Martinez
Refining Company

Martinez Refining Company LLC
3485 Pacheco Blvd
Martinez, CA 94553

Office 925.313.3601

www.martinezrefiningcompany.com

February 9, 2024

Dr. Philip Fine
Air Pollution Control Officer
Bay Area Air Quality Management District
375 Beale Street, Suite 600
San Francisco, CA 94104

Re: Martinez Refining Company LLC's Request for Approval of Alternative Emissions Monitoring System under Regulation 6, Rule 5-503.2

Dr. Philip Fine:

Martinez Refining Company LLC ("MRC") formally requests approval of an alternative emissions monitoring system ("AEMS") as described in the attached **Exhibit 1** for purposes of monitoring emissions of total particulate matter ("TPM") under Bay Area Air Quality Management District ("Air District") Regulation 6, Rule 5 ("Regulation 6-5"), specifically Reg. 6-5-503.2. As you are aware, over the preceding months, MRC has provided the Air District voluminous data supporting approval of the attached AEMS, including 127 source test results from the Carbon Monoxide Boilers ("COBs") that are connected to MRC's Fluidized Catalytic Cracking Unit ("FCCU"), which is subject to Regulation 6, Rule 5.

The sampled Total PM_{10} ("TPM") from the 127 source tests consisted of condensable particulate matter ("CPM") measured using US EPA Method 202 and filterable particulate matter ("FPM") measured using Method 5b as required by Regulation 6-5-604. The extensive source testing showed that the FPM portion of the TPM remains steady provided there is proper conditioning and proper FCCU electrostatic precipitators ("ESPs") operation. These source tests demonstrated that controlling appropriate parameters and keeping the ESPs operating properly ensures the lowest TPM possible to meet the 0.010 grains per dry standard cubic feet at 5% O2 on a rolling four-quarter average basis limit ("TPM Emission Limit") as required by Regulation 6-5.

However, the extensive testing also showed that the Regulation 6-5 required testing methodologies for TPM resulted in a high degree of variability at the TPM Emission Limit, and that such variability would make the required quarterly testing required in Regulation 6-5 highly variable and potentially inaccurate for compliance purposes.

To address this variability, based on scientific first principles and validated by the source testing, MRC developed the equation ("Correlation Equation") below that allows for measurement of CPM through data inputs as measured by the FCCU's online ammonia ("NH_3") and sulfur dioxide ("SO_2") analyzers.

