Bay Area Air Quality Management District
939 Ellis Street
San Francisco, CA 94109

Staff Report

Further Study Measure 9
Refinery Wastewater Treatment Systems

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I. EXECUTIVE SUMMARY

Each of the five Bay Area refineries has a system that collects and treats wastewater from refinery processes and operations prior to discharge as effluent into San Francisco Bay Area waters. Volatile organic compounds (VOC) are introduced into the wastewater system through refinery processes and are released into the atmosphere through volatilization from open tanks/ponds. The District regulates VOC emissions from wastewater collection and separation systems through Regulation 8, Rule 8. Currently, Regulation 8, Rule 8 requires the control of emissions and enclosure of all separator tanks, oil-water separators effluent channels, junction boxes, air-flotation units, and sludge-dewatering units.

In 2001, the District adopted the Revised San Francisco Bay Area 2001 Ozone Attainment Plan to attain the national one-hour ozone standard (the 2001 Ozone Plan). At that time, the District lacked adequate data to determine whether the imposition of controls or adoption of more stringent standards on then-uncontrolled components of a petroleum refinery's wastewater system would reduce volatile organic compound (VOC) emissions significantly at each of the five refineries. Accordingly, the District, jointly with the California Air Resources Board (CARB) undertook a two-phased study to investigate the wastewater collection and treatment systems components (Further Study Measure 9, "Refinery Wastewater Treatment Systems"). The District completed the first phase of the study in 2004, focusing primarily on wastewater collection systems that consist of drains from process units piped to mechanical separation, such as oil-water separators. On September 21, 2004, the District amended Regulation 8, Rule 8 to impose, among other measures, a more stringent vapor leak standard of 500 parts per million (ppm) on controlled wastewater collection systems components and oil-water separators and the requirement of a wastewater collection system inspection program. The District estimates that the September 2004 amendments to Regulation 8, Rule 8 will reduce VOC emissions by 2.1 tons per day (tpd).

This staff report describes the outcome from the study's second phase, which investigated whether there are potential significant VOC emissions reductions to be achieved from control of the refineries' secondary wastewater treatment components. Each refinery utilizes a treatment system that consists of various components, including oil-water separators, dissolved air/nitrogen flotation units, biological treatment units, clarifiers, and equalization ponds. To determine emissions from the uncontrolled units, District and CARB staff implemented a field investigation utilizing state-of-the art sampling and measurement techniques to collect direct vapor measurements from two of the refineries and wastewater samples from all five refineries. The field collected data were used in conjunction with refinery-specific process information to support development of a refinery-specific emission model for all five refineries. The District and CARB staff modeled the emissions from wastewater treatment systems because sampling at the large, open treatment units was physically infeasible, except at certain locations.

The District estimates a total of 0.24 tons per day (tpd) of VOC emissions from the uncontrolled treatment units located at the five refineries. Of that total, the dissolved air flotation unit vents and channel/weir at ConocoPhillips emit approximately 0.11 tpd. At the remaining four refineries, the biological treatment units cause most VOC emissions because of turbulent conditions in the units. The District selected for evaluation several control technologies known to reduce VOC emissions reliably and effectively from refinery wastewater streams. Staff considered installation of steam strippers and liquid phase carbon adsorption units to reduce the VOC content in the wastewater stream prior to its entry to secondary treatment and installation of aluminum domes over biological treatment tanks to reduce the wastewater stream's exposure to the atmosphere. District staff investigated the technical feasibility of installing these technologies at the specific refineries, the potential emission reductions to be achieved from these technologies, and the costs to install, operate and maintain them.

Assuming a VOC emissions reduction of 0.14 tpd, cost-effectiveness based on the installation of either a steam stripper or liquid phase carbon adsorption unit was estimated from $1.42 million to $1.35 million per ton of VOCs removed, respectively. For the doming option, only ConocoPhillips and Valero refineries have their treatment systems in tanks that are suitable for doming. The other refineries have bermed aeration lagoons and ponds that cannot accommodate a dome. The estimated cost-effectiveness to reduce emissions by doming the tanks is $25,000 per ton of VOCs reduced based on a total reduction of 0.025 tpd, not including the costs of vapor control and construction of additional infrastructure to support the domes.

