Petroleum Refinery Source Characterization and Emission Model for Residual Risk Assessment

Prepared for:

 Mr. Robert Lucas U.S. Environmental Protection Agency Office of Air Quality Planning and Standards Research Triangle Park, NC 27709

Prepared by:

RTI P.O. Box 12194 Research Triangle Park, NC 27709 Contract No. 68-D6-0014

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1.0 Model Overview

The Refinery Emission Model (REM) is an Access database model used to characterize hazardous air pollutant (HAP) emissions from all processes typically present at a petroleum refinery. The model has been designed to use reported emissions data, if they are available. When reported emissions data are not available, they are estimated using the best available data or algorithms (as described in Section 4), which are based on a variety of emission factors and calculation protocols developed and reported by the U.S. Environmental Protection Agency (EPA). Additional emission factors and calculation protocols were developed, as necessary, for a few emission sources. Emission factor development for these sources relied heavily on emissions reported by refineries in their Title V permit applications.

The overall database is based primarily on the information reported in the *Oil & Gas Journal* (OGJ) 2000 Worldwide Refining Survey (Stell, 2000a). This survey lists 155 refineries in the United States and it territories (Puerto Rico and the Virgin Islands). It also provides sitespecific process charge or production capacities for 18 refinery process units at these refineries. Data collected by EPA in developing other standards for the petroleum refining industry were used to supplement the database.

Using these data and the algorithms detailed in Section 4, the REM provides source characteristics and HAP emission estimates for each of the following emission sources:

- **Process heaters and boilers**
- Flares/thermal oxidizers (includes marine vessel loading emissions)
- Wastewater collection and treatment systems
- Cooling towers
- \blacksquare Fugitive equipment leaks
- Tanks (both storage and process tanks)
- Truck and rail (product) loading operations
- Catalytic reforming unit (CRU) catalyst regeneration vents
- Catalytic cracking unit (CCU) catalyst regeneration vents
- Sulfur recovery units (SRU) or sulfur plant vents.

A draft approach to estimating emissions from miscellaneous process vents is also provided in Section 4, but it has not been added to the REM.

The REM output file is based on the general structure of the National Toxic Inventory (NTI) database. This database provides a separate record for each chemical from each emission source at a given refinery.

One of the compounds most likely to drive risk at petroleum refineries is benzene because of its prevalence in emissions from petroleum refineries and its relatively high unit risk factor. Table 1-1 provides a comparison of benzene emissions calculated by REM and those reported by the refineries in their Title V applications.

Based on the comparison of calculated and reported benzene emissions for these refineries, the REM estimates appear to be accurate within a factor of 2 for each refinery emission point and for the total refinery emissions. In every case, the REM estimates are higher than the reported emissions. This is generally due to the inclusion of emission estimates for cooling towers, combustion sources, and other emission sources that were not reported by most refineries in their Title V permit applications.

Most of the emission discrepancies greater than a factor of 2 are readily explainable. First, the emissions reported by the Marathon–Garyville Refinery are substantially lower than those reported for other similar-sized refineries. This refinery was very active in the Early Reduction Program¹ and has implemented measures to reduce emissions from wastewater collection and treatment systems, marine vessel loading operations, and cooling towers, according to refinery personnel during an EPA site visit (Zerbonia and Coburn, 1995). This refinery is one of only a few refineries (if not the only refinery) that achieved the 90 percent emission reduction required by the Early Reduction Program. As such, it is understandable why this refinery's emissions are out-of-line compared with the emissions of other similar-sized refineries and why the REM overestimates this refinery's emissions. Because so few refineries qualified under the Early Reduction Program, the frequency of an emission discrepancy caused by a refinery controlling emissions well beyond what is currently required by law is considered to be very low. From a different perspective, Marathon–Garyville's emissions suggest that emission-reduction measures are available that could achieve emission reductions of roughly 65 percent compared with current (typical) industry practices.

The other significant discrepancy in reported versus predicted emissions is for the Exxon–Chalmette refinery. This refinery operates an aromatics unit and produces toluene and xylene, but no benzene. The REM cannot distinguish among the specific aromatics that are produced, so it assumes benzene, toluene, and xylene (BTX) are all produced. The REM estimates 5 tons/yr of benzene emissions occur from the benzene product storage tanks. Excluding this 5 tons/yr of benzene emissions from the storage tank emission estimates for the Exxon–Chalmette refinery yields tank emissions that are roughly within a factor of 2, and it significantly improves the overall refinery emission estimate. The inability to distinguish among the specific aromatics produced is one of the most significant shortcomings of the REM (at least in terms of BTX) emission estimates. Aromatics units operate at 20 percent of the U.S. refineries; data collection efforts targeted to these aromatics units would significantly improve REM emission estimates (not only for storage tanks, but also for wastewater treatment and fugitive process equipment leaks).

 1 The Early Reduction Program under Section 112(i) allows a qualifying facility to defer compliance with Maximum Achievable Control Technology (MACT) standards for 6 years if it reduces HAP emissions by 90 percent (95 percent for hazardous particulate emissions) before the applicable MACT is proposed.

2.0 Inputs and Outputs

There are four basic input files used by REM:

- 1. The actual reported emission database file;
- 2. The overall facility process capacity/production rate database file;
- 3. Unit-specific database files (for certain processes for which data are available); and
- 4. The emission factor database files (one file per emission source).

The actual reported emissions database file currently contains emissions data for nine Louisiana refineries for which Title V applications were obtained. This database will expand as more data are collected from the refineries or state agencies.

The overall and process-specific production rate databases are based on production and process charge capacities as reported in the OGJ 2000 Worldwide Refining Survey (Stell, 2000a). Process charge or production capacities are provided in the refining survey for the following process units:

- Crude unit
- Vacuum distillation unit
- Coking unit
- Thermal processes (thermal cracking and visbreaking)
- Catalytic cracking unit
- Catalytic reforming unit
- Catalytic hydrocracking unit
- Catalytic hydrotreating unit
- **Alkylation unit**
- Polymerization/dimerization unit
- **A**romatics unit
- **ISOMETER 1999** Isometization unit
- Lube plant
- Oxygenates unit
- Hydrogen plant
- \Box Coke plant
- Sulfur plant
- **Asphalt plant.**

Some unit-specific information was available for CCUs, CRUs, and SRUs based on previous Maximum Achievable Control Technology (MACT) standard development efforts. These additional data, which include the number of units, the type of unit, and the control devices used, are included in the unit-specific database files.

The emission factor input files were developed using the available data or estimation algorithms that are detailed in Section 4. The emission factors generally are formatted to provide HAP-specific emission estimates per unit throughput.

The REM output file is based on the general structure of the NTI database. This database provides a separate record for each chemical from each emission source at a given refinery. Table 2-1 lists the field names and descriptions for the output database file.

Based on the 2000 Worldwide Refining Survey (Stell, 2000a), the REM contains input/output information for 155 refineries located in the United States, Puerto Rico, and the Virgin Islands. Table 2-2 provides a listing of the refineries included in the REM.

Based on the available emissions data, HAP emissions estimates could be developed for 64 specific HAPs from the refinery emission sources. The HAPs included in REM input/output files are listed in Table 2-3.

| Field | Data Type | Description |
|------------------|---------------------|---|
| FacNum | Double | Unique facility ID number assigned by RTI, ranging from 1 to 155 |
| NTI_ID1 | Text | ID assigned to the facility in the 1996 NTI |
| NTI_ID2 | Text | Second NTI ID when more than one ID was assigned to the same facility |
| SCC | Text | Source classification code ¹ |
| SCC1_DESC | Text | Descriptor associated with first SCC digit |
| SCC3_DESC | Text | Descriptor associated with first three SCC digits |
| SCC6_DESC | Text | Descriptor associated with first six SCC digits |
| SCC8_DESC | Text | Descriptor associated with first eight SCC digits |
| AFSUNITS | Text | Units of measure associated with throughput—AIRS Facility Subsystem |
| MEASURE | Text | Units of measure associated with throughput |
| MATERIAL | Text | Material being measured |
| ACTION | Text | Action performed on the material |
| UnitID | Text | ID assigned to the process unit or group of units for which emissions are estimated |
| CASRN | Text | Chemical Abstract Service registration number for the chemical in the row |
| ChemName | Text | Name of the chemical for which emissions are estimated |
| Emissions | Double | Annual emissions of the chemical in tons per year |
| OpHours | Text | Number of hours per year that the process operates |
| Height | Text | Height of the emission point in feet |

Table 2-1. Fields in the Petroleum Refinery Output Database File

Table 2-1. (continued)

¹ The number of digits provided depends on how the emission points are grouped. For example, tanks are assigned three digits (403) because one estimate of emissions was made for all types of tanks (fixed-roof, floating-roof, etc.). On the other hand, process heaters are very specific and use eight digits (30600106).

Table 2-2. List of Refineries Included in the REM

| No. | Facility Name | City | State | Crude Capacity (bbl/day) |
|-----|---|----------------|--------------|---------------------------------------|
| 147 | Ergon-West Virginia, Inc. (formerly Quaker State Oil Refining Corp.) | Newell | WV | 11,500 |
| 148 | Murphy Oil USA, Inc. | Superior | WI | 33,250 |
| 149 | Frontier Oil & Refining Co. | Cheyenne | WY | 40,500 |
| 150 | Little America Refining Co. | Casper | WY | 22,000 |
| 151 | Sinclair Oil Corp. | Sinclair | WY | 22,000 |
| 152 | Wyoming Refining Co. | Newcastle | WY | 12,500 |
| 153 | Hovensa LLC (formerly Hess Oil) | St. Croix | V.Isl | 525,000 |
| 154 | Caribbean Petroleum Corp. | Bayamon | P.Rico | 49,000 |
| 155 | Sunoco, Inc. | Yabucoa | P.Rico | θ |

Table 2-2. (continued)

Table 2-3. (continued)

** Emissions for these compounds were based only on nondetect limits and are, therefore, biased high.

3.0 Assumptions and Limitations

In addition to the information and data discussed in Section 2, the REM contains various assumptions, most of which are more effectively described on a source-specific basis. The more general model assumptions are discussed in this section; the assumptions made in developing source-specific emission characteristics and emission factors are discussed in the source-specific subsections in Section 4.

As described previously, emissions are generally estimated based on production and process charge capacities as reported in the OGJ 2000 Worldwide Refining Survey (Stell, 2000a). This approach leads to two assumptions. The first is that the 2000 Worldwide Refining Survey includes all known U.S. petroleum refineries. In reviewing other EPA databases, it appears that several small companies (pipeline stations, gas stations, home heating fuel distributors, etc.) occasionally list themselves using the SIC code of 2911 (Petroleum Refineries). The 1996 version of the NTI appears to contain many such facilities. The OGJ survey was considered to provide the best reference for facilities that were actually petroleum refineries. In some instances, two or three nearby/neighboring refineries, which were originally separate facilities, have come under the control of a single company. These refineries were subsequently listed in the OGJ survey as a single refinery, and the process totals reflect that of the total combined refinery. In these cases, the refineries are modeled as one large refinery. This treatment is generally consistent with the definition of a facility under the Clean Air Act (CAA) because the refineries are generally adjacent, and the combined refinery is included in a single contiguous facility boundary. However, not all of the combined refineries were contiguously located.

The second assumption is that all refinery processes are operating at 100 percent capacity. In general, this assumption is valid based on process capacity utilization trends (Lidderdale et al., 1995; EIA, 2000); crude capacity utilization rates reached 96 percent in May 2000 (FTC, 2001). Although certain processes, such as sulfur production, have capacity utilization rates that are substantially less than 100 percent (Stell, 2000b), for most petroleum refining processes, especially those that contribute significantly to the HAP emissions (especially those HAPs with high unit risk factors), the assumption of 100 percent capacity utilization provides an accurate assessment of actual operating rates.

The REM currently uses reported emissions data (from Title V permit applications) as a priority over the refinery model emission estimates *for a given emission source*. This assumes that the reported data are superior to the model estimates and are complete. If the reported emissions data file contains tank emission estimates for BTX, tank emissions are output for only those three chemicals, even though tank emission factors were developed for a dozen HAPs. Also, the degree of documentation of the reported data is widely variant, and some reported

emissions have no documented basis. It is quite likely that many of the reported emissions rates are not actually measured data, but emission model estimates made by the refinery. The refinery does have better knowledge of equipment type and counts to run its emission estimates, but these fixed emissions data have some level of uncertainty associated with them.

All of the emission estimates developed for the REM assume that the process units and emission controls, if present, are operating normally. The model does not estimate episodic emission events that may result from process upsets or control device malfunctions.

Because of the lack of process-specific source locations or configurations at the refineries and the emission characteristics of certain sources, three general area sources were defined: the process equipment area, the tank farm area, and the wastewater treatment area. Although the equipment leak emissions were calculated on a process-specific basis, these emissions were summed and used to estimate the total emissions from the process area. Similarly, refinery fuel gas (RFG) use in combustion sources was calculated on a process-specific basis, but the RFG use was summed for all heaters, with a separate sum for boilers, and these totals were used to determine the number of stacks at the refinery; these stacks were assumed to be uniformly distributed in the process area of the refinery.

Tank farms were assumed to be one large area emission source rather than a large number of individual tank point (for fixed-roof tanks with or without internal floating roofs) and area sources (for external floating-roof tanks). Half of the wastewater treatment emissions were assumed to occur from the process area (i.e., from the wastewater collection system), and half of the emissions from the wastewater treatment area.

4.0 Source Characteristics and Emission Estimates

This section describes the source characteristics and algorithms used to estimate HAP emissions from each specific emission source. The emission sources considered in the REM are discussed in the following subsections:

Although not included in the preliminary REM, miscellaneous process vents not included in the emission sources listed above are discussed in a final subsection, Section 4.11.

4.1 Process Heaters and Boilers

Process heaters and boilers are vent (point) sources that occur throughout the process area of the refinery. The size of the vent stack varies with the size of the heater or boiler (typically measured in terms of the rate fuel is burned). For petroleum refineries, nearly all refinery process heaters and boilers use RFG as the primary fuel. Boilers are used to generate steam for various refinery operations, and theses sources are generally localized, e.g., in the boiler plant. Process heaters are used to preheat feedstock for a given process or to heat distillation columns (the latter are often termed reboilers); these emission sources are typically localized at or near the process requiring the heater (or reboiler).

4.1.1 Emission Estimation Methodology

The American Petroleum Institute (API), in conjunction with the Western States Petroleum Association (WSPA), has conducted numerous emission source tests of combustion sources and has compiled emission factors to be used for refinery combustion sources (Hansell and England, 1998). Separate emission factors were developed for different combustion sources based on the type of source and fuel used. Emission factors compiled for boilers using RFG are presented in Table 4-1; the emission factors compiled for process heaters using RFG are presented in Table 4-2.

