BAY AREA AIR QUALITY MANAGEMENT DISTRICT

Refinery Emissions Inventory Guidelines: An Assessment of EPA Document *Emission Estimation Protocol for Petroleum Refineries*

(Version 2.1.1, May 2011)

September 2013

Prepared by:

Thu Bui, Senior Air Quality Engineer
Brenda Cabral, Supervising Air Quality Engineer
Bhagavan Krishnaswamy, Senior Air Quality Engineer
Carol Lee, Senior Air Quality Engineer
Brian Lusher, Senior Air Quality Engineer
Juan Ortellado, Air Quality Engineering Manager
Greg Solomon, Supervising Air Quality Engineer
Greg Stone, Supervising Air Quality Engineer
Art Valla, Senior Air Quality Engineer

Reviewed by:

Pam Leong, Air Quality Engineering Manager
Jim Karas, Director of Engineering

Introduction

This report is a review of the document entitled *Emission Estimation Protocol for Petroleum Refineries* (version 2.1.1, May 2011) by the staff of the Bay Area Air Quality Management District (District). The *Emission Estimation Protocol for Petroleum Refineries* (EEPPR) was prepared by RTI International for U.S. EPA to provide guidance to petroleum refineries on how to calculate emission inventories, for the purpose of satisfying EPA's 2011 information collection request. We are reviewing this document to determine whether or not the District should use the EEPPR as a guidance document for refinery emission calculations.

The EEPPR is divided into several chapters covering common emission categories at refineries. Each chapter contains several options for calculating emissions, and ranks those options in order of preference. Staff reviewed the chapters to see how the various calculation methods compare to the way the District typically calculates emissions. For each chapter, staff prepared a summary report and provided recommendations on which method(s) in the EEPPR, if any, should be used by the District.

Overriding Principles

The following overriding principles should be considered when doing any type of emission calculation:

- The EEPPR and staff's corresponding recommendations are *guidelines* only, and do not necessarily dictate the emission calculation method in all possible cases. There are many variables at refineries that may warrant specific approaches not included in these recommendations.
- Direct measurement is preferable to calculated emissions.
- Continuous measurement is preferable to periodic testing.
- Periodic source testing should be representative of typical source operation (unless intentionally testing for atypical conditions).
- Emission factors that are based on source testing should be updated as processes change.
- Use default emission factors only when other data is not available. While it is desirable to avoid using default emission factors, it is impractical to directly measure or test all sources for all pollutants under all operating scenarios. However, such factors will not capture emission trends over time, due to changing operation.
- When multiple emission factors are available for a given criteria pollutant/toxic air contaminant, use the following order of preference: CATEF, EEPPR, AP-42.

Source-Specific Recommendations

The following is a summary of staff recommendations for each emission category, in the order that the corresponding chapters appear in the EEPPR. For each category, the summary includes the methods recommend by the EEPPR, followed by staff recommendations.

Fugitive Emission Leaks

Fugitive emission leaks occur throughout the refinery at various equipment components, including valves, flanges, pumps, compressors, relief valves, etc.

EEPPR Methods:

Table 2-1. Summary of Equipment Leak Emission Estimates

Rank	Measurement Method	Correlation Equations or Emission Factor	Compositional Analysis Data[a]
1	Direct measurement (high-volume sampler or bagging)	Not necessary	Speciation of collected gas samples
2	EPA Method 21	Correlation equation	a) Process-specific, equipment-specific concentrations b) Process-specific average concentrations c) Refinery average stream concentrations
3	EPA Method 21	Defaults creening ranges factors	
4	No monitoring; facility-specific component counts	Default average emission factors	a) Process-specific, service-specific concentrations b) Process-specific average concentrations c) Refinery average stream concentrations d) Default process compositions
5	No monitoring; default model process component counts	Default average emission factors	

[a] The letters represent ranking sublevels. For example, rank 2a consists of using the correlation equation to estimate total VOC emissions and using process-specific and equipment-specific process fluid concentration data to estimate speciated emissions.

