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**Subject: Air District Separate Statement
Valero Benicia Refinery
Stipulated Order of Abatement
Docket # 3731**

The Air District files this Separate Statement with the Hearing Board pursuant to Section 12, p. 10 of the Stipulated Order of Abatement (“SOA”) that was signed by the District and Valero on January 20, 2022, and filed with the Hearing Board on January 24, 2022. This Separate Statement provides important background to the SOA and explains why the Air District believes the SOA is an appropriate plan to address recurring violations of Air District rules.

Air District Background Statement:

The Valero Benicia Refinery was bought by Valero Refining Company – California from ExxonMobil on May 15, 2000. Valero is a Major Facility (“Title V”) petroleum refinery and is permitted with a maximum crude throughput rate of approximately 170,000 barrels of per day. Crude oil is processed through a series of complex operations at the refinery, which create various petroleum fractions that are sold to the market. The various process units operate over a wide range of temperatures and pressures.

A Notice of Violation (“NOV”) No. A58465 was issued on March 21, 2019, for a violation of Regulation 8-2-301, citing Valero for the period beginning on May 15, 2000, with no closure date.

Regulation 8-2-301 states:

***8-2-301 - Miscellaneous Operations:** A person shall not discharge into the atmosphere from any miscellaneous operation an emission containing more than 6.8 kg. (15 lbs.) per day and containing a concentration of more than 300 PPM total carbon on a dry basis.*

The NOV involves Valero’s two Hydrogen Plants (“H2U-A” and “H2U-B”; Source (S-1010), and the Naphtha Reformulation Unit (“NRU”; S-1004)) (collectively referenced herein as the “Hydrogen System”). These are process units that were part of the original construction of the Refinery.

Hydrogen is an essential component to various refining processes. It is widely used to de-sulfurize process feeds and to assist in cracking long-chain hydrocarbons to produce more desirable hydrocarbon molecules. The Valero Refinery in Benicia produces an average of 41,000 MMscf/year. Around 90% of the hydrogen is produced in the dedicated Hydrogen Unit (“H2U”). The hydrogen gas produced in the H2U is 95.5% pure hydrogen with the balance composed of 0.5% nitrogen, and

4% methane, which is exempt from Regulation 8-2-301 total carbon definition. The remaining 10% is produced as a byproduct of the NRU.

Valero's NRU is tasked with processing low-octane, heavy naphtha feeds and converting them into high-octane reformate. Reformate is a key gasoline blending component which is known to contain significant amounts of aromatic ring compounds including benzene, toluene, ethylbenzene, and xylene ("BTEX"). The process requires high temperatures and elevated pressures in the presence of hydrogen and a catalyst to "crack" long-chain hydrocarbons into shorter-chain, aromatic rings. A byproduct of the NRU process is impure hydrogen mixed with regulated air pollutants. The hydrogen being produced in the NRU is only about 87% pure hydrogen with the balance comprised of 5.3% methane, 5% C₂-C₆ hydrocarbons, and 3% nitrogen and other trace compounds.

The Valero Refinery hydrogen system is unique in the Bay Area in that the NRU hydrogen is combined with the produced hydrogen from the Hydrogen Plants before feeding a central compression facility. The H₂U and the NRU hydrogen streams are each sent to a series of hydrogen gas compressors which mix the two streams and distribute the combined stream into the hydrogen grid at ~1,900 pounds per square inch (pound) of pressure. Various process units consume this high-pressure hydrogen stream as needed and let down excess hydrogen to lower pressure grids for use in other units and processes. Due to fluctuating process demands, production of hydrogen is carefully maintained to provide a small surplus to the grid to ensure that supply is sufficient, and to avoid "starving" any hydrogen consumers of adequate hydrogen supply.

The combined hydrogen feeding the compression and distributed through the hydrogen grid averages about 90-95% hydrogen, 3.8-6.8% methane, and 0.25 to 2 % (2,500 to 20,000 ppm) Non-Methane Organic Compounds ("NMOC," often referred to as Volatile Organic Compounds ("VOCs") or Precursor Organic Compounds (POCs)). The NRU hydrogen itself averages about 5% (50,000 ppm) NMOC, some of which is BTEX.