Table 4-1. Summary of Emission Factors for Boilers Firing Refinery Fuel Gas

a CARB = California Air Resource Board

| | | | Emission Factor (lb/MMBtu) | | | Uncer- | | | |
|-----------------------------|------------------------------|-------------|-----------------------------------|----------------|----------|----------------|-----------------------|--------------------------|------------------------|
| Substance | CARB Rating | Mean | Median | Maximum | Minimum | Tests | RSD, $\frac{0}{0}$ | tainty, $\frac{0}{0}$ | Detect Ratio |
| Zinc | $C3-v0$ | 2.08E-05 | 2.58E-05 | 2.83E-05 | 8.48E-06 | 1 | 51.72 | 58.53 | $\mathbf{1}$ |
| Acenaphthene | $A2-v0$ | 2.36E-09 | 1.55E-09 | 5.61E-09 | 1.20E-09 | $\overline{4}$ | 69.14 | 40.86 | 0.95 |
| Acenaphthylene | $A2-v0$ | 1.55E-09 | 1.25E-09 | 2.74E-09 | 1.02E-09 | 4 | 41.7 | 24.64 | 0.51 |
| Anthracene | $A2-v0$ | 2.87E-09 | 2.30E-09 | 6.45E-09 | 1.09E-09 | $\overline{4}$ | 61.24 | 36.19 | 0.92 |
| Benzo(a)anthracene | $A1-v2$ | 3.21E-08 | 5.40E-09 | 3.39E-07 | 1.05E-09 | 9 | 265.3 | 101.97 | 1 |
| Benzo(a)pyrene | $A1-v3$ | 8.96E-08 | 1.73E-09 | 1.38E-06 | 1.02E-09 | 9 | 352.36 | 135.44 | 0.98 |
| Benzo(b)fluoranthene | $A1-v2$ | 4.04E-08 | 3.31E-09 | 4.87E-07 | 1.02E-09 | 9 | 314.58 | 120.92 | 0.99 |
| Benzo(g,h,i)perylene | $A2-v0$ | 1.17E-09 | 1.10E-09 | 1.40E-09 | 1.02E-09 | $\overline{4}$ | 11.55 | 6.82 | $\boldsymbol{0}$ |
| Benzo(k)fluoranthene | $A1-v2$ | 2.41E-08 | 2.18E-09 | 2.96E-07 | 1.02E-09 | 9 | 310.01 | 119.16 | 0.96 |
| Chrysene | $A2-v0$ | 1.63E-09 | 1.23E-09 | 4.79E-09 | 1.02E-09 | $\overline{4}$ | 66.84 | 39.5 | 0.63 |
| Dibenz(a,h)anthracene | $A1-v2$ | 1.02E-08 | 1.60E-09 | 1.37E-07 | 5.93E-10 | 9 | 279.09 | 107.28 | $\overline{0}$ |
| Fluoranthene | $A2-v0$ | 3.06E-09 | 3.14E-09 | 5.04E-09 | 1.85E-09 | 4 | 33.8 | 19.97 | 1 |
| Fluorene | $A2-v0$ | 1.08E-08 | 8.77E-09 | 2.74E-08 | 2.96E-09 | $\overline{4}$ | 70.62 | 41.74 | $\mathbf{1}$ |
| Indeno $(1,2,3$ -cd) pyrene | $A1-v3$ | 1.03E-07 | 1.75E-09 | 1.42E-06 | 1.02E-09 | 9 | 343.01 | 131.85 | 0.99 |
| Naphthalene | $A2-v0$ | 3.13E-07 | 2.61E-07 | 7.58E-07 | 1.19E-07 | $\overline{4}$ | 66.9 | 39.53 | $\mathbf{1}$ |
| Phenanthrene | $A2-v0$ | 1.46E-08 | 1.50E-08 | 2.25E-08 | 6.91E-09 | $\overline{4}$ | 32.6 | 19.27 | $\mathbf{1}$ |
| Pyrene | $A2-v0$ | 2.84E-09 | 2.72E-09 | 4.53E-09 | 1.87E-09 | 4 | 28.87 | 17.06 | 1 |
| Ethylbenzene | $A2-v1$ | 3.02E-05 | 1.79E-05 | 1.03E-04 | 2.72E-06 | $\overline{4}$ | 104.65 | 59.21 | 0.51 |
| Phenol | $C1-v1$ | 5.63E-06 | 3.14E-06 | 2.54E-05 | 2.84E-07 | 7 | 114.62 | 49.02 | 0.97 |
| Acetaldehyde | $B1-v3$ | 1.53E-05 | 8.12E-06 | 8.55E-05 | 8.41E-08 | 8 | 126.3 | 50.53 | 0.88 |
| Benzene | $B1-v1$ | 6.47E-05 | 5.49E-05 | 1.85E-04 | 2.54E-06 | 11 | 87.67 | 29.91 | 0.02 |
| Formaldehyde | $B1-v3$ | 1.11E-04 | 1.90E-05 | 1.34E-03 | 7.67E-07 | τ | 262.94 | 112.46 | $\mathbf{1}$ |
| Hydrogen sulfide | $A1-v1$ | 2.92E-04 | 2.46E-04 | 8.04E-04 | 1.76E-05 | 7 | 75.53 | 32.3 | $\boldsymbol{0}$ |
| Propylene | $A2-v0$ | 2.17E-06 | 2.22E-06 | 2.98E-06 | 1.08E-06 | 3 | 23.69 | 15.47 | 0.05 |
| Toluene | $D1-v2$ | 1.07E-04 | 7.00E-05 | 9.19E-04 | 4.04E-06 | 11 | 148.57 | 50.69 | 0.55 |
| Xylene (total) | $A2-v1$ | 3.73E-05 | 3.16E-05 | 1.08E-04 | 4.66E-06 | $\overline{4}$ | 99.32 | 56.19 | $0.6\,$ |

Table 4-2. (continued)

The median emission factors presented in Tables 4-1 and 4-2 were used for the preliminary emission estimates from heaters and boilers. Upon further review, it is noted that several of the emission factors presented by the California Air Resource Board (CARB)/API are based on method detection limits; consequently, all heater and boiler emission factors that have a detect ratio of 0 will provide emission estimates that are biased high. For example, the hexavalent chromium emission factor, which is based on nondetect values, is higher than the median total chromium emission factor. Consequently, additional data are needed to develop accurate emission factors for the compounds with a zero-detect ratio.

To use the CARB/API emission factors, RFG usage rates are needed. Data on combustion sources were available from selected Louisiana refineries' Title V applications. These data confirmed that RFG is used almost exclusively to fuel process heaters and boilers. These data also established a means to estimate the RFG usage rates of a specific refinery process based on the process capacity. The RFG usage rates reported in the Title V applications were sorted by emission source. The total RFG usage for a given process, for example the CRU, was calculated and divided by the total CRU capacity (as reported in Stell (2000a)) to calculate an RFG usage rate per unit capacity factor. Process-specific RFG usage rate factors were compared for different Louisiana refineries, and a representative factor was selected (typically the highest of the median or average); Table 4-3 summarizes the process-specific RFG usage rate factors calculated for the Louisiana refineries reporting combustion fuel usage rates in their Title V permit applications and the emission factor selected from these data. In general, the mean value was used unless the range of calculated fuel use factors spanned an order of magnitude or if one value appeared to be incongruent. Median and log-mean average values were also calculated. Mean, median, and log-mean values were also calculated with the apparent incongruent value omitted, and a value was selected that appeared to best represent the limited data available.

| | | | Process for | Process | Fuel Use Factor (MMBtu/bbl) | | |
|--------------------|--------------------|--------------|---------------------------|----------------------|---------------------------------------|-----------------|----------------|
| Plant | City | State | Fuel Use Factor | Capacity (bbl/cd) | Calculated | Selected | Comment |
| BP-Alliance | Belle Chase | LA | Alkylation | 38,000 | 0.0586 | 0.217 | median |
| ExxonMobil | Chalmette | LA | Alkylation | 12,500 | 0.2074 | | |
| Marathon Oil | Garyville | LA | Alkylation | 28,500 | 0.2265 | | |
| Murphy Oil | Meraux | LA | Alkylation | 7,650 | 0.5145 | | |
| BP-Alliance | Belle Chase | LA | Aromatics | 17,800 | 0.0998 | 0.0998 | |
| Marathon Oil | Garyville | LA | Asphalt | 39,900 | 0.1329 | 0.190 | mean |
| Pennzoil | Shreveport | LA | Asphalt | 540 | 0.2471 | | |
| ExxonMobil | Chalmette | LA | CO Boiler | 68,000 | 0.1129 | 0.219 | mean |
| Pennzoil | Shreveport | LA | CO Boiler | 10,800 | 0.3251 | | |
| BP-Alliance | Belle Chase | LA | Coking | 25,200 | 0.0200 | 0.0942 | mean |
| ExxonMobil | Chalmette | LA | Coking | 32,500 | 0.1684 | | |
| Exxon | Baton Rouge | LA | CRU | 70,000 | 0.3576 | 0.467 | median |

Table 4-3. Development of Fuel Use Factors

| | | | Process for Process Fuel Use Capacity | | Fuel Use Factor (MMBtu/bbl) | | |
|--------------------|--------------------|--------------|---|----------|---------------------------------------|-----------------|------------------|
| Plant | City | State | Factor | (bbl/cd) | Calculated | Selected | Comment |
| Marathon Oil | Garyville | LA | CRU | 42,800 | 0.4441 | | |
| BP-Alliance | Belle Chase | LA | CRU | 42,000 | 0.4476 | | |
| Murphy Oil | Meraux | LA | CRU | 16,200 | 0.4859 | | |
| ExxonMobil | Chalmette | LA | CRU | 46,000 | 0.5044 | | |
| Pennzoil | Shreveport | LA | CRU | 8,000 | 0.5064 | | |
| Citgo | Lake Charles | LA | Crude | 307,325 | 0.0282 | 0.0873 | mean w/o low # |
| ExxonMobil | Chalmette | LA | Crude | 182,500 | 0.0826 | | |
| Pennzoil | Shreveport | LA | Crude | 46,200 | 0.0836 | | |
| Marathon Oil | Garyville | LA | Crude | 232,000 | 0.0861 | | |
| BP-Alliance | Belle Chase | LA | Crude | 250,000 | 0.0888 | | |
| Murphy Oil | Meraux | LA | Crude | 95,000 | 0.0954 | | |
| Murphy Oil | Meraux | LA | FCCU^{a} | 34,200 | 0.0229 | 0.0505 | median |
| Marathon Oil | Garyville | LA | FCCU | 104,500 | 0.0505 | | |
| ExxonMobil | Chalmette | LA | FCCU | 68,000 | 0.0551 | | |
| ExxonMobil | Chalmette | LA | Hydrocrack | 18,500 | 0.0889 | 0.105 | mean |
| ExxonMobil | Chalmette | LA | Hydrocrack | 18,500 | 0.1204 | | |
| Marathon Oil | Garyville | LA | Hydrotreat | 181,500 | 0.0043 | 0.0179 | mean w/o low $&$ |
| BP-Alliance | Belle Chase | LA | Hydrotreat | 112,000 | 0.0153 | | high values |
| Murphy Oil | Meraux | LA | Hydrotreat | 58,050 | 0.0179 | | |
| ExxonMobil | Chalmette | LA | Hydrotreat | 111,500 | 0.0189 | | |
| Exxon | Baton Rouge | LA | Hydrotreat | 299,500 | 0.0193 | | |
| Pennzoil | Shreveport | LA | Hydrotreat | 21,560 | 0.0499 | | |
| ExxonMobil | Chalmette | ${\rm LA}$ | Isom | 9,500 | 0.1511 | 0.151 | |
| Pennzoil | Shreveport | $\rm LA$ | Lubes | 7,650 | 0.3683 | 0.368 | |
| Marathon Oil | Garyville | $\rm LA$ | Boiler/Misc | 232,000 | 0.0569 | 0.137 | logmean |
| Exxon | Baton Rouge | $\rm LA$ | Boiler/Misc | 485,000 | 0.1018 | | |
| Murphy Oil | Meraux | $\rm LA$ | Boiler/Misc | 95,000 | 0.1262 | | |
| ExxonMobil | Chalmette | $\rm LA$ | Boiler/Misc | 182,500 | 0.1855 | | |
| Pennzoil | Shreveport | $\rm LA$ | Boiler/Misc | 46,200 | 0.3514 | | |

Table 4-3. (continued)

| | | | Process for Fuel Use | Process | Fuel Use Factor (MMBtu/bbl) | | |
|--------------------|--------------------|--------------|---------------------------------------|----------------------|---------------------------------------|-------------------|----------------|
| Plant | City | State | Factor | Capacity (bbl/cd) | Calculated | Selected | Comment |
| Exxon | Baton Rouge | LA | SRU | $675^{\rm b}$ | 1.9911 ^c | 3.08 ^c | mean w/o high |
| ExxonMobil | Chalmette | LA | SRU | 465 ^b | 2.4103° | | |
| BP-Alliance | Belle Chase | LA | SRU | 70 ^b | 3.8057° | | |
| Murphy Oil | Meraux | LA | SRU | 120 ^b | 4.1000 ^c | | |
| Pennzoil | Shreveport | LA | SRU | 10 ^b | 15.1200° | | |
| ExxonMobil | Chalmette | LA | Vacuum | 102,000 | 0.0424 | 0.0838 | median |
| Pennzoil | Shreveport | LA | Vacuum | 23,085 | 0.0438 | | |
| Marathon Oil | Garyville | LA | Vacuum | 118,800 | 0.0687 | | |
| Murphy Oil | Meraux | LA | Vacuum | 47,500 | 0.0990 | | |
| BP-Alliance | Belle Chase | LA | Vacuum | 92,000 | 0.1137 | | |
| Citgo | Lake Charles | LA | Vacuum | 79,800 | 0.1504 | | |

Table 4-3. (continued)

 ${}^{\textrm{a}}$ FCCU = fluid CCU

b Capacity in long-tons/cd

c Fuel use factor in MMBtu/long-ton

Unclassified or miscellaneous RFG combustion sources were classified together with boilers to develop an overall boiler/miscellaneous RFG usage rate factor (based on crude throughput), and the boiler emission factors were applied to this combined group. Process heater emission factors were applied for all other RFG fuel usage rates. Table 4-4 provides a sample calculation of process heater and boiler emission estimates for benzene from a model refinery.

4.1.2 Source Characteristics

Data on combustion sources using RFG as reported in the Louisiana Title V applications were reviewed to develop process heater and boiler vent characteristics. The summary statistics for the process heater and boiler source vents are presented in Table 4-5. Based on these statistics, all process heater stacks were assumed to be 128 ft high and to operate at a stack temperature of 550°F. Process boilers were assumed to be 65 ft high and to operate at a stack temperature of 350°F.

Because the process heater fuel use was calculated on a process-specific basis, the number of process vents was initially going to be calculated on a process-specific basis (e.g., four vents per CRU, one vent for most other processes, three to four boiler vents, etc.). However, because no information was available to locate the process heater vents for most of the refineries and because uniform stack height and temperatures were assumed, the total RFG use rate for process heaters was calculated. A simple algorithm was developed to estimate the number of stacks based on the total RFG use rate by assuming the standard process heater burned

^a Capacity in long-tons/cd

^b Fuel use factor in MMBtu/long-ton

^c Assumed to be the same fuel use factor as coking

| Type | Stat | Ht(ft) | \mathbf{D} ia (ft) | $T(^{\circ}F)$ | ft/s | acfm |
|----------------|-------------|--------|----------------------|----------------|------|---------|
| Heaters and | Mean | 129 | 6 | 600 | 24 | 38,800 |
| Reboilers | Median | 128 | 5.3 | 550 | 18 | 23,600 |
| | Std Dev. | 53 | 3 | 215 | 24 | 44,600 |
| | Minimum | 24 | 1.5 | 140 | 0.3 | 37 |
| | Maximum | 257 | 15 | 1200 | 222 | 295,000 |
| Boilers | Mean | 89 | 6.5 | 500 | 27 | 60,100 |
| | Median | 64 | 6 | 340 | 20 | 41,800 |
| | Std Dev. | 59 | 2.8 | 325 | 16 | 48,100 |
| | Minimum | 25 | 3.5 | 270 | 11 | 7,300 |
| | Maximum | 205 | 13 | 1100 | 50 | 156,000 |

Table 4-5. Summary Statistics for Process Heater and Boiler Stacks

100 MMBtu/hr of RFG (2,400 MMBtu/cd), which translates to roughly 45,000 acfm at 550°F. Based on analysis of the flow rate data and fuel use rate data, along with theoretical calculations, a flow rate factor of 235 scfm per MMBtu/hr was determined (standard conditions defined as 1 atmosphere and 68°F). This flow rate factor was used to determine the process heater (or boiler) vent flow rate. The mean process heater stack diameter of 6 ft was used because the assumed flow rate per stack was a slightly larger-than-average stack flow rate.