District Recommendations:

- Use direct measurement for components with potentially significant emissions (high flow rate, high concentrations, etc.)
- Correlation equations (Rank Method 2) for components that are monitored (EPA Method 21 LDAR), including factors for zero and pegged leakers (10,000 ppm);
- Default average emission factors (Rank Method 4) for components that are not monitored;
- For speciation of individual compounds, use process specific or equipment specific analyses of process streams

Storage Tanks

EEPPR Methods:

Table 3-1. Summary of Typical Hierarchy of Storage Tank Emission Estimates

Rank	Methodology Description	Application	Data Requirements
1	Direct measurement	Covered and vented storage tanks	Constituent concentration and flow rate
2	Tank-specific modeling	All petroleum liquid storage tanks	Tank type, tank dimensions, stored liquid properties and constituent concentrations, tank condition/fitting information, throughput
3	Default tank modeling	Not applicable for refinery ICR emission estimates	

District Recommendations:

Use EPA Tanks 4.09D program (Rank Method 2) or subsequent revision. The District currently uses an older version of the TANKS model, which will have to updated at some point in the near future. However, it should also be noted that the TANKS 4.09 D model has known problems as pointed out in page 3-3 of the protocol document. For example, the model underestimates emissions from heated tanks, it does not account for monthly variations in emissions, etc.

Stationary Combustion

EEPPR Methods:

Table 4-1. Summary of Typical Hierarchy of Stationary Combustion Source Emission Estimates

Rank	Measurement Method	Additional Data Needed
1	Direct measurement (continuous emission monitoring systems [CEMS]) for both flow rate and gas composition	▪ Pressure, temperature, and moisture content (depending on the monitoring system)
2	Direct measurement (CEMS) for gas composition Use of F factors	▪ Fuel usage ▪ Heat content of fuel (depending on units of source-specific emission factors)
3A	Fuel analysis/mass balance	▪ Fuel usage ▪ Assumed destruction efficiency
3B	Source-specific stack testing to calculate source-specific emission correlations or factors	▪ Fuel usage ▪ Heat content of fuel (depending on units of source-specific emission factors)
4	Default emission factors	▪ Fuel usage

District Recommendations:

Staff recommends using the same calculation hierarchy as above:

- CEM and flue gas flow measurements (Rank Method 1)
- CEM and calculated Fd factor based on fuel gas composition (Rank Method 2)
- Stoichiometric calculations (Rank Method 3A)

- Source Test to develop source-specific emission factors (Rank Method 3 B), provided test is representative of operating conditions
- Default emission factors (Rank Method 4)

Process Vents

Typically, vent gases are collected and routed to a vapor recovery or fuel gas system. This section is for estimating emissions from vent gasses that are not collected. There are calculation methods specific to several different process units.

EEPPR Methods:

Table 5-1. Summary of Typical Hierarchy of Process Vent Emissions Estimates

Rank	Flow Estimate Method	Compositional Analysis Data
1	Continuous flow meter	Continuous gas composition analyzer
2	Engineering estimates (e.g., F factor)	Continuous gas composition analyzer
3	Continuous flow meter or engineering estimates	Occasional grab samples
4	Measured process rates	Site-specific emissions factor based on source test
5	Measured process rates	Default emissions factors

District Recommendations:

Staff agrees with the calculation procedures identified in the EEPPR.

Flares

EEPPR Methods:

Table 6-1. Summary of Flare Emissions Estimate Methodologies

Rank	Measurement Method	Additional Data Needed
1	Continuous composition monitoring (or manual sampling at least once every 3 hours during flaring events) and continuous flow rate monitoring of the gas sent to the flare	▪ Combustion efficiency (based on results of a direct measurement test, if available, or a default assumption)
2	Continuous flow rate monitoring and daily or weekly compositional analysis	▪ Representative sample (grab or integrated) ▪ Assumed combustion efficiency
3	Continuous flow rate and heating value monitoring	▪ Emission factors based on heating value
4	Engineering calculations	▪ Process knowledge of units connected to flare (e.g., volume, composition of process streams) ▪ Temperature and pressure monitoring data or other process operating data as needed ▪ Assumed combustion efficiency
5	Emission factors based on energy consumption	▪ Flow estimates (not continuous) ▪ Heat value estimates (not continuous)
6	Default emission factors based on refinery or process throughput	▪ Refinery or process throughput

District Recommendations:

- Rank Method 1, because District Regulation 12-11 requires the monitoring of flare gas composition and flow rate when the flare gas exceeds 330 scfm.
- Assume 98% combustion efficiency for properly operated flare (40 CFR 60.18), unless otherwise indicated.
- Calculate SO_2 emissions based on total sulfur compounds in flare gas, not just H_2S.
- Develop HAP emission factors based on periodic analyses of flare gas.

