table 1 summarizes the emissions by source category for each of the 10 petroleum refineries in the study area. These emission estimates are from recent agency inventories for either calendar year 2000 or 2001. To determine the emission estimation methods used, we first examined the estimation codes in each agency's electronic database. We reviewed agency files to gather additional data since the codes in database usually don't provide enough detail regarding how emissions were calculated. As questions arose, we consulted with agency permit writers, inspectors, or inventory preparation personnel to obtain clarifications. MACTEC did not contact the refineries directly to obtain additional information. Rather, the agencies contacted the refineries to obtain clarifications when appropriate.

TABLE 1 – COMPARISON OF VOC EMISSIONS (tons/year) BY REFINERY AND PROCESS

Refinery	Atmospheric Distillation Capacity (barrels/day)	Boilers and Process Heaters	Cokers, FCCs, and CO Boilers	Other Process Units	Process Equipment Leaks	Water Treatment	Cooling Towers	Flares	Storage	Unloading & Loading	Plant Total
Motiva Delaware City	185,000	35	219	1 ^a	37	260	4	1	123	9	690
Sunoco Marcus Hook	185,000	34	<1	<1	100	46	25	3	140	30	376
ConocoPhillips Trainer	190,000	43	<1	3	53	28	8	67	84	4	290
Sunoco Philadelphia	355,000	67	50	<1	220	25	54	2	170	40	628
Citgo Asphalt Paulsboro	30,500	3	(b)	2	8	2	0 ^d	<1	25	<1	40
Coastal Eagle Point, Westville	146,000	88	41	1	31	111	0 ^d	315	205	6	798
Valero Refining Paulsboro	172,600	52	32	7	57	282	0 ^d	<1	399	<1	829
Amerada Hess Port Reading	0 ^c	1	50	3	6	1	0 ^d	6	261	40	370
Chevron Perth Amboy	83,000	1	(b)	1	47	422	0 ^d	1	60	1	532
ConocoPhillips Linden	263,000	37	13	1	1,132	111	0 ^d	28	368	21	1,711
Totals	1,610,100	361	405	19	1,691	1,288	91	421	1,835	151	6,264

a) The 1999 inventory included 149 tons/year from sulfur removal process. There were no emissions from this process in 2001.

b) These two refineries do not have thermal or catalytic cracking units.

c) The refinery was converted from a crude oil refinery and reopened in 1984 processing only refined intermediates.

d) Cooling tower emissions listed as insignificant activities.

COMBUSTION SOURCES

There are a number of different types of combustion sources in a typical refinery. These sources are categorized by and the fuel. Refinery combustion devices include boilers, heaters, gas turbines, and engines. Fuels are typically residual oil, distillate oil, refinery gas, or natural gas.

Boilers/Heaters Fired with Natural Gas or Refinery Gas

VOC emissions from boilers and heaters fired with either natural gas or refinery (process) gas are usually calculated by multiplying an emission factor by the amount of gas consumed. In some cases, source test data is available. EPA publishes emission factors in two standard references: the Factor Information Retrieval (FIRE) database and AP-42. The factors change over time as new and better test data become available.

Table 2 compares the VOC emission factors and how they have changed over time. Currently, the standard AP-42 VOC emission factor (7/98 version) is 5.5 lbs/mmft³ for natural gas combustion. No distinction is made on the size of the boiler. AP-42 also presents a total organic compound factor of 11 lbs/mmft³. In earlier editions of AP-42 (10/96 version), the VOC emission factor was either 1.4 lbs/mmft³ for boilers >100 million Btu/hour heat input or 2.8 lbs/mmft³ for boilers less than 100 million Btu/hour heat input. AP-42 does not present a factor for refinery (process) gas combustion, but FIRE generally assumes that the factor for refinery (process) gas is the same as for natural gas. It appears that there is an inconsistency in EPA's FIRE database. FIRE Version 6.23 appears to still use the outdated 2.8 lbs/mmft³ factor for refinery (process) gas boilers and heaters.

Table 3 compares the VOC emission factors used by each refinery. Several of the refineries are using out-of-date emission factors. In some case, the use of outdated emission factors results in under reporting of emissions. For example, the Motiva refinery uses two out-of-date factors, resulting in a possible under reporting by 20 tons per year. The Sunoco-Philadelphia refinery also uses the outdated 2.8 lbs/mmft³ for all boilers/heaters, resulting in a possible under reporting by about 27 tpy. On the other hand, Citgo-Paulsboro uses the emission factor for total organic compounds, thus over reporting VOC emissions.

Oil-fired Boilers/Heaters

VOC emissions from oil-fired boilers/heaters are usually calculated by multiplying an emission factor by the amount of oil consumed. In some cases, source test data is available. Emission factors are from EPA's two standard references: the FIRE database and AP-42. The factors have not changed recently. There is a distinction made between utility and industrial boilers in AP-42. Table 4 compares the VOC emission factors in FIRE and AP-42. The utility boiler emission factor is 0.76 lbs/1000 gallons irrespective of type of oil burned. The industrial boiler factor is 0.28 lbs/1000 gallons for No. 6 and No. 5 oil, and 0.2 lbs/1000 gallons for No. 4 and distillate oil. AP-42 states "emissions can increase by several orders of magnitude if the boiler is improperly operated or is not well maintained". AP-42 does not present a factor for process heaters, but FIRE uses 0.3 lbs/1000 gallons. Table 3 compares the VOC emission factors used by each refinery.

**TABLE 2 - COMPARISON OF EPA VOC EMISSION FACTORS FOR
NATURAL GAS AND REFINERY (PROCESS) GAS FIRED BOILERS/HEATERS**

SCC	Fuel	VOC Emission Factor (lbs/million cubic feet burned)			
		FIRE 5.0	FIRE 6.23	AP-42 Oct 1996	AP-42 Jul 1998 ^c
1-01-006-01	Nat. Gas	1.4	5.5	1.4	5.5
1-01-006-02	Nat. Gas	2.8	5.5	2.8	5.5
1-01-006-04	Nat. Gas	1.4	5.5	2.8	5.5
1-01-007-01	Process Gas	1.4	5.5 ^a	--	--
1-01-007-02	Process Gas	2.8	5.5 ^a	--	--
1-02-006-01	Nat. Gas	1.4	5.5	1.4	5.5
1-02-006-02	Nat. Gas	2.8	5.5	2.8	5.5
1-02-006-03	Nat. Gas	5.3	5.5	2.8	5.5
1-02-006-04	Nat. Gas	2.8	5.5	2.8	5.5
1-02-007-01	Process Gas	2.8	2.8	--	--
3-06-001-04	Gas-fired	2.8	5.5 ^b	--	--
3-06-001-05	Nat. Gas	2.8	2.8	--	--
3-06-001-06	Process Gas	2.8	2.8	--	--

a) FIRE 6.23 footnote says process gas factor assumed to be the same as natural gas factor.

b) FIRE 6.23 footnote says derived from values for 1-01-006-02.

c) AP-42 also reports a Total Organic Compound emission factor of 11 lbs/mmft³.

**TABLE 3 - VOC EMISSION FACTORS USED BY REFINERIES FOR
NATURAL GAS AND REFINERY (PROCESS) GAS FIRED BOILERS/HEATERS**

Refinery	Emission Factors Used
Motiva-Delaware City, DE	For boilers, old AP-42 factor of 1.4 lbs/mmft ³ . For process heaters, old AP-42 factor of 2.8 lbs/mmft ³ .
Sunoco-Philadelphia, PA	Old AP-42 - 2.8 lbs/mmft ³
Sunoco-Marcus Hook, PA	Current AP-42 - 5.5 lbs/mmft ³
ConocoPhillips-Trainer, PA	Current AP-42 - 5.5 lbs/mmft ³
Amerada Hess-Port Reading, NJ	Source test value of 0.0014 lbs/mmBtu, which is roughly equivalent to 1.4 lbs/mmft ³
Chevron-Perth Amboy, NJ	Source test value of 0.0933 lbs/hour.
Citgo-Paulsboro, NJ	Current AP-42 total organic compound factor - 11 lbs/mmft ³ .
Coastal Eagle-Westville, NJ	Current AP-42 - 5.5 lbs/mmft ³ , or source test data
ConocoPhillips-Linden, NJ	Source tests - 0.012 to 0.07 lbs/hour
Valero-Paulsboro, NJ	Old AP-42 - 1.4 lbs/mmft ³ or manufacturer's data - 8.3 lbs/mmft ³

**TABLE 4 - COMPARISON OF VOC EMISSION FACTORS FOR
OIL-FIRED BOILERS/HEATERS**

Source	Fuel	VOC ^a Emission Factor (lbs/1000 gallons burned)			
		FIRE 5.0	FIRE 6.23	AP-42 Oct 1996	AP-42 Sep 1998
Utility	No. 6	0.76	0.76	0.76	0.76
Utility	No. 5	0.76	0.76	0.76	0.76
Utility	No. 4	0.76	0.76	0.76	0.76
Industrial	No. 6	0.28	0.28	0.28	0.28
Industrial	No. 5	0.28	0.28	0.28	0.28
Industrial	No. 4	0.2	0.2	0.2	0.2
Industrial	Distillate	0.2	0.2	0.2	0.2
Heater	Oil	0.3	0.3	--	--

a) Neither AP-42 nor FIRE 6.23 have a VOC factor per se; rather, they report a total non-methane organic compounds factor, which is equivalent to VOC

**TABLE 5 - VOC EMISSION FACTORS USED BY REFINERIES FOR
OIL-FIRED BOILERS/HEATERS**

Refinery	Emission Factors Used
Motiva-Delaware City, DE	For Boilers #1-#4 fired with no. 6 oil - 0.76 lbs/1000 gallons. It appears that Motiva did not use any oil in process heaters in 2001.
Sunoco-Philadelphia, PA	FIRE - 0.3 lbs/1000 gallons
Sunoco-Marcus Hook, PA	AP-42 - 0.28 lbs/1000 gallons
ConocoPhillips-Trainer, PA	AP-42 - 0.28 lbs/1000 gallons
Amerada Hess-Port Reading, NJ	State factor – 0.34 lbs/1000 gallons
Chevron-Perth Amboy, NJ	Did not operate oil-fired units in 2001
Citgo-Paulsboro, NJ	AP-42 - 0.252 lbs/ 1000 gallons
Coastal Eagle-Westville, NJ	Source test data
ConocoPhillips-Linden, NJ	Did not operate oil-fired units in 2001
Valero-Paulsboro, NJ	Manufacturer's data – 1.4 lbs/1000 gallons

FCC UNITS, COKING, AND CARBON MONOXIDE BOILERS

VOC emissions primarily originate from fluid catalytic cracking (FCC) processes and thermal cracking (coking) processes as by-products of coke combustion during the regeneration of catalysts used in the cracking process. There are two basic types of regenerators: complete combustion (full burn) regenerators and partial combustion regenerators. Most partial combustion regenerators employ secondary combustion devices (referred to as CO boilers) to recover the latent heat in the flue gas. The fuel used in the CO boiler consists of the process gas from the catalyst regenerator and an auxiliary fuel source. Data included in the EPA's Background Information Document (BID) for the Subpart UUU MACT standard indicated that organic emissions from complete combustion (full burn) regenerators are comparable to a partial combustion regenerator vented to a CO boiler.

According to both AP-42 and the *Air Pollution Engineering Manual*, "combusting the gas in the boiler reduces emissions of VOCs to negligible levels". The AP-42 emission factor for total hydrocarbons for an uncontrolled unit is 220 lbs/1000 bbl (5.23 lbs/1000 gallons).

The FIRE database lists VOC emission factors for CO boilers under SCC 1-02-014-01 (natural gas), 1-02-014-02 (process gas), 1-02-014-003 (distillate oil), and 1-02-014-04 (residual oil). The FIRE emission factor for natural gas and process gas (2.8 lbs/mmft³) was "transferred from natural gas burning boilers assuming process similarity". The FIRE factor appears to be outdated, and should be replaced by the current 5.5 lbs/mmft³ factor. The FIRE emission factor for distillate oil (0.2 lbs/1000 gallons) and residual oil (0.28 lbs/1000 gallons) were also "transferred from other oil-burning boilers assuming process similarity".

The EPA BID for the Subpart UUU BID presents emission factors in the range of 0.078 to 1.24 lbs/1000 bbl of unit throughput. These factors represent VOC emissions after the CO boiler or complete combustion unit.

The Texas Natural Resource Conservation Commission (TNRCC) suggests that VOC emissions from CO boilers should be calculated in the following manner:

- VOC resulting from refinery fuel gas combustion can be estimated by using the AP-42 emission factor for nonmethane volatile organics (i.e., the 5.5 lbs/mmft³ factor)
- Regenerator-related VOC in the CO boiler outlet can be estimated by applying the Destruction Removal Efficiency (DRE) of the combustion device (typically 99 to 99.9 percent) to the VOC waste load of the inlet flue gas (about 220 lbs of VOC per 1,000 bbl fresh feed), resulting in controlled emissions of 0.22 to 2.2 lbs/ 1,000 bbl fresh feed).

Table 6 summarizes information about the coker and FCC units at each refinery. The table also shows the VOC emissions and emission estimation method.

Motiva has two CO boilers – one on the coking unit and one on the FCC unit. For the CO boiler on the coking unit, Motiva reports emissions using the FIRE emission factors for three SCCs: 1-02-014-02 (process gas), 1-02-014-04 (residual oil), and 1-02-014-02 (natural gas). In the 2001 inventory, Motiva reported 110 tons per year of VOC from coker off-gas combustion and 109 tons per year of VOC from the cracker CO boiler. As mentioned earlier, the FIRE emission

TABLE 6 - VOC ESTIMATION METHODS FOR COKERS/FCC UNITS AND CO BOILERS

Refinery	Unit	Capacity (Barrels per Day)	Unit Type/ Control Device	VOC Emissions (tons/year)	Estimation Methodology
Motiva Delaware City, DE	FCC	82,000	CO Boiler	109	FIRE factor - 2.8 lbs/mmft ³
	Coker (thermal cracker)	54,000	CO Boiler	110	FIRE factor - 2.8 lbs/mmft ³
Sunoco Philadelphia, PA	FCC-Girard Point	73,500	CO Boiler	50	Stack test – 8.0 lbs/hr
	FCC-Point Breeze	47,500	Full-burn	0	Stack test “VOC not detected”
Sunoco Marcus Hook, PA	FCC	115,000	CO Boiler	0 in 2000 10.7 in 2002	Source test – 0.83 lbs/hr
ConocoPhillips Trainer, PA	FCC	52,000	CO Boiler	3	Source test – 0.73 lbs/hr
Amerada Hess Port Reading, NJ	FCC	62,500	?	50	CEM
Chevron Perth Amboy, NJ	None	---	---	---	None
Citgo Paulsboro, NJ	None	---	---	---	None
Coastal Eagle Westville, NJ	FCC	55,000	CO Boiler	41	Source test – 9.45 lbs/hour
ConocoPhillips Linden, NJ	FCC	145,000	CO Boiler	13	Source test – 3.0 lbs/hour (total hydrocarbons)
Valero Paulsboro, NJ	FCC	54,000	Full burn	32	Source test – 7.05 lbs/hour
	Coker (thermal cracker)	24,500	?	1	AP-42 Factor

factor of 2.8 lbs/mmft³ for process gas appears to be outdated, and should be replaced by the 5.5 lbs/mmft³. If the newer factor was used, VOC emissions would increase by about 105 tons per year for the coker CO boiler and 105 tons per year for the FCC CO boiler.

Motiva also reports emissions for periods when the CO boiler is not operational. During periods when the coker CO boiler is not in operation, a back-up incinerator is in operation. During periods when the FCC CO boiler is not in operation, the operation of the unit changes to a full burn mode of operation. In 2001, VOC emissions when the CO boilers were not in operation were reported to be less than 1 ton per year per unit. However, in the 1999 inventory VOC emissions from the FCC regenerator bypass were reported to be 68.4 tons per year, so there is potential for significant emissions when the CO boilers are not operational.

The Sunoco-Philadelphia refinery has a CO boiler associated with the Unit 1232 FCC at Girard Point. VOC emissions are calculated using the FIRE emission factors for three SCCs: 3-06-001-03 (oil-fired process heater), 3-06-001-06 (gas-fired process heater), and 3-06-001-06 (gas-fired process heater). In the 2000 inventory, VOC emissions were reported as 50 tons per year of VOC from Unit 1232 FCC CO boiler. It appears from Sunoco's backup calculation spreadsheet that emissions are based on the results of a stack test. When the CO boiler is not working, the Unit 1232 FCC can be operated at full burn with the addition of a CO promoter catalyst. The inventory does not appear to account for periods of time when the CO boiler is not in operation.

The Sunoco Philadelphia refinery also has the Unit 868 FCC at Point Breeze. This FCC does not vent to a CO boiler, but rather is a "full-burn" unit. VOC emissions are reported as zero in the PAMS database, and Sunoco's backup calculations report the VOC emissions from Unit 868 FCC as "not detected".

The FCC unit at the Sunoco Marcus Hook refinery is controlled with a CO boiler. CO Boiler emissions are reported under two SCCs – 1-02-008-02 (coke) and 3-06-002-01 (FCC unit) through Stack 60. There are no VOCs emissions reported in the 2000 inventory. There was a stack test conducted in February 2001 showing 0.83 lbs/hr of non-methane VOCs. For 2002, PADEP indicates that the refinery is reporting 10.7 tpy for the FCCU. At times, the CO boiler is not operational and emissions are vented through the FCC bypass Stack 61. There were no VOC emissions reported through the FCC bypass stack in the 2000 inventory. PADEP's understanding is that the bypass stack is very rarely used.