This fixed-stack method was satisfactory for large refineries but provided single-stack estimates for small refineries. Consequently, the fixed-stack method was altered slightly so that all refineries had at least two process heater stacks. The final algorithm for determining the number of stacks for process heaters (PH) is as follows:

For boilers, three or four boiler stack vents were assumed per refinery. Refineries with less than 7,200 MMBtu/cd (300 MMBtu/hr, or approximately 50,000 bbl/cd crude capacity) were assumed to have three boilers and three boiler stacks; all other were assumed to have four boilers

and four boiler stacks. Because the boiler stack flow rates for large refineries could vary widely based on the essentially fixed number of boiler stacks, two different model boiler stack diameters were used for the large refineries. Boilers processing less than 4,800 MMBtu/cd per boiler were assumed to have 5 ft diameter stacks; boilers processing 4,800 MMBtu/cd per boiler or more were assumed to have 7.5 ft diameter stacks.

For both process heater and boiler stacks, the flow rate was calculated using Equation 4-1. The stack velocity was calculated based on the flow rate and stack diameter using Equation 4-2.

$$
Q_{\text{stack}} = \frac{235 \text{ scfm}}{MM\text{Btu}} \times \frac{(460 + T_{\text{stack}})}{528}
$$

where

$$
Q_{\text{stack}} = \text{flow rate of stack (acfm)}T_{\text{stack}} = \text{temperature of stack (°F)}
$$

$$
V_{\text{stack}} = \frac{Q_{\text{stack}}}{\pi \left(\frac{d_{\text{stack}}}{2}\right)^2} \times \frac{1 \text{ min}}{60 \text{ sec}}
$$

where

 V_{stack} = velocity of stack emissions (ft/sec) $d_{\text{stack}} =$ diameter of stack (ft)

Based on this methodology, the average model process heater stack (one model stack per refinery for all petroleum refineries) has a flow rate of 39,500 acfm and an average stack velocity of 23 ft/sec. Similarly, the average model boiler stack (one model stack per refinery for all petroleum refineries) has a flow rate of 58,000 acfm and an average stack velocity of 30 ft/sec.

4.1.3 Uncertainty in Estimates

The primary uncertainties are in the emission factors and the fuel use factors; there are also uncertainties in the number and characteristics of stacks. Statistics for the emission factors are provided in Tables 4-1 and 4-2. Care should be taken in using the uncertainties associated with the metals analyses because only one test was performed for process heaters and only one for boilers. Consequently, the statistics for metals presented in these tables illustrate the uncertainty and variability of a single process in the very short term. In general, the emission factors employed are considered central tendency values. However, for compounds with a detect ratio of zero (or close to zero), the emission factors are based on the analytical detection limits. Therefore, the emission factors for these compounds are biased high.

Because both process heaters and boilers are large combustion units firing the same fuel, the process heater and boiler emission factors are expected to be similar. It is encouraging to see that the metal emission factors developed for process heaters and for boilers (i.e., two separate tests) resulted in median or average emission factors that are generally within a factor of 2 or 3. A more complete analysis of uncertainty can be made by reviewing the uncertainties associated with the emission factors for VOCs for both process heaters and boilers and for the polycyclic aromatic hydrocarbons (PAHs) for process heaters. By evaluating the standard deviations for the emission factors for these chemicals, by comparing the median and average values within a test group, and by comparing the same central tendency indicator across test groups (i.e., process heaters versus boilers), the data provide compelling evidence that the central tendency emission factors are accurate within a factor of 2 or 3.

As presented in Tables 4-1 and 4-2, the maximum and minimum values represent the results of a single test run and not the results of a single source test (three-run average emission factor). As such, the maximum and minimum "emission factors" likely accentuate the variability of the process and the test methods rather than characterizing true process emissions variability. For example, in a single test run (see emission factors for metals where the detect ratio is 1), the maximum and minimum values roughly span an order of magnitude. These single sampling events provide an assessment of the short-term variations in process operations and uncertainties associated with the process emissions, but they may not provide good measures of long-term emission variablity. Nonetheless, based on the data presented in Tables 4-1 and 4-2, the high and low extreme values are roughly one order of magnitude greater than or less than the median value, respectively.

Although very limited data were used to develop the RFG use factors, with some fuel use factors based on single observations, only three processes significantly contribute to the overall fuel use rates for most refineries. As seen in the sample calculation for a "model" refinery presented in Table 4-4, CRU process heaters have the highest fuel use factor and generally dominate the process heater fuel usage. This was expected because the CRU is an endothermic reaction carried out in three to four reactors in series; before/between each reactor, the process stream is heated in a process heater to raise (or re-raise) the temperature of the process stream prior to the next reactor. The other major contributors to the refineries' fuel usage are the crude heaters and the boilers (which includes miscellaneous combustion vents) primarily because crude capacity is generally significantly larger than other process capacities. Therefore, the best measure of the accuracies and uncertainties associated with the overall RFG usage rates is the fuel usage factors developed for these three contributors.

Based on the data presented in Table 4-3, the fuel use factors for crude and CRU process heaters are very consistent. For CRUs, the factors range from 0.36 to 0.51; excluding the apparently low value, the range is very tight (0.44 to 0.51). Based on the energy requirements of the CRU, this tight range of fuel use factors is expected. Similarly, the crude unit process heater fuel use factors are expected to be consistent because the energy required to preheat the crude and operate the atmospheric distillation column should be universal for all refineries. Omitting the uniquely low value, the crude process heater fuel use factors range only from 0.83 to 0.95.

The boiler (and miscellaneous combustion source) fuel use factors exhibit a broader range of values than the crude and CRU process heaters; the high-low values differ from the central tendency value by a factor of 2.5. Although this may be partially due to differences in how refineries characterized their emission sources (i.e., which sources could be attributed to specific processes and which were included as miscellaneous sources), a given refinery may likely have significantly different steam generation and use requirements that affect the magnitude of its boiler plant (e.g., whether the CCU vent stream is used to generate steam). Consequently, the boiler fuel use rate factors are likely accurate only to a factor of 2 or 3. However, because the boiler contributes roughly 30 percent of the total RFG usage, the overall refinery fuel use rate is more certain, based on the tight range of factors for crude and CRU process heaters. The overall fuel usage rate for a given refinery is expected to be within ± 50 percent. (Based on the similarity of emission factors for process heaters and boilers, minimal uncertainty is introduced by including miscellaneous RFG combustion sources with the boiler fuel use estimates.)

In summary, the emission factors are estimated to be accurate within a factor of 2 to 3, and the overall fuel usage rate for a given refinery is expected to be within ± 50 percent. Taken together, the combined uncertainty of the process heater and boiler emission estimates is roughly a factor of 3 to 5. This uncertainty directly affects the emission estimates of the PAHs; other sources of PAH emissions are minor compared to the combustion sources. Process heater and boiler emissions of volatile organic HAPs are a very small contributor to the refinery's overall emissions of volatile organic HAPs. Metal HAP emissions from combustion sources have a direct impact on the total metal HAP emissions for refineries that do not have a CCU. For refineries with CCUs, the CCU metal HAP emissions are generally a factor of 2 to 5 times higher than the process heater and boiler emission estimates, so that the uncertainties in the risk associated with metal HAP emissions are more closely linked to the uncertainties in the CCU emission estimates.

4.2 Flares and Thermal Oxidizers

Flares and thermal oxidizers are used at petroleum refineries to destroy organic compounds in vapor streams of purged products or waste products that are vented from various processes. For example, flares are commonly used on the vapor recovery system associated with marine vessel loading and some process vents, and thermal oxidizers are used to destroy volatile organic compounds (VOCs) from enclosed wastewater treatment systems. Most flares have a natural gas pilot flame and use the fuel value of the vapor to sustain combustion. Thermal oxidizers (vapor incinerators) often use natural gas or other fuel to destroy vapors that often would not support combustion alone.

4.2.1 Emission Estimation Methodology

Accurate estimates of emissions from flares are difficult to obtain because they do not lend themselves to conventional emission testing techniques and only a few attempts have been made to characterize flare emissions. Some EPA tests have been attempted, and the results were used in AP-42 (U.S. EPA, 1995a; Section 13.5) to estimate a destruction efficiency of 98 percent

Table 4-6. Estimates of HAP Emissions from Flares and Thermal Oxidizers from Title V Permit Applications

and an emission factor of 0.14 lb total hydrocarbons per million Btu. This emission factor requires site-specific knowledge of the energy consumption of each flare, and the total hydrocarbons must be speciated to obtain estimates of HAP emissions. There are insufficient data to apply this technique to each of the 155 petroleum refineries.

Site-specific estimates, however, were obtained for seven Louisiana refineries from their Title V permit applications and are summarized in Table 4-6. The company estimates were generated using AP-42 procedures and, generally, speciation based on the vapor composition.

The estimates for BP-Belle Chasse (now Tosco) were accompanied by the most complete description of how they were done. A summary is provided below for the flare associated with marine vessel loading:

First, a vessel and material-specific emission factor is generated from the AP-42 methodology (Section 5.2) for loading petroleum liquid. Then, the total VOC emission rates are calculated by multiplying the appropriate emission factor by the product throughput. Speciated emissions of the VOC are calculated by multiplying the species weight (from site-specific composition data) by the total VOC emission rate. The heat input is calculated from the fuel usage rate and vapor heating value. Finally, VOC and species emissions are calculated from the AP-42 procedures for flares (Section 13.5).

The best information on hand to estimate emissions from flares and thermal oxidizers is the site-specific estimates shown in Table 4-6. These results were extrapolated to other refineries by assuming that emissions from flares are proportional to the size of the refineries, i.e., larger refineries generate and burn more waste vapors in flares than do small refineries, assuming that operating practices are equivalent. The emission rates were normalized by the crude oil capacity to generate emission factors in tpy of HAP per barrel (bbl) of crude oil capacity. The recommended emission factors are shown in the bottom half of Table 4-6, and most are within an order of magnitude of the extreme values that were derived.

The application of the emission factor is straightforward, as illustrated below for benzene for a refinery with a capacity of 100,000 bbl/day:

Benzene emissions (tpy) = 100,000 bbl/day \times 1E-5 tpy/bbl/day = 1.0 tpy.

4.2.2 Source Characteristics

Site-specific information was obtained for 27 flares and thermal oxidizers at seven refineries. The number of flares at each facility is given in Table 4-7. The larger refineries appear to have more than smaller refineries. To extrapolate to other refineries, a total of four flares were assigned to refineries less than 200,000 bbl/day capacity, and a total of six (four flares and two thermal oxidizers) were assigned for the larger refineries.

Source characteristics for flares and thermal oxidizers are also given in Table 4-7. All of the flares and thermal oxidizers are elevated (i.e., no ground-level flares were reported). Default values were chosen from the median values of 150 ft in height, 4 ft in diameter, and a temperature of 1,600°F. To estimate a default volumetric flow rate, the reported flow rates were examined and normalized by crude oil capacity. A value of 5 acfm per bbl/day was used to estimate volumetric flow rate. The linear velocity (ft/s) was then calculated from the volumetric flow rate, diameter, and number of flares at each plant.

4.2.3 Uncertainty in Estimates

As discussed earlier, emission estimates for flares are highly uncertain because the emissions are difficult to impossible to measure. The emission factors derived in this approach introduce variability when they are applied to other refineries. Even if the site-specific estimates in Table 4-6 are accurate, there can be an order of magnitude of variability in applying these sitespecific estimates to other refineries for which there are no data. However, the emission factors are a best estimate of the midrange value, and no attempt was made to bias them high or low. In addition, the site-specific emission estimates for flares indicates they are not a significant source of emissions relative to other sources, such as fugitive equipment leaks, wastewater, and storage

Table 4-7. Source Characteristics for Flares and Thermal Oxidizers (from Title V permit applications)

tanks; consequently, the error in flare emissions should not result directly in large errors for the total facility emissions.

Several factors affect the uncertainty in emission estimates for flares. These factors include the HAP concentration in the vapor being flared, its variability, the destruction efficiency, formation of products of incomplete combustion, combustion conditions, and how uniformly they are maintained.

For the source characteristics, the information in Table 4-7 appears to be a reasonable sample, and the refinery size spans an order of magnitude (from about 50,000 to 500,000 bbl/day). Consequently, the statistical summary in Table 4-7 should provide insight into the variability of source characteristics.

4.3 Wastewater Collection and Treatment Systems

The wastewater treatment plant is typically a collection of treatment processes located in a common area and generally distinct from the process area. The wastewater treatment plant receives wastewater from the oil-water separator and various process wastewater and storm water collection points contained in the process area. Previous experience and emission modeling of wastewater collection and treatment suggest that a large portion of the emissions from wastewater occur during the collection phase. Emissions from both the collection and treatment of wastewater are subject to the requirements of the Benzene Waste Operations National Emission Standard for Hazardous Air Pollutants (NESHAP) (40 CFR, Part 61, Subpart FF). All refineries that have more than 10 megagrams per year (Mg/yr) of benzene in their wastewater are required under this rule to employ certain wastewater collection and treatment equipment to reduce the emissions of benzene.

4.3.1 Emission Estimation Methodology

The "uncontrolled" or pre-Benzene Waste Operations NESHAP (pre-BWON) emissions were estimated following the methodology described in EPA's *Locating and Estimating Air Emissions from Sources of Benzene* (hereafter, the Benzene L&E document; U.S. EPA, 1998a). This methodology provides estimates of the amount of wastewater produced per unit throughput of various refinery processes (average flow factors) along with an estimate of that process wastewater stream's benzene content (see Table 4-8). The average flow factors are simply multiplied by the corresponding process capacities to calculate the rate of wastewater production for each process. These wastewater production rates are multiplied by the average benzene concentration for each stream to calculate the loading rate of benzene into the wastewater system by process. These process wastewater loading rates were summed to calculate the total loading rate of benzene into the wastewater system. This total loading rate was multiplied by 0.85 (fraction emitted) to calculate the "uncontrolled" emission rate. (Benzene loadings from methyl ethyl ketone (MEK) dewaxing units were several orders of magnitude less than those from other processes so that no error was introduced in not using the 0.49 emission factor suggested for that process (see Table 4-8).)

Table 4-8. Model Process Unit Characteristics for Petroleum Refinery Wastewater

Source: U.S. EPA (1998a)

^a All flow factors were derived from Section 114 questionnaire responses

 β gal/bbl = gallons of wastewater per barrel of capacity at a given process unit

c Average concentration in the wastewater

 d ppmw = parts per million by weight

 e^{t} 114 = Section 114 questionnaire response; 90-day = 90-day BWON report;

 $Eq. = equilibrium calculation; and Ratio = HAP-to-benzene ratio (4.48)$

f These factors are given in lbs HAP emitted/lbs HAP mass loading

 \textdegree This flow factor is given in gal/MM ft³ of gas production

^h This flow factor is given in gal/ton of sulfur

ⁱ Fraction emitted as reported in U.S. EPA (1998a); for computational ease, the REM uses a fraction emitted of 0.85 for all sources.

For some processes, the average flow factors and average wastewater benzene concentrations had to be estimated (e.g., aromatics and oxygenates); for other activities, the process throughput had to be estimated in order to use the given flow factors (e.g., product blending and tank draw down). The assumptions used to make these estimates are outlined below:

- The benzene wastewater loading rate for aromatics was estimated using an average flow factor of 3 (because a wide variety of processes had production rates between 2.5 and 3) and a benzene wastewater concentration based on the value for CRUs (the highest benzene content of all process wastewater streams except tank drawdown).
- The benzene wastewater loading rate for oxygenates was estimated using the average flow factor and average benzene concentration value for full-range distillation.
- The benzene wastewater loading rate for coke plants was estimated using the average flow factor and average benzene concentration value for SRU.
- The product blending and tank drawdown throughputs were estimated as the larger of either
	- The crude capacity $/ 12$, or
	- (CCU capacity) / $4 + (oxygenates production) / 4 + (CRU capacity) / 8$.
- The MEK dewaxing throughput was estimated as the lube oil production rate.