Wastewater

Wastewater systems consist of a variety of components, including collection systems, weirs, oil-water separators, flotation units, biological treatment and polishing. Because of the Benzene Waste NESHAP requirements, many of the components (equalization tanks, oil-water separators, flotation units) are enclosed and/or abated, and therefore, can be measured directly. Emissions from open units can be calculated using predictive modeling or emission factors.

EEPPR Methods:

Table 7-1. Summary of Wastewater Treatment Emission Estimates

Rank	Measurement Method	Application	Data Requirements
1	Direct measurement	Covered and vented units	▪ Constituent load and speciation of collected gas samples
2a	Predictive modeling with site-specific factors and biodegradation rates followed by validation	Uncovered units	▪ Constituent load and speciation of process wastewaters ▪ Site-specific biodegradation rates ▪ Model validation by a direct measurement method
2b	Predictive modeling with site-specific factors and biodegradation rates	Uncovered units	▪ Constituent load and speciation of process wastewaters ▪ Site-specific biodegradation rates
2c	Predictive modeling with site-specific factors	Uncovered units	▪ Constituent load and speciation of process wastewaters
3a	Engineering estimates based on wastewater treatment plant load	Uncovered units	▪ Constituent load and speciation of process wastewaters
3b	Engineering estimates based on crude throughput	Uncovered units	▪ Crude throughput

District Recommendations:

- For covered and vented units use Direct Measurement (Rank Method 1).
- For uncovered units:
  - Predictive modeling (Rank Method 2) – Long term goal.
  - Emission factors (Rank Method 3) – Short term.
- Estimate HAPs from benzene concentration data in wastewater.

Cooling Towers

This section estimates POC, HAP, chlorine and particulate emissions from cooling towers. Organic contaminants are introduced into the cooling water through leaks in heat exchangers and condensers, and then stripped out of the cooling water to the atmosphere.

EEPPR Methods:

Table 8-1. Summary of Cooling Tower Emissions Estimation Methodologies

Rank	Measurement Method or Emission Factor	Compositional Analysis Data
1	▪ Air stripping simulation using Appendix P, Modified El Paso method (speciated VOC) [a] ▪ Water recirculation rate	▪ Speciation of collected gas samples with EPA TO-14 or TO-15 methods, with EPA Method 18, or with a portable (not handheld) gas chromatograph/flame ionization detector
2	▪ Air stripping simulation using Appendix P, Modified El Paso method[a], using a flame ionization detection analyzer (total VOC) ▪ Water recirculation rate	▪ Process-specific, service-specific concentrations ▪ Process-specific average concentrations ▪ Site-specific refinery average stream concentrations ▪ Default process compositions
3	▪ Direct water measurement by EPA Method 8260B[b] before and after exposure to the atmosphere (e.g., at the cooling tower return line and at the outlet of cooling tower) ▪ Water recirculation rate	▪ Speciation of collected water samples
4	▪ Direct water measurement by EPA Method 8260B[b] before exposure to the atmosphere (e.g., at the heat exchanger exit line, or at the cooling tower return line) ▪ Water recirculation rate	▪ Speciation of collected water samples
5	▪ AP-42 emission factor for VOC, PM_{10}, and chlorine ▪ Water recirculation rate OR ▪ Material balance	▪ Process-specific, service-specific concentrations ▪ Process-specific average concentrations ▪ Site-specific refinery average stream concentrations ▪ Default process compositions

[a] Source: TCEQ, 2003.
[b] Source: U.S. EPA, 1996.

District Recommendations:

- Rank 1 is most appropriate to use for determining volatile organic HAP and VOC emissions.
- Rank 5C is simplest to use to estimate cooling tower PM emissions and would likely overestimate PM emissions.

Loading Operations

Organic and HAP emissions result from the loading of liquids into trucks, railcars and marine vessels.

