Addressing Air Emissions from the Petroleum Refinery Sector
Risk and Technology Review and New Source Performance Standard Rulemaking

Public Outreach Presentation
US Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, NC
Purpose of this Webinar

- To engage communities, particularly environmental justice communities, in a dialog about the development of this rulemaking early in the process
- Part of EPA’s overall outreach strategy to stakeholders
- Builds on EPA’s earlier Clean Air Act 101 webinar for communities
- Rulemaking combines several regulatory programs including programs that look at risk and those that don’t
Outline

► The Petroleum Refining Sector
► The Clean Air Act and Refinery Rulemakings
► Refinery Process and Emissions
► Health Effects
► Potential Amendments
► Public Involvement in the Upcoming Rulemaking
► Q and A
► Appendix with Reference Materials
  ► Process Units and Controls
  ► Additional GHG Information
Petroleum Refinery Background

- Approximately 90% of the petroleum products produced in the United States are fuels.
- Motor vehicle gasoline accounts for about 40% of the total output from refineries.
- Located near crude oil sources or in heavily industrialized areas.
- Near East and West Coast population centers, along the Gulf Coast, and throughout the Midwest.
- Go to [http://www.eia.gov/neic/rankings/refineries.htm](http://www.eia.gov/neic/rankings/refineries.htm) for a current list of top refineries, their locations, and throughputs.
Refineries Emit a Wide Variety of Pollutants

- Criteria Air Pollutants (CAP)
  - Sulfur dioxide $\text{SO}_2$
  - Oxides of Nitrogen $\text{NO}_x$
  - Carbon Monoxide $\text{CO}$
  - Particulate Matter (PM)

- Volatile Organic Compounds (VOC)
  - Organic compounds that are photochemically reactive

- Other Pollutants
  - Greenhouse Gases (GHG)
  - Hydrogen Sulfide ($\text{H}_2\text{S}$)

- Hazardous Air Pollutants (HAP)
  - Carcinogenic HAP, including benzene, naphthalene, 1,3-butadiene, PAH
  - Non-carcinogenic HAP, including HF and HCN
  - Persistent bioaccumulative HAP, including mercury
The Petroleum Refinery Sector

- 150 domestic refineries
- 17 MMbbls/day crude throughput, refining ~20% of world crude production
- Refineries have hundreds of emission points
- Second largest industrial source of GHGs

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>2005 National Emissions Inventory (NEI) Emissions (TPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOₓ</td>
<td>146,185</td>
</tr>
<tr>
<td>SO₂</td>
<td>247,239</td>
</tr>
<tr>
<td>VOCs</td>
<td>114,852</td>
</tr>
<tr>
<td>HAP</td>
<td>14,000</td>
</tr>
<tr>
<td>PM₂.₅</td>
<td>30,333</td>
</tr>
<tr>
<td>(GHGs)</td>
<td>220 MMTCO₂e</td>
</tr>
</tbody>
</table>
The Clean Air Act and Refinery Rulemakings
What does the Clean Air Act (CAA) Require?

- **New Source Performance Standards (NSPS)**
  - CAA Section 111(b) requires the EPA to set and periodically review, emission standards for new sources of criteria air pollutants (CAP), volatile organic compounds (VOC), and other pollutants.

- **Air Toxics Rules: Maximum Achievable Control Technology (MACT) and Residual Risk and Technology Reviews**
  - CAA Section 112(d) requires the EPA to set emissions standards for hazardous air pollutants (HAP) emitted by major stationary sources based on performance of the maximum achievable control technology (MACT).
  - EPA is required to conduct 2 reviews and update the existing standards if necessary
    - **Residual Risk Assessment**: To determine whether additional emission reductions are warranted to protect public health or the environment. This is a one-time review.
    - **Technology Reviews**: To determine if better emission control approaches, practices, or processes are now available. Technology reviews are required every eight years.
What We Have Done So Far

NSPS
► 1974 NSPS – covers fuel gas combustion devices, FCCU, and sulfur plants
► 2008 NSPS – covers same above and delayed cokers, flares and process heaters specifically
  ► Received 3 petitions for reconsideration
  ► Addressed a portion of the reconsideration issues