More than 30 percent of the total benzene loading is produced from crude distillation. Thermal cracking and catalytic reforming are responsible for another 32 percent of the total benzene load to wastewater. Vacuum distillation, catalytic cracking, hydrotreating, aromatics, asphalt production, and product blending each contribute between 4 and 8 percent of the total benzene loading. All other processes contribute roughly 1 percent or less to the total benzene loading. Therefore, most of the assumptions outlined above have little impact on the total benzene loading rate to the wastewater treatment system.

The benzene loading and emission estimates following this procedure are expected to represent uncontrolled or pre-BWON emissions. The uncontrolled emissions were compared to 90-day reports prior to the implementation of the BWON. The range of refinery emissions and the total nationwide emissions for benzene from wastewater using the methodology described above compared well with the pre-BWON benzene emissions. Review of 90-day reports after implementation of the BWON and a review of the emissions reported by the Louisiana refineries suggest that refineries subject to the BWON have wastewater benzene emissions of between 5 and 10 tons per year (tpy). Therefore, a hypothetical correlation was developed to calculate the benzene emissions from wastewater after implementation of the BWON.

If a refinery's total benzene loading rate was 10 tpy or less, then the "uncontrolled" emissions rate (i.e., 85 percent of benzene loading rate) was output for that refinery directly. If a refinery's total benzene loading rate exceeded 10 tpy, then the "uncontrolled" emissions rate was adjusted as follows to calculate a controlled emission rate after implementation of the BWON:

$$
EmBz_{post-BWON} = \frac{EmBz_{pre-BWON}}{20} + 4.5
$$
 4-3

where

 $EmBz_{post-BWON}$ = benzene wastewater emissions after implementation of BWON (tpy) $EmBz_{pre-BWON}$ = benzene wastewater emissions calculated using the Benzene L&E method (tpy)

Once the benzene emission rates were estimated, these emission rates were used to project the emissions of other compounds. The average concentration of liquid refinery streams as developed for the refinery MACT I (Murphy, 1993) was used as a starting point for these projections (see Table 4-9). To account for the various compounds' affinity for water, the average concentrations were divided by the octanol-water partition coefficient to estimate "equilibrium" wastewater concentrations. These equilibrium wastewater concentrations were normalized by the calculated equilibrium wastewater concentration for benzene to develop a wastewater concentration ratio (also provided in Table 4-9).

(continued)

| CASRN | HAP | Average Concen- tration ^a $(wt\%)$ | Log $(K_{ow})^b$ | Waste- water Concen- tration Ratio | HLC _p | Ratio to Benzene Waste- water Emission Factor ^c | Waste- water Treatment Emission Multiplier |
|---------------|-----------------------------|--|---------------------|---|------------------|--|---|
| 1634-04-4 | Methyl tertiary butyl ether | 0.71 | 1.901 | 0.747192 | 0.000555 | 0.8 | 0.5978 |
| $91 - 20 - 3$ | Naphthalene | 0.37 | 3.36 | 0.013532 | 0.000483 | 0.8 | 0.0108 |
| $108-93-0$ | Phenol | 0.09 | 1.48 | 0.249699 | 3.97E-07 | 0.05 | 0.0125 |
| $100-42-5$ | Styrene | 0.72 | 2.94 | 0.069264 | 0.00275 | | 0.0693 |
| 108-88-3 | Toluene | 5.64 | 2.75 | 0.840337 | 0.00664 | | 0.8403 |
| 1330-20-7 | Xylene | 5.58 | 3.17 | 0.316088 | 0.00604 | | 0.3161 |

Table 4-9. (continued)

^a Average concentration of all refinery liquid streams as reported by Murphy (1993)

b Physical properties for chemicals as contained in CHEMDAT8 (U.S. EPA, 1994)

c Representative ratio of emission fractions for compound to that for benzene based on CHEMDAT8

model runs for two select aerated tanks

Not only do the different chemicals have a different affinity for water, they also have a different affinity for volatilization from wastewater, as seen by the different values for their Henry's law constant (HLC). Two different wastewater treatment systems (one with high biological activity and one with low biological activity) were developed and projected 85 percent emissions for benzene using the CHEMDAT8 model for aerated tanks (U.S. EPA, 1994). The emission fraction for the other compounds was calculated and compared to the emission fraction for benzene. Based on these evaluations, an emission ratio (relative to benzene) was established. By combining the concentration ratio and the emission ratio, a multiplying factor was developed to project the emissions of other compounds based on the estimated emissions of benzene (see Table 4-9).

4.3.2 Source Characteristics

The wastewater treatment in the petroleum refinery industry is typically effected by biological treatment in activated sludge systems. These systems generally operate a series of open tanks such that the wastewater treatment system is best characterized as a large area source. Some refineries may employ a steam stripper to remove benzene and other VOCs prior to other wastewater treatment operations; for these refineries, a portion of the total benzene emissions would originate from a stack.

Previous emission modeling of wastewater collection and treatment suggests that a large portion of the emissions from wastewater occur in the collection phase. These collection areas are located within the process equipment area, whereas the wastewater treatment plant is generally a distinct portion of the refinery. The collection area emissions are again essentially all area source emissions. For this application, half of the estimated wastewater emissions were

assumed to occur from areas within the process equipment and half from the actual wastewater treatment plant area.

The area of the wastewater treatment plant was estimated based on three model refinery plot plans developed by EPA (U.S. EPA, 1978). The model refinery plot plans were also used to estimate the area of the wastewater collection system within the process area of the plant based on oil-water separators located within the equipment area. From this analysis, three model wastewater treatment areas were established. The collection areas estimated were very similar to the wastewater treatment plant area, so the wastewater treatment areas were used for both the wastewater and the collection areas. Table 4-10 provides the model wastewater treatment areas and the refinery crude capacity ranges used to assign the model areas to each refinery.

| Model Unit Crude Capacity | Model Unit Applied to Refineries with Crude Capacity in Range | Wastewater Collection Area (MM ft ²) | Wastewater Treatment Area (MM ft ²) |
|--|--|---|--|
| 50,000 | 0 to $<$ 125,000 | 0.34 | 0.34 |
| 200,000 | 125,000 to $\langle 225,000 \rangle$ | 1.0 | 1.0 |
| 250,000 | \geq 225,000 | 2.0 | 2.0 |

Table 4-10. Model Plant Areas for Wastewater Collection and Treatment

4.3.3 Uncertainty in Estimates

Many assumptions were used to develop the emission estimates from wastewater. The L&E methodology appeared to provide only "uncontrolled" emission estimates for benzene, and a simple correlation was used to reduce the refinery's benzene emissions to between 5 and 10 tpy (depending on its uncontrolled emissions) if the facility was anticipated to be subject to the BWON. Finally, the benzene emissions were used to project the emission of other compounds using theoretical partitioning considerations. Given these assumptions, it is difficult to assess the uncertainties in the model without a comparison of the model results with those reported or measured at selected refineries.

Table 4-11 provides a comparison of emissions of benzene, toluene, and hexane calculated from the model with those reported for nine Louisiana refineries in their Title V applications. The emissions for benzene reflect inaccuracies in the L&E method and the BWON correction correlation. The emissions for toluene and hexane provide insight into the uncertainty of the combined methodology for nonbenzene compounds. Of the 13 compounds for which wastewater emissions are projected, benzene has the highest emission potential (as indicated by the multiplication factor) and the highest unit risk factor. Therefore, the benzene emissions will drive the risk from wastewater. Except for the one very low benzene emission rate reported by

Table 4-11. Comparison of Wastewater Emission Model Estimates and Reported Wastewater Emissions

 $NR = not reported$

^a Data reported in the Title V permit applications for selected Louisiana refineries

b Predicted wastewater treatment emission estimates from the emissions model algorithm

c Includes emissions from fugitive equipment leaks; model estimates for benzene from fugitives and wastewater treatment are 17.4 tons/yr

Murphy Oil, the modeled benzene emissions are within a factor of 2 of the reported benzene wastewater emissions. The emission estimates of toluene also appear to be within a factor of 2, but toluene partitioning and volatility are reasonably similar to those for benzene. The reported emissions for hexane confirm that hexane wastewater emissions are significantly lower than those for benzene, but perhaps not to the extent predicted by the model. These lower hexane wastewater emissions can only be attributed to its lower affinity for water (hexane has higher concentrations in process streams and is more volatile from wastewater than benzene), so the oilwater partitioning is important. Based on this comparison, the REM nonbenzene wastewater emission estimates are likely accurate to within a factor of 5, whereas the benzene wastewater emissions, which drive the wastewater risk, are accurate to within a factor of 2.

There is also uncertainty in the precise split of emissions between the collection system (area within the process equipment) and the physical wastewater treatment plant. The 50:50 split is a rough approximation based on engineering judgment and experience with wastewater emission model results that consider the collection system components in series with the wastewater treatment tanks. Based on this experience, the total wastewater emission result is expected to have more uncertainty than is associated with the 50:50 split assumption. Therefore, the model emission estimate for the collection system for benzene is considered to be accurate to within a factor of 2, and the emission estimate for the wastewater treatment system is considered to be accurate within a factor of 2.

4.4 Cooling Towers

Cooling water is used in refineries in heat exchangers and condensers to cool or condense various product streams. The cooling water is usually sent to cooling towers where it is cooled to ambient temperature, then recycled to the process or to refrigeration units for additional cooling before reuse.

4.4.1 Emission Estimation Methodology

VOCs are picked up by cooling water when leaks occur in heat exchangers or condensers. Product on the high-pressure side leaks through the exchanger and contaminates the water. VOCs are then stripped from the water and emitted in the cooling tower. Emissions on the order of tons per year can occur for even low levels of contamination because refineries use large volumes of cooling water. For example, a refinery with 100,000 bbl/day of crude oil capacity typically uses about 170 MMgal/day cooling water (from AP-42 (U.S. EPA, 1995a), the cooling water rate is about 40 times the crude oil capacity). If this water is contaminated with easily strippable hydrocarbons at 1 ppm, the emission potential is 260 tpy.

The emission estimating methodology for cooling towers is given in AP-42 (U.S. EPA, 1995a; Section 5.1). For this assessment, the uncontrolled emission factor of 6 lb of total hydrocarbons (THC) per million gallons of water (MM gal) was used (a concentration in the water of 0.7 ppm). The controlled emission factor, based on monitoring for hydrocarbons and fixing leaks when they occur, is 0.7 lb/MM gal, a reduction of 88 percent. For petroleum refineries, the AP-42 section recommends a cooling water rate of 40 times the crude oil capacity. In terms of crude oil capacity, the emission factor for THC translates to 0.0018 tpy THC per bbl/day crude oil capacity.

Site-specific information on the composition of process streams cooled in heat exchangers and condensers is not currently available. However, an average composition of all process streams at a refinery was developed to estimate emissions for the Petroleum Refinery MACT I (40 CFR Part 63, Subpart CC). This average composition was used to speciate the THC and to generate the HAP emission factors given in Table 4-12.

An example calculation is given below for benzene from cooling towers at a refinery with a capacity of 100,000 bbl/day of crude oil:

Benzene (tpy) = 100,000 bbl/day \times 3E-5 tpy/bbl/day = 3 tpy.

4.4.2 Source Characteristics

To develop source characteristics, the EPA document, "Development of Petroleum Refinery Plot Plans," was reviewed (U.S. EPA, 1978). For a refinery of 200,000 bbl/day crude oil capacity, the document suggests a total of five cooling towers with a total flow rate of 8 MM bbl/day and a total cross-sectional area of 46,737 ft². The total cross-sectional area of all cooling towers is expected to be a function of refinery size (i.e., larger refineries have more or larger

cooling towers). For this analysis, the total cross-sectional area of cooling towers at each refinery was estimated from 0.2 ft² per bbl/day crude oil capacity based on the refinery described above.

The height for cooling towers at the 200,000 bbl/day refinery ranged from 20 ft to 30 ft. For comparison, the default height assigned in the 1996 NTI database was 32 ft. For this assessment, a default height of 30 ft was used. The only readily available information on exit velocity was the default value in the $NTI - 11$ ft/s.

4.4.3 Uncertainty in Estimates

There is a great deal of uncertainty in the emission estimates for cooling towers because of the scarcity of data. Emissions will depend on many site-specific features for which we have few data, such as the composition of products streams and water usage rates or measured contamination rates in cooling towers. If a given refinery has a program in place to detect leaks into cooling tower water and take corrective actions when necessary, the emission estimates may be somewhat conservative (high). We also have few data on the source characteristics of cooling towers, and these features likely vary from refinery to refinery. To reduce or quantify the uncertainty associated with these estimates for cooling towers, much more detailed, site-specific information is needed.

The permit applications for five of the Louisiana refineries contained emission estimates for cooling towers. Two of the refineries stated they used the controlled emission factor from

AP-42, and the others also appear to be based on the controlled emission factor. The estimates they provided for benzene ranged from 0.2 to 1.2 tpy. For comparison, the approach described earlier would estimate a range of 1.5 to 15 tpy for uncontrolled emissions for refineries of similar size. This comparison suggests that if most refineries actually have a leak detection and repair program in place to reduce cooling water contamination, then the estimates derived in this section are high (perhaps by a factor of 10) because the emissions are assumed to be uncontrolled. Based on the uncontrolled emission factors employed, cooling towers contribute roughly 20 percent of the refineries' benzene emissions. For certain chemicals, such as 2,2,4- Trimethylpentune, the contribution of uncontrolled cooling tower emissions can approach 50 percent of the refineries' total 2,2,4-Trimethylpentane emissions.

4.5 Fugitive Equipment Leaks

Equipment leaks are small point or area sources that occur throughout the process area of the refinery. Because of the large number of potentially leaking equipment components for any given process, let alone the entire refinery, fugitive equipment leaks are most appropriately modeled as a large area source. Leaking equipment may directly release gas or liquid; it is generally assumed that all released liquid eventually evaporates so that 100 percent of equipment leaks contribute to refinery emissions.

4.5.1 Emission Estimation Methodology

The fugitive equipment leak emissions were estimated using the revised equipment leak protocol developed for the petroleum refinery industry (U.S. EPA, 1995b) and model refinery equipment component counts and process streams composition data for benzene presented in EPA's L&E document (U.S. EPA, 1998a). The total fugitive equipment leak emissions calculated for benzene were then used to estimate the emissions for other HAPs using the average liquid stream compositions for refinery streams developed for the refinery MACT I standard (Murphy, 1993).

Table 4-13 presents the equipment leak rates for the revised refinery protocol (U.S. EPA, 1995b). These leak rates are used with equipment component counts and process stream concentrations to estimate emissions according to Equation 4-4:

$$
EmR_{Bz} = EqLR_{C, level} \times N_{C, level} \times BzConc_C
$$
 4-4

where

| EmR_{Bz} | = the emission rate of benzene (kg/hr) |
|------------------|---|
| $EqLR_{C,level}$ | = the equipment leak rate from Table 4-13 for the specified organic concentration measured by the monitoring device for that component (kg/hr/source) |

^a As reported in U.S. EPA (1995b)

 b SV is the screening value (SV, ppmv) measured by the monitoring device

 ϵ The "other" equipment type was developed from instruments, loading arms, pressure relief devices, stuffing boxes, vents, compressors, dump lever arms, diaphrams, drains, hatches, meters, and polished rods. This "other" equipment type should be applied to any equipment other than connectors, flanges, open-ended lines, pumps, or valves

The median equipment component counts for "small" refineries (less than 50,000 bbl/cd) and "large" refineries (greater than 50,000 bbl/cd) as presented in the Benzene L&E document (U.S. EPA, 1998a) are presented in Tables 4-14 and 4-15, respectively. The Benzene L&E document also presents average process stream benzene concentrations based on the stream type or "service" (i.e., if the process stream is a gas, a light liquid, or a heavy liquid). These data are presented in Table 4-16.