EEPPR Methods:

Table 9-1. Summary of Loading operations Emission Estimates

Rank	Measurement Method or Emission Factor	Compositional Analysis Data
1A	Direct measurement (CEMS) for both flow rate and gas composition	▪ Pressure, temperature, and moisture content (depending on the monitoring system)
1B	Direct measurement (CEMS) for both flow rate and THC	▪ Process-specific, service-specific concentrations based on measurement data
2	Direct measurement by EPA Method 18 (site-specific emission factor) and loading rate	▪ Not applicable
3	Direct measurement by EPA Method 25, Method 25A, or Method 25B (site-specific emission factor) and loading rates	▪ Process-specific, service-specific concentrations ▪ Process-specific average concentrations ▪ Site-specific refinery average stream concentrations ▪ Default process compositions
4	AP-42 emission factor (default emission factor) and loading rates	▪ Process-specific, service-specific concentrations ▪ Process-specific average concentrations ▪ Site-specific refinery average stream concentrations ▪ Default process compositions

District Recommendations:

Staff recommends the following for the methods ranked above:

- Method 1A: unlimited use
- Method 1B above: use with limitations (unlimited use for THC emissions)
- Method 2: use with assurances of applicability
- Method 3: use with assurances of applicability
- Method 4: use not recommended
- For methods ranked 1B, 2 and 3 above, the samples to determine speciation need to ensure TAC emissions are adequately trended.

Fugitive Dust

This section provides particulate emission calculations for three operations at refineries: roads (paved and unpaved), FCCU catalyst handling, and coke handling and storage.

EEPPR Methods:
Use fugitive emission calculations in AP-42, Chapter 13, along with the refinery-specific default values provided in Table 10-1 of the EEPPR.

District Recommendations:

- The use of AP-42, Chapter 13 for Fugitive Dust Sources is consistent with the current District procedure with the exception of Table 10-1, Default Values for Fugitive Dust Emission Estimates (outdated values which were revised in January 2011 for paved and unpaved roads).
- For stockpiles, use the default factor in the District's Permit Handbook Chapter.

Startup & Shutdown

This section provides emission estimates for process vessel depressurization and purging.

EEPPR Methods:
Initially, vessels are depressurized to the refinery fuel gas system or to the flare. Those emissions should be accounted for as part of combustion or flaring. Use the equations provided in this section to calculate emissions to atmosphere from:

- Gaseous process vessel depressurization (based on Ideal Gas Law)
- Liquid process vessel depressurization (which includes liquid "heel")

District Recommendations:

- The EEPPR calculations are based on generally recognized methods and are usable.

Malfunctions & Upsets

Emissions from all types of malfunctions and upsets should be included in the refinery emission inventory. However, due to the complexity of a refinery, the EEPPR does not provide calculations for all possible types of malfunctions/upsets.

EEPPR Methods:

Emission calculation protocols are provided for:

- Control device failure;
- Vessel over pressurization (if not accounted for as part of flare);
- Spills.

District Recommendations:

- The calculation methods in the EEPPR can be used to estimate emissions form malfunctions and upsets.
- For small spills (<500 gallons), assume 100% of material evaporates.
- For large spills (>500 gallons), use mass transfer equation provided.
- For a flare that is operating outside of the design conditions in 40 CFR 60.18, assume an efficiency of 93%.
- For a flare in an over-steaming condition, assume an efficiency of 80%.

Next Steps

Upon approval, there are several things that the District should do to incorporate the EEPPR and staff recommendations for refinery emission calculations.

- Compare EEPPR reported emissions for each Bay Area refinery with Data Bank emissions
- Incorporate calculation protocols into our Permit Handbook, as applicable
- Update Data Bank specific emission factors based on reported emissions from refineries
- Update default emission factors to reflect approved protocol or latest AP-42
- Review the following source categories, which are widely inconsistent:

Wastewater

Short Term (Emission Factors) – Update the emission factors currently used in Data Bank to calculate emissions from wastewater systems. The types of calculations and the emission factors are not consistent among refineries, and the bases for the emission factors are not well defined. Review the emission factors for all refinery wastewater systems to ensure that:

- Emissions are calculated in a consistent manner for the same wastewater components for each refinery.
- Emission factors are based on site-specific data when available.
- Default emission factors are based on latest available factors.

Long Term (Predictive Modeling) – Convert from the current calculation method (emission factors) to a predictive model. Staff will need to develop a better understanding of available models: Water 9, TOXCHEM or RWET (refinery wastewater emission tool - which is a simplified model included as part of the EEPPR)

Cooling towers

- The guidance document suggests estimating non-volatile organic compounds, such as polycyclic organic matter (POM) which has low volatility by modifying Equation 8-9. If no data is available to estimate TDS concentration in the cooling water, then the default average AP-42 PM10 emission factors should be used.
- The use of site-specific material balance to estimate cooling tower chlorine emissions is suggested. However, there are no chlorine emission factors for cooling towers at this time, and they may be developed by the EPA in the near future.

- Compare basis for different sets of HAP emission factors – which to use?