The Hydrogen System is designed to vent excess hydrogen to atmosphere through process vent ST-302, which is located remote from the hydrogen plant itself in the hydrogen grid. The excess hydrogen venting occurs via a pressure controller on the highest-pressure header in the hydrogen grid. When the hydrogen supply from the hydrogen and reformer plants exceeds the hydrogen demand in the process consumers, the pressure control valve will vent the excess hydrogen to the atmosphere through the process vent ST-302.

Investigation:

In November of 2018, the Air District began an investigation to determine if Valero was venting hydrogen mixed with regulated air pollutants directly to the atmosphere. During the investigation, the Air District learned that Valero has been conducting

periodic sampling at their sampling station on the combined hydrogen stream for hydrocarbon content since 2003 and the sample results showed that there were elevated levels of POCs in their hydrogen line which were being vented to atmosphere.

Air District Regulation 8-2-301 Miscellaneous Operations was adopted on December 19, 1979. Section 301 was last amended on May 21, 1980. The rule is considered a “backstop” rule aimed at limiting NMOC or POC emissions from miscellaneous sources not covered by other District Rules and Regulations.

In 1976, the Air District began requiring all facilities to submit information for well-defined emission points such as stacks or chimneys. The information to be submitted with new applications to construct and are used for modelling and emissions accounting purposes. For sources that were already installed prior to 1976, the Air District requested all facilities to provide information for all existing emission points in the facility. The Air District searched for but found no documentation showing that ST-302 was a permitted emission point. Further Valero could not produce any records demonstrating that Valero had identified this emission point, ST-302 to the Air District.

In March 2019, the Air District requested and received process data from Valero. A review of the submitted process data indicates that over the 3-year look-back period (December 14, 2015 through December 13, 2018), the ST-302 vent continuously emitted over 5.6 million pounds of total carbon POCs with an average concentration of 13,350 ppm as defined in Reg. 8-2. This equates to an approximate average of 5,200 pounds (2.6 tons) per day emitted to the atmosphere over the 3-year time period examined.

Table 1 below summarizes the total carbon emissions from ST-302. The results are based upon flow data calculated off valve position and NMOC concentration data obtained from Valero’s weekly sample results for the 3-year lookback period.

Table 1 – Survey Response #3 H2P017 Total Carbon Emissions

| Date Range | Reg 8-2 Average NMOC Concentration (ppm) | Average Vent Flow (SCFD) | Reg 8-2 NMOC Mass Emissions (tons) |
|-------------------|------------------------------------------|--------------------------|------------------------------------|
| 12/14/15-12/13/16 | 19,148 | 2,707,275 | 1,036 |
| 12/14/16-12/13/17 | 13,545 | 4,326,304 | 1,538 |
| 12/14/17-12/13/18 | 7,370 | 2,295,304 | 255 |
| | | Total = | 2,829 |

The 3-year look-back data showed that mass emissions were around 1,036 tons in 2016, 1,538 tons in 2017, and 255 tons in 2018. POC emissions were over the 15 lbs./day and 300 ppm concentration limit all three years.

Table 2 below summarizes the hydrogen venting emissions estimated by the Air District for the period of 2003 through 2020.

Valero has provided detailed calculations for the estimates of the 8-2 carbon emissions to the Air District. POC and toxic air contaminant (“TAC”) emission estimates have also been included. POC emission estimates are based on detailed weekly vent stream composition data Valero provided for 2013 through 2020 and the Valero mass emission calculations. For the period of 2003 through 2012, the detailed weekly or monthly vent stream composition data Valero provided was used to estimate emissions using the same mass emissions calculation methodology Valero used for the 2013 through 2020 mass emission estimates.