Given these data, the equipment leak emissions for benzene can be calculated for each process in the model refineries once the number of leaking components is determined. For the preliminary analysis, it was assumed that 97 percent of the components were not leaking (i.e., used the default zero leak rate), 2 percent were leaking at the 10,000 ppmv pegged emission rate, and 1 percent were leaking at the 100,000 ppmv pegged emission rate. There is some disparity between the leak rates reported by refineries and those observed by EPA. For 17 refineries investigated by the EPA, the average leak rate reported by the facilities was 1.3 percent, whereas the average leak rate determined by EPA (and confirmed by the facilities) was 5 percent (U.S. EPA, 1999). The assumed 3 percent leak rate is a midrange value between these two reported values.

| | Weight % Benzene in Stream Type: | | | |
|--------------------------------|---|-----------|---------------------|--|
| Process Unit | Gas | Light | Heavy Liquid | |
| Crude | 1.3 | 1.21 | 0.67 | |
| Alkylation (sulfuric acid) | 0.1 | 0.23 | 0.23 | |
| Catalytic Reforming | 2.93 | 2.87 | 1.67 | |
| Hydrocracking | 0.78 | 1.09 | 0.1 | |
| Hydrotreating/Hydrorefining | 1.34 | 1.38 | 0.37 | |
| Catalytic Cracking | 0.39 | 0.71 | 0.2 | |
| Thermal Cracking (visbreaking) | 0.77 | 1.45 | 1.45 | |
| Thermal Cracking (coking) | 0.24 | 0.85 | 0.18 | |
| Product Blending | 1.2 | 1.43 | 2.15 | |
| Full-Range Distillation | 0.83 | 1.33 | 1.08 | |
| Vacuum Distillation | 0.72 | 0.15 | 0.22 | |
| Isomerization | 2.49 | 2.49 | 0.62 | |
| Polymerization | 0.1 | 0.1 | 0.1 | |
| MEK Dewaxing | 0.36 | NR | NR | |
| Other Lube Oil Processing | 1.2 | 1.2 | 0.1 | |

Table 4-16. Concentration of Benzene in Refinery Process Unit Streamsa

a Data reported in U.S. EPA (1998a)

NR - not reported

Some processes did not have any benzene concentration data. These processes were assumed to have benzene concentrations of 0.01 percent, except for asphalt. The benzene concentration in asphalt (all streams) was assumed to be 0.03 percent based on the weight percent of benzene in asphalt product as reported in the Benzene L&E document (U.S. EPA, 1998a).

Using the data from Tables 4-13 through 4-16 and the 97, 2, and 1 percent leak rate assumption, the benzene emissions could be calculated for each process in the model refineries. The results of these calculations are presented in Table 4-17. These emission rates were applied to each refinery on a process-specific basis. That is, if a refinery operates two CCUs, then the CCU equipment leaks were calculated for each CCU and summed together for that refinery. In order to do this, "small" and "large" processes needed to be defined. Using the relative U.S. capacities of crude and other processes as reported in the 2000 Worldwide Refining Survey (Stell, 2000a), average process-specific capacity limits were derived based on a refinery with a crude capacity of 50,000 bbl/cd. These process-specific capacities used to distinguish "small" and "large" processes are presented in Table 4-17. The "small" process emission rate was

applied when the refinery's process capacity was at or below the cutoff limit; "large" process emission rates were applied when the process capacity exceeded the cutoff limit. Using processspecific capacities provided a more facility-specific analysis based on the presence, number, and capacity of the individual processes at the refinery.

| | Size Cutoff | Benzene Emissions (tons/yr) | | |
|--------------------------------|--------------------|------------------------------------|-------------|--|
| Process Unit | (bbls/cd) | Small | Large | |
| Crude Distillation | 50,000 | 0.452 | 0.962 | |
| Vacuum Distillation | 25,000 | 0.053 | 0.221 | |
| Thermal Cracking (coking) | 10,000 | 0.174 | 0.339 | |
| Thermal Cracking (visbreaking) | 10,000 | 0.362 | 0.604 | |
| Catalytic Cracking | 17,500 | 0.377 | 0.349 | |
| Catalytic Reforming | 10,000 | 1.386 | 1.726 | |
| Hydrocracking | 5,000 | 0.641 | 0.776 | |
| Hydrotreating/Hydrorefining | 35,000 | 0.441 | 0.593 | |
| Alkylation | 5,000 | 0.159^{a} | 0.154^{a} | |
| Polymerization | 1,000 | 0.037 | 0.045 | |
| Aromatics | 5,000 | 1.386^{b} | 1.726^b | |
| Isomerization | 2,500 | 1.332 | 0.904 | |
| Other Lube Oil Processes | 5,000 | 0.292 | 0.255 | |
| Full-Range Distillation | 5,000 | 0.436 | 0.914 | |
| Hydrogen Plant | 10 ^c | 0.002 | 0.003 | |
| Coke | $375^{\rm d}$ | 0.003e | 0.003e | |
| Sulfur Plant | 75 ^d | 0.003 | 0.003 | |
| Asphalt Plant | 5,000 | 0.017 | 0.003 | |
| Product Blending | 5,000 | 0.635 | 0.862 | |
| MEK Dewaxing | 5,000 | 0.135 | 0.204 | |

Table 4-17. Model Process Equipment Leak Emission Rates for Benzene

^a Average of emission rates calculated for sulfuric acid alkylation and HF alkylation

^b Component counts for aromatics unavailable; set equal to emission rate from CRU

c Production rate in MMcf/day

d Production rate in tonnes/day

e Component counts for coke were unavailable; set equal to emission rate from SRU

Once the total benzene equipment leaks emissions were calculated for a given refinery (based on the type, number, and size of process units), the total benzene emissions were multiplied by a concentration ratio to estimate the equipment leak emissions of other compounds. The concentration ratio was based on the average composition of all liquid waste streams as presented in a MACT I project memorandum (Murphy, 1993). The reported average concentrations and the calculated concentration ratio are presented in Table 4-18.

4.5.2 Source Characteristics

All fugitive process equipment leaks were characterized as one large area emission source originating from the process area. The process area was estimated based on model refinery plot plans developed by EPA (U.S. EPA, 1978). The three model plants and their respective process equipment areas are provided below in Table 4-19.

4.5.3 Uncertainty in Estimates

There are several sources of uncertainty in the REM equipment leak emission estimates, including the equipment component counts, the benzene stream composition, the equipment leak emission rates, the assumptions of leaking frequency, and the ratios used to translate benzene emissions to the emissions of other compounds. The uncertainty resulting from equipment component counts is one source of uncertainty but appears to be limited based on a comparison of the benzene emission factors developed for the two model plant/process sizes (most small and large benzene emission factors are within approximately 30 percent of each other, with a few varying by a factor of 2). Process benzene concentrations are also uncertain. Although the raw data used to develop the model stream composition were not available for review, average waste stream compositions for these processes probably do not vary by more than a factor of 2 between refineries. The largest uncertainties lie with the assumptions used regarding the equipment leak rates, the emission factor developed for aromatics units (where no equipment component counts or stream composition data were available, but where benzene concentration could potentially approach 100 weight percent), and the concentration ratios used to project the emissions of compounds other than benzene.

Based on the number of assumptions used to develop the emission estimates from equipment leaks, the equipment leak emission estimates could vary by a factor of 5 or more. To better understand the uncertainty in the process equipment leak emission estimates, a complete review of the data used to develop the component counts and process stream concentrations, as well as Method 21 data on equipment leaks (to better determine the range of percent leaking components), would be needed. By defining the range of values, a Monte Carlo or "boot strap" analysis could be performed to characterize the uncertainty in the final equipment leak emission factors. However, a comparison of the equipment leak emissions estimated for the nine Louisiana refineries for which Title V permit application data were available provides a simpler method of assessing the inaccuracies in the emission estimation methodology. Table 4-20 presents the reported equipment leak emissions with those calculated using the methodology described in this section. The REM equipment leak emission estimates for benzene agree better

Table 4-18. Concentration Ratios Used for Equipment Leak Emission Estimates

^a Average composition of all liquid process streams as reported by Murphy (1993)

b Ratio of average liquid concentration of selected HAP to average liquid concentration for benzene

with reported emissions than the layers of uncertainty in the analysis suggest; many of the predicted emissions are within 30 percent of the reported values, and the largest discrepancies are roughly a factor of 2.

However, based on the comparison of refinery reported-equipment leak rates versus equipment leak rates determined by EPA (U.S. EPA, 1999), the equipmet leak rates reported by the refineries for which we have data may underestimate actual equipment leak emissions if they are similarly underreported. The data in Table 4-20 also indicate that the emission estimates for HAPs other than benzene are more highly variable; the inaccuracies for these compounds generally vary between a factor of 2 and a factor of 5. This is somewhat expected because the benzene emissions used process-specific benzene concentrations, and the ratio of the HAP concentration to benzene will vary by process. It might be possible to improve the emission estimates for these other compounds if more process-specific compositional data were available. Nonetheless, because benzene is the compound with the highest risk factor of the compounds listed in Table 4-18, these additional data may not be critical to improving the overall risk analysis.

Table 4-20. Comparison of Fugitive Equipment Leak Model Estimates and Reported Equipment Leak Emissions

^a Data reported in the Title V permit applications for selected Louisiana refineries

 $\rm ^b$ Predicted fugitive equipment leak emission estimates from the emissions model algorithm

c Includes emissions from wastewater treatment; model estimates for benzene from

fugitives and wastewater treatment are 17.4 tons/yr

4.6 Tanks

Tanks are used to store crude oil prior to refining, intermediates between refining processes, and refined product streams (e.g., gasoline, diesel fuel, fuel oil, etc.). Nearly all storage tanks in the petroleum refinery industry used to store liquid material have been converted to floating-roof tanks. As the fluid levels in the tank rise and fall, a thin film of the contained liquid may remain on the tank walls and evaporate. Because storage tanks in the petroleum industry are generally 30 to 40 feet in diameter, these tank emissions occur over a reasonably large surface area. Additionally, except for a few process storage tanks, the storage tanks are generally located together in what is referred to as the "tank farm." Consequently, the tank farm can be considered one large area source and all tank emissions are assumed to come from this area.

4.6.1 Emission Estimation Methodology

Emission factors for tanks were developed from the Title V permit data reported for the Louisiana refineries. Based on a preliminary review of the data, four "classes" of tanks were designated based on the differences in the emissions from these tanks and the availability of data to characterize and apply the resulting emission factors. The four classes are

- Crude storage tanks;
- Light and intermediate product tanks (e.g., gasoline, diesel, jet fuel, and fuel oil);
- Heavy product tanks (lube oil and asphalt); and
- **EXECUTE:** Aromatic product tanks.

Emissions reported for intermediate process storage tanks were included with the light and intermediate product tank emission totals.

In order to develop and employ emission factors for storage tanks, the throughput of crude, light and intermediate products, heavy products, and aromatic products was needed. Crude capacity and aromatic production capacity were used to normalize crude and aromatic tank emissions. A few refineries report no crude capacity but have significant capacities for other processes. To estimate tank emissions, the crude capacity was estimated as the sum of the reported vacuum and coking capacities for refineries with no reported crude capacity. The heavy-product tank emissions were normalized by the sum of the lube oil and asphalt production capacities. Light and intermediate production capacities were estimated based on the crude capacity (as calculated for tanks) minus the heavy product and aromatic product capacities. This methodology was devised based on product production rates reported in a limited number of the Title V applications; the data reviewed are summarized in Table 4-21. Because the "lights" plus "heavies" were essentially equal to the crude processing rate (except for the anomalous lube production rate reported by Murphy Oil), the crude minus the "aromatics" and "heavies" was used to estimate light and intermediate production capacities. Aromatic tanks were treated separately because these tanks have a much higher emission rates based on the high HAP concentrations of the aromatic material stored.

Using the data reported in the 2000 Worldwide Refining Survey (Stell, 2000a), the crude capacities and production rates for each refinery were used to calculate the throughput rates for each tank class. These throughput rates were used in conjunction with the reported emissions data for tanks, to develop emission factors for the different types of tanks. The Louisiana refinery emissions data, as extracted from the Title V permit applications, are presented in Appendix A. The emissions factors were calculated for each tank class for each refinery reporting tank data; these emission factors, along with associated statistics, are provided in Table 4-22.

Although all nine Louisiana refineries had reported storage tank emissions in their Title V permit applications, only six of the refineries provided sufficient detail to divide or classify the reported emissions into the four "classes" of storage tanks needed for the emissions model. For

Table 4-22. Emission Factors for Storage Tanks1

(continued)

| | Tank Souce/ | Emission Factor (lbs/MMbbl) | | | | No. | |
|------------------|------------------------|------------------------------------|--------------------------|----------------|------------------|----------------------|--|
| CASRN | Chemical | Average ² | Median ² | Maximum | Minimum | Nonzero ³ | |
| | Heavies | | | | | | |
| $71-43-2$ | Benzene | 39.96 ⁴ | 4.12 | 75.80 | $\boldsymbol{0}$ | 2 of 3 | |
| 108-88-3 | Toluene | 29.19 ⁴ | 17.44 | 40.95 | $\boldsymbol{0}$ | 2 of 3 | |
| 1330-20-7 | Xylene | 25.58 ⁴ | 14.97 | 36.20 | $\boldsymbol{0}$ | 2 of 3 | |
| 110-54-3 | Hexane | 4.24 | 0.00 | 12.71 | $\boldsymbol{0}$ | 1 of 3 | |
| $91 - 20 - 3$ | Naphthalene | 2.66 | 2.20 | 5.77 | $\boldsymbol{0}$ | 2 of 3 | |
| $100 - 41 - 4$ | Ethylbenzene | 2.81 | 3.16 | 5.29 | $\boldsymbol{0}$ | 2 of 3 | |
| $95 - 63 - 6$ | 1,2,4 Trimethylbenzene | 1.96 | 0.00 | 5.89 | $\boldsymbol{0}$ | 1 of 3 | |
| $92 - 52 - 4$ | Biphenyl | 0.23 | 0.00 | 0.69 | $\boldsymbol{0}$ | 1 of 3 | |
| 98-82-8 | Cumene | 0.14 | 0.00 | 0.41 | $\boldsymbol{0}$ | 1 of 3 | |
| | PNA/PAH | 5.77 | 0.00 | 17.30 | $\boldsymbol{0}$ | 1 of 3 | |
| Aromatics | | | | | | | |
| $71-43-2$ | Benzene | 2,864 | 526 | 8,067 | $\boldsymbol{0}$ | 2 of 3 | |
| 108-88-3 | Toluene | 6,630 | $\overline{}$ | 19,890 | $\boldsymbol{0}$ | 1 of 3 | |
| 1330-20-7 | Xylene | 4,827 | 80 | 14,400 | $\boldsymbol{0}$ | 2 of 3 | |
| $100 - 41 - 4$ | Ethylbenzene | 957 | \blacksquare | 2,871 | $\boldsymbol{0}$ | 1 of 3 | |
| $95 - 63 - 6$ | 1,2,4 Trimethylbenzene | 66 | | 197 | $\boldsymbol{0}$ | 1 of 3 | |

Table 4-22. (continued)

¹ Emission factors used in the model are bolded

2 Average and medians include zero values unless otherwise noted

³ Number of refineries reporting nonzero emissions of number of refineries reporting emissions for a given tank class

4 Average based on the two nonzero emission factors

crude and light-product tanks, six refineries reported data for most of the more volatile organic chemicals; only one refinery reported any semivolatile emissions from the light-product tanks. It is uncertain whether the semivolatile tank emissions from the one refinery were based on some standard emission factor, a site-specific emission estimate, or actual measurements. These emissions were reported for some "fixed-roof distillates" tanks. Based on the lack of semivolatile emissions from the other light-end tanks, it was decided to use the average emission factor, including the zero values for the other refineries.

For the heavy-product storage tanks, only two of the three refineries that had heavy production capacity (as calculated using the 2000 Worldwide Refining Survey data). A third refinery, Murphy Oil, had reported emissions of naphthalene and PAH/polynuclear aromatic hydrocarbons (PNAs) from "heavy oil" tanks. Although this refinery does not have "heavies

production," as calculated in the model, Murphy Oil had reported heavy production (albeit a questionably high value) in its Title V Permit application. Consequently, either the average or the maximum value reported for the two refineries projected to have "heavies" emissions was used; and only the emissions for PAH/PNAs reported by Murphy Oil were used to develop an emission factor. For this emission factor, "heavies production" was estimated as 1 percent of the crude capacity.