MACT
► Promulgated 2 MACT Standards for Refineries
  ► 1995 MACT (known as MACT 1) covers non-combustion or evaporative sources, such as equipment leaks, tanks, wastewater, miscellaneous process vents; amended to cover heat exchange systems, including cooling towers.
  ► 2002 MACT (known as MACT 2) covers combustion sources: Catalytic Cracking Units, Catalytic Reforming Units, and Sulfur Recovery Units

Risk and Technology Review (RTR)
► 2007 proposed Risk and Technology Review amendments for non-combustion sources
► 2009 withdrew amendments related to risk review due to insufficient data; amendments promulgated for heat exchanger systems.
What This Rulemaking Will Do

► NSPS - Address remaining reconsideration issues, including GHG
► MACT 1 and 2 - Propose and promulgate RTR amendments and evaluate whether additional rule revisions are necessary
► Respond to issues raised in litigation and petitions
Refinery Processes and Emissions
How much HAP do these sources emit with existing controls in place?

Petroleum Refinery HAP Emissions (tons per year)

- Flares: 1184 tons
- Equipment Leaks: 4018 tons
- Cooling towers: 2303 tons
- Wastewater Treatment: 3992 tons
- Storage: 1714 tons
- Combustion: 2105 tons
- FCCU: 2825 tons
- Miscellaneous: 1385 tons

Source: ICR data, 2010
How much GHG do these sources emit?

- Combustion: 67.7%
- Fluid Catalytic Cracking Units: 25.2%
- Other: 0.8%
- Sulfur Plant: 1.9%
- H2 Plant: 2.7%
- Flaring: 1.6%
- Cat Coke: 0.10%
- Blowdown: 0.014%
- Asphalt Blowing: 0.018%
- Cooling Towers: 0.003%
- Delayed Coking: 0.058%
- Equipment Leaks: 0.014%
- Storage Tanks: 0.007%
- Wastewater Treatment: 0.43%

August 8, 2008; TECHNICAL SUPPORT DOCUMENT FOR THE PETROLEUM REFINING SECTOR: PROPOSED RULE FOR MANDATORY REPORTING OF GREENHOUSE GASES
Health Effects of Refinery Emissions
# Health Effects of Criteria Air Pollutants

<table>
<thead>
<tr>
<th>Compound</th>
<th>Health Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur Dioxide (SO₂) and Oxides of Nitrogen (NOₓ)</td>
<td>Array of adverse respiratory effects, airway inflammation in healthy people, increased respiratory symptoms in people with asthma</td>
</tr>
<tr>
<td>Carbon Monoxide (CO)</td>
<td>Harmful health effects associated with the reduction of oxygen delivery to the body's organs (heart and brain) and tissues</td>
</tr>
<tr>
<td>Particulate Matter</td>
<td>Increased respiratory symptoms, irritation of the airways, coughing, or difficulty breathing, decreased lung function; aggravated asthma; development of chronic bronchitis; irregular heartbeat; nonfatal heart attacks; and premature death in people with heart or lung</td>
</tr>
</tbody>
</table>
## Health Effects of Risk Driving HAP

<table>
<thead>
<tr>
<th>Compound</th>
<th>Acute</th>
<th>Chronic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>Neurological effects, irritation of the eye, skin and respiratory tract</td>
<td>Blood disorders (reduced number of red blood cells and aplastic anemia), cancer</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>Irritation of the eyes, throat and respiratory tract</td>
<td>Cardiovascular effects, leukemia, cancer</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>Hemolytic anemia, damage to the liver, neurological effects</td>
<td>Cataracts, damage to the retina, hemolytic anemia, cancer</td>
</tr>
<tr>
<td>PAHs</td>
<td>Skin disorders, depression of the immune system</td>
<td>Skin disorders (dermatitis, photosensitization), depression of the immune system, damage to the respiratory tract, cataracts, cancer</td>
</tr>
</tbody>
</table>
# Health Effects of Other Pollutants

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mechanism</th>
<th>Health Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile Organic Compounds (VOC)</td>
<td>Combine with NOx in sunlight to create ozone</td>
<td>Significantly reduce lung function and induce respiratory inflammation in normal, healthy people during periods of moderate exercise, symptoms include chest pain, coughing, nausea, and pulmonary congestion</td>
</tr>
<tr>
<td>Greenhouse gases (GHG), including Methane (CH$_4$), Carbon Dioxide (CO$_2$), Nitrous Oxide (N$_2$O)</td>
<td>Compounds with high global warming potential contribute to climate change</td>
<td>Increase in average temperatures, higher levels of ground-level ozone, increased drought, harm to water resources, ecosystems and wildlife, health risk to sensitive populations</td>
</tr>
</tbody>
</table>
Basics of Risk and Technology Review