In May of 2019 and continuing, the Air District and Valero collected samples from Valero’s hydrogen stream. The purpose of the sampling was to see if there were any TACs of BTEX compounds as listed in District Regulation 2, Rule 5 being emitted out of the hydrogen vent along with the POCs which were already quantified. All samples were taken to an independent laboratory for analysis. Results of the testing showed that there were again detectable concentrations of POC and detectable concentrations of BTEX compounds. Valero has provided BTEX lab analytical data summaries or reports for weekly samples starting in October 2019. Results are both higher and lower than the May/June 2019 sample averages. Sufficient information was not provided by Valero for Air District validation, so the results are not used in the emission estimates. Valero has not provided any BTEX lab analytical reports for venting that occurred during 2003 through 2018.

Table 2 - Summary of Valero ST-302 Hydrogen Venting Emissions 2003 through 2020

| CY | ST302 | Total 8-2 Carbon | | Total POC | | Benzene | Ethylbenzene | Toluene | Xylenes |
|------------------------|---------------|-------------------|--------------|-------------------|---------------|---------------|---------------|----------------|---------------|
| | MMscf | lbs | tons | lbs | tons | lbs | lbs | lbs | lbs |
| 2003 | 414.0 | 2,183,855 | 1,092 | 2,656,719 | 1,328 | 3,748 | 893 | 7,599 | 2,763 |
| 2004 | 333.2 | 1,146,268 | 573 | 1,397,461 | 699 | 3,016 | 719 | 6,116 | 2,224 |
| 2005 | 100.6 | 245,225 | 123 | 298,929 | 149 | 911 | 217 | 1,846 | 671 |
| 2006 | 63.2 | 197,280 | 99 | 242,204 | 121 | 572 | 136 | 1,159 | 421 |
| 2007 | 215.5 | 288,269 | 144 | 329,102 | 165 | 1,950 | 465 | 3,954 | 1,438 |
| 2008 | 273.8 | 1,198,433 | 599 | 1,458,012 | 729 | 2,478 | 591 | 5,025 | 1,827 |
| 2009 | 214.1 | 224,440 | 112 | 273,866 | 137 | 1,938 | 462 | 3,929 | 1,429 |
| 2010 | 552.8 | 1,459,327 | 730 | 1,783,810 | 892 | 5,004 | 1,193 | 10,146 | 3,689 |
| 2011 | 206.7 | 287,821 | 144 | 351,582 | 176 | 1,871 | 446 | 3,793 | 1,379 |
| 2012 | 195.4 | 663,168 | 332 | 802,582 | 401 | 1,768 | 421 | 3,585 | 1,304 |
| 2013 | 299.1 | 788,064 | 394 | 802,582 | 470 | 2,708 | 645 | 5,490 | 1,996 |
| 2014 | 401.7 | 679,170 | 340 | 822,209 | 411 | 3,636 | 867 | 7,372 | 2,680 |
| 2015 | 656.7 | 1,159,426 | 580 | 1,407,503 | 704 | 5,945 | 1,417 | 12,053 | 4,383 |
| 2016 | 982.7 | 2,044,739 | 1,022 | 2,480,704 | 1,240 | 8,895 | 2,120 | 18,036 | 6,558 |
| 2017 | 1364.2 | 3,023,303 | 1,512 | 3,664,625 | 1,832 | 12,348 | 2,943 | 25,038 | 9,104 |
| 2018 | 847.3 | 523,640 | 262 | 640,316 | 320 | 7,670 | 1,828 | 15,551 | 5,654 |
| 2019 | 464.1 | 566,485 | 283 | 680,058 | 340 | 4,201 | 1,001 | 8,518 | 3,097 |
| 2020 | 43.8 | 169,941 | 85 | 193,344 | 97 | 396 | 94 | 804 | 292 |
| Total 2003-2020 | 7628.7 | 16,848,854 | 8,424 | 20,285,607 | 10,211 | 69,054 | 16,459 | 140,014 | 50,910 |

The Air District has issued various NOV's to Valero related to the Hydrogen System and this SOA. Those NOV's are set forth in Table 3:

Table 3 - Valero Refinery - Notices of Violation Issued

| NOV# | Source | Regulation | Comment |
|--------|---------------------------------|--------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| A58465 | S-1010 HYDROGEN PLANT | 8-2-301 | A person shall not discharge into the atmosphere from any miscellaneous operation an emission containing more than 6.8 kg. (15 lbs.) per day and containing a concentration of more than 300 PPM total carbon on a dry basis. |
| A59512 | S-1004 CATALYTIC REFORMER | 8-18-401.2 8-18-402.1 | <u>8-18-401.2 Inspection:</u> Failure to inspect quarterly all valves, pressure relief devices, pumps or compressors subject to this Rule. <u>8-18-402 Identification:</u> Failure to identify all valves, connectors, pressure relief devices, pumps and compressors subject to the regulation in their database. |
| A59627 | S-1004 CATALYTIC REFORMER | 8-18-402.1 | Same as above |
| A59609 | S-1010 HYDROGEN PLANT | 8-28-406 8-28-407 | <u>8-28-406 Monitoring System Demonstration Report:</u> Failure to submit a Monitoring System Demonstration Report that identifies each pressure relief device subject to this Rule. <u>8-28-407 Process Unit Identification Report:</u> Failure to submit a report listing all process units equipped with atmospheric PRDs, all associated pressure relief devices subject to this Rule identified in accordance with Section 8-28-404. Valero failed to identify 27 atmospheric PRD's |
| A59513 | S-1010 HYDROGEN PLANT | 1-441 | <u>1-441 Right of Access to Information:</u> Failure to provide information requested by the APCO shall be provided as soon as reasonable possible, but in any event within 30 days from the date of receipt of the request. |

In July of 2019, the Air District Engineering Division performed a Health Risk Assessment (“HRA”) based on sampling results and issued its findings in late August of 2019. Due to the results of the HRA and the volume of pollutants being continuously emitted from ST-302 vent, the Air District sent Valero an information request letter pursuant to Air District Regulation 1, Section 441, *Right of Access to Information*: In late December 2019 Valero finally fulfilled the information request after repeated requests to gather additional data for the investigation.

In early October 2019, a meeting was held with Valero's Management, and they informed the Air District of the interim testing steps they had taken to test a bypass line to minimize atmospheric venting at ST-302 by installing a "jump over" line to redirect the emissions "during normal" operations. A permit application was submitted and approved. On October 17, 2019, after months of testing the viability of a bypass pipeline, Valero installed a permanent bypass pipeline and began routing this high-pressure hydrogen excess directly to the low-pressure grid instead of venting the excess off to atmosphere. However, anytime there is a unit startup, shutdown, or malfunction ("SSM"), large hydrocarbon excess mass emissions events from ST-302 will occur.

In late May 2020, the Air District held another meeting with Valero to discuss the ongoing violation. Valero reported that the emissions to the atmospheric vent had been reduced since the installation of the jump-over line and that they were still trying to determine a solution which would comply with Regs. 8-2, 8-28, and the proposed Reg. 13-5 hydrogen venting rule. Data presented showed that the vent had emitted 7,828 lbs. of NMOC from January 1 to May 30, 2020, which equates to a daily average of 55 lbs./day or 9.6 tons/year over that period. This is a large reduction in emissions when compared to the 2015-2018 data which indicated a 2.6 tons per day emission rate of total carbon, but still a significant amount of emissions for a five-month period. Therefore, this SOA was agreed upon by the parties because compliance will not be achieved until the next refinery-wide maintenance turnaround.

The harm caused by this alleged violation, which led to NOV A58465, was the excess release of POCs to the atmosphere. POCs are non-methane hydrocarbons that contribute to the formation of ground-level ozone, which has negative effects on human health and the environment, especially on hot, sunny days. The total POC emissions associated with this violation between December 14, 2015 and December 31, 2020 were calculated by Valero and verified by BAAQMD to be 3,266 tons. In addition, a portion of the POCs emitted to atmosphere with this violation consist of BTEX compounds that on certain days exceed health risk assessment standards and daily federal reportable quantities.

Regards,

Edward Giacometti
Manager of Compliance and Enforcement