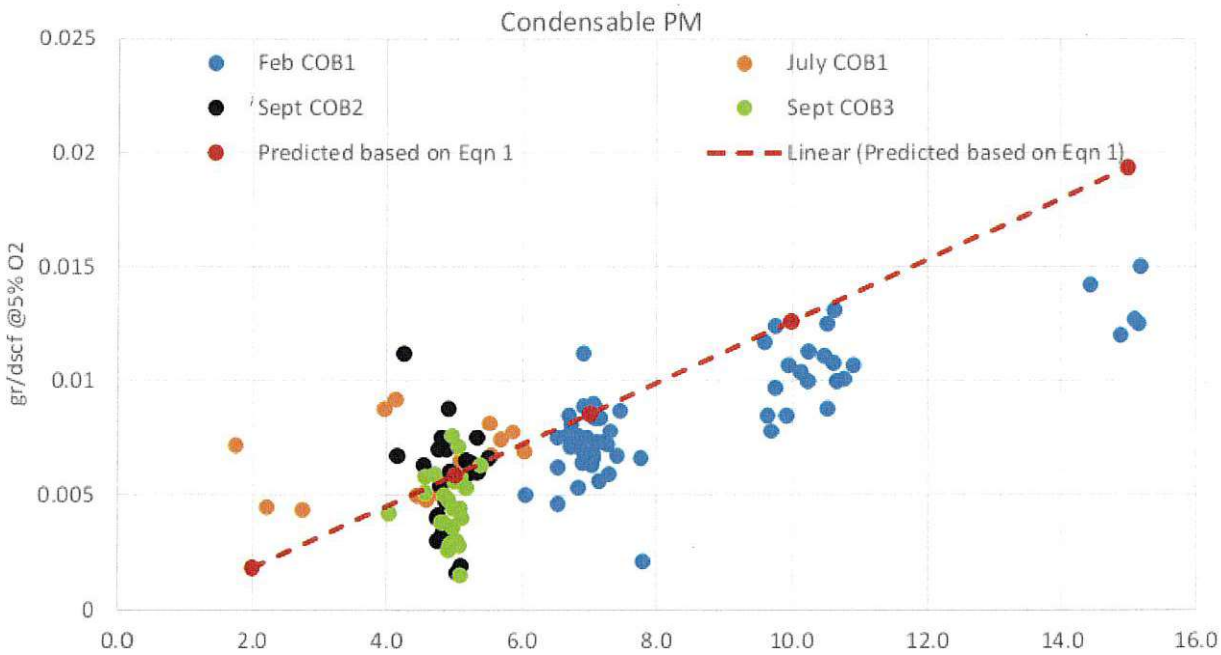
Correlation Equation

$$CPM\ gr/dscf = \left(\frac{1}{379.5}\right) * \left(\left(\frac{NH3\ ppmv}{1{,}000{,}000}\right) - \left(\frac{SO2\ ppmv}{1{,}000{,}000} * 0.03\right)\right) * \left(\frac{123.5}{1.5}\right) * 7000$$

Where:

- CPM gr/dscf = Calculated CPM at 5% O2
- 1/379.5 = ratio of moles per one dscf using the idea gas law
- NH_3 ppmv = measured NH3 concentration corrected to 5% O2 as measured by COB Continuous Emission Monitoring System ("CEMS")
- SO_2 ppmv = measured SO_2 concentration corrected to 5% O2 as measured by COB CEMS
- 1/1,000,000 = conversion from ppm to fraction
- 0.03 = ratio of sulfur trioxide ("SO_3") formed to SO_2 in stack
- 123.5 = average molecular weight between ammonium bisulfate and ammonium sulfate based on source test data which shows a ratio of 1.5 between NH_3 and SO_4. This would indicate for every one mole of ammonium bisulfate [$(NH_4)HSO_4$] there is one mole of ammonium sulfate [$(NH_4)2SO_4$]
- 1.5 = ratio between NH_3 and SO_4 based on source test data
- 7000 = conversion from pounds to grains

The following graph demonstrates the accuracy of the Correlation Equation as compared to the 127 source tests MRC conducted in developing the AEMS:



Using the Correlation Equation for CPM and MRC's historic FPM levels, the AEMS will more accurately measure compliance with Regulation 6-5's TPM Emission Limit in comparison to the methodologies required in Regulation 6-5-604. The determination of compliance with the TPM Emission Limit under the AEMS will consist of the following, which is described more fully in the attached **Exhibit 1**:

- Use of the equation above, derived from the 127 source tests conducted to date using Regulation 6-5 testing methodologies;
- Using the FCCU online NH_3 and SO_2 CEMS for each COB to acquire continuous data that would be input in Correlation Equation to determine the quarterly TPM average for the COBs;
- Incorporating a constant FPM for each COB.
- Taking the sum of the average CPM and the average FPM to determine the TPM for each COB.

Please let me know if you any questions regarding this request for approval of MRC's proposed AEMS.