► Risk Review
  ► CAA Section 112 (f)(2) requires EPA to review the MACT standard 8 years after it is promulgated to determine if the MACT standard is sufficiently protective for human health and the environment
  ► If any person is exposed to a risk greater than 1 in a million, EPA goes through a 2-step process to evaluate whether that risk can be reduced
    ► Step 1 – Tighten MACT standard if any person exposed greater than 100 in a million
    ► Step 2 – Tighten MACT standard to reduce individual risk and population risk to the greatest extent possible considering costs, technical feasibility and other impacts

► Technology Review
  ► NSPS - Section 111(b)(1)(B) requires EPA to periodically review and revise these standards of performance, as necessary, to reflect improvements in methods for reducing emissions.
  ► MACT – Section 112(d)(6) requires EPA to review the MACT standard every 8 years considering advances in technologies and operational practices
What will the risk results show?

- The CAA requires us to determine the highest risk or the Maximum Individual Risk (MIR) expressed as “x in a million”.
- This represents the highest excess cancer risk for a receptor from the refinery source category with a 70 year period exposure period taking into account the distance from the refinery to the receptor and site-specific meteorological conditions.
- In our analysis we will identify the risk-driving HAP and specific source risk contribution.
- We also perform a demographic analysis of risk.
Potential Amendments
Rulemaking Strategy

• Make refineries subject to uniform standards
• Amend MACT and NSPS to cover the remaining emission points of concern
• Address rule gaps
• Address startup, shutdown and malfunction (SSM) provisions
What are Uniform Standards?

- EPA developed consistent emission source standards to replace existing standards across the chemical and refinery sectors.
- They apply to:
  - equipment leaks
  - storage vessels and transfer operations
  - closed vent systems and control devices (flares)
  - heat exchange systems
- Strengthen requirements considering technologies and costs
- Satisfy technology review requirements for MACT and NSPS
Other Amendments to MACT and NSPS

- Emission points not covered by uniform standards:
  - Delayed cokers
  - Fluid catalytic cracking units (FCCU)
    - NO\textsubscript{X} and PM limits
  - Reformers
- Fenceline monitoring
- GHG standards
- Other NSPS reconsideration Issues
- SSM and rule gaps
Fenceline Monitoring Approach

- Refineries contain hundreds of emission points (air toxics and criteria pollutants)
- Some emission points are well-understood and well-characterized
- Others (mostly fugitive ground-level sources) not well characterized in the inventories
  - Fugitives from process piping
  - Wastewater sources
  - PRV releases
  - Tankage
  - Unplanned or unknown emission sources (e.g., not on the books)
- Highest concentrations of these ground-level sources outside the facility likely occur by the property boundary near ground level
- Air monitoring at the property boundary can provide a direct measure of the annual average concentrations of these air toxics directly surrounding the refinery
- Provides a more certain measure of the risk from these sources than our current approach
How Does it Work?

- Passive sorbent sampling
- Two week sampling time
- Costs for one year monitoring at a refinery: ~$105,000

The one-year validation study used Carbopak X sorbent tubes, deployed by LDAR contractor, shipped to RTP for analysis.
GHG Approaches

► Energy management
  ► Framework for managing energy and promoting continuous improvement
  ► ANSI, ANSI MSE 2001:200 ISO, ISO 50001
  ► Do not guarantee GHG reductions or standards

► Intensity Benchmarking
  ► Captures whole facility
  ► Simple means of comparing emissions from different types and sizes of refineries
  ► For refineries, benchmarks based on emissions per processing intensity