The FCC unit at the ConocoPhillips Trainer refinery is controlled with a CO boiler. Emissions are reported under SCC 3-06-002-01 (FCC unit). VOC emissions are based on an emission factor of 0.73 lbs/hour, which was based on an emission testing program conducted in December 1994 when the refinery was owned and operated by BP Oil Company. The emission rate was confirmed by an emission testing program conducted by ConocoPhillips in 2002. The Trainer refinery does not have the capability of bypassing the CO boiler. BP Oil removed the CO boiler bypass in 1994. ConocoPhillips has no reason to believe that significant VOC emissions are missing from the emission inventory for this source. In inventories dating back to the 1990/1991 time frame, VOC emissions from the FCC unit were reported as about 600 tons per year.

According to the RADIUS database, VOC emissions from the FCC unit at Amerada Hess-Port Reading were determined through the use of a continuous emission monitor.

According to the RADIUS database, VOC emissions at the Coastal Eagle-Westville refinery were determined from company source test data.

Source test data was used to determine emissions from the FCC unit at Valero-Paulsboro. The FCC unit is not vented to a CO boiler. VOC Emissions from the coker unit are less than 1 tpy in the inventory.

Emissions for the FCC at ConocoPhillips-Linden were determined from company source test data where USEPA Methods were used to determine the total hydrocarbon emission rate. The FCC unit is vented to two CO boilers.

There are no cokers or FCC units at Chevron-Perth Amboy or Citgo-Paulsboro.

FLARES

Flares are commonly used for the disposal of waste gases during process upsets (e.g., start-up, shutdown) and emergencies. They are basically safety devices that also are used to destroy organic constituents in waste emission streams. Flares provide for the safe disposal of hydrocarbons, both liquid and gases, that are either automatically vented from the process units through pressure relief valves, control valves, or manually drawn from units. Flare systems gather relief flow, separate liquid from vapors, recover any condensable oil and water, and discharge the vapors to a flare for combustion and release to the atmosphere.

Table 13.5-1 of AP-42 has a total hydrocarbon factor of 0.14 lbs/10⁶ Btu. Table 13.5-2 of AP-42 shows that, on average, 55% of the hydrocarbon flare emissions are methane. This factor is based on a 1983 EPA flare efficiency study.

FIRE 6.23 has emission factors for refinery flares under the SCC 3-06-009-xx. FIRE lists a factor of 5.6 lbs/mmft³ of natural gas or process gas burned. This is roughly equivalent to 0.0056 lbs/mmBtu, significantly less than the factor listed in Table 13.5-1 of AP-42. The emission factor quality rating is “U”, meaning unknown quality. There is no documentation in FIRE as to the origin of the 5.6 lbs/mmft³ emission factor.

Finally, Table 5.1-1 of AP-42 presents a factor of 0.8 lbs/1000 bbl refinery feed for blowdown systems vented to a flare. A blowdown system provides for the safe disposal of hydrocarbons discharged from pressure relief devices. Blowdown material is separated into vapor and liquid cuts, and the gaseous cuts are often flared.

TNRCC suggests an alternative method that uses the flare destruction efficiency to calculate VOC emissions. Volumetric flow rates are converted to mass flow rates using the ideal gas law, and then a destruction efficiency in the range of 98 to 99.5 percent is applied to calculate VOC emissions. One of the main problems with current flares is that their efficiencies are essentially

unknown. Estimates of efficiency range from 20 % to 99 % and this leads to large uncertainties as to the effects of flaring on the environment. (See Reference 6 for information about TNRCC's approach to calculating emissions from flares).

Based on a recent study conducted by the BAAQMD, emissions from flares appear to be under reported. BAAQMD's analysis suggests that flare emissions are much higher than previously thought. Their analysis suggests that average daily VOC emissions from flares at four Bay Area refineries range from 2-13 tons per day (equivalent to 730 to 4,745 tons per year). Emissions from refinery flares in the Philadelphia area are reported to be much lower than these estimates for Bay Area refineries. (See Reference 7 for further information about BAAQMD's analysis).

Table 7 summarizes VOC emissions and emission estimation methodology at each refinery. There is considerable variation in the methods used and resulting emission estimates.

The Motiva Delaware City refinery uses the FIRE emission factor of 5.6 lbs/mmft³ of gas burned for purge gas combustion. The estimated annual purge gas usage is 108 mmft³. Emissions from purge gas combustion are reported under Group ID #80. Any waste material combusted in the flare is reflected under the accidental releases emission point. The refinery did not provide any details on how these emissions are calculated.

The Sunoco Philadelphia refinery estimates emissions from flaring based on AP-42 emission factors, operating records, and engineering estimates. For pilot purge gas combustion at both Point Breeze and Girard Point, the refinery uses the AP-42 total hydrocarbon factor of 0.14 lbs/mmBtu. For waste gas combustion from the blowdown system, the refinery uses the AP-42 a factor of 0.8 lbs/1000 bbl refinery feed for blowdown systems vented to a flare. Pilot gas flows are monitored, as is the refinery feed at each area of the refinery.

The Sunoco Marcus Hook refinery calculates emissions using a company derived emission factor (which appears to be about 0.26 lbs/mmBtu). There refinery operates flares at the 10 plant, the 12 plant, and the ethylene complex. The ethylene complex flare, located in Delaware, has a flow meter as it is the primary flare. The 10 plant and 12 plant flares do not have flow meters. The volumetric flow rates for the 10 and 12 plant flares were estimated in 1995 based on typical pilot and purge gas flow rates and other normal loadings. Emissions from the 10 and 12 plant flares were about 3 tpy in 2000.

The Conoco Phillips Trainer refinery VOC emission estimate for Emission Point 103 (Main Flare) is based upon the AP-42 total hydrocarbon factor of 0.14 lbs/mmBtu. The emission estimates are based on volumetric flow rates determined by ultrasonic flow meters for each of the three flare headers and estimated gross calorific value for the flare gas stream. For the 2000 inventory, the volumetric flow was 1,122 mmscf/yr and the heating value was 857 Btu/scf. Using this data with the 0.14 lbs/mmBtu emission factor yields 67.3 tpy of VOC.

VOC emissions in the 2001 RADIUS emission statement at the Amerada Hess Port Reading refinery for Emission Unit U9 (refinery plant flare system) were 5.8 tpy. The emission factor listed in RADIUS is the AP-42 total hydrocarbon factor of 0.14 lbs/mmBtu. We have no information on how the volumetric flow rates are determined.

TABLE 7 - VOC EMISSIONS AND ESTIMATION METHODS FOR FLARES

Refinery	VOC Emissions (tons per year)	Emission Factor Used	Methodology to Determine Amount of Material Flared
Motiva Delaware City, DE	1	FIRE emission factor of 5.6 lbs/mmft ³ for purge gas combustion. Unknown for waste gas combustion in the flare	Unknown
Sunoco Philadelphia, PA	2	AP-42 factor of 0.14 lbs/10 ⁶ Btu for pilot gas. AP-42 factor of 0.8 lbs/1000 bbl refinery feed for the blowdown system.	Pilot gas flow rate is monitored, as is the refinery feed used for the waste gas emission calculations
Sunoco Marcus Hook, PA	6.6	Company developed factor, which appears to be 0.26 lbs/mmft ³	Volumetric flow rates were estimated in 1995 based on typical flow rates and loadings
ConocoPhillips Trainer, PA	67.3	AP-42 factor of 0.14 lbs/10 ⁶ Btu	Ultrasonic flow meters for each of the three flare headers
Amerada Hess Port Reading, NJ	5.8	AP-42 factor of 0.14 lbs/10 ⁶ Btu	Unknown
Chevron Perth Amboy, NJ	1	AP-42 factor of 0.14 lbs/10 ⁶ Btu	Fuel flow rates for natural gas purge and pilot are monitored. Waste gas rate are not monitored; they are estimated from operating records and process knowledge.
Citgo Paulsboro, NJ	0.03	AP-42 factor of 0.14 lbs/10 ⁶ Btu	Purge gas flow to the flare is monitored continuously. Flows from emergency venting are calculated based on which safety valve is relieving to the flare system, the maximum design flow rate, and the discharge duration
Coastal Eagle Westville, NJ	315	Unknown	Unknown
ConocoPhillips Linden, NJ	28	AP-42 Section 13.5 factor of 0.14 lbs/mmBtu for pilot gas. For flared material, use AP-42 Section 1.4 natural gas boiler factor of 5.5 mmft ³ (roughly 0.0055 lbs/mmBtu)	Pilot gas flow rate is the design flowrate. For flared material, estimate is that 0.07% of received crude is lost due to flaring
Valero Paulsboro, NJ	0.52	AP-42 factor (RADIUS says 1.4 lbs/mmBtu, probably should be 0.14 lbs/mmBtu)	Historical estimate, adjusted annually based on refinery fuel gas production

The Chevron Perth Amboy refinery estimates emissions from flaring based on AP-42 emission factors, operating records, and engineering estimates. Several different scenarios can lead to flaring and the calculation approach varies accordingly. Fuel flow rates for natural gas purge and pilot are monitored. Waste gas rate are not monitored; they are estimated from operating records and process knowledge. The refinery uses the AP-42 total hydrocarbon factor of 0.14 lbs/mmBtu. VOC emissions in the 2001 RADIUS emission statement were only 1 tpy.

The Citgo Asphalt Paulsboro refinery uses the AP-42 total hydrocarbon factor of 0.14 lbs/mmBtu. The purge gas flow to the flare is monitored continuously. Flows from emergency venting are calculated based on which safety valve is relieving to the flare system, the maximum design flow rate from the valve, and the discharge duration. Citgo used 98% destruction efficiency for its steam assisted flare for VOC. VOC emissions in the 2001 RADIUS emission statement were less than 1 tpy.

VOC emissions in the 2001 RADIUS emission statement at the Coastal Eagle Point refinery VOC emissions for Emission Unit U52 (refinery plant flare system) were 315 tpy. These estimates are extremely high compared to other refineries. There is not sufficient documentation to determine whether these estimates are correct.

The Conoco Phillips Linden (Bayway) refinery estimates flaring emissions from combustion of both pilot gas and from flared material. For pilot gas, the refinery uses the AP-42 total hydrocarbon factor of 0.14 lbs/mmBtu, multiplied by the pilot gas design flow rate and the average heating value of the pilot gas. For flared material, waste gas fuel flow rates are not directly measured, so the refinery estimates that 0.07% of the received crude is lost due to flaring. Using this estimate with the 0.14 lbs/mmBtu emission factor yields 28 tpy of VOC. The destruction efficiency used to estimate these emissions is assumed to be 98%.

The Valero Refining Paulsboro refinery estimates flare emissions based on a historical volumetric flow estimate, adjusted annually based on refinery fuel gas production. The refinery believes that the historical estimate is conservatively high. The estimate is based on emission factors from AP-42 (exact factor not provided by refinery; RADIUS has 1.4 lbs /mmBtu, which probably should be the 0.14 lbs/mmBtu factor from Table 13.5-1. AP-42 assumes a 98% destruction efficiency for a properly operated flare.

PROCESS EQUIPMENT LEAKS

Process fugitive emissions typically result from leaking valves, flanges, pumps, connectors, and compressors. Although the release from each individual source may be small, there are usually thousands of these components in a refinery and the total emissions from these sources can be significant. Most refineries have a leak detection and repair (LDAR) program that is structured to detect and repair equipment that are identified as leaking. Most federal equipment leak control programs have quarterly or monthly monitoring requirements. However, the LDAR monitoring frequency and leak definitions at some state equipment leak control programs may be different from federal programs. LDAR programs involve monitoring using a portable flame ionization detector (FID) designed to record screening values (ppmv) around each component

There are four basic approaches for estimating emissions from equipment leaks in a specific processing unit. The approaches, in order of increasing refinement, are:

- Average emission factor approach;
- Screening ranges approach;
- EPA correlation approach; and
- Unit-specific correlation approach.

The approaches increase in complexity and in the amount of data collection and analysis required. All the approaches require some data collection, data analysis and/or statistical evaluation. References 8 and 9 provide a full description of the methods, which are briefly summarized below.

The average emission factor approach is commonly used to calculate emissions when site-specific LDAR screening data are unavailable. The emission rate for all equipment in the stream of a given equipment type is obtained by multiplying the applicable average emission factor by the average weight fraction of VOC in the stream and by the number of pieces of the applicable equipment type in the stream. Table 4.5-2 of Reference 8 presents the refinery average emission factors for each type of equipment and type of service (i.e., gas, light liquid, heavy liquid).

The screening ranges (i.e., leak/no leak method) approach requires LDAR screening data to be collected for the equipment in the process unit. This approach is applied in a similar manner as the average emission factor approach in that equipment counts are multiplied by the applicable emission factor. However, two emission factors are used: one factor for equipment where screening data are "greater than or equal to 10,000 ppmv" and a second factor where screening data are "less than 10,000 ppmv." Emission factors are provided in Table A-3 of Reference 9.

The EPA correlation equation approach is the preferred method when actual LDAR screening values are available. This approach involves entering each individual screening value into the correlation equation, which predicts the mass emission rate based on the screening value. If no emission are detected by the FID, then the "Default Zero Emission Rate" emission factors are used. If pegged screening values are detected (i.e., level is above the upper detection limit of the FID), the "Pegged Emission Rate" emission factors are used. This approach offers a good refinement to estimating emissions from equipment leaks by providing an equation to predict mass emission rate as a function of screening value for a particular equipment type. Correlation equations, for the petroleum industry that apply to refineries, marketing terminals, and oil and gas production operations data are available for: (1) valves; (2) connectors; (3) flanges; and (4) pump seals; (5) open-ended lines; and (6) other. Table 4.4-4 of Reference 8 provides the correlation equations to be used for this approach.

Finally, the correlation equations may be developed for specific units rather than using correlation equations developed by the EPA. Methodologies for generating leak rate/screening value correlations with mass emissions data and screening values are presented in Appendix B of the *1995 Protocol* document. Once correlations are developed using the methodologies outlined in Appendix B, they are applied in the same manner as described in the example for the EPA correlations.

Table 8 shows the VOC emissions and estimations methods used in the study area.

TABLE 8 - VOC EMISSIONS AND ESTIMATION METHODS FOR PROCESS EQUIPMENT LEAKS

Refinery	VOC Emissions (tons per year)	Emission Estimation Methodology
Motiva Delaware City, DE	37	Used the refinery or SOCFI (where applicable) emission correlation equations from EPA <i>Protocol for Equipment Leak Emission Estimates</i> . Backup calculations not available , but are based on the EPA <i>Protocol</i> document.
Sunoco Philadelphia, PA	220	Used emission factors from EPA <i>Protocol for Equipment Leak Emission Estimates</i> . Backup calculations not available , but are based on the EPA <i>Protocol</i> document.
Sunoco Marcus Hook, PA	100	Used emission correlation equations from Table 2-9 of the EPA <i>Protocol for Equipment Leak Emission Estimates</i> for SOCFI components. Backup calculations not available for non-SOCFI components, but are based on the EPA <i>Protocol</i> document.
ConocoPhillips Trainer, PA	53	Used emission correlation equations from Table 2-10 of the EPA <i>Protocol for Equipment Leak Emission Estimates</i> .
Amerada Hess Port Reading, NJ	6.5	No information in RADIUS on estimation method and refinery did not provide any supporting documentation. .
Chevron Perth Amboy, NJ	47	Used EPA's <i>Protocol for Equipment Leak Emission Estimates</i> . For valves and pumps, use 1,000 ppm leak definition and factors from Table 5-5 of the EPA document. For pressure relief valves and compressor seals, use the screening range factors from Table 2-6. For flanges, use the average emission factors from Table 2-2.
Citgo Paulsboro, NJ	8.3	Used EPA's <i>Protocol for Equipment Leak Emission Estimates</i> . Uses 1,000 ppm leak definition and factors from Table 5-5 of the EPA document.
Coastal Eagle Westville, NJ	30.7	No information in RADIUS on estimation method and refinery did not provide any supporting documentation. .
ConocoPhillips Linden, NJ	1,132	Uses screening ranges approach from Table 2-6 of EPA's <i>Protocol for Equipment Leak Emission Estimates</i> . "Leak" emission factors for components measured at >1,000 ppm; "no-leak" factors for components measured at <1,000 ppm, non-detects, and components not measured.
Valero Paulsboro, NJ	57	No information in RADIUS on estimation method and refinery did not provide any supporting documentation.

The Motiva Delaware City refinery uses the correlation equations from EPA's *Protocol for Equipment Leak Emission Estimates*. The actual screening values are stored in LEAKDAS (the LDAR database) and are used with the correlation equations to calculate emissions. The default zero emission rate and pegged emission rate are also from the EPA's *Protocol* document.

The Sunoco Philadelphia refinery uses techniques from EPA's *Protocol for Equipment Leak Emission Estimates*. The refinery did not provide any supporting documentation regarding the exact methods used to calculate process fugitive emissions.

The Sunoco Marcus Hook refinery uses techniques from EPA's *Protocol for Equipment Leak Emission Estimates*. For applicable areas of the refinery, the SCOMI leak rate/screening value correlation equations from Table 2-9 of the EPA document are used, with the default zero emission rates from Table 2-11 and the pegged values from Table 2-13. For SOCOMI components not monitored, the SOCOMI average emission factors from Table 2-1 of the EPA document are used. There are about 6,531 SOCOMI fugitive components. For non-SOCMI components, the exact equations or emissions factors used were not available.

The ConocoPhillips Trainer refinery uses the correlation equations from Table 2-10 of EPA's *Protocol for Equipment Leak Emission Estimates*. The actual screening values are used with the equations from Table 2-10 to calculate emissions. For unmonitored components (flanges), an assumption is made that the flanges have a 2% leak rate (at 10,000 ppm) using the flange factor from Table 2-10. The default zero emission factor provided in Table 2-12 is used for the remaining flanges. The refinery will make the screening values available for review by PADEP, if desired.