Sincerely

Daniel Ingram
Refinery Manager
Martinez Refining Company LLC

<u>Exhibit 1</u>

Regulation 6: Particulate Matter, Rule 5

Alternative Emissions Monitoring System

1. General Overview.

a. This Alternative Emissions Monitoring System ("AEMS") applies for purposes of demonstrating compliance with the Bay Area Air Quality Management District ("Air District") Regulation 6: Particulate Matter, Rule 5: *Particulate Emissions from Petroleum Refinery Fluidized Catalytic Cracking Units* ("Regulation 6-5") Total PM10 ("TPM") limit of 0.010 grains per dry standard cubic feet, as currently contained in Regulation 6-5, Section 5-301.3 ("TPM Emission Limit").

b. This AEMS shall apply to the refinery located at 3485 Pacheco Boulevard in Martinez, California, that is owned and operated by Martinez Refining Company LLC ("MRC").

c. Compliance with this AEMS shall satisfy and constitute compliance with all monitoring, reporting, and recordkeeping requirements of Regulation 6-5 with respect to TPM, including without limitation the provisions of Regulation 6-5, Sections 6-5-503, 6-5-504, and the provisions 6-5-600 with respect to the TPM Emissions Limit.

2. Alternative Emissions Monitoring System.

a. This AEMS will demonstrate compliance with the TPM Emissions Limit.

b. <u>Data Collection</u>. MRC will utilize continuous emissions monitoring systems ("CEMSs") installed at the Fluidized Catalytic Cracking Unit ("FCCU") and/or the Carbon Monoxide Boilers ("COBs"), which will collect continuous data related to (i) ammonia ("NH_3") and (ii) sulfur dioxide ("SO_2").

   i. The SO_2 and NH_3 CEMSs will be certified and operated in accordance with 40 CFR Part 60, Appendix B, Performance Specifications 2, 3, and 18, Appendix F, Quality Assurance, and the District's MOP Volume V, as applicable. The annual Relative Accuracy and Field Accuracy Tests of the SO_2 and NH_3 CEMSs will meet an alternative standard of 10%.

   ii. SO_2 and NH_3 data will be measured and collected as specified in MRC's Title V Permit or monitoring plans approved by the Air District or, if none specified, then within the standard collection frequencies of the SO_2 and NH_3 CEMSs.

c. <u>Use of Data</u>. Data collected from the SO_2 and NH_3 CEMSs will be input into the "Correlation Equation" (below).

d. Correlation Equation. Pursuant to this AEMS, TPM will be calculated as the sum of the condensable particulate matter ("CPM") plus filterable particulate matter ("FPM"), as determined by the "Correlation Equation" below:

Correlation Equation

$$TPM\,\frac{gr}{dscf} = \left(\left(\frac{1}{379.5}\right) * \left(\left(\frac{NH3\ ppmv}{1{,}000{,}000}\right) - \left(\frac{SO2\ ppmv}{1{,}000{,}000} * 0.03\right)\right) * \left(\frac{123.5}{1.5}\right) * 7000\right) + FPM$$

$$CPM\,\frac{gr}{dscf} = \left(\left(\frac{1}{379.5}\right) * \left(\left(\frac{NH3\ ppmv}{1{,}000{,}000}\right) - \left(\frac{SO2\ ppmv}{1{,}000{,}000} * 0.03\right)\right) * \left(\frac{123.5}{1.5}\right) * 7000\right)$$

$FPM\,\frac{gr}{dscf} =$

COB1	*COB2*	*COB3*
0.0038	*0.0047*	*0.0059*

3. Compliance Demonstrations and Recordkeeping.

a. Implementation of this AEMS. MRC will employ the AEMS, the Correlation Equation, and relevant inputs described herein to calculate quarterly TPM averages for the FCCU.

b. Reporting. MRC will submit quarterly reports to the Air District's Air Pollution Control Officer that document TPM emissions as calculated pursuant to Section 2(d) of this AEMS, on a rolling four-quarter average basis, for the FCCU. Such reporting shall satisfy the requirements of Regulation 6-5, Section 6-5-503.

c. Recordkeeping. MRC will maintain supporting emissions data from the SO_2 and NH_3 CEMSs for a minimum of five (5) years, and shall make that information available to the Air District within thirty (30) days of a written request by the Air District for such information. Such recordkeeping will satisfy the requirements of Regulation 6-5, Section 6-5-504 with respect to the TPM recordkeeping provisions of Regulation 6-5, Section 6-5-301.3.