► Unit/Equipment specific requirements

References:
► AVAILABLE AND EMERGING TECHNOLOGIES FOR REDUCING GREENHOUSE GAS EMISSIONS FROM THE PETROLEUM REFINING INDUSTRY, EPA, OCTOBER 2010.
Public Involvement in the Upcoming Rulemaking
<table>
<thead>
<tr>
<th>EPA Rulemaking Activity</th>
<th>Opportunities For Public Involvement</th>
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<tbody>
<tr>
<td>Phase 1. EPA begins to develop a rule</td>
<td>Check EPA’s Regulatory Development and Retrospective Review Tracker for rules of interest at yosemite.epa.gov/opei/RuleGate.nsf/. Contact and work with rule development group to provide input and community and tribal perspectives. Ask for technical assistance if you need it in order to participate in a meaningful way. <strong>Participate in EPA webinars, if offered.</strong> Ask for web address that will post updates on the rulemaking.</td>
</tr>
<tr>
<td>Phase 2. EPA develops draft rule and publishes it in the Federal Register. Public comment period is set.</td>
<td>Ask for a community meeting and/or a public hearing. Review draft rule on line, along with supporting documents. Participate in meeting and/or public hearing and submit written comments. Check EJAir web and links there to see if EPA will offer webinars on the proposal. <strong>Note:</strong> EPA plans to offer a webinar on petroleum refinery rulemaking early in the public comment period.</td>
</tr>
<tr>
<td>Phase 3. Final rule is published in the Federal Register.</td>
<td>Public has the right to seek judicial review of the final rule. Work with EPA and state to understand and participate in monitoring how well the rule is working.</td>
</tr>
</tbody>
</table>
How do I Comment on the Upcoming Rulemaking?

- To download the proposed rule before it’s published in the Federal Register (FR) go to http://www.epa.gov/ttn/oarpg/t3pfpr.html on December 10, 2011.
- It can take up to 2 weeks after the rule is signed by the Administrator for the rule to be published in the FR.
- EPA will set a public comment period, which will be published in the Federal Register.
- Comments may be submitted by one of the following methods
  - Snail mail: EPA, Mail Code 2822T, 1200 Pennsylvania Ave., NW, Washington, DC 20460 (send 2 copies)
  - Via fax: 202-566-9744
  - Via email: www.epa.gov/oar/docket.html, or A-and-r-docket@epa.gov
  - In person: EPA/DC, EPA West, Room 3334, 1301 Constitution Ave., NW. Washington DC 20460
  - Online: www.regulations.gov. Highlight “submit a comment” and add the docket (ID) number

- Docket ID number for this rulemaking is EPA-HQ-OAR-2010-0682
What Happens After I Comment?

► After the comment period closes, EPA will review every comment that was submitted on time
► Taking those comments into consideration, EPA will begin to develop the final rule
► EPA will prepare a “Response to Comments” document that describes how our final rule either
  ► takes the comment into account, or
  ► why we were unable to take the comment into account

► For more information
  ➢ Contact Brenda Shine of EPA's Office of Air Quality Planning and Standards at (919) 541-3608 or shine.brenda@epa.gov
Q & A
APPENDIX
Refinery Process Units
Crude Desalting

- Contaminants in crude oil can cause corrosion of equipment and processing problems
- Crude oil is washed with water
- Water is separated and now contains contaminants
- Largest source of wastewater at the refinery
- Largest source of benzene in wastewater
- Air emissions
  - Benzene, VOC, other air toxics
  - Source: Wastewater
  - Control Technology: Steam stripper/Biotreatment

Source: Wastewater
Catalytic Reforming

- Converts naptha-boiling range molecules into higher octane reformate
- Produces hydrogen as a byproduct that can be used in hydrotreaters or the hydrocracker
- Uses catalysts that can be regenerated

Air emissions
- CAP (CO, No\textsubscript{x}), HAP (benzene, toluene, xylene, naphthalene), VOC, dioxins (?)
- Control Technology: Scrubber
Fluid Catalytic Cracking

- Upgrades heavier fractions into lighter, more valuable products
- **Feedstocks**
  - Gas oils (from vacuum & atmospheric distillation, coker)
  - Vacuum tower bottoms
- Uses a fluidized catalyst to contact the feedstock at high temperature and moderate pressure to vaporize long chain molecules and break them into shorter molecules
- Largest source of emissions of \( SO_2 \), \( NO_x \), CO, PM, and metals at the refinery
- **Air emissions**
  - CAP (\( SO_2 \), \( NO_x \), CO, PM), HAP (metals, ammonia), VOC
  - Control Technology: Scrubber, ESP
Sulfur Recovery

- H$_2$S removal and recovery using an amine treating unit and the Claus process

► Air emissions
  - CAP (SO$_2$, NO$_x$, CO), HAP (carbonyl sulfide, carbon disulfide)
  - Control Technology: Scrubber

http://upload.wikimedia.org/wikipedia/commons/8/88/CLAUSPLANT.png

http://upload.wikimedia.org/wikipedia/commons/8/88/CLAUSPLANT.png
Thermal Processing