The Amerada Hess Port Reading refinery did not provide any supporting documentation regarding process fugitive emission calculations.

The Chevron Products Perth Amboy refinery uses techniques from EPA's *Protocol for Equipment Leak Emission Estimates*. Valves and pumps in applicable VOC service are calculated using the average leak rate for a 1,000 ppm leak definition based on the equations found in Table 5-5 of the EPA document. Pressure relief valves and compressor seals are calculated using refinery screening range emission factors from Table 2-6 of the EPA reference. Flanges are estimated using refinery average emission factors from Table 2-2 of the EPA reference. Component counts were not available.

The Citgo Asphalt Paulsboro refinery uses emission factors from EPA's *Protocol for Equipment Leak Emission Estimates*. Specifically, they use the factors from Table 5-5 with a leak rate of 0.5% and a leak definition of 1,000 ppm. For other components that were determined not to be leaking during the year, Citgo uses the default zero emission factors from Table 2-12 of the EPA document. The refinery has about 6,309 fugitive emission components.

The Coastal Eagle Point refinery did not provide any supporting documentation regarding process fugitive emission calculations.

The Conoco Phillips Linden (Bayway) refinery estimates process fugitive emissions using the screening ranges emission factors from Table 2-6 of EPA's *Protocol for Equipment Leak Emission Estimates*. Emission factors are separated into two categories – “leak” and “no-leak”. “Leak” emission factors are used for components which have been tested and measured at a rate greater than 1,000 ppm. “No leak” emission factors apply for components which are tested and found to be leaking less than 1,000 ppm (including non-detects). This method is conservative (i.e., generates higher VOC emission estimates) since the EPA emission factors are based on a leak rate of 10,000 ppm, not 1,000 ppm. Leak rates for components not monitored are determined for different areas of the refinery. For example, if 100 components at the Powerformer are test and 5 components are found to be leaking greater than 1,000 ppm, then a 5% leak rate is applied to the components not tested.

Fugitive emissions at the terminal facilities are calculated in a slightly different manner. The basis for terminal fugitive emissions is obtained from API Publication #4588 *Development of Fugitive Emission Profiles for Petroleum Marketing Terminals*. There is a single emission factor for each type of component (i.e., flanges, valves, pumps), and leak/no leak rates don not apply.

ConocoPhillips Linden refinery estimates that there are 62,295 fugitive components at the refinery, including the two marketing terminals. Its emissions are substantially higher than any other refinery in the study area. ConocoPhillips believes this is because of the large size and complexity of the refinery, and that the emission statement includes two marketing terminals. Also, the facility does not apply a 0% leak rate to components not tested, but rather uses the average leak rate for the process area.

The Valero Refining Paulsboro refinery did not provide any supporting documentation, although they will make is available for review by NJDEP.

WASTEWATER TREATMENT

During this refining process, a significant quantity of industrial wastewater is produced. This wastewater typically passes through a complex series of on-site collection and treatment units. Many of these collection and treatment units are open to the atmosphere and allow for volatilization of VOCs from the wastewater. The design of the wastewater treatment systems is dictated by the types of pollutants in the waste stream. Drain systems, oil-water separators, and air flotation systems are generally included. The majority of VOC emissions result from the evaporation from the surfaces of waste water in open drains, separators, and aerated basins. The factors influencing emissions from these systems are waste water composition, equipment design, and climatic factors. Each refinery's wastewater treatment system is unique.

There are five basic approaches for estimating emissions from wastewater treatment processes. The approaches, in order of increasing refinement, are:

- Average emission factors;
- Material balance;
- Manual calculations
- Emission models
- Source testing

The approaches increase in complexity and in the amount of data collection and analysis required. All the approaches require some data collection, data analysis and/or statistical evaluation. References 8 and 9 provide a full description of the methods, which are briefly summarized below.

Both AP-42 and FIRE present average emission factors process. Table 5.1-2 of AP-42 presents two emission factors for oil/water separators. The first factor is 5 lbs/1000 gallons wastewater processed and is for uncontrolled operations. The second factor is 0.2 lbs/1000 gallons wastewater and is for covered separators and/or vapor recovery systems. FIRE has a factors of 0.03 lbs/1000 gallons wastewater processed and 0.7 lbs/1000 barrels refinery feed processed for wastewater treatment activities without an oil/water separator, but the origin of these factors is unknown. AP-42 Table 5.1-3 also presents a factor of 0.064 lbs per drain per day for process drains.

The second estimation method to determine VOC emissions from wastewater collection systems is through material balance. Material balance relies on wastewater flow rate and influent and effluent liquid-phase pollutant concentrations. Compound mass that cannot be accounted for in the effluent is assumed to be volatilized. However, the use of this methodology assumes that both the influent and effluent concentrations at each point in the wastewater collection system are known. Furthermore, an accurate mass balance requires collection and analysis of many samples over a long period, because refinery wastewater concentrations are constantly changing, so they must be averaged before calculating removals. Because of these limitations, this VOC estimation method has limited usefulness.

Several EPA documents are available that provide theoretical equations that may be used to calculate emissions from WWCT. These include *Industrial Wastewater Volatile Organic Compound Emissions - Background Information for BACT/LAER Determinations* (EPA-450/3-90-004), AP-42 Chapter 4.3, and *Air Emissions Models for Waste and Wastewater* (EPA-453/R-94-080A). The equations are based on mass transfer and liquid-gas equilibrium theory and use individual gas-phase and liquid-phase mass transfer coefficients to estimate overall mass transfer coefficients. Calculating air emissions using these equations is a complex procedure, especially if several systems are present, because the physical properties of the numerous contaminants must be individually determined.

Because of the great deal of complexity involved, computer programs are available that incorporate these equations to estimate emissions.

- EPA recommends the use of the WATER9, a Windows based computer program and consists of analytical expressions for estimating air emissions of individual waste constituents in wastewater collection, storage, treatment, and disposal facilities; a database listing many of the organic compounds; and procedures for obtaining reports of constituent fates, including air emissions and treatment effectiveness. To obtain these emission estimates, the user must identify the compounds of interest and provide their concentrations in the wastes. The identification of compounds can be made by selecting them from the database that accompanies the program or by entering new information describing the properties of a compound not contained in the database. See Reference 13 for details of the equations and input parameters necessary to run the WATER9 program.

- The American Petroleum Institute (API) initiated a project to develop a mathematical model that would predict accurate emissions from refinery process drains. A mechanistic model was developed to predict VOC and HAP emissions from refinery process drains using mass transfer fundamentals based on conservation of mass. See Reference 12 for more details.

Estimating emissions using models is data intensive, requires site-specific information, and information on the chemical constituents of the waste stream.

Finally, source tests can be used to determine the emissions of VOCs from each wastewater collection component. Air samples are collected from the various emission points in the wastewater collection system (drains, sumps, manholes, etc). These air samples are analyzed for VOC concentration. Other information such as airflow rates for each sample point combined with the air sample concentrations is used to determine the emissions for each emission point in the wastewater collection system. While this methodology is highly accurate in determining individual emission points of the refinery wastewater collection systems, it is not a practical methodology to use. Since the wastewater collection system consists of thousands of components at each refinery, this methodology is too time and resource consuming to be the sole methodology used to estimate emissions from wastewater collection systems. However, a limited and focused source testing program can provide valuable data to estimate emissions from an entire refinery wastewater collection system using emission estimation models.

Table 9 summarizes the VOC emissions and emission estimation methods used by each refinery.

The Motiva Delaware City refinery uses the EPA's WATER9 model to calculate VOC emissions from wastewater treatment plant components. The total water flow rate to the treatment plant is 6.04 mmGal/day. Output from the model was available for review, but input parameters were not available. It is not clear whether emissions from process drains are accounted for in the WATER9 modeling or are included under the process fugitive emission point.

The Sunoco Philadelphia refinery uses the FIRE emission factors to calculate VOC emissions from wastewater treatment operations at both Girard Point and Point Breeze. The factor is 0.03 lbs/1000 gallons water processed. This factor has a quality rating of "U", meaning unknown quality. The average water flow rate to the treatment plant at Girard Point is 4.16 mmGal/day. The average water flow rate to the treatment plant at Point Breeze is 4.5 mmGal/day. While both areas use the same emission factors and the water flows are similar, the emissions are not. There appears to be an error in the oil/water separator emission calculations at Girard Point. VOC emissions in 1998 were about 22 tpy, but were 0 in the 2000 inventory. This difference appears to be caused by an error in Sunoco's emission calculation spreadsheet where the annual water flow to the oil/water separators appears to be incorrectly calculated. Emissions from Girard Point oil/water separators should be able 31 tpy in 2000.

Emissions from process drains at both Girard Point and Point Breeze are included with fugitive emissions, according to Sunoco's backup spreadsheet. VOC emissions from unmonitored process drains at Point Breeze appear to be missing from 2000 inventory. These emissions are included under process fugitive emissions. Sunoco's backup calculation spreadsheet showed 38.4 tpy from process drains in 1999, but were 0 tpy in the 2000 inventory.

**TABLE 9 - VOC EMISSIONS AND ESTIMATION METHODS FOR
WASTE WATER TREATMENT**

Refinery	VOC Emissions (tons per year)	Emission Estimation Methodology
Motiva Delaware City, DE	260	Used EPA WATER9 model (resulting in a factor of 0.35 lbs/1000 gals)
Sunoco Philadelphia, PA	24.7	Point Breeze uses FIRE factor of 0.03 lbs/1000 gallons, which they claim is for covered separators vented to carbon canister control
	0.05	Girard Point separators 4a and 2B also use FIRE factor of 0.03 lbs/1000 gallons; apparent error in emission calculations, if corrected, would result in about 31 tpy of VOC for these separators
Sunoco Marcus Hook, PA	46	Used EPA's AP-42 emission factor (resulting in a factor of 0.035 lbs/1000 gals), which includes a 95% control efficiency for covered separators
ConocoPhillips Trainer, PA	28	Used EPA's WATER8 model, and used a 96.2% control efficiency for covered separators
Amerada Hess Port Reading, NJ	1	RADIUS has of factor of 0.265 lbs per hour factor of unknown origin
Chevron Perth Amboy, NJ	422	Based on <i>Air Emissions Models for Waste and Wastewater</i> ; calculations were prepared for the facility-wide permit, and annual updates are prorated based on the loading of oil to the treatment plant.
Citgo Paulsboro, NJ	2	RADIUS has 0.111 lbs/1000 gallons for biological treatment and 0.0004 lbs/1000 gallons for air filtration unit; based on WATER9 model and sampling data
Coastal Eagle Westville, NJ	111	RADIUS has 29.8 tpy from API separator, 27.5 from API thickener, and 52.6 tpy from aeration basin, all calculated using a material balance; details of calculations were not provided.
ConocoPhillips Linden, NJ	111	RADIUS has emission factors ranging from 0.4 to 5.5 lbs/hour, based on use of unspecified EPA computer program
Valero Paulsboro, NJ	282	RADIUS has an emission factor of 64.4 lbs/hour, basis appears to be EPA's WATER8 model

The Sunoco Marcus Hook refinery estimates VOC emissions from the wastewater treatment facility by multiplying the volumetric flow rate to the POTW by and AP-42 emission factor. The inventory includes a control efficiency of 95%, but the exact emission factor used has not been documented.

The ConocoPhillips Trainer refinery estimates VOC emissions from wastewater treatment operations using the EPA WATER8 model. The inputs for WATER8 are based on monthly samples (VOC scan analysis) of the API separator effluent. The VOC emissions from process drains are calculated based on the WATER8 input data and emission factors for drains, manholes, and sewers developed by the BP Oil Company. The sample analysis, wastewater throughputs, and model outputs are entered into a spreadsheet to calculate the VOC emissions. The model inputs, outputs, analytical and process data are all available for review by PADEP, upon request. The inventory for years 1997 and earlier used the AP-42 factor of 0.2 lbs/mmGal for the API separator and an emission factor from FIRE for process drains.

For the Amerada Hess Port Reading refinery, RADIUS has of factor of 0.265 lbs per hour factor of unknown origin, and emissions of less than 1 tpy. No other information is currently available.

The Chevron Products Perth Amboy refinery calculates VOC emissions from the effluent treatment plant based on the 1994 EPA document entitled *Air Emissions Models for Waste and Wastewater*, which formed the basis for EPA's WATER8 model. Calculations were prepared for the facility-wide permit, and annual updates are prorated based on the loading of oil to the treatment plant. Flow rate is about 0.72 mmGal/day.

The Citgo Asphalt Paulsboro refinery calculates VOC emissions from wastewater using EPA's WATER9 model. Citgo monitors the inlet and outlet of its wastewater treatment plant for VOCs. Samples are collected once a month to comply with the Title V air permit. The monthly VOC concentrations are used as input to the WATER9 emissions model. Citgo began collecting VOC wastewater data for Title V compliance in April 2002.

According to RADIUS, the Coastal Eagle Point refinery has 29.8 tpy from API separator, 27.5 from API thickener, and 52.6 tpy from aeration basin, all calculated using a material balance. Details of the emission calculations are not currently available. The flow to the API separator is about 3.2 mmGal/day.

The ConocoPhillips Linden (Bayway) refinery calculates VOC emissions from wastewater treatment operations using EPA modeling software (version number not provided). VOC emissions at the main bays of the API separators are determined by sampling at the influent to the API. Sampling data is reduced and used as inputs to the water modeling software, which calculates a VOC emission factor which is applied to the wastewater flow rate. Wastewater treatment plant emissions rose from 44 tpy in 2000 to 111 tpy in 2001, possible because of due to increased skimming facility outages in 2001. The water model is also used to determine an emission factor at the biox lagoons downstream of the API separators, where biological treatment takes place. Input data to the water modeling software comes from reduction of sampling data at the inlet to the biox.

The Valero Refining Paulsboro refinery had a study of wastewater VOC emissions conducted as part of its 1995 VOC RACT submittal. The study used the EPA's WATER8 model. Current emissions from wastewater treatment operations are estimated using the results of the WATER8 modeling as a baseline and adjusting based on wastewater treatment plant discharges.

COOLING TOWERS

Refineries use large quantities of water for cooling throughout the refining process. Cooling towers are used to transfer heat from the cooling water to the atmosphere by allowing water to cascade through a series of decks and slat-type grids. Water that enters the cooling tower may contain hydrocarbons from leaking heat exchangers. VOC emissions occur as VOCs are stripped from the cooling water as the air and water come into contact.

AP-42 Table 5.1-2 presents an emission factor of 6 lbs/10⁶ gallons cooling water processed for uncontrolled operations. For controlled conditions, the emission factor is 0.7 lbs/10⁶ gallons cooling water processed. Control of cooling tower emissions is accomplished by reducing the contamination of cooling water through the proper maintenance of heat exchangers and condensers. The effectiveness of cooling tower controls is highly variable, depending on refinery configuration and existing maintenance practices.

TNRCC (Reference 14) suggests the values presented in AP-42 are very general and should be replaced by actual test data from the tower once it is in operation. Specifically, the VOC concentration in the water coming to and leaving a cooling tower should be determined so that an emission rate can be calculated. TNRCC suggests a test method developed by El Paso Products Company can be used to determine VOC emissions from a cooling tower.

Table 10 summarizes the VOC emissions and emission estimation methods used by each refinery. The emissions vary widely, and several different emission estimation methods are used.

The Motiva Delaware City refinery uses a material balance based on measured cooling tower flow rates and sampling to determine VOC content of the cooling water. The details of the calculations made are not available.

The Sunoco Philadelphia refinery uses the AP-42 emission factor of 0.7 lbs/10⁶ gallons cooling water processed, which is the controlled emission factor where the applicable control technology is to minimize hydrocarbon leaks into the cooling water system. There are four cooling towers Girard Point and four towers at Point Breeze. The total water circulation rate is 189,000 gal/min at Girard Point, compared to 105,600 at Point Breeze.

The Sunoco Marcus Hook refinery also estimates cooling tower emissions using the AP-42 emission factor of 0.7 lbs/10⁶ gallons cooling water processed, which is the controlled emission factor where the applicable control technology is to minimize hydrocarbon leaks into the cooling water system.

TABLE 10 - VOC EMISSIONS AND ESTIMATION METHODS FOR COOLING TOWERS

Refinery	VOC Emissions (tons per year)	Emission Estimation Methodology
Motiva Delaware City, DE	3.7	RFG cooling tower based on measured water flow and lab analyzed samples of VOC content of cooling water
Sunoco Philadelphia, PA	35 Girard Point 19 Point Breeze	AP-42 controlled factor of is 0.7 lbs/10 ⁶ gallons cooling water processed is used at both Girard Point and Point Breeze
Sunoco Marcus Hook, PA	25	AP-42 controlled factor of is 0.7 lbs/10 ⁶ gallons cooling water processed
ConocoPhillips Trainer, PA	8	Factor used was 0.83 lbs/10 ⁶ gallons cooling water processed
Amerada Hess Port Reading, NJ	0	No cooling towers in inventory
Chevron Perth Amboy, NJ	4.4	Cooling tower emissions are reported as insignificant activity; company estimated 1.0 lbs/hr in 2001 inventory; no VOC present in cooling tower water in 2002
Citgo Paulsboro, NJ	0	No cooling towers; cooling is performed using a closed looped ethylene glycol system
Coastal Eagle Westville, NJ	3.6	Listed as insignificant source in permit, emissions based on uncontrolled AP-42 factor of 6 lbs/10 ⁶ gallons cooling water processed
ConocoPhillips Linden, NJ	0	No cooling towers in 2001 RADIUS emission statement inventory
Valero Paulsboro, NJ	0	Cooling tower listed as insignificant activity; no emissions reported

The ConocoPhillips Trainer refinery also estimates cooling tower emissions using the AP-42 emission factor of 0.7 lbs/10⁶ gallons cooling water processed, which is the controlled emission factor where the applicable control technology is to minimize hydrocarbon leaks into the cooling water system.