All three refineries expected to have aromatic production reported emissions from their aromatics product tanks. However, each of these refineries produced a different mix of aromatics. One refinery only produced benzene; one refinery produced benzene and xylene; and the third produced toluene and xylenes. The limited available data were assumed to be representative of the different mixes of product so that the emission factors developed included zeros for the refineries that did not make that product.

Given the emission factors presented in Table 4-22, the storage tank emissions can be calculated using the production capacity data reported in the 2000 Worldwide Refining Survey (Stell, 2000a) for each storage tank class. The emissions for each storage tank class were then summed to develop the total tank farm emissions.

4.6.2 Source Characteristics

The emissions from the storage tanks were modeled as one large area source representative of the total tank farm area. Model tank farm areas were estimated based on model refinery plot plans developed by EPA (U.S. EPA, 1978). The three model plants and their respective tank farm areas are provided below in Table 4-23.

4.6.3 Uncertainty in Estimates

Table 4-22 provides some measure of the uncertainty in the storage tank emissions. Based on a comparison of the average and median values for crude tanks, it appears that different crude stocks vary significantly in aromatic content, while the hexane content is fairly consistent (save one very low value). For nearly all refineries, the "lights" throughput capacity is essentially equal to the refinery's crude capacity, and benzene drives the risks for the organic HAPs emitted

from storage tanks. The emissions from light-product storage tanks are roughly an order of magnitude greater than the emissions from crude storage tanks. Therefore, because emissions are being modeled from the entire tank farm, the uncertainties in the crude storage tank emission factors are not of particular concern.

The central tendency indicators for VOCs from light-product storage tanks agree well, and these central tendency indicators are generally within a factor of 2 of the maximum value and a factor of 4 of the minimum value. Again, for most refineries and essentially all large refineries (i.e., those with catalytic cracking, reforming, or other refinery stream upgrade processes), the emissions from the light-product tanks will dwarf the emissions from crude and heavy-product storage.

There is a high level of uncertainty associated with the heavy-product storage tank emission factors, based on the limited number of data that were available for these tanks. Nonetheless heavy-product storage tank emissions will only make a very small contribution to tank farm emissions for most refineries. Only five refineries had heavy-production capacities of 30 percent of their crude capacity or more. All of these refineries have crude capacities of less than 12,000 bbl/cd. None of the Louisiana refineries for which Title V permit application data were available are very representative of these small, essentially "straight-run" refineries. Consequently, the emission factors selected from the limited data set were chosen using a more conservative high-end approach than was used for the other tank classes.

The uncertainty in the aromatics emissions is both large and significant. There are 30 refineries reporting aromatics production capacity. Based on the benzene emission factors for aromatics and light-product storage tanks, aromatics will contribute at least 25 percent of the tank farm's benzene emissions if aromatics production is only 1 percent of the "lights" production (true for 29 of the 30 refineries with aromatic production); they will contribute 50 percent or more of the tank farm's emissions if aromatics production is 3.5 percent or more of the lights production (true for 24 of the 30 refineries with aromatic production). The uncertainty in the emission factors for aromatic product storage tanks, as encountered in reviewing the limited data available for these tanks, is that the aromatics products may differ by refinery. The 2000 Worldwide Refining Survey (Stell, 2000a) provides some additional detail about the type of aromatic process employed, classifying the production capacities for the following aromatic units: BTX, hydrodealkylation (which produces benzene), cyclohexane, and cumene. This added level of detail regarding the aromatic units was not used for several reasons. First, no data were available to characterize cyclohexane and cumene product storage tank emissions. Moreover, all 30 refineries that had aromatics production capacity specified at least some production of BTX, and the BTX aromatics production capacity was 80 percent of the total aromatics production capacity. Thus, for the most significant aromatics production unit (BTX), which was listed for all refineries with aromatics production capacity, there was little option available other than to estimate emissions for all three aromatics (i.e., benzene, toluene, and xylene). Consequently, it is quite likely that for any given refinery, the REM estimates emissions of an aromatic product that the refinery does not have, and it is equally likely that the REM underestimates the emissions of the aromatic products that they do have. Although a slightly more refined analysis could be implemented that uses the additional information available about

the type of aromatic unit, this refined approach would also require additional emissions data to implement, and it would not alleviate the uncertainty for BTX units. Aromatic product storage tanks appear to be one area where a focused information collection effort could significantly improve the emission estimates and associated risk from storage tanks.

Table 4-24 provides a comparison of the overall tank farm emissions for benzene, toluene, and hexane as calculated by the model versus those reported in the Title V permit applications for the Louisiana refineries. The emissions are generally accurate within a factor of 2 to a factor of 5; the largest discrepancies stem from differences in aromatics production and the emissions reported by Shell, where three fixed-roof tanks are responsible for 60 to 70 percent of the reported benzene and toluene emissions. Most of the reported tank emissions are based on tank throughput capacity; the reported emissions may overstate actual emissions if the tanks are not used to capacity (e.g., if a refinery still has fixed-roof tanks, but rarely uses them).

4.7 Product Loading Operations

Product loading emissions occur when vapor is displaced by the liquid product when it is loaded into tank trucks, rail cars, and marine vessels. The vapor may contain constituents from the material previously transported and from the product being loaded.

Table 4-24. Comparison of Tank Farm Model Estimates and Reported Tank Emissions

 $NR = not reported$

a Data reported in the Title V permit applications for selected Louisiana refineries

^b Predicted tank farm emission estimates from the emissions model algorithm

c Includes "fugitive tank farm" emissions, which are roughly 25 percent of total tank farm emissions

^d Refineries with aromatics production units; aromatics produced in parenthesis:

 $B =$ benzene, T=toluene, X=xylene(s)

4.7.1 Emission Estimation Methodology

A review of the permit applications for the nine Louisiana refineries for which we had data showed that eight reported marine vessel loading operations, and all of them captured emissions and vented them to a flare. Consequently, emissions from marine vessel loading are included in the emission factor for flares derived from these plants. For the ninth plant, which is the second smallest of the nine (crude capacity of 78,000 bbl/cd), loading emissions were reported separately and were not identified as from marine vessel loading.

Emissions from gasoline loading racks are regulated under MACT I for petroleum refineries (40 CFR Part 63, Subpart CC) and are limited to 10 mg of THC per liter of gasoline. For this analysis, a conservative assumption was made that all gasoline is loaded through these loading racks and that emissions occur at the allowable level (10 mg THC/L). The emission limit converts to 6.4E-4 tpy THC for each bbl/day of gasoline loaded.

Data were available for the estimated vapor-phase HAP composition of gasoline. The vapor-phase composition in Table 4-25 was multiplied by 6.4E-4 to generate the emission factors shown in the table in terms of tpy per bbl/day of material loaded. The "lights" production rate, as calculated for storage tanks (Section 4.6), was used to estimate the amount of material produced/loaded at each refinery. An example calculation is given below for benzene from loading emissions at a refinery producing 100,000 bbl/day of gasoline and other light distallate products:

Benzene (tpy) = 100,000 bbl/day \times 6.1E-6 tpy per bbl/day = 0.6 tpy.

For comparison, five of the Louisiana refineries reported benzene emissions from loading operations that were calculated from site-specific information—0.01, 0.05, 0.14, 0.22, and 0.51 tpy. The approach, based on an emission limit of 10 mg/L, appears to be conservative (high) relative to the estimates in permit applications.

4.7.2 Source Characteristics

Estimates of source characteristics were developed from review of the EPA document "Development of Petroleum Refinery Plot Plans" (U.S. EPA, 1978) and Title V permit applications. The model modules for plot plans described two sizes of truck loading racks, one that was 7×30.5 m (an area of 2,300 ft²) and another that was 13.7×70.1 m (10,000 ft²). Only one of the Louisiana facilities provided information on the truck loading area $(5,000 \text{ ft}^2)$. A midrange value of $5,000$ ft² was chosen as the default value.

The model modules were assigned heights of 4.6 m (15 ft) and 6.1 m (20 ft). One of the Louisiana permit applications provided a height of 10 ft and a second was 15 ft. A midrange value of 15 ft was assigned as the default height.

4.7.3 Uncertainty in Estimates

Accurate estimates of loading emissions require site-specific data, such as the composition of the product, vapor pressures of the components, quantity loaded, loading procedure, and the effectiveness of the capture and control systems in place. This information was not available for this analysis. Consequently, the default approach used to estimate loading emissions may result in a great deal of uncertainty for a specific site. If we assume the estimates of loading emissions provided by five Louisiana refineries are based on site-specific information, comparisons can be made for benzene, which is a carcinogen of primary interest. The sitespecific estimates for benzene ranged from 0.01 to 0.5 tpy for refineries with capacities of about 50,000 to 500,000 bbl/day. The default approach described earlier would estimate a range of benzene emissions of 0.3 to 3 tpy. This comparison suggests the default approach is conservative (high) with respect to estimating emissions from loading. However, loading emissions are not a significant contributor to the total facility emissions.

4.8 Catalytic Reforming Unit (CRU) Catalyst Regeneration Vents

The CRU is a series of catalytic reactors that turn naphtha into high-octane gasoline. There are no direct atmospheric vents from the naphtha reforming process, but the catalyst activity slowly diminishes with time and the catalyst must be regenerated. There are three basic types of CRU catalyst regeneration: continuous, cyclic, and semiregenerative. Continuous CRU catalyst regenerators operate continuously with a small slip stream of catalyst being recirculated between the CRU and the regenerator. Cyclic CRU essentially involves an extra CRU reactor. When regeneration is needed, one reactor is cycled offline and regenerated. The regeneration of the offline reactor is a batch process. When complete, the reactor is returned to service and the next reactor is cycled offline and regenerated. The process continues until all reactors are regenerated. In a cyclic CRU, regeneration may occur for 1,000 to 4,000 hours per year. The

semiregenerative CRU operates without regeneration for 8 to 18 months, then the entire unit is brought offline, and the entire unit is regenerated. The overall regeneration cycle typically takes 1 to 2 weeks.

During regeneration, there are several potential atmospheric vents. Although the location of the emission points might vary depending on whether catalyst regeneration is semiregenerative, cyclic, or continuous, emissions can occur regardless of the regenerator type at three times during the regeneration process. These three emission points are (1) the initial depressurization and purge vent; (2) the coke burn pressure control vent; and (3) the final catalyst purge vent.

The initial depressurization and purge cycle removes the hydrocarbons from the catalyst prior to CRU catalyst regeneration. The vent gases from this initial purge may have high levels of organic HAPs, such as BTX and hexane. This vent is typically vented to the refinery's fuel gas system or directly to a combustion device (e.g., flare or process heater). The coke burn cycle is typically the largest (in terms of gas volume) emission source of the overall catalyst regeneration cycle. The primary HAPs contained in the CRU coke burn vent are hydrogen chloride (HCl) and chlorine $(Cl₂)$, which are produced when the water formed during combustion leaches chloride atoms from the CRU catalyst. The final purge and reduction cycle removes oxygen and any remaining chorination agent from the system and reduces the catalyst prior to returning CRU catalyst to the reforming process or bringing the unit back online. The vent gases from this final purge may have low levels of the chlorinating agent (usually an organic HAP, such as trichloroethene of perchloroethene) and residual HCl or Cl₂ remaining in the system. This vent is typically vented to the atmosphere or the refinery's fuel gas system, depending on the oxygen content of the vent gases (safety considerations restrict the venting of oxygen-containing gases to the fuel gas system).

The 2000 Worldwide Refining Survey data were supplemented with data available from the MACT II project database (Hansell, 1997). The additional data provided information on the number of CRUs at each refinery, the capacity for each CRU, and the type of control device used for the purge and coke-burn emission vents. Control device information was available for approximately 80 percent of the CRU based on capacity.

4.8.1 Emission Estimation Methodology

Few data are available to characterize the emissions from the CRU catalyst regeneration vent because venting is infrequent, the vent flow rates are slow and usually variable, and the vents have small diameters. All of these factors make traditional source testing difficult. Most of the available data are for HCl and Cl₂ emissions from "uncontrolled" coke burn (20 data) available for HCl emissions; 10 data available for $Cl₂$). A few data were available for limited VOCs. These data are compiled in the background information document (BID) for the proposed MACT II rule (U.S. EPA, 1998b). During the MACT II project, the CARB, with funding assistance from EPA, conducted a source test of a continuous CRU catalyst regenerator coke burn vent for dioxins/furans, polychlorinated biphenyls (PCBs), and PAHs. The results from this source test, which were not yet available for inclusion into the MACT II BID, were used to

develop emission factors for these compounds. The emission factors used for the "uncontrolled" coke burn emissions are presented in Table 4-26. These emission factors are normalized by the CRU process throughput and were assumed to apply equally for all types of CRU regenerators.

| CASRN | Chemical Name | Emission Factor (lb/1000 bbl) ^a |
|----------------|-----------------------------|--|
| 1746-01-6 | Dioxin TEQ ^b | 5.68E-09 |
| 1336-36-3 | Total PCBs ^c | 2.62E-06 |
| $91 - 20 - 3$ | Naphthalene | 3.51E-05 |
| $91 - 57 - 6$ | 2-Methylnaphthalene | 1.29E-06 |
| 208-96-8 | Acenaphthylene | 3.03E-08 |
| 83-32-9 | Acenaphthene | 4.28E-08 |
| 86-73-7 | Fluorene | 1.95E-07 |
| $85 - 01 - 8$ | Phenanthrene | 6.12E-07 |
| $120 - 12 - 7$ | Anthracene | 9.14E-08 |
| 206-44-0 | Fluoanthene | 1.01E-07 |
| 129-00-0 | Pyrene | 1.51E-08 |
| $56 - 55 - 3$ | Benzo(a)anthracene | 8.95E-10 |
| 218-01-9 | Chrysene | 2.87E-09 |
| 205-99-2 | Benzo(b)fluoranthene | 1.54E-09 |
| 207-08-9 | Benzo(k)fluoranthene | 7.48E-10 |
| 192-97-2 | Benzo(e)pyrene | 2.91E-09 |
| 193-39-5 | Indeno $(1,2,3-c,d)$ pyrene | 1.74E-09 |
| $53 - 70 - 3$ | Dibenzo(a,h)anthracene | 7.79E-10 |
| 191-24-2 | $Benzo(g,h,i)$ perylene | 4.04E-09 |
| $71-43-2$ | Benzene | 0.004 |
| 108-88-3 | Toluene | 0.0096 |
| 1330-20-7 | Xylene | 0.007 |
| 7647-01-0 | HCl | 4.225 ^d |
| 7782-50-5 | Chlorine | 0.225 ^d |

Table 4-26. Emissions Factors for CRU Catalyst Regeneration Vent

^a Emission factor in lbs pollutant emitted per 1,000 bbl of CRU process capacity b Dioxin TEO = toxicity equivalence to 2.3.7 8-tetrachloro-dibenzo-p-dioxin use

Dioxin TEQ = toxicity equivalence to $2,3,7,8$ -tetrachloro-dibenzo-p-dioxin used for risk analysis; specific dioxin/furan isomer emissions data are available

 c Sum total of all chlorinated biphenyl emission factors; data available for each class of chlorinated biphenyls (mono-, di-, tri-, decachlorobiphenyl)

d Emission factor for "uncontrolled" coke burn vent; "controlled" emissions estimated based on minimum control device efficiencies

The most prevalent control device used in association with the coke burn vent is a wet scrubber. The dioxin/furan emissions source tests, as well as the volatile organics source tests were performed on a system controlled by a wet scrubber. Because of the limited solubilities of these chemicals and the scrubbing medium recirculation rate used for wet scrubbers on this vent stream, the scrubber is assumed to be ineffective at reducing the emissions of these chemicals. Therefore, the same emission factor was used for these chemicals for both controlled and uncontrolled CRUs. The scrubbers are expected to reduce the emissions of HCl and $Cl₂$. The scrubbers used for these vents were characterized into two classes: single-stage scrubbers and multiple-stage scrubbers. Single-stage scrubbers were estimated to reduce HCl and Cl₂ emissions by 92 percent, and the multiple-stage scrubbers were estimated to reduce HCl and $Cl₂$ emissions by 97 percent. For units with no control device information available, the emissions were estimated assuming 40 percent reduction efficiency (because control devices are used for just over 40 percent of the CRU capacity for which control device information is available).