► Converts heavy fractions into lighter products

► Types
  ► Delayed coking
  ► Fluid coking (no emissions)
  ► Visbreaking (no emissions)
  ► Flexicoking (no emissions)

► Air emissions
  ► Delayed coking unit emits CAP (SO$_2$, NO$_x$, PM), HAP (metals), VOC
  ► Control Technology: Flares
Delayed Coking Unit

- Heavy residues are thermally cracked in a furnace with multiple parallel passes (semi-batch process), which cracks the heavy, long chain hydrocarbon molecules into gas oil and petroleum coke.
- Potentially significant source of emissions.
- Air emissions:
  - Steam vents
  - Coke drill
  - Coke pit

Note: All pressures are absolute pressures. The quench system in the upper left corner is used only when a drum is being steamed prior to de-cokeing.
Refinery Process Unit Controls
Flares

- Combustion control device used to burn waste gases in both normal and process upset conditions
Scrubbers

- Removal of material from the gas phase to the liquid phase
  - $\text{SO}_2$ removal from stack gases
  - removal of organics from vent gases
Steam Strippers

 ► A distillation process whereby gases and other unwanted organics are removed from water
   ► Benzene removal from wastewater
   ► removal of other organics from water
Electrostatic Precipitators (ESP)

► PM control device that uses an induced electrostatic charge to remove small particles from gases (similar to static electricity)
More Info on GHG
GHG Emissions from the Industrial Sector

Misc Info
Rules Affecting the Sector

- **MACT**
  - Subpart CC – Miscellaneous sources
  - Subpart UUU – FCCU, SRU, Reformer (three vents)
  - Subpart EEE - Organic Liquids Distribution
  - Subpart DDDDD - Boilers and Process Heaters

- **Benzene NESHAP**
  - Subpart FF - Benzene Waste Operations NESHAP (BWON)
  - Subparts for tanks, equipment leaks, and storage

- **New Source Performance Standards**
  - Subpart J - miscellaneous sources
  - Subpart QQQ – wastewater separators
  - Subpart GGG – equipment leaks
  - Subpart Kb – storage tanks
  - Subpart Db - boilers
Refinery Sector Emission Trends
Summary of Reconsideration Issues on NSPS Ja appendix

- EPA published a final rule on June 24, 2008 promulgating a new and more stringent NSPS.

- We received three timely petitions for reconsideration on the following issues:
  1. The definition of “modification” for flares.
  2. The definition of “flare.”
  3. The fuel gas combustion device (FGCD) sulfur limits for flares.
  4. The flow limit for flare systems.
  5. The total reduced sulfur and flow monitoring requirements for flares.
  6. The nitrogen oxide (NO\textsubscript{X}) limit for process heaters.
  7. The depressurization work practice standard for delayed coking units (DCU).
  8. The NO\textsubscript{X} limit for fluid catalytic cracking units (FCCU).
  9. The particulate matter (PM) limit for FCCU.
  10. EPA’s decision not to promulgate NSPS for GHG emissions from refineries

- We received a timely supplemental PFR that included 82 detailed issues covering six different topic areas that overlap with the previous ten issues.

- On September 26, 2008, EPA granted reconsideration and initiated a stay of Issues 1-6 and denied a stay of the effectiveness of the provisions implementing Item 7.

- On December 22, 2008, EPA proposed revisions that address Issues 1-6 and extended the stay until final action is taken.

- On December 29, 2009, EPA granted reconsideration on all remaining issues.
Refinery Process Emissions

- Crude Oil Storage
- Desalter
- Distillation Tower
  - Butane and lighter
  - Naphtha
  - Light straight run gasoline/isomerate
  - Reformate
  - Alkylation
    - Alkylate
    - Kerosene
    - Diesel
  - Fluid Catalytic Cracking Unit (FCCU)
  - FCC gasoline
- Vacuum Tower
- Delayed Coker
- Coke
- Sulfur Recovery/Tail Gas Treatment
- Sulfur
- Refinery Fuel gas
- Amine treating
- LPG
- Storage and loading
- All wastewater
- All heat exchange systems
- Equipment Leaks
- MACT 1 (CC)
- MACT 2 (UUU)
- NSPS Ja