The 2001 RADIUS emission statement for the Amerada Hess Port Reading refinery does not list any cooling towers in the inventory.

There is one cooling tower at the Chevron Products Perth Amboy refinery. It is listed as an insignificant activity and its emissions are combined with all other insignificant activities in the emission statement. In the past, emissions have been based on calculations contained in the facility-wide permit application (i.e., 1.0 lbs/hour based on existing Subchapter 8 permit no 13831). This results in an annual emission rate of 4.4 tpy. According to the company, there was no indication of the presence of VOC in the cooling tower in 2002, so no VOC emissions were reported.

There are no cooling towers at the Citgo Asphalt Paulsboro refinery. Cooling is performed using a closed looped ethylene glycol fan system.

The 2001 RADIUS emission statement for the Coastal Eagle Point refinery lists cooling towers as insignificant sources in the inventory. Emissions in 2001 were 3.63 tpy, based on the AP-42 factor of 6 lbs/10⁶ gallons cooling water processed for uncontrolled operations.

The RADIUS emissions statement for ConocoPhillips Linden (Bayway) does not list any cooling towers in the inventory. Their response to NJDEP's inquiry stated that they "do not have cooling tower emissions to quantify prior to RY 2003". We cannot determine whether this means that they do not have any cooling towers, or that they have not been able to quantify VOC emissions from existing cooling towers.

The Valero Refining Paulsboro refinery states that "we do not have VOC emissions from cooling towers under normal operating conditions". Cooling towers are listed as an insignificant source in the RADIUS 2001 emission statement.

STORAGE TANKS

Storage tanks are significant sources of VOC emissions at refineries. Storage tank emissions are attributed to breathing and working losses. Breathing losses result from vapor volume and pressure variations caused by diurnal temperature changes. Working losses result from tank-filling operations where hydrocarbon vapors are displaced from the tank because of the rising liquid surface. VOC emissions depend upon the design of the tank, the product stored, and ambient meteorological conditions.

There are six basic tank designs used for organic liquid storage vessels: fixed roof (vertical and horizontal), external floating roof, domed external (or covered) floating roof, internal

floating roof, variable vapor space, and pressure (low and high). A brief description of each tank is provided in AP-42 Section 7.1.

Organic liquids at refineries include both petroleum liquids, generally are mixtures of hydrocarbons having dissimilar true vapor pressures (for example, gasoline and crude oil), and volatile organic liquids, composed of pure chemicals or mixtures of chemicals with similar true vapor pressures (for example, benzene or a mixture of isopropyl and butyl alcohols).

The emission estimating equations presented in Section 7.1 of AP-42 for storage tanks were developed by the American Petroleum Institute (API). These equations have been incorporated into a computer program maintained by EPA called TANKS. The software is designed for use by local, state, and federal agencies, environmental consultants, and others who need to calculate air pollutant emissions from organic liquid storage tanks. The current version of TANKS is Version 4.09b. The TANKS program undergoes frequent update to correct minor errors and improve the user interface. The last major changes (from Version 3 to Version 4) occurred in September 1999.

TANKS 4.09b allows users to enter specific information about a storage tank (dimensions, construction, paint condition, etc.), the liquid contents (chemical components and liquid temperature), and the location of the tank (nearest city, ambient temperature, etc.), and generate an air emissions report. Report features include estimates of monthly, annual, or partial year emissions for each chemical or mixture of chemicals stored in the tank.

Table 11 summarizes the VOC emissions, number of tanks, and version of the TANKS program used at each refinery.

UNLOADING AND LOADING OPERATIONS

The transportation and marketing of petroleum liquids involve many distinct operations, each of which represents a potential source of evaporation loss. Crude oil is transported from production operations to a refinery by tankers, barges, rail tank cars, tank trucks, and pipelines. Refined petroleum products are conveyed to fuel marketing terminals and petrochemical industries by these same modes. From the fuel marketing terminals, the fuels are delivered by tank trucks to service stations, commercial accounts, and local bulk storage plants.

Loading losses are the primary source of evaporative emissions from rail tank car, tank truck, and marine vessel operations. Loading losses occur as organic vapors in "empty" cargo tanks are displaced to the atmosphere by the liquid being loaded into the tanks. These vapors are a composite of (1) vapors formed in the empty tank by evaporation of residual product from previous loads, (2) vapors transferred to the tank in vapor balance systems as product is being unloaded, and (3) vapors generated in the tank as the new product is being loaded.

TABLE 11 - VOC EMISSIONS AND ESTIMATION METHODS FOR STORAGE TANKS

Refinery	VOC Emissions (tons per year)	Number of Storage Tanks	Emission Estimation Methodology
Motiva Delaware City, DE	123	124	TANKS Version 3.1; does not include tanks at the nearby Motiva Enterprises Marketing Terminal, which is a separate facility in the inventory.
Sunoco Philadelphia, PA	170	91 Point Breeze 66 Girard Point	Version of TANKS not provided; does not include 45 tanks at adjacent Schuylkill River Tank Farm, which is a separate facility
Sunoco Marcus Hook, PA	140	84	TANKS Version 4.09b
ConocoPhillips Trainer, PA	84	34	TANKS Version 4.06
Amerada Hess Port Reading, NJ	261	68	Version of TANKS not provided
Chevron Perth Amboy, NJ	59	134	Version of TANKS not provided
Citgo Paulsboro, NJ	25	39	Version of TANKS not provided
Coastal Eagle Westville, NJ	205	170	Version of TANKS not provided
ConocoPhillips Linden, NJ	368	225	TANKS Version 4.0; includes emissions from Linden Marketing terminal and Tremley Point terminal
Valero Refining Paulsboro, NJ	399	367	Version of TANKS not provided

Section 5.2 of AP-42 provides a fuller description of the emission generating processes. The AP-42 loading equation listed in Chapter 5.2 is typically used to calculate emissions from loading operations:

$$LL = 12.46 \text{ SPM/T}$$

where:

LL = Loading Loss (lb/103 gal of liquid loaded)

S = Saturation factor from AP-42, Table 5.2-1

P = True vapor pressure of liquid loaded (psia)

M = Molecular weight of vapors (lb/lb-mol)

T = Temperature of bulk liquid loaded (°R)

Loading operations are typically controlled using a vapor recovery unit (VRU) or backup vapor combustion unit (VCU). Stack tests are normally conducted to determine the control efficiency of the device. Loading of products with relatively low volatilities, such as heating oil or diesel, sometimes occur without the use of the control equipment.

Table 12 summarizes the VOC emissions from truck/railcar loading operations, emission controls, and emission estimation method used at each refinery. Table 13 summarizes the VOC emissions from marine vessel loading operations, emission controls, and emission estimation method used at each refinery.

TABLE 12 - VOC EMISSIONS AND ESTIMATION METHODS FOR TRUCK/RAILCAR LOADING OPERATIONS

Refinery	VOC Emissions (tons per year)	Emission Controls	Emission Estimation Methodology
Motiva Delaware City, DE	0	None	No truck loading operations in the inventory. Presumably truck loading occurs at the adjacent Motive Marketing Terminal, which is a separate facility in the DNREC inventory
Sunoco Philadelphia, PA	0.1		No truck loading is performed at Point Breeze. At Girard Point, AP-42 equation is used. No loading of gasoline in 2000 at Girard Point, the only loading by tank truck is the cumene rack
Sunoco Marcus Hook, PA	1.3	99.9% carbon adsorber	Appears to be AP-42 equation.
ConocoPhillips Trainer, PA	3.1	None provided	Title V permit does not list any truck loading operations. Railcar loading is listed at LPG and Butane loading. Estimation method appears to be AP-42 equation.
Amerada Hess Port Reading, NJ	12.0	None listed in RADIUS	RADIUS has truck loading rack emissions based on State emission factor of 8.36 lbs/10 ⁶ gallons transferred.
Chevron Perth Amboy, NJ	0	None	RADIUS has loading racks as emission point U6 with no VOC emissions or control device information
Citgo Asphalt Paulsboro, NJ	0.1	None	RADIUS lists as insignificant sources truck loading of #6 oil, asphalt, kerosene, and #2 fuel oil
Coastal Eagle Westville, NJ	3.9	90% VCU	RADIUS has emissions based on either source tests or AP-42 equation. Control device listed in RADIUS is a flare with 90% control efficiency
ConocoPhillips Linden, NJ	7.6	99.7% LMT VRU 99.9% LMT VCU 99.9% TPT VRU	AP-42 equation is used. Emission statement includes truck loading racks at Linden Marketing Terminal (LMT) and Tremley Point Terminal (TPT). No truck loading occurs at the refinery. Uncontrolled loading occurs occasionally at each source for diesel, kerosene, etc.
Valero Paulsboro, NJ	0		RADIUS does not list any truck loading operations.

VRU – vapor recovery unit
VCU – vapor combustion unit

TABLE 13 - VOC EMISSIONS AND ESTIMATION METHODS FOR MARINE VESSEL LOADING OPERATIONS

Refinery	VOC Emissions (tons per year)	Emission Controls	Emission Estimation Methodology
Motiva Delaware City, DE	8.9	MVRU efficiency not provided	Emissions based on source tests while loading both gasoline and methanol. In 1999, MVRU was used for gasoline loading but not methanol loading. In 2001, the MVRU was used for both gasoline loading and methanol loading.
Sunoco Philadelphia, PA	1.2 Point Breeze	99.9% MVRU	AP-42 equation is used.
	38.3 Girard Point	Uncontrolled?	AP-42 equation is used. Emission calculations do not include control efficiency.
Sunoco Marcus Hook, PA	23.1	None listed	Marine vessel loading of gasoline (ID#115) has been inactive since 2000. Marine vessel loading of other products appear to be based on AP-42 equation.
ConocoPhillips Trainer, PA	0.4	99.9% MVRU	Estimation method appears to be AP-42 equation.
Amerada Hess Port Reading, NJ	27.8	MVRU efficiency not provided	RADIUS has marine loading emissions based on State emission factor of 8.36 lbs/10 ⁶ gallons transferred.
Chevron Perth Amboy, NJ	0.63	MVCU efficiency not provided	RADIUS has emissions based on source tests. Control device listed in RADIUS is a thermal oxidizer – no control efficiency provided
Citgo Asphalt Paulsboro, NJ	0.05	MVCU efficiency not provided	RADIUS has emissions based on material balance and emissions controlled by thermal oxidizer – no control efficiency provided
Coastal Eagle Westville, NJ	2.4	99.9% MVCU	RADIUS has emissions based on either source tests or AP-42 equation. Control device listed in RADIUS is a thermal oxidizer with 99% control efficiency
ConocoPhillips Linden, NJ	13.3	99.9% TPT MVCU 99.9% refinery MVCU	AP-42 equation is used. Barge loading occurs at the Tremley Point Terminal (TPT) and the refinery's marine loading dock. No barge loading occurs at Linden Marketing Terminal. Uncontrolled loading occurs occasionally at each source for diesel, kerosene, etc.
Valero Paulsboro, NJ	<0.01	MVRU efficiency not provided	RADIUS has emissions based on source test – 0.92 lbs/hour.

VRU – vapor recovery unit
VCU – vapor combustion unit

MVRU – marine vapor recovery unit
MVCU – marine vapor combustion unit

REFERENCES

1. *Air Pollution Engineering Manual, Chapter 17 – The Petroleum Industry*, J. Eldon Rucker and Robert P Strieter, published by the Air and Waste Management Association, 1992.
2. *Compilation of Air Pollutant Emission Factors, AP-42, 5th Edition*, published by the U.S. Environmental Protection Agency, RTP, NC. [TTN CHIEF | Compilation of Air Pollutant Emission Factors](#)
3. *FIRE Version 5.0 Source Classification Codes and Emission Factor Listing for Criteria Air Pollutants* (EPA-454/R-95-012), August 1995, U.S. Environmental Protection Agency, RTP, NC.
4. *Uncontrolled Emission Factor Listing for Criteria Air Pollutants* (EIIIP Volume II: Chapter 14, July 2001, Emission Inventory Improvement Program. http://www.epa.gov/ttn/chief/eiip/techreport/volume02/ii14_july2001.pdf
5. *Technical Guidance Package for Chemical Sources: Fluid Catalytic Cracking Units* (Draft RG-110), February 2001, Texas Natural Resource Conservation Commission. http://www.tnrcc.state.tx.us/permitting/airperm/nsr_permits/files/fccu.pdf
6. *Petroleum Refineries Background Information for Proposed Standards – Catalytic Cracking Units, Catalytic Reforming Units, and Sulfur Recovery Units* (EPA-453/R-98-003), June 1998, U.S. Environmental Protection Agency, RTP, NC.
7. *Technical Guidance Package for Chemical Sources: Flares and Vapor Oxidizers* (Draft RG-109), October 2000, Texas Natural Resource Conservation Commission. http://www.tnrcc.state.tx.us/permitting/airperm/nsr_permits/files/flares.pdf
8. *Draft Technical Assessment Document: Further Study Measure 8 Flares*, December 2002, Bay Area Air Quality Management District. <http://www.baaqmd.gov/enf/refineryfsm/Flares/FlaresTAD.pdf>
9. *Preferred and Alternative Methods for Estimating Fugitive Emissions from Equipment Leaks*, (EIIIP Volume II: Chapter 4, November 1996, Emission Inventory Improvement Program. http://www.epa.gov/ttn/chief/eiip/techreport/volume02/ii04_a.pdf and http://www.epa.gov/ttn/chief/eiip/techreport/volume02/ii04_b.pdf
10. *Protocol for Equipment Leak Emission Estimates*, (EPA-453/R-95-017), November 1995, U.S. Environmental Protection Agency, RTP, NC. http://www.epa.gov/ttn/chief/efdocs/lks95_ch.pdf
11. *Development of Fugitive Emission Factors and Emission Profiles for Petroleum Marketing Terminals, Volume 1*, (API #4588), May 1993, American Petroleum Institute, Washington, DC.
12. *Preferred and Alternative Methods for Estimating Air Emissions from Wastewater Collection and Treatment*, (EIIIP Volume II: Chapter 5, March 1997, Emission Inventory Improvement Program. <http://www.epa.gov/ttn/chief/eiip/techreport/volume02/ii05.pdf>

13. *Draft Technical Assessment Document: Potential Control Strategies to Reduce Emissions from Refinery Wastewater Collection and Treatment Systems*, January 2003, Bay Area Air Quality Management District.
<http://www.baaqmd.gov/enf/refineryfsm/WasteWater/WasteWaterTAD.pdf>
14. *Fugitive Emissions from Refinery Process Drains Volume I, Fugitive Emission Factors for Refinery Process Drains*, Publ 4677, American Petroleum Institute. [Air Emission Model for Predicting Emissions from Refinery Process Drains](#)
15. *WATER Model, Industrial Wastewater Volatile Organic Compound Emissions - Background Information for BACT/LAER Determinations* (EPA-450/3-90-004), and *Air Emissions Models for Waste and Wastewater* (EPA-453/R-94-080A). U.S. Environmental Protection Agency, RTP, NC. [EPA |TTN CHIEF | WATER9](#)
16. *Air Quality Permit Technical Guidance for Chemical Sources: Cooling Towers*
http://www.tnrcc.state.tx.us/permitting/airperm/nsr_permits/files/ctower.pdf
17. Various e-mails concerning VOC emissions from the Sunoco Marcus Hook Refinery from Mr. David Brown, PADEP Air Quality Specialist, to Mr. Edward Sabo, MACTEC, dated May 23, May 28, and May 30, 2003.
18. *Response to June 6, 2003 Request for Information*, letter from Mr. John Deemer, Conoco Phillips Trainer Refinery, to Ms. Cynthia Neger, PADEP Air Quality Specialist, dated July 8, 2003.
19. *Exhibit 1 – Questions for States/locals and Refineries Regarding Emission Estimation Methods: Motiva Enterprises, Delaware City*, contained in a Fax from Mr. Bruce Steltzer, DNREC, to Mr. Edward Sabo, MACTEC, dated July 14, 2003.
20. *Responses to Annual Emission Statement MARAMA Project Questions*, e-mail from Conoco Phillips Linden (Bayway) Refinery to Mr. Danny Wong, NJDEP Emission Statement Program.
21. Letter from Mr. Michael Pesch, Valero Paulsboro Refinery, to Mr. Danny Wong, NJDEP Emission Statement Program, dated July 9, 2003.
22. *Response to Questions of Reasonableness Concerning the 2002 Emission Statement*, letter from Mr. Richard Roat, Citgo Asphalt Paulsboro Refinery, to Mr. Danny Wong, NJDEP Emission Statement Program, dated June 23, 2003.
23. *Response to NJDEP Questions on the 2002 Emission Statement*, letter from Mr. Mark Sullivan, Chevron Products Company Perth Amboy Refinery, to Mr. Danny Wong, NJDEP Emission Statement Program, dated July 10, 2003.