Because most emissions from the purge cycles are vented to the RFG system or a flare, emissions from this source are not covered separately here; these emissions are presumably included in the RFG combustion sources (process heaters and boilers) or flares emissions estimates. No data are available to characterize the small portion of venting that occurs directly to the atmosphere from these purge cycles; no estimates of these emissions were included in the preliminary emissions estimates.

4.8.2 Source Characteristics

The CRU catalyst regeneration vent is generally a small-diameter (3 to 9 inch) stack or pipe. Except for the continuous CRU, the CRU catalyst regeneration vent only operates periodically throughout the year. Three model stacks were developed—one model stack for each type of CRU. The model stacks were developed based on information collected during site visits perfomed during the MACT II rulemaking, limited source test data for these vents, and limited data reported by the Louisiana refineries in their Title V applications. The model stack parameters are presented in Table 4-27.

Continuous CRU regenerators that did not have a wet scrubber to remove HCl generally had hooks at the end of the CRU so that rain would not fall into the system. Condensed water in the system would absorb HCl and corrode the pipes. Therefore, as indicated in Table 4-27, when no scrubber is present, the gas is vented at roughly 800°F. When a scrubber is used, the scrubbing medium (caustic water solution) cools the gas to approximately 150°F.

4.8.3 Uncertainty in Estimates

Based on the limited amount of data available to set the emission factors, there are large uncertainties in the emissions from the CRU vent for most chemicals, except perhaps for HCl and $Cl₂$. One other source test measuring dioxin/furans from a CRU has been performed; the dioxin TEQ emissions from this source test are roughly two orders of magnitude lower than the dioxin emission factors employed in the REM. The source test data used for the emission factors

in the REM were for a continuous CRU; this second test was performed on a semiregenerative CRU. Some differences in emissions are likely based on the CRU regenerator type. Continuous and cyclic CRUs process naphtha under more "severe" conditions than semiregenerative CRU because the frequency of regeneration does not have a significant impact on the process throughput for these units. Therefore, it is likely that these units may burn off more coke per bbl of CRU naphtha processed. The two orders-of-magnitude difference likely results from a combination of the differences in CRU regenerator type and the variability in the process emissions in general.

The "uncontrolled" emission factors associated with HCl and $Cl₂$ emissions were developed using a midrange estimate. As such, the emissions are generally within a factor of 2 of the highest measured emission factor, but can be an order of magnitude greater than the lowend value. The arithmetic average emission factor is roughly a factor of 2 less than the midrange value for HCl. As such, the lumped control factor applied to the emissions for units that did not report control device information still yields results that are generally characteristic of uncontrolled emissions. Very few emissions data are available for HCl from controlled CRUs; the few data available suggest that the control efficiencies for HCl wet scrubbers are generally higher than the control factors applied in the emission estimates. As such, the coke burn emission factors used in this analysis are considered to be biased high. This level of conservatism was considered appropriate because of the general lack of available data and lack of emission estimates for purge streams that are vented directly to the atmosphere.

There are also uncertainties in the stack parameters. This uncertainty arises from the limited amount of data available to characterize these sources. Particularly, uncertainties exist primarily in the stack height, flow rate/stack velocity, and operating hours (for noncontinuous CRUs). An example of this uncertainty is for a class of CRUs referred to as platformers. In platformers, the CRU reactors are positioned horizontally. These platformers are generally continuous CRUs, and the regenerator may be located several hundred feet in the air.

4.9 Catalytic Cracking Unit (CCU) Catalyst Regeneration Vents

The CCU (fluid or other) is used to upgrade the heavy distillates to lighter, more useful distillates, such as heating oils or gasoline. Nearly all CCU systems operate as fluidized-bed

reactors and use air or oil gas flow to transport the catalyst between the CCU reactor and the CCU regenerator. These fluid CCU (FCCU) systems represent more than 97 percent of the U.S. CCU capacity. A few thermal CCU (TCCU) exist, which use larger catalyst particles and moving bed reactors. Although the attributes of particulate matter emissions from FCCU and TCCU regenerators can differ widely, the HAP constituents emitted from the regeneration process are essentially the same.

During the cracking process, coke is deposited on the catalyst, and catalyst activity decreases. Therefore, the catalyst is recirculated between the reactor and the regenerator to burn off the coke deposits and reactivate the catalyst. There are two basic types of CCU regenerators: complete combustion regenerators and partial combustion regenerators. In a complete combustion regenerator, the regenerator is typically operated at approximately 1,200 to 1,400°F with excess oxygen and low levels $(< 500$ ppmv) of carbon monoxide (CO) in the exhaust flue gas. In a partial (or incomplete) combustion regenerator, the regenerator is typically operated at approximately 1,000 to 1,200°F under oxygen-limited conditions and relatively high levels (1 to 3 percent) of CO. Nearly all partial combustion CCU regenerators operate a CO boiler, incinerator, or other thermal combustion unit to complete the combustion of CO and to destroy products of incomplete combustion.

 There are two general classes of HAP emissions from the CCU catalyst regenerator: metal HAPs (such as nickel, manganese chromium, and lead) that are associated with catalyst particles entrained in the exhaust gas; and organic HAPs (such as benzene, formaldehyde, hydrogen cyanide, phenol, and PAHs) that result from the incomplete combustion of coke or other impurities in the CCU reactor feed that deposits on the catalyst particles.

The 2000 Worldwide Refining Survey data were supplemented with data available from the MACT II project database. The additional data provided information on the number of CCUs at each refinery, the capacity for each CCU, the type of regenerator (complete vs. partial combustion), and the presence of additional control devices effective for the organic or metal HAP emission control. Organic HAP control device information was available for approximately 95 percent of the CCUs based on capacity, and metal HAP control device information was available for all CCUs.

4.9.1 Emission Estimation Methodology

For organic emissions, emission factors developed during the MACT II rulemaking were used. These emission factors, which are presented in Table 4-28, were developed based on data for units controlled for organic HAPs (i.e., either complete combustion or partial combustion followed by additional combustion). The emission factors for VOCs are generally based on five to six emission source tests; the emission factors for PAHs and furans are generally based on one or two emission source tests. Emissions of uncontrolled organic HAPs were estimated assuming a control efficiency of 98 percent (so that uncontrolled emissions are 50 times higher than controlled emissions); based on the current MACT II data, only one FCCU is uncontrolled for organic HAPs.

Table 4-28. Organic HAP Emission Factors for CCU Catalyst Regenerator Vent

(continued)

| CASRN | Compound | Emission Factor (lb/MMbbl) ^a |
|----------------|-----------------------------|---|
| 191-24-2 | Benzo(g,h,i)perylene | 0.0046 |
| 207-08-9 | Benzo(k)fluoranthene | 0.00272 |
| 218-01-9 | Chrysene | 0.00327 |
| $53 - 70 - 3$ | Dibenz(a,h)anthracene | 0.0042 |
| $206 - 44 - 0$ | Fluoranthene | 0.221 |
| 86-73-7 | Fluorene | 0.058 |
| 193-39-5 | Indeno $(1,2,3$ -cd)pyrene | 0.00438 |
| $91 - 20 - 3$ | Naphthalene | 1.12 |
| $85-01-8$ | Phenanthrene | 0.353 |
| 129-00-0 | Pyrene | 0.00327 |
| $91-57-6$ | 2-Methylnaphthalene | 0.0261 |
| $65 - 85 - 0$ | Benzoic acid | 79.3 |
| 117-81-7 | Bis(2-ethyl hexyl)phthalate | 2.84 |
| 84-74-2 | Di-n-butylphthalate | 1.98 |
| 84-66-2 | Diethylphthalate | 0.282 |

Table 4-28. (continued)

^a Emission factors for CCUs controlled for organics in lbs per million barrels of CCU capacity

Estimates of metal HAP emissions were based on the emissions of nickel (Ni) estimated from a Monte Carlo simulation of CCU emissions developed during the MACT II rulemaking. Nickel emissions were based on actual emissions data or on a hierarchy of available data for each CCU. This hierarchy is as follows:

- 1. Actual Ni emissions test data for that CCU;
- 2. Actual particulate matter test data for the CCU combined with reported equilibrium catalyst (E-Cat) Ni concentrations;
- 3. Actual particulate matter test data for the CCU and a randomized Ni fines concentration based on the distribution of fines data obtained from catalyst vendor;
- 4. Random particulate matter emission rate based on the presence of a particulate matter control device and particulate matter emission distributions for controlled

and uncontrolled units combined with reported E-Cat Ni concentrations for that CCU; and

5. Random particulate matter emission rate based on the presence of a particulate matter control device and particulate matter emission distributions for controlled and uncontrolled units combined with a randomized Ni fines concentration based on the distribution of fines data obtained from catalyst vendor.

An arithmetic average emission rate for each CCU was calculated from the 1,000 randomized runs performed for the Monte Carlo analysis, and these emission rates were directly input into the CCU emissions database. There are 127 CCUs in the database; direct Ni emissions data were available for 22 CCUs. Particulate matter emissions data were available for 51 refineries, and Ni E-Cat concentrations were available for 61 refineries.

Once the Ni emissions were included in the database, emissions from other metal HAPs were estimated based on the ratio of emission rates measured for these compounds to the emissions of Ni. Approximately 10 emission source tests measured multiple metal HAPs. The ratios used to estimate the emissions of the metal HAPs based on Ni emissions are presented in Table 4-29.

Table 4-29. Ratio of CCU Metal HAP Emissions to Nickel Emissions

4.9.2 Source Characteristics

Stack parameters were available for roughly 30 CCUs based a preliminary risk assessment performed by API. Additional stack parameters are likely available in the particulate matter emissions source test reports, but these were not reviewed and compiled. Using these data, along with the process operating parameters collected in the MACT II rulemaking, the model stack parameters provided in Table 4-30 were developed.

Table 4-30. Model Stack Parameters for CCU Catalyst Regeneration Vent

^a Stack diameter calculated based on calculated flow rate and assumed stack velocity

 b Default temperature for units with a wet scrubber (WS) is 300 \degree F; default temperature for all other control device configurations is 550°F

 c Flow rate calculated based on CCU capacity (CCU_{cap}) based on correlation developed from process data

4.9.3 Uncertainty in Estimates

Compared with many other sources, the CCU catalyst regenerator vent is relatively datarich, especially with respect to Ni emissions, which are expected to be one of the main risk drivers from this source. Additionally, the relative ratio of Ni to other metal HAPs is generally consistent based on analysis of fines collected by particulate matter control devices on the CCU catalyst regenerator vent. The largest uncertainty lies with the emissions for mercury because mercury is not expected to be controlled well by the particulate matter control devices used for this vent (i.e., electrostatic precipitators (ESPs) or venturi scrubbers). Nonetheless, using the measured/calculated Ni emission rate and the emission ratios presented in Table 4-29, the nationwide mercury emissions from the CCU catalyst regenerator vent was estimated to be 1.29 tons/year. This emission rate is only 2.3 times lower than the emissions projected using the single highest emission factor derived from the mercury emissions data. Although the uncertainties increase when a given facility's emissions parameters are randomly assigned, the metal HAP emission estimates are considered to be accurate within a factor of 2 for most CCUs.

The CCU catalyst regenerator vent is the driving emission source for metal HAPs from the refinery. Therefore, the relatively high level of data and associated confidence in the metal HAP emissions for the CCU catalyst regenerator vent leads to a relatively high level of confidence for the refinery-wide metal HAP emissions.

The organic emission factors for volatiles are based on midrange estimates, so the highend emissions are generally no more than a factor of 2 higher than those estimated. The low-end emissions may be an order-of-magnitude less than those estimated using the emission factors presented in Table 4-28. The highest uncertainty lies with emissions that are uncontrolled for HAPs. Fortunately, only one facility is currently projected to be uncontrolled for organic HAPs. Uncontrolled formaldehyde emissions are most suspect. Formaldehyde is generally formed as a combustion product with some excess oxygen, and it is unlikely that uncontrolled formaldehyde emissions are 50 times those of controlled units. Additionally, because the industry trend has been toward complete combustion CCUs, the one CCU uncontrolled for organics should be contacted to verify that it has not modified its CCU operation (i.e., it still uses a partial combustion unit with no postcombustion device). The CCU regenerator vent is a relatively minor contributor to the overall benzene emission, but it is a major contributor to formaldehyde, cyanide, and hydrogen cyanide (HCN) emissions.

Based on the lack of data for the PAH and furan emissions, the emission estimates for these compounds have high uncertainties, likely an order of magnitude either high or low. The CARB, with the support of EPA, did conduct an emissions source test at a complete combustion FCCU (with no postcombustion device). The only dioxin isomer detected in all runs was OCDD (octachloro-dibenzo-p-dioxin); OCDF (octachloro-dibenzo-p-furan) and hetpa-CDD (hetpachloro-dibenzo-p-dioxin) were detected in one run; all dioxin/furan quantities that were detected were detected at levels below the method quantitation limit for the analysis. All PCBs isomers were below detection limits; data for PAHs have not yet been reported. This additional source test was not included in the development of the MACT II emission factors, but it confirms low emissions of these compounds from the CCU catalyst regenerator vent.

4.10 Sulfur Recovery Unit (SRU) / Sulfur Plant Vents

All crude oils contain some sulfur compound impurities. Sulfur compounds are converted to hydrogen sulfide (H_2S) in the cracking and hydrotreating processes of the refinery. The H₂S or "acid gas" is removed from the process vapors using amine scrubbers. The amine scrubbing solution is subsequently heated to release the H_2S , and the acid gas is treated in the sulfur recovery plant to yield high-purity sulfur that is then sold as product. The sulfur recovery plant consists of one or more SRUs operated in parallel and may also contain one or more catalytic tail gas treatment units and/or a thermal oxidizer.

The primary HAP components of the final sulfur plant vent are carbonyl sulfide (COS) and carbon disulfide (CS_2) . These HAP components are by-products of the SRU and tail gas treatment unit (TGTU) reactions; COS may also be a product of incomplete combustion from a thermal oxidizer.

The 2000 Worldwide Refining Survey data were supplemented with data available from the MACT II project database. The additional data provided information on the number of SRUs
at each refinery, the capacity for each SRU, the type of SRU (most are Claus units), and the presence and type of TGTU and/or thermal oxidizer. Process-specific information was available for approximately 90 percent of the SRUs based on sulfur production capacity.

4.10.1 Emission Estimation Methodology

The MACT II BID (U.S. EPA, 1998b) presents a range of total sulfur HAP compound emission factors for SRU controlled by an incinerator. Based on the data presented and additional concentration data submitted by National Petrochemical and Refiners Association (NPRA), it was assumed that 75 percent of the sulfur HAPs emitted in COS and 25 percent in CS₂. Emissions of uncontrolled sulfur HAPs were estimated assuming a control efficiency of 98 percent (so that uncontrolled emissions are 50 times higher than controlled emissions). The emission factors used in the analysis are presented in Table 4-31. The controlled emission factors are based on summary data reported for five SRUs.

a Emission factor in lbs HAP per long-ton of sulfur produced

b Values estimated at 50 times the controlled SRU emission factor

The controlled emission factor was applied for all units that operated a TGTU, an incinerator, or both. For units for which control device information was unavailable, 50 percent of the uncontrolled emission factor was used. This is likely an overestimate of the emissions because every SRU for which information was available operated either a TGTU or an incinerator.