APPENDIX G

FINAL TECHNICAL MEMORANDUM #6

**EVALUATION OF EMISSION ESTIMATION METHODS FOR
PETROLEUM REFINERIES
IN DELAWARE, NEW JERSEY, AND SOUTHEASTERN PENNSYLVANIA**

**TECHNICAL MEMORANDUM #6
FINAL**

**EVALUATION OF EMISSION ESTIMATION METHODS FOR
PETROLEUM REFINERIES
IN DELAWARE, NEW JERSEY, AND SOUTHEASTERN PENNSYLVANIA**

Prepared for:

Susan S.G. Wierman, Executive Director
Mid-Atlantic Regional Air Management Association (MARAMA)
711 W. 40th Street
Suite 318
Baltimore, MD 21211-2109

October 13, 2003
5925.006

Submitted by

Edward Sabo
MACTEC Federal Programs, Inc.
560 Herndon Parkway
Suite 200
Herndon, VA 20170
(703) 471-8383, FAX (703) 481-8296
EJSabo@mactec.com

TABLE OF CONTENTS

	Page
INTRODUCTION	1
OVERVIEW OF EMISSION ESTIMATION METHODOLOGIES	3
EXTERNAL AND INTERNAL COMBUSTION SOURCES	6
MACT I PROCESS VENTS	9
MACT II PROCESS VENTS	9
FLARES	11
PROCESS EQUIPMENT LEAKS	13
WASTEWATER TREATMENT	17
COOLING TOWERS	20
STORAGE TANKS.....	21
LOADING OPERATIONS	22
MARINE VESSEL BALLASTING	23
NON-ROUTINE RELEASES	24
REFERENCES	26

TABLES

	Page
Table 1. Typical Air Emission Sources in the Petroleum Industry.....	2
Table 2. General Point Source Emission Estimation Methods	5
Table 3. AP-42 Emission Factors for External and Internal Combustion	8

FIGURES

	Page
Figure 1. Emission Estimation Approaches	4

INTRODUCTION

Recent ozone air quality investigations indicate the potential for underestimation of volatile organic compound (VOC) emissions from petroleum refineries. As part of the *Texas Air Quality Study 2000*, airplane measurements of ambient concentrations of VOC and highly photochemically reactive compounds were compared to the reported emission inventory estimates. The comparison indicated that VOC emissions may be significantly under-reported, specifically for industrial sources. Similar aircraft measurements in the Philadelphia area also found a substantial ozone plume downwind of the Delaware/Southeast Pennsylvania/New Jersey industrial area. VOC emissions from petroleum refineries comprise a significant portion of the total industry related VOC emissions in this area. Finally, the Bay Area Air Quality Management District, the Texas Commission on Environmental Quality, and the U.S. Environmental Protection Agency have all acknowledged the potential for underestimation of VOC emissions from petroleum refineries.

In Technical Memorandum #2, we identified petroleum industry facilities in the MARAMA states and New York. Technical Memorandum #3 focused on identifying individual emission processes at the 10 refineries and other petroleum industry facilities located in Delaware, New Jersey, and southeastern Pennsylvania. Technical Memorandum #4 identified individual VOC sources that are potentially not accounted for in the existing emission inventories. Technical Memorandum #5 described the VOC emission estimation methods currently being used for each source category within the refineries.

This report, Technical Memorandum #6, evaluates the methods identified in Memorandum #5 and other methods that are available for estimating VOC emissions from petroleum refineries. The specific objectives of this memorandum are to:

- Describe and evaluate emission estimation methodologies currently being used
- Compare the methods used to available methodologies in EPA and State agency guidance
- Suggest ways to improve emission estimates

This memorandum begins with a brief discussion of the general types of methodologies used to estimate emissions. The remainder of this document provides a description of the methods used to estimate VOC emissions from sources typically found at petroleum refineries. The sources listed in Table 1 are addressed. A general discussion is provided for each emission source type, outlining optional estimation techniques, where applicable. Emission factors are listed and referenced. Where possible, this memorandum provides multiple estimation approaches for each category of emissions. These approaches are generally presented in terms of a preferred approach and alternate approach(es) for estimating VOC emissions.

This memorandum is intended to help promote consistent estimation of VOC emissions from petroleum refineries in the MARAMA region. We recognize that each facility should decide which emission estimation technique is appropriate for their specific sources and available data. For example, if site specific data such as stack testing or emissions monitoring is available, it would provide more accurate emission estimates than the use of AP-42 emission factors. Also, some facilities may have detailed engineering calculations or process simulations that may better characterize the emissions than the general methods presented in this document. Alternative methods may be equally acceptable if they are based on sound engineering assumptions or data.

TABLE 1

TYPICAL AIR EMISSION SOURCES IN THE PETROLEUM INDUSTRY

<p>External Combustion Sources Boilers Furnaces Process heaters</p> <p>Internal Combustion Sources Gas turbines Reciprocating engines</p> <p>MACT I Process Vents^a Alkylation units Blending units Catalytic hydrotreating Catalytic hydrocracking Chemical treatment units Crude distillation Lube oil production Hydrogen production Isomerization Polymerization Solvent extraction Vacuum distillation</p> <p>MACT II Process Vents^b Catalytic cracking unit (CCU) catalyst regeneration vent (fluid and thermal units) Catalytic reformer unit (CRU) catalyst regeneration vents Sulfur recovery unit</p>	<p>Flares</p> <p>Process Equipment Leaks Pump seals Compressor seals Valves Pressure relief devices Flanges Open-ended lines Sampling connections</p> <p>Wastewater Treatment Process drains and collectors Oil-water separators Air flotation systems Surface impound basins and ponds Cooling water towers</p> <p>Storage Vessels Fixed roof External floating roof Internal floating roof</p> <p>Loading Operations Marine vessels (tankers and barges) Marine vessel ballasting Rail tank cars Tank trucks</p> <p>Non-Routine Operations Accidental Releases Maintenance Operations</p>
---	--

- a) Miscellaneous process vents covered by 40CFR Part 63 Subpart CC - National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries (commonly referred to as MACT I Standard)
- b) Sources covered by 40CFR Part 63 Subpart UUU - National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries – Catalytic Cracking (fluid and Other) Units, Catalytic Reforming Units, and Sulfur Plants (referred to as MACT II Standard)

OVERVIEW OF EMISSION ESTIMATION METHODOLOGIES

The joint STAPPA/ALAPCO/EPA Emission Inventory Improvement Program (EIIP) has identified general methods¹ for developing point source emission inventories. The EIIP suggests that selecting a method to estimate source specific emissions warrants a case-by-case analysis considering the cost and required accuracy in the specific situation. When selecting an emissions estimation method, the tradeoffs between cost and accuracy of the resulting estimates should be considered. The EIIP document identifies several considerations:

- Availability of quality data needed for developing emissions estimates;
- Practicality of the method for the specific source category;
- Intended end use of the inventory (e.g., an inventory in support of significant regulatory implications such as residual risk or environmental justice issues may require that more accurate and costly emission estimation methods be used than would an inventory intended for simply a source characterization);
- Source category priority (e.g., if a source category is of relatively high priority, it may require a more accurate emission estimation method);
- Time available to prepare the inventory; and
- Resources available in terms of staff and funding.

Figure 1 (from Reference 1) depicts the relative costs versus quality of the various types of emission estimation methodologies. Table 2 provides a general description of the emission estimation methods available for point sources.

In general, continuous emissions monitoring (CEM) is the most accurate methodology for obtaining actual emissions measurements. The CEM concentration data can be converted to mass emission rates provided the air volume through the monitor is also known. However, the use of CEMs imposes significant data requirements and higher costs. Another form of continuous monitoring is parametric monitoring. This type of monitoring does not directly measure emissions, but rather measures a surrogate parameter that can be used to help quantify emissions.

In cases where CEM or parametric monitoring data are unavailable or impractical to collect, source test data may be available. A source test is conducted over a discrete, finite period of time, while CEM is continuous. Source tests generally require substantial resources (both time and equipment), but can provide representative site-specific data. An alternative, emerging alternative to traditional stack sampling is the use of Fourier transform infrared (FTIR) spectroscopy. FTIR testing has the potential to be used for both measurement of stack emissions (extractive FTIR) and fugitive emissions (open-path FTIR).

If site-specific measurements are not available, another method must be used to estimate emissions. The three principal methods for estimating emissions in such cases are material balances, emission factors, and an engineering estimate based on available process, physical, chemical, and emission knowledge may be used. Emission models may be used to estimate emissions in cases where the calculation approach is burdensome.

RISK SENSITIVITY EMISSION ESTIMATION APPROACHES

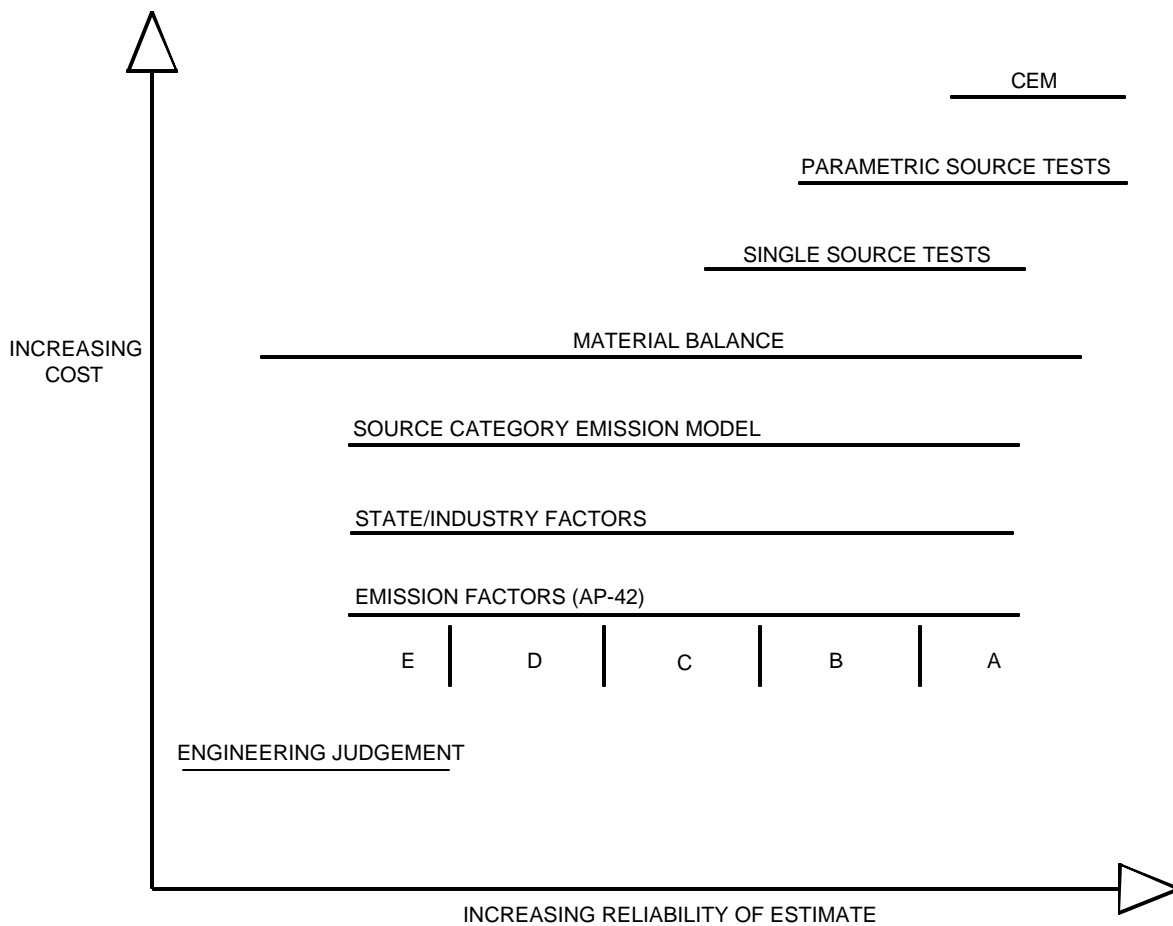


FIGURE 1 – RISK SENSITIVITY EMISSION ESTIMATION APPROACHES
(from Reference 1)

TABLE 2

GENERAL POINT SOURCE EMISSION ESTIMATION METHODS

<p>Continuous Emissions Monitors (CEM) measure and record actual emissions during the time period the monitor is operating and the data produced can be used to estimate emissions for different operating periods. CEMs are typically used to measure stack gas concentrations of NO_x, CO₂, CO, SO₂, and total hydrocarbons (THC). CEMs can either be permanently installed to generate data 24-hours a day or they can be used during a defined source testing period (e.g., 1 to 4 hours). Continuous parametric monitoring does not directly monitor emissions, but rather some surrogate parameter that can be used to help quantify emissions.</p>
<p>Source tests are short-term emission measurements taken at a stack or vent. The essential difference between a source test and CEM is the duration of time over which measurements are conducted. A source test is conducted over a discrete, finite period of time, while CEM is continuous. Due to the substantial time and equipment involved, a source test requires more resources than an emission factor or material balance emission estimate. Test data gathered on-site for a process is generally preferred. The second choice is to use test data from similar equipment and processes on-site, or to use pooled source tests or test data taken from literature. The reliability of the data may be affected by factors such as the number of tests conducted and the test methodology used.</p>
<p>Fourier Transform Infrared Spectroscopy (FTIR) is an emerging technology that has recently been applied to source monitoring. Extractive FTIR monitoring refers to systems that remove gas from the stack or duct, filter out particulate matter and transport the gas through a sample line to a remote location for continuous, "real time" analysis by an FTIR spectrometer. In 1999, EPA approved use of Test Method 320 for measurement of vapor phase organic emissions using extractive FTIR. Open-path FTIR offers the ability to monitor refinery components from a distance and identify leaking components within the line of sight of the optical imager. The remote sensing and instantaneous detection capabilities of optical imaging technologies allow an operator to scan areas containing tens to hundreds of potential leaks, thus eliminating the need to visit and manually measure all potential leak sites. EPA has not yet developed a protocol for the use open-path FTIR to supplement to current leak detection and evaluation methods.</p>
<p>Material balances determine emissions by knowing the amount of a certain material that enters a process, the amount that leaves the process by all routes, and the amount shipped as part of the product itself. The simplest method of material balance is to assume that all organics consumed by a source process will evaporate during the process.</p>
<p>Emission models are used to estimate emissions in cases where the calculation approach is burdensome, or in cases where a combination of parameters have been identified which affect emissions but, individually, do not provide a direct correlation. For example, the TANKS program incorporates variables such as tank color, temperature, and wind speed to calculate emissions.</p>
<p>Emission factors are used to estimate the rate at which a pollutant is released to the atmosphere as a function of some process activity. For example, the emission factor for NO_x emissions from the combustion of anthracite coal is 9 pounds of NO_x per 1 ton of coal burned (9 lb/ton). The use of emission factors is relatively straightforward and uncomplicated.</p>
<p>A best approximation or engineering judgment is a final option for estimating emissions, although it is considered the least desirable method. A best approximation or engineering judgment is an emission estimate based on available information and assumptions.</p>

Based primarily on Section 4 of Reference 1.

EXTERNAL AND INTERNAL COMBUSTION SOURCES

There are a number of different types of combustion sources in a typical refinery. These sources are categorized by equipment type and the type of fuel combusted. Refinery combustion devices include boilers, heaters, gas turbines, and engines. Fuels are typically residual oil, distillate oil, refinery gas, or natural gas. Combustion devices do not normally have controls for organics or VOCs since the combustion process destroys most organic pollutants, although there are residual amounts of organics in the exhaust streams.

The EIIP boiler guidance document² states that the use of site-specific emission data (recent stack tests) is preferred over the use of industry-averaged data such as emission factors. However, depending upon available resources, site-specific data may not be cost effective to obtain. The alternative is to use emission factors to calculate emissions from combustion devices when site-specific stack monitoring data are unavailable. Emission factors may come from equipment vendors or EPA's *Compilation of Air Pollutant Emission Factors*, AP-42 document³.

It should be noted that EIIP prefers the use of CEMS for measuring emissions of total hydrocarbons, but not for measuring VOC emissions since there is no direct measurement method for VOC. VOC is defined by EPA as those volatile organic compounds that are photo reactive and contribute to ozone formation. There are two common ways for determining VOC. The first is to measure as many of the individual organic compounds as possible and add those that are considered VOC. The second is to measure total hydrocarbons, subtract methane and ethane, and add formaldehyde. The second procedure is more of an estimate of VOC, but is considered acceptable.

The 10 refineries in the Philadelphia/Delaware/New Jersey area use three different methods for estimation VOC emissions. The predominant method is the use of emission factors (although some of the refineries are using outdated AP-42 emission factors). Some refineries base the emission estimates on source test data or manufacturer's emission factor data. None of the refineries use CEMs to monitor VOC emissions from combustion units.

Preferred Method – Stack Sampling Data

Stack sampling is the preferred emission estimation methodology for VOC. There are currently no CEM methods for directly measuring VOC, so the use of short-term, site-specific stack test data is preferred over using industry average emission factors for a particular equipment/fuel type. Stack sampling test reports often provide emissions in terms of lbs/hr or lb/mmBtu.

There are three issues to be aware of when using stack test data to estimate VOC emissions. First, test data for the specific units are preferred over tests of similar units since burner/boiler maintenance greatly affects VOC emissions. Proper maintenance includes keeping the air/fuel ratio at the manufacturer's specified setting, having the proper air and fuel pressures at the burner, and maintaining the atomizing air pressure on oil burners at the correct levels. According to one manufacturer's literature, an improperly maintained boiler/burner package can result in VOC levels over 100 times the normal levels⁴.

Secondly, VOC emissions are affected by operating load condition. In most cases, stack tests are performed under a maximum load condition to determine compliance with a permit condition or a short-term maximum emissions rate. In other cases, the testing is done at different operating load conditions to determine the maximum emission rate. Thus, the stack test data may not accurately reflect the annual emission rate that would result under normal operating conditions. When using stack sampling test data to estimate emissions, the test reports should be reviewed to determine whether the tests were conducted under “normal” operating conditions or “maximum” conditions. Engineering judgment should be used to determine the appropriate manner for calculating the annual emission rate.

The third issue when using stack test data to determine VOC emissions is to find out whether the test measured VOCs or total hydrocarbons. If the test measured total hydrocarbons, then the TCEQ⁵ suggests that an adjustment be made for this by multiplying the hydrocarbon factor by the following ratio: AP-42 VOC factor / AP-42 TOC factor.

Alternative Method – Vendor Data

Equipment manufacturers and vendors can often provide emission factor data for the combustion units in their product line. The emission factors are typically based upon tests of the specific make and model or on tests of units with similar size and design. Most vendors provide “guaranteed” emission factors, which typically include a safety factor to ensure that emissions will be at or below the normal full load operating emission levels.

Alternative Method – EPA Emission Factors

The EPA’s AP-42 document is the standard reference for emission factors. Table 3 lists the current AP-42 emission factors for the common equipment and fuel types used in petroleum operations. These factors are appropriate for both external combustion (e.g., boilers and heaters) as well as internal combustion (e.g., engines and turbines).

AP-42 generally provides hydrocarbon emission factors in several forms, depending on the measurement technique used in the underlying data. The general forms are total hydrocarbons (THC), total organic gas (TOG), nonmethane hydrocarbons (NMHC), and volatile organic compounds (VOC). State/local emission inventory guidance requests estimates for VOC, which excludes some hydrocarbons (methane, ethane, and other compounds such as chlorinated hydrocarbons) that are less ozone-forming than other hydrocarbons. Generally, AP-42 emission factors for VOC result from subtracting methane and ethane from the TOG emission estimates.

It is important to note that there are no published emission factors specific to the use of “refinery fuel gas”. Factors are available for the combustion of natural gas. In situations where refinery gas is being used as a fuel, the emissions should be calculated using the natural gas emission factors adjusted for the difference in the heat contents of the two types of fuels.

EPA also publishes emission factors in the Factor Information Retrieval (FIRE) database⁶. However, AP-42 emission factors are preferred since there are some inconsistencies in the FIRE database. For example, FIRE Version 6.23 appears to still use the outdated 2.8 lbs/mmft³ factor for refinery (process) gas boilers and heaters.

TABLE 3 – AP-42 EMISSION FACTORS FOR EXTERNAL AND INTERNAL COMBUSTION

Equipment Type	Fuel Type	Emission Factor		AP-42 Reference		
		TOC	VOC	Rating	Table	Last Update
Boilers and Heaters Utility, > 100 mmBtu/hr	No.6 Oil	1.04 lbs/1000 gal	0.76 lbs/1000 gal	A	1.3-3	9/98
	No. 5 Oil	1.04 lbs/1000 gal	0.76 lbs/1000 gal	A	1.3-3	9/98
	No. 4 Oil	1.04 lbs/1000 gal	0.76 lbs/1000 gal	A	1.3-3	9/98
	Natural Gas	11 lbs/mmscf	5.5 lbs/mmscf	B, C	1.4-2	7/98
	Refinery Gas	Use natural gas factors adjusted for the difference in the heat contents of the fuels.				
Boilers and Heaters Industrial, 10-100 mmBtu/hr	No.6 Oil	1.28 lbs/1000 gal	0.28 lbs/1000 gal	A	1.3-3	9/98
	No. 5 Oil	1.28 lbs/1000 gal	0.28 lbs/1000 gal	A	1.3-3	9/98
	No.4 Oil	0.252 lbs/1000 gal	0.2 lbs/1000 gal	A	1.3-3	9/98
	Distillate	0.252 lbs/1000 gal	0.2 lbs/1000 gal	A	1.3-3	9/98
	Natural Gas	11 lbs/mmscf	5.5 lbs/mmscf	B, C	1.4-2	7/98
	Butane	0.6 lbs/1000 gal	0.4 lbs/1000 gal	E	1.5-1	10/96
	Propane	0.5 lbs/1000 gal	0.3 lbs/1000 gal	E	1.5-1	10/96
	Refinery Gas	Use natural gas factors adjusted for the difference in the heat contents of the fuels.				
Boilers and Heaters Commercial, 0.3-10 mmBtu/hr	No.6 Oil	1.605 lbs/1000 gal	1.13 lbs/1000 gal	A	1.3-3	9/98
	No. 5 Oil	1.605 lbs/1000 gal	1.13 lbs/1000 gal	A	1.3-3	9/98
	No.4 Oil	0.556 lbs/1000 gal	0.34 lbs/1000 gal	A	1.3-3	9/98
	Distillate	0.556 lbs/1000 gal	0.34 lbs/1000 gal	A	1.3-3	9/98
	Natural Gas	11 lbs/mmscf	5.5 lbs/mmscf	B, C	1.4-2	7/98
	Butane	0.6 lbs/1000 gal	0.4 lbs/1000 gal	E	1.5-1	10/96
	Propane	0.5 lbs/1000 gal	0.3 lbs/1000 gal	E	1.5-1	10/96
	Refinery Gas	Use natural gas factors adjusted for the difference in the heat contents of the fuels.				
Gas Turbines	Natural Gas	0.011 lbs/mmBtu	0.0021 lbs/mmBtu	B, D	3.1-2a	4/00
	Distillate	0.004 lbs/mmBtu	0.00041 lbs/mmBtu	C, E	3.1-2a	4/00
RICE, 2 stroke, lean burn	Natural Gas	1.64 lbs/mmBtu	0.12 lbs/mmBtu	A, C	3.2-1	7/00
RICE, 4 stroke, lean burn	Natural Gas	1.47 lbs/mmBtu	0.118 lbs/mmBtu	A, C	3.2-2	7/00
RICE, 4 stroke, rich burn	Natural Gas	0.358 lbs/mmBtu	0.0296 lbs/mmBtu	C	3.2-3	7/00
IC Engines, < 250 hp	Gasoline	3.03 lbs/mmBtu	---	D	3.3-1	10/96
IC Engines, < 600 hp	Diesel	0.36 lbs/mmBtu	---	D	3.3-1	10/96
IC Engines, > 600 hp	Diesel	0.09 lbs/mmBtu	0.082 lbs/mmBtu	C, E	3.4-1	10/96

MACT I PROCESS VENTS

There are a number of specialized process vents in refineries. In developing the MACT standards for petroleum refineries, EPA developed two separate standards for process vents. The first standard covers separation, conversion, and treatment process vents that emit primarily organic HAPs (40CFR Part 63 Subpart CC - National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries, commonly referred to as MACT I standard). Process vents covered under this rule have low inorganic HAP emissions relative to organic HAP emissions. The second standard (the MACT II standard) covered process vents that also emit inorganic HAPs (40CFR Part 63 Subpart UUU - National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries – Catalytic Cracking (fluid and Other) Units, Catalytic Reforming Units, and Sulfur Plants). MACT II process vents are discussed in the next section.

The 10 refineries in the Philadelphia/Delaware/New Jersey area reported very little VOC emissions from MACT I process vents. No refinery reported more than 5 tons per year from miscellaneous process vents. Typically, atmospheric vents should not have emissions except during upsets. Normally, the exhaust streams from these process vents are diverted to the refinery fuel gas system and combusted in boiler or process heaters to recover the fuel value while destroying the VOCs. The MACT I rules require that process vent streams be controlled by either reducing organic HAPs by 98% using incinerators, boilers, process heaters, or other devices. Some streams are not suitable for control by boilers/heaters, including those with varying flow rate and/or heating value, high volume/low heating value streams, and streams with corrosive compounds. Flares are often used to control these streams. The emissions from MACT I process vents are generally included under the boiler/heater and flare categories, and the emission estimation methods for those source categories should be used.

MACT II PROCESS VENTS

The three process vents associated with this MACT standard are: (1) the catalytic cracking unit (CCU) catalyst regeneration process vent, (2) the catalytic reforming unit (CRU) catalyst regeneration process vent, and (3) the sulfur recovery plant (SRU) vent. These process vents were excluded from the MACT I rule because of the unique characteristics of the inorganic emissions from each of these vents.

VOC emissions originate from fluid catalytic cracking (FCC) processes and thermal cracking (coking) processes as by-products of coke combustion during the regeneration of catalysts used in the cracking process. There are two basic types of regenerators: complete combustion (full burn) regenerators and partial combustion regenerators. Most partial combustion regenerators employ secondary combustion devices (referred to as CO boilers) to recover the latent heat in the flue gas. The fuel used in the CO boiler consists of the process gas from the catalyst regenerator and an auxiliary fuel source such as refinery fuel gas. On very rare occasions, the exhaust from the FCC unit may bypass the CO boiler and may vent directly to the atmosphere

Data included in the EPA's Background Information Document (BID)⁷ for the MACT II standard indicate that organic emissions from the CRU and SRU vents are rather small (i.e., less

than one ton per year for the typical refinery). The emission inventories for the 10 refineries in the Philadelphia/Delaware/New Jersey area also show very little VOC emissions from the CRU and SRU process vents. For these reasons, the remainder of this section will focus on emissions from the FCC units.

All but one the refineries in the study area base their emissions on source test data. The VOC emission rates obtained via source testing range from “not detected” to 9.45 lbs/hour (0 to 41 tons per year). VOC emissions from the Motiva Delaware City refinery are calculated using EPA emission factors, and are significantly higher than the emission estimates for the refineries that use stack test data to estimate emissions.

Preferred Method – Stack Sampling Data

Most of the refineries in the study area base their emission estimates for FCC units on stack test data. It should be noted, however, that stack sampling provides a snapshot of emissions at the test conditions and does not address potential variability over time. CEMs are not required for VOC, although many refineries are required by NSPS Subpart J to have CEMs for opacity, CO, SO₂, and NO_x.

Alternative Method – EPA AP-42 Emission Factors

Table 5.1-1 of AP-42 presents an emission factor for total hydrocarbons for an uncontrolled FCC unit of 220 lbs/1000 bbl (5.23 lbs/1000 gallons). Section 5.1 of AP-42 states that CO waste heat boilers reduce the “hydrocarbon emissions from FCC units to negligible levels. However, the Texas Commission on Environmental Quality (TCEQ)⁸ suggests that VOC emissions from FCC units equipped with CO boilers should be calculated in the following manner:

- VOC resulting from refinery fuel gas combustion can be estimated by using the AP-42 emission factor for nonmethane volatile organics (i.e., the 5.5 lbs/mmft³ factor)
- Regenerator-related VOC in the CO boiler outlet can be estimated by applying the Destruction Removal Efficiency (DRE) of the combustion device (typically 99 to 99.9 percent) to the VOC waste load of the inlet flue gas (about 220 lbs of VOC per 1,000 bbl fresh feed), resulting in controlled emissions of 0.22 to 2.2 lbs/1,000 bbl fresh feed).

It should be noted that the FIRE database lists VOC emission factors for CO boilers under SCC 1-02-014-01 (natural gas), 1-02-014-02 (process gas), 1-02-014-003 (distillate oil), and 1-02-014-04 (residual oil). The FIRE emission factor for natural gas and process gas (2.8 lbs/mmft³) was “transferred from natural gas burning boilers assuming process similarity”. The FIRE factor appears to be outdated, and should be replaced by the current 5.5 lbs/mmft³ factor. The FIRE emission factor for distillate oil (0.2 lbs/1000 gallons) and residual oil (0.28 lbs/1000 gallons) were also “transferred from other oil-burning boilers assuming process similarity”.

Alternative Method – EPA MACT Emission Factors

In developing the MACT II standard, EPA developed organic HAP emission factors for these three process units using section 114 responses and follow-up surveys by the API and National Petroleum Refiners Association. These emission factors were documented in the MACT II

background information document. Data included in the EPA's Background Information Document (BID) for the Subpart UUU MACT standard indicated that organic emissions from complete combustion (full burn) regenerators are comparable to a partial combustion regenerator vented to a CO boiler. The EPA BID presents emission factors in the range of 0.078 to 1.24 lbs/1000 bbl of unit throughput. These factors represent VOC emissions either after the CO boiler or for a complete combustion unit.

FLARES

Flares are used to manage the disposal of hydrocarbon products from routine operations, upsets, or emergencies via combustion. There is a wide variety of flare types used in the industry. Combustion efficiency, and therefore flare performance, is highly variable, primarily dependent on the flame stability. This, in turn, depends on the gas velocity, heat content, and wind conditions. In addition, the actual flow rates to the flare and the specific composition of the gas routed to the flare can be highly variable.

The EIIP oil and gas industry guidance document⁹ states that the preferred approach for estimating VOC and HAP emissions from sources venting to flares is based on the gas processing rate and the destruction and removal efficiency (DRE) of the flare. The alternative emissions calculation approach is to use the AP-42 emission factor, which is based on an estimated 98% combustion efficiency.

Most refineries in the study area use a simple AP-42 total hydrocarbon emission factor to calculate VOC emissions. This factor was developed in the early 1980's and has not been updated by EPA since then. The emission factor does not take into consideration the flare efficiency or the composition of the material being flared. While most refineries monitor the pilot gas flow rate, waste gas flow rates and composition are determined using several different approaches, ranging in accuracy from continuous monitoring to the use of historical estimates and engineering assumptions.

Preferred Method – Gas Processing Rate and Destruction/Removal Efficiency Data

According to the EIIP, the preferred approach for estimating VOC emissions from sources venting VOC to flares is based on the gas processing rate and the destruction and removal efficiency of the flare. The following equation can be applied:

$$E_x = Q * y_x * 1/C * MW_x * (1 - DRE/100)$$

where:

E_x = Emission estimate for pollutant x, lb/hr

Q = Gas process rate, scf/hr

y_x = Mole fraction of pollutant x in inlet stream, lb-mole x/lb-mole

C = Molar volume of ideal gas, 379 scf/lb-mole @ 60 degrees Fahrenheit

MW_x = Molecular weight of pollutant x

DRE = Destruction and removal efficiency, %

To obtain the most accurate emissions estimate, the TCEQ^{10,11} recommends that the above calculation be based on the actual flow rate and the specific composition of the gas routed to the flare. The generally preferred methods of obtaining pilot gas and flared gas flow rate and composition data are, in order of preference:

1. Continuous monitoring with quality assured instruments
2. Continuous monitoring with instruments that may not meet all quality assurance tests
3. Periodic testing with instruments and laboratory analytical methods
- 4-a. Engineering estimates based on detailed process evaluation
- 4-b. One time performance test conducted during the inventory year

Selection of the most accurate method may sometimes require exercising scientific judgment. For example, when using the results of a one-time performance test, the test conditions should be compared to the flare's actual operating conditions during the inventory year to determine whether the test accurately represents the flare's performance. If test conditions do not accurately model flare operation, then engineering estimates based on detailed process evaluation may provide the best data.

Since flare gas flow rate and composition are highly variable, the TCEQ suggests that emission estimates should not be based on annual average conditions. Instead, the emissions should be calculated for short time segments during which the flare flow rate and composition are relatively constant, and then those short-term emissions be summed to obtain an annual total. This calculation guidance is especially important for ozone season emission calculations.

Estimates of the DRE of the flare can also be highly variable. According to the American Petroleum Institute¹², the general industry practice relies on the widely accepted AP-42 document which states: "properly operated flares achieve at least 98 percent combustion efficiency" (AP-42 Section 13.5). The TCEQ also recommends the 98% DRE factor, but considers claims for DREs greater than 98% on a case-by-case basis. The TCEQ recommends

- A general method that uses vendor supplied test data for flares of a similar design and waste stream composition;
- A 99.5% DRE justification method may be claimed where the refinery can show that (a) the VOC compounds in the waste stream are not difficult to combust, (b) the waste stream composition does not vary excessively, and (3) the flare will meet the flow and heating value requirements of 40 CFR 60.18 via monitoring of the waste stream flow rate and Btu content;
- A DRE of greater than 98% can also be claimed if the refinery can provide test results from similar facilities and waste streams and the certain other conditions are met.

The API recommends vendor specific information as the preferred method for estimating flare efficiencies. In the absence of vendor information, the API recommends that the alternative approach is based on an estimated 98% combustion efficiency. As part of the Houston-Galveston Air Quality Study, research is being conducted on using passive FTIR technology to measure flare efficiency¹³. Results from this research are still being compiled.

Alternative Method – EPA Emission Factors

Table 13.5-1 of AP-42 has a total hydrocarbon factor of 0.14 lbs/10⁶ Btu. Table 13.5-2 of AP-42 shows that, on average, 55% of the hydrocarbon flare emissions are methane. This factor is based on a 1983 EPA flare efficiency study. If no flow rate or composition data are available, then engineering estimates should be used to account for the amount of gas flared.

The FIRE 6.23 database provides a factor of 5.6 lbs/mmft³ of natural gas or process gas burned. This is roughly equivalent to 0.0056 lbs/10⁶ Btu, significantly less than the AP-42 factor. There is no documentation in FIRE as to the origin of the 5.6 lbs/mmft³ emission factor.

PROCESS EQUIPMENT LEAKS

Process fugitive emissions typically result from leaking valves, flanges, pumps, connectors, and compressors. Although the release from each individual source may be small, there are usually thousands of these components in a refinery and the total emissions from these sources can be significant. As a result of the adoption by EPA of the Refinery MACT Rule, nearly every refinery must have a leak detection and repair (LDAR) program that is structured to detect and repair equipment that are identified as leaking. In addition to the MACT requirements, there are state and local regulations that may apply to leak monitoring. Each regulation may have different leak definitions or monitoring frequencies. Sometimes more than one regulation (with different standards) may apply to the same component at the same time. This makes it difficult to directly compare emissions between refineries, as each refinery may be subject to different sets of monitoring standards, record-keeping and reporting requirements.

LDAR programs involve monitoring using EPA Method 21. This method involves placing a portable flame ionization detector (FID) at the surface of each piping component seal and measuring the VOC concentration as the probe is moved along the surface of the seal. The instrument readings, referred to as screening values, are in volume parts-per-million (ppmv). EPA and some state/local agencies have established the level of screening value VOC concentration which determines a leak. These range from 1,000 to 10,000 ppmv. If the measured VOC concentration at a piping component is above the level defining a leak, the component must be repaired or replaced to reduce the concentration to below the acceptable level. A correlation has been established relating the mass rate of VOC leaking from the component to the maximum screening value concentration measured by the instrument.