4.10.2 Source Characteristics

The few stack parameters that were available for the SRU vent all employed a thermal oxidizer. From these data, the model stack parameters presented in Table 4-32 were developed. These model stack parameters are suitable for units with an incinerator (the most prevalent control device), but the stack temperatures may be high for certain types of TGTUs.

 a^2 Flow rate calculated based on SRU production capacity (SRU_{cap}) based on correlation developed from available process data

4.10.3 Uncertainty in Estimates

The HAP emission factors for SRU vents are based on limited data. However, the emission data that were available were rather consistent so that the controlled emission factors are likely accurate to within a factor of 2. The uncontrolled emission factors are more highly speculative. These emission factors were divided by 2 and applied to units that did not report TGTU or incinerator information. Although control device configuration information was available for more than 90 percent of the sulfur production capacity, the high emission factors attributed to those units without information resulted in two-thirds of the SRU HAP emissions originating from those units. Based on the prevalence of controls at units that have control configuration information, the application of half the uncontrolled emission factor for SRUs with missing data is considered to be a highly conservative assumption.

4.11 Miscellaneous Process Vents

Miscellaneous process vents include those associated with distillation units, flash or knockout drums, reactors, caustic wash accumulators, and overheads from scrubbers, strippers, and wash towers. Process vents associated with catalyst regeneration for catalytic reforming and catalytic cracking and the sulfur recovery vent were addressed separately, as previously described. There were few data available to characterize these miscellaneous process vent emissions, and the preliminary emissions estimates provided for the risk assessment runs did not include estimates for these emission sources. Based on information from Petroleum Refinery MACT I, most of these process vents are controlled. A methodology is presented to estimate emissions from these vent sources based on current information.

4.11.1 Emission Estimation Methodology

Accurate estimates of emissions from process vents are difficult to obtain because of the lack of HAP data and site-specific information on whether they are controlled. A review of the permit applications for the nine Louisiana refineries indicated they did not report any miscellaneous process vents with significant HAP emissions. Several plants reported process

vents that were vented to some type of combustion device. For example, the noncondensibles or tail gas from the vacuum and crude distillation units were sent to the RFG system at one plant, and another plant burned them in a process heater. Other process vents were also reported to be sent to the RFG system or to a flare. Although process vents at these plants appear to be controlled, other plants for which we have little information may vent certain units to the atmosphere. The effort is also complicated by the lack of information on how plants implemented the requirements for Petroleum Refinery MACT I. The rule requires that process vents at existing sources be controlled if they contain 20 ppmv or more VOCs and emit 33 kg/day or more VOCs.

The approach used to estimate emissions relies on the nationwide estimates of the impacts of MACT I. The estimates before and after control (i.e., before and after MACT I) are given in Table 4-33. These emissions were distributed among the 155 refineries in the database using the crude oil capacity. The estimates for "after control" were divided by the nationwide crude oil capacity (17 million bbl/day) to generate the emission factors in the table. An example calculation is given below for benzene emissions from process vents at a refinery with 100,000 bbl/day crude oil capacity:

Benzene (tpy) = 100,000 bbl/day \times 1.8E-5 tpy/bbl/day = 1.8 tpy.

Table 4-33. Process Vent Emission Estimates from MACT I

4.11.2 Source Characteristics

As with HAP emissions data, there is little information with which to characterize process vents. The characteristics are expected to be quite variable, depending on the specific plant and associated processes. The only process vent found in the 1996 NTI was for the condenser on vacuum distillation units. The vent height ranged from 10 ft to 200 ft, and the diameter ranged from 1.5 ft to 11 ft. The velocity ranged from 13 ft/s to 56 ft/s. Midrange values of 105 ft in height, 6 ft in diameter, and 35 ft/s are recommended.

4.11.3 Uncertainty in Estimates

As discussed earlier, the HAP emission estimates for process vents are uncertain because of the lack of site-specific information, including which vents at which plants are uncontrolled. The emission estimates for MACT I suggest that the nationwide emissions of HAP from process vents are not as significant as other emission points at refineries. However, process vent emissions may make a significant contribution to emissions at any refineries where these vents are not controlled. Site-specific information on uncontrolled process vents could provide a significant improvement in the emission estimates and reduce uncertainty.

5.0 Additional Data Collection

The database documented in this report is expected to be an improvement over other available databases for petroleum refineries because it is more complete with respect to the populations of refineries, emission points, and HAPs. However, during the development of this database, which took place over a relatively short time frame, some weaknesses were identified that may merit the collection of additional information to provide more accurate and defensible estimates. In addition, areas where additional information would be of little value were also identified to assist in focusing any additional data collection effort.

5.1 Recommendations for Additional Data Collection

The recommendations focus on the emission points that are the biggest contributors to HAP emissions and also those for which data should be available at individual refineries to improve the estimates. Information that would improve the estimates of **fugitive equipment leaks** includes Method 21 inspection results (site-specific data on leak frequency and screening levels when leaks are detected), HAP composition of process streams, and counts of individual components (such as pumps, valves, and flanges) by process. These data are especially needed for aromatic units because no process component counts or compositional data are currently available for aromatics units. For **wastewater treatment processes**, information on the quantity of HAPs processed in open wastewater collection and treatment systems and emissions from any control devices (such as thermal oxidizers or strippers) would be helpful. Additionally, wastewater generation rates and composition data for aromatics units are needed. For **process and storage tanks**, site-specific emission estimates generated by the companies using EPA's AP-42 procedures (*TANKS* software) would improve the estimates. Such site-specific estimates are likely to have been generated already for state or Toxics Release Inventory (TRI) emission inventories, and the companies are in the best position to develop accurate estimates based on their knowledge of throughput and composition. Specific product production rates for aromatic compounds could greatly improve product storage tank emission estimates. In general, **aromatic units** could be targeted for the collection of more-detailed, process-specific data.

Site-specific data for **cooling towers** could significantly improve emission estimates, especially for plants that monitor the cooling water. This information would include the volumetric flow rate for the water and the composition of the process streams where it is used. Any measurement data on the HAP content or THC before the water is exposed to the atmosphere would also be helpful. Finally, information on **uncontrolled process vents** is needed. Plants could identify the processes and vents, describe their use (e.g., whether continuous or periodic or infrequent venting), and provide emissions data or estimates for THC or specific HAPs. With respect to characteristics of emission points, additional information for cooling towers and uncontrolled process vents is needed to supplement the sparse available data. This information would include height, area, linear flow rate, volumetric flow rate, and temperature.

5.2 Recommendations for Not Collecting Additional Data

There are likely to be no additional useful emissions data for process **heaters, boilers, and flares**. A detailed study has already been performed for process heaters and boilers, and flares are not amenable to testing. In addition, the characteristics of these emission points are reasonably well characterized from available data.

The available data for the **MACT II emission points** also appear adequate and already include many site-specific features. Additional HAP emissions data are not likely to be obtained because the nine Louisiana refineries generally did not include them in their permit applications, and other databases, such as the TRI, generally do not include emissions estimates for the full range of HAPs emitted from these sources. These vents include the **catalytic regeneration vents** associated with catalytic cracking and catalytic reforming, and the **sulfur recovery vent**.

The review of available data indicates that emissions from **loading product** into marine vessels, tank trucks, and rail cars are generally controlled. Because these emissions appear to make only a small contribution to total emissions, additional information would probably be of little value. In addition, **process vents that are controlled** by venting to a combustion device do not make a significant contribution to total emissions, and to some extent, their contribution is accounted for in the emission factors for process heaters, boilers, and flares.

6.0 References

- EIA (Energy Information Administration). 2000. *Oil Market Basics*. Report available at http://www.eia.doe.gov/pub/oil_gas/petroleum/analysis_publications/oil_market_basics/ Refining text.htm#U.S.%20Refining%20Capacity. Graph of capacity and utilization rates available at: http://www.eia.doe.gov/pub/oil_gas/petroleum/analysis_publications/ oil market basics/Ref image Crude runs.htm.
- FTC (Federal Trade Commission). 2001. *Midwest Gasoline Price Investigation*. Final Report. March 29, 2001. Available at http://www.ftc.gov/os/2001/03/mwgasrpt.htm.
- Hansell, D. 1997. Letter from Energy and Environmental Research to B. Lucas (U.S. EPA). American Petroleum Institute CCU and CRU Database Summary, version 3. April 11, 1997.
- Hansell, D., and G. England. 1998. *Air Toxic Emission Factors for Combustion Sources Using Petroleum Based Fuels, Volume 2: Development of Emission Factors Using CARB Approach*. Prepared by EER for S. Folwarkow, Western States Petroleum Association, Concord, CA, and K. Ritter, American Petroleum Institute, Washington, DC.
- Lidderdale, T., N. Masterson, and N. Dazzo. 1995. U.S. refining capacity utilization. *Energy Information Administration/Petroleum Supply Monthly.* Available at http://www.eia.doe.gov/pub/pdf/feature/lidder3.pdf.
- Murphy*,* P. 1993. Letter from P. Murphy (Radian) to J. Durham (EPA). *Average Weight Percent HAPs in Refinery Streams.* Providing emission estimates for Petroleum Refinery MACT I (Subpart CC). August 10, 1993.
- Stell, J. 2000a. 2000 Worldwide Refining Survey. Survey Editor. *Oil & Gas Journal*, December 18, 2000. pp. 66-120.
- Stell, J. 2000b. Worldwide Sulfur Production. Survey Editor. *Oil & Gas Journal*, June 26, 2000. pp. 66-120.
- U.S. EPA (Environmental Protection Agency). 1978. *Development of Petroleum Refinery Plot Plans*. EPA-450/3-78-025. Office of Air Quality Planning and Standards, Research Triangle Park, NC.
- U.S. EPA (Environmental Protection Agency). 1994. *Air Emissions Models for Waste and Wastewater*. EPA-453/R-94-080A. Office of Air Quality Planning and Standards, Research Triangle Park, NC.
- U.S. EPA (Environmental Protection Agency). 1995a. *Compilation of Air Pollutant Emission Factors*. *Sections 5.1, 5.2, and 13.5.* AP-42. Office of Air Quality Planning and Standards, Research Triangle Park, NC.
- U.S. EPA (Environmental Protection Agency). 1995b. *Protocol for Equipment Leak Emission Estimates*. EPA-453/R-95-017. Office of Air Quality Planning and Standards, Research Triangle Park, NC.
- U.S. EPA (Environmental Protection Agency). 1998a. *Locating and Estimating Air Emissions from Sources of Benzene*. EPA-454/R-98-011. Office of Air Quality Planning and Standards, Research Triangle Park, NC.
- U.S. EPA (Environmental Protection Agency). 1998b. *Petroleum Refineries: Catalytic Cracking (Fluid and Other) Units, Catalytic Reforming Units, and Sulfur Recovery Units – Background Information for Proposed Standards*. EPA-454/R-98-003. Office of Air Quality Planning and Standards, Research Triangle Park, NC.
- U.S. EPA (Environmental Protection Agency). 1999. Proper Monitoring Essential to Reducing "Fugitive Emissions" under Leak Detection and Repair Programs. *Enforcement Alert.* 2(9):1-4. October.
- Zerbonia, R., and J. Coburn. 1995. *Site Visit—Marathon Oil Company, Garyville, LA.* Memorandum from RTI to R. Lucas, U.S. EPA, Office of Air Quality Planning and Standards, Research Triangle Park, NC. September 28, 1995.

Appendix A. Data Extracted from Louisiana Permit Applications

A.1 Overview

Personnel from EC/R visited the Office of Air Quality at the Louisiana Department of Environmental Quality and extracted information from their files. One of the most useful items was an emission inventory questionnaire that petroleum refineries submitted for each emission point in their application for a Part 70 operating permit. The questionnaire included a description of the emission point, its UTM coordinates, and characteristics (stack height and diameter, exit temperature, flow rate, velocity, operating time, and operating rate). For combustion sources, the type of fuel and heat input were specified, and for tanks, the volume was reported. The questionnaire also included a list of the pollutants emitted, the average and maximum rates (lb/hr), and annual average rate (tpy). Most of these applications were submitted in the 1996 to 2000 time frame. Figure A-1 shows an example of a questionnaire response.

The applications were obtained for nine refineries that spanned a wide range of crude oil capacity (from 50,000 to 500,000 bbl/day). The refineries have a representative mix of processes typical of refineries nationwide. This information was used to characterize the emissions and emission points at these refineries in great detail and were also used to extrapolate to other refineries for which information was not available. The most useful information was for emissions from fugitive equipment leaks, wastewater treatment, storage and process tanks, product loading, and flares.

A.2 Details

The emission estimates provided by the companies were generally developed from EPA estimating procedures using site-specific data. However, not all emission points or HAP were included. For example, the company estimates were supplemented by the estimating procedures described in Section 4 to fill in data gaps for HAP from heaters and boilers, catalyst regeneration vents, and sulfur recovery. The results for benzene emissions (a HAP found at all refineries that is a carcinogen of primary interest) are shown in Figure A-2 and tabulated in Table A-1 by emission point. The diamond data points represent the company's estimates and show internal consistency in that (as would be expected) benzene emissions increase with refinery capacity. The circles are the estimates derived for the risk assessment and include emission points that were not in the questionnaire responses. The results for benzene emissions for Marathon Oil appear to somewhat out of line with the others in terms of capacity.

Table A-2 gives plant totals for emissions of the most commonly reported HAPs. One of the most detailed responses was that for BP Oil – Belle Chasse (now Tosco Refining). Tables A-3 through A-6 provide a summary of emissions by type of emission point for different processes and provides insight into the major contributors to HAP emissions. This level of detail was not available for all of the plants. Table A-7 is a listing of each of the emission points reported by the nine refineries and the characteristics. Table A-7 gives the HAP emissions estimates for each emission point. (The key to the facility ID is given in Table A-1.)

FIGURE A-1. EXAMPLE OF EMISSION INVENTORY FORM

A-2

FIGURE A-2. BENZENE EMISSION ESTIMATES FOR LA REFINERIES

Crude oil capacity (bbl/day)

◆ Company permit application ○ Estimate for risk analysis

| ID | Refinery | Benzene emissions (tons/yr) | | | | | |
|----|-----------------------|-----------------------------|---------------|--------------|---------------|------------------|--------------|
| | | Fugitives | Wastewater | Tanks | Flares | Loading | Total |
| 70 | Pennzoil, Shreveport | 3.0 | 3.2° | 1.5 | 0.7 | -- | 8.4 |
| 74 | Valero, Krotz Springs | 5.1 | 9.8 | 0.8 | $- -$ | 0.5 | 16 |
| 68 | Murphy, Meraux | 9.0 | 0.4 | 0.6 | 0.08 | 0.2 | 10 |
| 64 | Exxon, Chalmette | 15.8^{b} | $-$ | 1.5 | $-$ | 0.01 | 17 |
| 67 | Shell, Norco | 9.6 | $- -$ | 15.6 | 2.4 | 0.22 | 28 |
| 65 | Marathon, Garyville | 2.0 | 3.6 | 1.8 | 0.03 | 2.1 | 9.5 |
| 73 | BP, Belle Chase | 9.3 | 9.2 | 8.3 | $- -$ | 4.3 ^a | 31 |
| 61 | Citgo, Lake Charles | 13.2 | 4.4 | 21.7 | 1.3 | 0.2 | 41 |
| 63 | Exxon, Baton Rouge | 12.9 | 14.1 | 18.8 | | 1.8 | 48 |

TABLE A-1. BENZENE EMISSION POINTS

^a Includes flares; ^b Includes wastewater treatment; ^c Inludes cooling tower

TABLE A-2. HAP EMISSION ESTIMATES FROM TITLE V PERMIT APPLICATIONS

* The emissions of ketones are associated with dewaxing processes at these plants.

TABLE A-3. BP EQUIPMENT LEAKS - FUGITIVE EMISSIONS

TABLE A-4. EMISSIONS FROM BP WASTEWATER TREATMENT

TABLE A-5. EMISSIONS FROM BP TANKS

TABLE A-6. EMISSIONS FROM BP MARINE VESSEL LOADING

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