The EIIP equipment leaks document¹⁴ suggests that there are four basic approaches for estimating emissions from equipment leaks in a specific processing unit. The approaches, in order of increasing refinement, are:

- Average emission factor approach;
- Screening ranges approach;
- EPA correlation approach; and
- Unit-specific correlation approach.

The approaches increase in complexity and in the amount of data collection and analysis required. All the approaches require some data collection, data analysis and/or statistical

evaluation. The EPA correlation equation approach is the preferred method when actual screening values are available. The EPA's *Protocol for Equipment Leak Emission Estimates*¹⁵ provides a full description of the methods, which are briefly summarized below.

All of the refineries in the Philadelphia/Delaware/New Jersey area use approved approaches from EPA's *Protocol for Equipment Leak Emission Estimates*. Some refineries base their emissions on EPA's preferred correlation equation approach that uses actual LDAR screening values to estimate emissions. Other refineries use the alternative "leak/no leak" method to calculate emissions. There are differences in how an individual refinery treats non-detects and components not monitored. VOC process equipment leak emissions vary widely from refinery to refinery due to differences in the size (number of equipment components monitored), liquid and gas streams processed, LDAR monitoring program requirements, and emission estimation approaches used.

Preferred Method – EPA Correlation Equations

The EPA correlation equation approach is the preferred method when actual LDAR screening values are available. This approach involves entering each individual screening value into the correlation equation, which predicts the mass emission rate based on the screening value. The TCEQ¹⁶ summarizes the approach for estimating emissions using the correlation equations:

- For each component with a non-zero screening value, enter the screening value into the correlation to determine a mass emission rate. Sum the individual mass emission rates to determine a total leak rate. Please note that each individual screening value must be entered into the correlation to predict a component's leak rate. Averaged screening values may not be used to estimate emissions.
- For each component with a screening value of zero, please note that although the correlations predict a leak rate of zero for screening values of zero, the EPA data suggest that this prediction is incorrect. To account for screening values of zero, the EPA has established a default zero leak rate which should be applied to each component whose screening value was zero.
- For each component with a screening value above 100,000 ppm, use a default 100,000 ppm pegged leak rate. Note that if a pegged value of 10,000 ppm is indicated (e.g., a dilution probe was not used to quantify the screening value between 10,000 ppm and 100,000 ppm), then the default 100,000 ppm pegged leak rate must be used. The default 10,000 ppm pegged leak rate may not be used.

The correlation equations, default zero emission rate, and pegged emission rates for the petroleum industry are presented in Table 4.4-4 of Reference 15. Similar correlation equations to be used for the SOCOMI industry are presented in Table 4.4-3 of Reference 15.

Note that the correlation equations estimate emissions of total organic compounds, not VOCs. A correction is necessary if some of the organic compounds in the equipment are not classified as VOCs (such as methane and ethane). The correction is to multiply the total organic mass emissions by the ratio of the VOC weight percent to the TOC weight percent.

Most LDAR regulations allow for decreased monitoring frequency if certain performance standards are consistently achieved. For example, monitoring frequency is decreased from quarterly to annual monitoring if less than two percent of the valves within a process unit are found leaking. Conversely, if greater than two percent of the valves are found to be leaking, monitoring must be conducted quarterly. Monitoring showing a greater than two percent leak rate has resulted in refineries reverting back to quarterly monitoring. Since a component's screening concentration may vary from one monitoring period to another, emissions for each monitoring period should be based upon each component's screening concentration for that period. These period-specific emission rates should then be summed to obtain an annual emission rate.

Sometimes screening data cannot be collected for all pieces of equipment, especially if the equipment is deemed difficult or unsafe to screen. For these equipment pieces, the average emission factors discussed later in this section should be used to estimate emissions.

Recent studies in Texas¹⁷ have identified two major issues where fugitive emissions may be underestimated using currently available techniques. First, the TCEQ has begun to consider emissions from non-traditional piping sources. While these sources have not historically been included in the emissions inventory process, TCEQ indicates that recent scientific studies and equipment monitoring have indicated that these sources do release emissions. Although component-specific factors do not exist for non-traditional components, the TCEQ has identified appropriate substitute factors based on component, leak potential, and leak mechanism similarity. The second issue is the potential underestimation of large leaks (i.e., those that peg the monitor and large visual leaks). Other issues are also identified in Reference 17.

The EPA Office of Regulatory Enforcement¹⁸ conducted a study of refinery LDAR programs that led to the conclusion that “the number of leaking valves and components is up to 10 times greater than had been reported by certain refineries ... EPA estimates that the failure to identify and repair leaks at petroleum refineries could be resulting in additional VOC emissions of 80 million pounds annually” nationally. Common compliance issues identified by EPA include:

- Failure to identify process units and components that must be monitored;
- Failure to follow prescribed monitoring procedures;
- Use of incorrect or expired calibration gasses;
- Failure to repair components within specified timeframes; and .
- Failure to submit quarterly reports and maintain appropriate calibration and/or monitoring records.

By not fully identifying all leaking components, EPA believes that refineries are likely causing the unnecessary release of excess hydrocarbons.

Alternative Method – Unit-Specific Correlation

Facilities may choose to develop correlation equations for specific units rather than using correlation equations developed by the EPA. Methodologies for generating leak rate/screening

value correlations with mass emissions data and screening values are presented in Appendix B of the *1995 Protocol* document. Once correlations are developed using the methodologies outlined in Appendix B, they are applied in the same manner as described in the example for the EPA correlations.

Alternative Method – Screening Values

The screening ranges (i.e., leak/no leak method) approach requires LDAR screening data to be collected for the equipment in the process unit. This approach is applied in a similar manner as the average emission factor approach in that equipment counts are multiplied by the applicable emission factor. However, only two emission factors are used: one factor for equipment where screening data are "greater than or equal to 10,000 ppmv" and a second factor where screening data are "less than 10,000 ppmv."

Emission factors are provided in Reference 14. Table 2-5 of Reference 14 has the SOCFI screening ranges emission factors, in terms of total organic compound emission rates. Table 2-6 of Reference 14 has the refinery screening ranges emission factors, in terms of non-methane organic compound emissions. Table 2-7 of Reference 14 has the marketing terminal screening ranges emission factors, in terms of total organic compound emission rates.

Since a component's leak status may vary from one monitoring period to another, emissions for each monitoring period should be based upon each component's leak status for that period. These period-specific emission rates should then be summed to obtain an annual emission rate. For example, if components are monitored quarterly, one should determine each component's quarterly leak status, estimate its quarterly emissions, and then sum the quarterly emission rates to obtain the component's annual emission total.

Alternative Method – Average Emission Factors

The average emission factor approach is an accepted approach to calculate emissions when site-specific LDAR screening data are unavailable. The emission rate for all equipment in the stream of a given equipment type is obtained by multiplying the applicable average emission factor by the average weight fraction of VOC in the stream and by the number of pieces of the applicable equipment type in the stream.

Emission factors are provided in Reference 14. Table 2-1 of Reference 15 has the SOCFI average emission factors, in terms of total organic compound emission rates. Table 2-2 of Reference 15 has the refinery average emission factors, in terms of non-methane organic compound emissions. Table 2-3 of Reference 15 has the marketing terminal average emission factors, in terms of total organic compound emission rates.

Chapter 5 of Reference 15 provides alternative average emission factors for facilities that have implemented LDAR programs but do not use the screening values directly to calculate emissions. Table 5-4 of Reference 15 provides equations relating average leak rate to the fraction of components leaking at SOCFI units. Table 5-5 of Reference 15 provides equations relating average leak rate to the fraction of components leaking at refinery units. Table 5-6 of

Reference 15 provides equations relating average leak rate to the fraction of components leaking at marketing terminal units.

Alternative Method – Open-Path FTIR and Smart LDAR

There is considerable uncertainty associated with current methods to estimate process fugitive equipment leaks, as well as concern about the cost/difficulty of implementing LDAR programs. As a result, current research is focusing on alternative or supplemental methods to current LDAR methods. One area of research is to use optical imagers, such as open-path FTIR monitoring, to identify leaking components. The remote sensing and instantaneous detection capabilities of optical imaging technologies allow an operator to scan areas containing tens to hundreds of potential leaks, thus eliminating the need to visit and manually measure all potential leak sites. Refer to the TCEQ study¹⁹ and Exxon-Mobil paper²⁰ for examples of current research on potentially improved leak detection methods and emission estimation methodologies.

WASTEWATER TREATMENT

During the petroleum refining process, a significant quantity of industrial wastewater is produced. This wastewater typically passes through a complex series of on-site collection and treatment units. Many of these collection and treatment units are open to the atmosphere and allow for volatilization of organics from the wastewater. The design of the wastewater collection and treatment system is dictated by the types of pollutants in the waste stream, and includes the following types of collection and treatment devices:

<u>Collection Devices</u>	<u>Treatment Devices</u>
Process Drains	Oil/Water Separators
Manholes	Equalization Basins
Reaches	Clarifiers
Junction Boxes	Biological Treatment Basins
Lift Stations	Sludge Digesters
Trenches	Treatment Tanks
Sumps	Surface Impoundments
Weirs	Air and Steam Stripping

The majority of VOC emissions result from the evaporation from the surfaces of waste water in open drains, separators, and aerated basins. The factors influencing emissions from these systems are waste water composition, equipment design, and climatic factors.

The EIP wastewater collection and treatment document²¹ identifies five basic approaches for estimating emissions from wastewater processes. The approaches, in order of increasing refinement, are:

- Average emission factors;
- Material balance;
- Manual calculations
- Emission models
- Source testing

The approaches increase in complexity and in the amount of data collection and analysis required. All the approaches require some data collection, data analysis and/or statistical evaluation. The EIIP document provides a full description of the methods, which are briefly summarized below.

The refineries in the Philadelphia/Delaware/New Jersey area use either an EPA-approved emission model (such as WATER8 or WATER9) or AP-42 emission factors. The model inputs and outputs were not available for review, so it was not possible to determine whether all wastewater treatment components (process drains, oil/water separators, refinery-specific treatment processes) are included in the inventory. The AP-42 emission factors for oil/water separators are very simplistic and dated (they have not changed since the 1980 edition of AP-42).

Preferred Method – Emission Models

EPA recommends the use of the WATER9, a Windows based computer program and consists of analytical expressions for estimating air emissions of individual waste constituents in wastewater collection, storage, treatment, and disposal facilities. Several EPA documents are available that provide theoretical equations that provide the basis for the water models. These include *Industrial Wastewater Volatile Organic Compound Emissions - Background Information for BACT/LAER Determinations* (EPA-450/3-90-004), AP-42 Chapter 4.3, and *Air Emissions Models for Waste and Wastewater* (EPA-453/R-94-080A). The model calculates average emission rates for each of the wastewater collection/treatment system components and applies these emission rates to each component at the refinery to determine the overall wastewater system emissions. To obtain these emission estimates, the user must provide the following inputs:

- Wastewater collection system layouts. A refinery wastewater collection system can comprise hundreds of acres with hundreds of individual collection devices. The user must provide the physical properties of each wastewater stream.
- Wastewater flow parameters. It is necessary to input for each component information on pipe diameters of the lines, temperature, flowrate, sewer channel slope, type of control system installed (if any) etc.
- Wastewater composition. The user must provide the type and concentration of petroleum products in the wastewater. In WATER9, the identification of compounds can be made by selecting them from the database that accompanies the program or by entering new information describing the properties of a compound not contained in the database.

The use of site-specific data is preferred, but in many cases the models will provide default values for many parameters.

Alternative Method – Manual Calculations

The equations are based on mass transfer and liquid-gas equilibrium theory and use individual gas-phase and liquid-phase mass transfer coefficients to estimate overall mass transfer coefficients. Calculating air emissions using these equations is a complex procedure, especially if several systems are present, because the physical properties of the numerous contaminants must

be individually determined. Because of the great deal of complexity involved, computer programs are available that incorporate these equations to estimate emissions.

Alternative Method – Source Testing

Source tests can be used to determine the emissions of VOCs from each wastewater collection component. Air samples are collected from the various emission points in the wastewater collection system (drains, sumps, manholes, etc). These air samples are analyzed for VOC concentration. Other information such as airflow rates for each sample point combined with the air sample concentrations is used to determine the emissions for each emission point in the wastewater collection system. While this methodology is highly accurate in determining individual emission points of the refinery wastewater collection systems, it is not a practical methodology to use. Since the wastewater collection system consists of thousands of components at each refinery, this methodology is too time and resource consuming to be the sole methodology used to estimate emissions from wastewater collection systems. However, a limited and focused source testing program can provide valuable data to estimate emissions from an entire refinery wastewater collection system using emission estimation models.

Alternative Method – Material Balance

Another method to determine VOC emissions from wastewater collection systems is through material balance. Material balance relies on wastewater flow rate and influent and effluent liquid-phase pollutant concentrations. Compound mass that cannot be accounted for in the effluent is assumed to be volatilized. However, the use of this methodology assumes that both the influent and effluent concentrations at each point in the wastewater collection system are known. Furthermore, an accurate mass balance requires collection and analysis of many samples over a long period, because refinery wastewater concentrations are constantly changing, so they must be averaged before calculating removals. Because of these limitations, this VOC estimation method has limited usefulness.

Alternative Method – Average Emission Factors

Both AP-42 and FIRE present average emission factors for wastewater treatment processes. Table 5.1-2 of AP-42 presents two emission factors for oil/water separators. The first factor is 5 lbs/1000 gallons wastewater processed and is for uncontrolled operations. The second factor is 0.2 lbs/1000 gallons wastewater and is for covered separators and/or vapor recovery systems. AP-42 Table 5.1-3 also presents a factor of 0.064 lbs per drain per day for process drains. These factors have a quality rating of “D” and have not been updated since the early 1980’s.

FIRE has factors of 0.03 lbs/1000 gallons wastewater processed and 0.7 lbs/1000 barrels refinery feed processed for wastewater treatment activities without an oil/water separator, but the origin and quality of these factors are unknown.

COOLING TOWERS

Refineries use large quantities of water for cooling throughout the refining process. Cooling towers are used to transfer heat from the cooling water to the atmosphere by allowing water to cascade through a series of decks and slat-type grids. Water that enters the cooling tower may contain hydrocarbons from leaking heat exchangers. Once the hydrocarbon-contaminated cooling water reaches the tower, the VOCs either flash out of the water or are stripped out by the tower's air flow.

Available methods for estimating VOC emissions from cooling towers include the use of VOC concentration data in the cooling water and the use of AP-42 emission factors. According to the TCEQ²², emissions estimates based on actual measured cooling water VOC concentrations and flow rate data are preferred when the data are available. The TCEQ further states that the values presented in AP-42 are very general and should be replaced by actual test data from the tower once it is in operation.

VOC emissions for cooling towers at the three Pennsylvania refineries are based on AP-42 controlled emission factors, resulting in emission estimates from 8 to 54 tons per year. Emissions from the refineries in Delaware and New Jersey are either very small (< 5 tons per year) or listed as insignificant sources. The emission estimation methodologies for the refineries in Delaware and New Jersey have not been fully described.

Preferred Method – Use of VOC Concentration Data

The TCEQ²³ preferred method uses the VOC concentration in the water coming to and leaving a cooling tower to calculate an emission rate. The TCEQ suggests that a test method developed by El Paso Products Company can be used to determine VOC emissions from a cooling tower. The difference in VOC between the inlet and outlet of the cooling water can be converted to a pounds per hour VOC mass emission rate for the cooling tower.

Alternative Method – AP-42 Emission Factors

AP-42 Table 5.1-2 presents an emission factor of 6 lbs/10⁶ gallons cooling water processed for uncontrolled operations. For controlled conditions, the emission factor is 0.7 lbs/10⁶ gallons cooling water processed. Control of cooling tower emissions is accomplished by reducing the contamination of cooling water through the proper maintenance of heat exchangers and condensers. The effectiveness of cooling tower controls is highly variable, depending on refinery configuration and existing maintenance practices.

The TCEQ does not allow the use of the “controlled” factor (0.7 lb/MMgal) since it is contingent upon the use of applicable control technology to minimize hydrocarbon leaks into the cooling water system and the monitoring of cooling water for hydrocarbons. If a monitoring system is sufficient to provide such “control”, then the associated data should be sufficiently detailed to allow for the derivation of an emission rate. If the monitoring system is insufficient to provide data for determining emissions, then the system is insufficient to provide reliable “control” and so the “uncontrolled” VOC emission factor is appropriate.

STORAGE TANKS

Storage tanks are significant sources of VOC emissions at refineries. Storage tank emissions are attributed to breathing and working losses. Breathing losses result from vapor volume and pressure variations caused by diurnal temperature changes. Working losses result from tank-filling operations where hydrocarbon vapors are displaced from the tank because of the rising liquid surface. VOC emissions depend upon several parameters, including:

- the physical design of the tank;
- the product stored and its chemical characteristics;
- the product throughput; and,
- ambient meteorological conditions.

There are six basic tank designs used for organic liquid storage vessels: fixed roof (vertical and horizontal), external floating roof, domed external (or covered) floating roof, internal floating roof, variable vapor space, and pressure (low and high). A brief description of each type of tank is provided in AP-42 Section 7.1.

Organic liquids at refineries include petroleum liquids (which are generally mixtures of hydrocarbons having dissimilar true vapor pressures, for example, gasoline and crude oil), and volatile organic liquids (composed of pure chemicals or mixtures of chemicals with similar true vapor pressures, for example, benzene or a mixture of isopropyl and butyl alcohols).

The preferred method for estimating emissions are the equations presented in Section 7.1 of AP-42 for storage tanks that were developed by the American Petroleum Institute (API). These equations have been incorporated into a computer program maintained by EPA called TANKS²⁴. The software is designed for use by local, state, and federal agencies, environmental consultants, and others who need to calculate air pollutant emissions from organic liquid storage tanks.

The current version of TANKS is Version 4.09b. The TANKS program undergoes frequent update to correct minor errors and improve the user interface. The last major changes (from Version 3 to Version 4) occurred in September 1999, which moved the TANKS program from a DOS to a Windows environment. The emission calculations in TANKS Version 3 and Version 4 are virtually the same. The last major revision of loss factors and equations occurred between TANKS 2 and TANKS 3.0. Relatively minor differences between TANKS 3.0 and TANKS 3.1.

PADEP conducted a TANKS version sensitivity analysis on nine crude tanks at Sunoco Marcus Hook. PADEP used the various versions of TANKS with the same input data to compare differences in emission estimates. Their analysis showed that the emissions more than double from TANKS Version 2 to Tanks Version 3. Smaller variations occur between later versions.

TANKS 4.09b allows users to enter specific information about a storage tank (dimensions, construction, paint condition, etc.), the liquid contents (chemical components and liquid temperature), product throughputs, and the location of the tank (nearest city, ambient temperature, etc.), and generate an air emissions report. Report features include estimates of monthly, annual, or partial year emissions for each chemical or mixture of chemicals stored in

the tank. A large amount of detail concerning tank configuration (seam length, fittings count) and material stored is required for accurate estimates for each tank. Using default data instead of actual plant specific data may lead to inaccuracies.

All of the refineries in the Philadelphia/Delaware/New Jersey area use the TANKS program to estimate emissions, but very few are using the most current version. However, all of the refineries are using fairly recent versions of the model and differences in the version of TANKS used should not create drastic inconsistencies. Emissions from storage tanks appear to be reasonably consistent from refinery to refinery when one factors in the differences in refinery size, the number of tanks at the refinery, and the products stored.

LOADING OPERATIONS

The transportation and marketing of petroleum liquids involve many distinct operations, each of which represents a potential source of evaporation loss. Crude oil is transported from production operations to a refinery by tankers, barges, rail tank cars, tank trucks, and pipelines. Refined petroleum products are conveyed to fuel marketing terminals and petrochemical industries by these same modes. From the fuel marketing terminals, the fuels are delivered by tank trucks to service stations, commercial accounts, and local bulk storage plants.

Loading losses are the primary source of evaporative emissions from rail tank car, tank truck, and marine vessel operations. Loading losses occur as organic vapors in "empty" cargo tanks are displaced to the atmosphere by the liquid being loaded into the tanks. These vapors are a composite of (1) vapors formed in the empty tank by evaporation of residual product from previous loads, (2) vapors transferred to the tank in vapor balance systems as product is being unloaded, and (3) vapors generated in the tank as the new product is being loaded. Section 5.2 of AP-42 provides a fuller description of the emission generating processes.

The EIIP oil and gas industry guidance document⁹ states that there are two preferred approaches for estimating VOC from loading operations: (1) the loading loss equation from AP-42 Section 5.2, or (2) source testing measurements.

The refineries in the Philadelphia/Delaware/New Jersey area generally calculate their VOC emissions using an AP-42 material balance calculation and product transfer rates. Most of the operations are controlled, and the efficiency of the control device is frequently based on source testing. In some cases, the source tests are used to directly develop the VOC emission estimates.

Preferred Method – AP-42 Loading Equation

Emissions from loading petroleum liquid can be estimated (with a probable error of ±30 percent) using the following expression from AP-42 Section 5.2:

$$LL = 12.46 * S * P * M * 1/T * (1 - DRE/100)$$

where:

LL = Loading Loss (lb/10³ gal of liquid loaded)

S = Saturation factor from AP-42, Table 5.2-1

P = True vapor pressure of liquid loaded (psia)
M = Molecular weight of vapors (lb/lb-mol)
T = Temperature of bulk liquid loaded (R)
DRE = Destruction and removal efficiency, %

The control efficiency term is included in the loading loss emission factor equation because most loading operations are controlled using various collection systems, such as a Vapor Recovery Unit (VRU) or a Vapor Combustion Unit (VCU). VRUs capture organic vapors displaced during loading operations and recover the vapors by the use of refrigeration, absorption, adsorption, and/or compression. The recovered product is piped back to storage. Vapors can also be controlled through combustion in a VCU, with no product recovery. If applicable, the overall estimated control efficiency for the particular control system should be used, accounting for the capture efficiency of the collection system as well as both the control efficiency and any downtime of the control device.

Source testing is usually conducted to determine the DRE of the control device. According to AP-42, control efficiencies for VRUs range from 90 to over 99 percent, depending on both the nature of the vapors and the type of control equipment used. However, only 70 to 90 percent of the displaced vapors reach the control device, because of leakage from both the tank truck and collection system. The collection efficiency should be assumed to be 90 percent for tanker trucks required to pass an annual leak test. Otherwise, 70 percent should be assumed.

Preferred Method – Source Test Data

Source tests can be used to either directly determine the mass VOC emissions (lbs/hr or lbs/10³ gal) or to determine the DRE of the control device. As with all source test data, there are three issues to be aware of when using stack test data to estimate VOC emissions. First, test data for the specific units are preferred over tests of similar units since the control device performance greatly affects VOC emissions. Secondly, VOC emissions are affected by operating load condition. In most cases, stack tests are performed under a maximum load condition to determine compliance with a permit condition or a short-term maximum emissions rate. In other cases, the testing is done at different operating load conditions to determine the maximum emission rate. Thus, the stack test data may not accurately reflect the annual emission rate that would result under normal operating conditions. When using stack sampling test data to estimate emissions, the test reports should be reviewed to determine whether the tests were conducted under “normal” operating conditions or “maximum” conditions. Engineering judgment should be used to determine the appropriate manner for calculating the annual emission rate. The third issue when using stack test data to estimate VOC emissions is to determine whether the test measured VOCs rather than total hydrocarbons. If the test measured total hydrocarbons, then an adjustment must be made to convert the TOC emissions to VOC emissions.

MARINE VESSEL BALLASTING

Ballasting operations may be a source of evaporative emissions associated with the unloading of petroleum liquids at marine terminals. It is common practice to load several cargo tank compartments with sea water after the cargo has been unloaded. This water, termed "ballast",

improves the stability of the empty tanker during the subsequent voyage. Although ballasting practices vary, individual cargo tanks are ballasted typically about 80 percent, and the total vessel 15 to 40 percent, of capacity. Ballasting emissions occur as vapor-laden air in the "empty" cargo tank is displaced to the atmosphere by ballast water being pumped into the tank. The EIIP²⁵ marine vessel document states that controls for emissions from ballasting include using segregated non-contaminated ballast tanks, or placing the ballast between hulls on double-hulled ships. If ballasting only occurs using segregated ballast tanks, it is not necessary to estimate ballasting emissions. However, if ballasting uses the empty cargo tank, emissions will occur, and must be calculated.

The preferred method for estimating VOC emissions from ballasting is the use of the AP-42 equation presented in Section 5.2. No alternative methods are available.

The refineries in the Philadelphia/Delaware/New Jersey area reported very little VOC emissions from ballasting operations. It appears that most marine vessels use segregated non-contaminated ballast tanks. For example, the marine vessels unloading at the Sunoco Marcus Hook refinery have been using segregated tanks since 1994.

Preferred Method – AP-42 Equation

The AP-42 equation in Section 5.2 was developed from test data to calculate the ballasting emissions from crude oil ships and ocean barges:

$$LB = 0.31 + 0.20 * P + 0.01 * PUA$$

where:

LB = ballasting emission factor, lb/10³ gal of ballast water

P = true vapor pressure of discharged crude oil, psia

UA = arrival cargo true ullage, measured from the deck, feet;

The term "ullage" here refers to the distance between the cargo surface level and the deck level.

NON-ROUTINE RELEASES

Non-routine emissions involve blowdown or venting emissions, either directly to the atmosphere, to the refineries fuel gas system, or to a flare. The API¹¹ groups non-routine emissions into the following two categories:

- Maintenance and turn-around activities may result in intentional releases of process gas to the environment to provide a safer work environment. For example, the gas blowdown of process equipment may be necessary to safely perform maintenance work. When the process equipment is put back in service following maintenance work, it may be necessary to purge the lines or equipment with process gas to prevent a flammable mixture of gas and oxygen from forming. An inert gas, such as nitrogen, or natural gas can be used for the purging process. If natural gas is used for purging equipment directly to the atmosphere, then VOC emissions will result.

- Emergency or upset conditions are examples of other non-routine releases that can occur. Often, these conditions automatically trigger the depressurization of process equipment to ensure safe operating conditions. For example, pressure relief valves (PRVs) and emergency shutdown systems (ESDs) are installed to relieve pressure during emergency conditions.

Blowdown systems provide for the safe disposal of hydrocarbon liquids and gasses vented during non-routine activities. According to API, gas releases from these sources are generally controlled by routing to the finery fuel gas system or to a flare. Therefore, emissions from these sources would be included with the combustion source or flare emission estimates. However, direct release to the atmosphere can occur during non-routine activities.

The EIIP oil and gas industry guidance document⁹ states that there are two preferred approaches for estimating VOC from non-routine operations: (1) a displacement equation, or (2) AP-42 emission factors.

The refineries in the Philadelphia/Delaware/New Jersey area do not report emissions from non-routine activities in a consistent manner. Some refineries, such as Sunoco Marcus Hook, group emissions from purging/sampling activities with other fugitive releases. Other refineries, such as ConocoPhillips Trainer, report emissions from purging/sampling as a distinct emission point. Sunoco Philadelphia has an emission point for blowdown systems. Motiva Delaware City has an emission point for accidental releases. Some of the New Jersey refineries reported accidental releases, while others do not.

Preferred Method – Displacement Equation

Since non-routine releases are episodic in nature, the use of a displacement equation is the preferred method for estimating VOC emissions for each event. The following equations can be applied to estimate emissions when no chemical conversion occurs:

$$E_x = Q * MW * X_x * 1/C$$

where:

E_x = Emissions of pollutant x

Q = Volumetric flow rate/volume of gas processed

MW = Molecular weight of gas

X_x = Mass fraction of pollutant x in gas x

C = Molar volume of ideal gas, 379 scf/lb-mole at 60 degrees Fahrenheit and 1 atmosphere

Engineering assumptions may be required to estimate the volume and components of the gas released. For example, the volume released may be based on the internal volume of a piece of equipment or the volume contained within a pipe section and converted from actual cubic feet of gas to standard cubic feet using the density of the gas.

Alternative Method – AP-42 Emission Factor

Table 5.1-1 of AP-42 presents a total hydrocarbon factor of 580 lbs/1000 bbl refinery feed for uncontrolled blowdown systems. A blowdown system provides for the safe disposal of hydrocarbons discharged from pressure relief devices. Blowdown material is separated into vapor and liquid cuts, and the gaseous cuts are often flared. If the materials is flared, then it should be accounted for in emissions for the flare source category.

REFERENCES

1. *Introduction to Stationary Point Source Emission Inventory Development* (EIIP Volume II: Chapter 1), prepared by Eastern Research Group, prepared for Point Sources Committee, Emission Inventory Improvement Program, May 2001.
http://www.epa.gov/ttn/chief/eiip/techreport/volume02/ii01_may2001.pdf
2. *Preferred and Alternative Methods for Estimating Air Emissions from Boilers*, (EIIP Volume II: Chapter 2, January 2001, Emission Inventory Improvement Program.
<http://www.epa.gov/ttn/chief/eiip/techreport/volume02/ii02.pdf>
3. *Compilation of Air Pollutant Emission Factors, AP-42, 5th Edition*, published by the U.S. Environmental Protection Agency, RTP, NC. [TTN CHIEF | Compilation of Air Pollutant Emission Factors](#)
4. *Emissions*, Cleaver-Brooks Package Boilers web site: [Cleaver Brooks: EMISSIONS](#)
5. *2002 Emissions Inventory Guidelines, Appendix A, Technical Supplement 1: Internal and External Combustion Sources* (RG-360/02), Texas Commission on Environmental Quality, December 2002. http://www.tnrcc.state.tx.us/air/aqp/eidata/rg_360_02.PDF
6. *Factor Information Retrieval (FIRE) Data System*, Version 6.23, October 2000, published by the U.S. Environmental Protection Agency, RTP, NC. [EPA | TTN CHIEF | Factor Information REtrieval \(FIRE\)](#)
7. *Petroleum Refineries Background Information for Proposed Standards: Catalytic Cracking (Fluid and Other) Units, Catalytic Reforming Units, and Sulfur Recovery Units*, EPA-453/R-98-003, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1998.
8. *Technical Guidance Package for Chemical Sources: Fluid Catalytic Cracking Units* (Draft RG-110), February 2001, Texas Natural Resource Conservation Commission.
http://www.tnrcc.state.tx.us/permitting/airperm/nsr_permits/files/fccu.pdf
9. *Preferred and Alternative Methods for Estimating Air Emissions from Oil and Gas Field Production and Processing Operations* (EIIP Volume II: Chapter 10), prepared by Eastern Research Group, prepared for Point Sources Committee, Emission Inventory Improvement Program, September 1999. <http://www.epa.gov/ttn/chief/eiip/techreport/volume02/ii10.pdf>
10. *2002 Emissions Inventory Guidelines, Appendix A, Technical Supplement 4: Flares* (RG-360/02), Texas Commission on Environmental Quality, December 2002.
http://www.tnrcc.state.tx.us/air/aqp/eidata/rg_360_02.PDF
11. *Technical Guidance Package for Chemical Sources: Flares and Vapor Oxidizers* (Draft RG-109), October 2000, Texas Natural Resource Conservation Commission.
http://www.tnrcc.state.tx.us/permitting/airperm/nsr_permits/files/flares.pdf
12. *Compendium of Greenhouse Gas Emission Estimation Methodologies for the Oil and Gas Industry, Section 4 – Emissions Estimation Methods* (API Product Number Z00100), American Petroleum Institute, Washington DC, April 2001.
13. *Flare Efficiency by Passive FTIR*, presentation by Bob Spellacy at the Houston-Galveston Air Quality Study Ozone Science Study Workshop (November 20-21, 2002), [Spellacy-FTIR Flare Efficiency.pdf on ftp.tnrcc.state.tx.us](#)

14. *Preferred and Alternative Methods for Estimating Fugitive Emissions from Equipment Leaks*, (EIIIP Volume II: Chapter 4, November 1996, Emission Inventory Improvement Program. http://www.epa.gov/ttn/chief/eiip/techreport/volume02/ii04_a.pdf and http://www.epa.gov/ttn/chief/eiip/techreport/volume02/ii04_b.pdf
15. *Protocol for Equipment Leak Emission Estimates*, (EPA-453/R-95-017), November 1995, U.S. Environmental Protection Agency, RTP, NC. http://www.epa.gov/ttn/chief/efdocs/lks95_ch.pdf
16. *2002 Emissions Inventory Guidelines, Appendix A, Technical Supplement 3: Equipment Leak Fugitives*, (RG-360/02), Texas Commission on Environmental Quality, December 2002. http://www.tnrcc.state.tx.us/air/aqp/eidata/rg_360_02.PDF
17. *Overview of Equipment Leaks Emission Estimation*, Powerpoint Presentation by Buzz Harris of URS Corporation at the Houston-Galveston Air Quality Study Emission Inventory Factor Workshop Feb. 7-8, 2002), [Overview of Fugitive Equipment Leaks.pdf on ftp.tnrcc.state.tx.us](ftp://www.tnrcc.state.tx.us)
18. *Proper Monitoring Essential to Reducing “Fugitive Emissions” Under Leak Detection and Repair Program*, (EPA-300-N-99-914), October 1999, U.S. Environmental Protection Agency, Washington, DC. <http://www.epa.gov/compliance/resources/newsletters/civil/enfalert/emissions.pdf>
19. *Project Abstract: Development of Emission Factors and/or Correlation Equations for Gas Leak Detection, and the Development of an EPA Protocol for the Use of a Gas-Imaging Device as an Alternative or Supplement to Current Leak Detection and Evaluation Methods*, TCET RFP 02-R04, Environ, January 2003. http://www.tcet.state.tx.us/RFPS/Abstracts/Abstract_Environ_02R04-01G.pdf
20. *Development of Smart LDAR for Fugitive Emissions Control*, Paper #P0056, Jeffrey Siegell, ExxonMobil Research & Engineering Company, et. al., November 2000. [EC Systems](#)
21. *Preferred and Alternative Methods for Estimating Air Emissions from Wastewater Collection and Treatment*, (EIIIP Volume II: Chapter 5), March 1997, Emission Inventory Improvement Program. <http://www.epa.gov/ttn/chief/eiip/techreport/volume02/ii05.pdf>
22. *2002 Emissions Inventory Guidelines, Appendix A, Technical Supplement 2: Cooling Towers*, (RG-360/02), Texas Commission on Environmental Quality, December 2002. http://www.tnrcc.state.tx.us/air/aqp/eidata/rg_360_02.PDF
23. *Air Quality Permit Technical Guidance Package for Chemical Sources: Cooling Towers* (Draft RG-108), February 2001, Texas Natural Resource Conservation Commission. http://www.tnrcc.state.tx.us/air/aqp/eidata/rg_360_02.PDF
24. *User’s Guide to TANKS*, Version 4.0, September 1999, U.S. Environmental Protection Agency, Washington, DC. [EPA |TTN CHIEF | TANKS Emission Estimation Software](#)
25. *Marine Vessel Loading, Ballasting, and Transit*, (EIIIP Volume III: Chapter 12), January 2001, Emission Inventory Improvement Program. http://www.epa.gov/ttn/chief/eiip/techreport/volume03/iii12_apr2001.pdf