Since the beginning of this study, the District and CARB have invited representatives from the five Bay Area petroleum refineries, the Western States Petroleum Association (WSPA), the Regional Water Quality Control Board, Communities for a Better Environment (CBE), and outside environmental consultants to participate in technical working group meetings. The staff convened four working group meetings in 2005 to discuss the phase two work plan, proposed emissions models, sampling plan and methodology, and the control technologies and associated costs. In addition, the District held a Public Workshop on October 27, 2005 to solicit comments from the public on the District's determination not to amend the existing regulation. Summaries of public comments, with the staff's responses are included in Attachment A.

District staff has concluded that the estimated emissions reductions of 0.14 tpd to be achieved from additional controls of refinery wastewater treatment systems are not significant and that pursuant to Further Study Measure 9, additional amendments to Regulation 8, Rule 8 are not warranted at this time. The current costs to install, operate and maintain what are generally known as the proven wastewater treatment system control technologies and the uncertainty of their compatibility with the refineries' existing treatment systems do not render additional controls viable at this time. Therefore, at this time, the District staff does not recommend any further rule amendments to existing Regulation 8, Rule 8.

II. BACKGROUND

The District committed in its Revised San Francisco Bay Area 2001 Ozone Attainment Plan to examine whether the imposition of controls or adoption of more stringent standards on uncontrolled components of a petroleum refinery's wastewater system would reduce VOC emissions significantly at each of the five refineries. There are five petroleum refineries located within the District, which are owned and operated by Chevron, ConocoPhillips, Shell, Tesoro, and Valero. Each petroleum refinery has a unique configuration and system for collection and treatment of wastewater from refinery operations and processes. At the time of adoption of the 2001 Plan, the District lacked adequate data about each refinery to confirm whether there were significant VOC emissions from the refineries' wastewater systems.

Accordingly, the District and the California Air Resources Board (CARB) undertook a two-phased study to investigate the wastewater collection and treatment systems components (Further Study Measure 9, "Refinery Wastewater Treatment Systems"). In 2004, the District completed the study's first phase, which focused primarily on wastewater collection systems. Wastewater collection systems consist of drains from petroleum operations and process units that collect and transport effluent to the primary treatment systems. As a result of the study's first phase, District staff proposed amendments to the District's Regulation 8, Rule 8 pertaining to wastewater systems. The District's Board of Directors adopted the proposed amendments on September 21, 2004.

In 2005, the District and CARB staff commenced phase two of the study, pertaining to wastewater treatment processes. This Staff Report presents staff's findings.

A. Description of Petroleum Refinery Wastewater Treatment Systems

Each Bay Area petroleum refinery collects wastewater from various refinery operations and transports it as influent to its wastewater treatment system. Figure 1 presents a simplified generic petroleum refinery wastewater treatment system. Each of the Bay Area refineries has a unique combination and configuration of some or all of the treatment processes shown in Figure 1.

Generally, primary wastewater treatment consists of oil-water separators and dissolved nitrogen flotation (DNF) or dissolved air flotation (DAF) units. An oil-water separator removes suspended solids and sludge, oil, and water from the influent. In the calm environment of the oil-water separator tanks, heavy organics and solids settle to the bottom and are removed as sludge or solids.

Lighter oils and organics float to the surface and are removed by mechanical skimmers and sent to slop oil tanks. In the slop oil tanks, the slop oil is treated for recycling or de-watered for disposal. The wastewater at all of the refineries undergoes oil-water separation. Regulation 8, Rule 8 requires enclosure of oil-water separators, oil-water separator effluent channels, and slop oil tanks.

Typically, the oil-water separator effluent is piped directly to DNF or DAF units. In the DAF and DNF units, air or gas percolates through the wastewater stream, causing floating oils and other floating liquid organic materials to float to the surface for removal by skimmers to slop oil tanks. Regulation 8, Rule 8 requires enclosure of DAF and DNF units to reduce VOC emissions. Shell, Tesoro, and Valero petroleum refineries operate DNF units. Vapor recovery systems abate VOC emissions from the DNF units. The ConocoPhillips petroleum refinery operates a four-cell DAF unit, which includes four uncontrolled, passive atmospheric vents to prevent the buildup of oxygen. A grated channel and a weir (channel/weir) transport the wastewater effluent from the DAF unit to secondary treatment. The Chevron petroleum refinery operates neither a DAF unit nor a DNF unit in its treatment system. The oil-water separator effluent is piped directly to the refinery's secondary treatment units.

Secondary treatment commences where wastewater leaves the dissolved gas flotation units or, in the case of the Chevron refinery, where the wastewater leaves the oil-water separator, and enters either equalization tanks or begins biological treatment. Equalization, which reduces fluctuations in the wastewater flow rate and organic content, results in a more uniform effluent quality for biological treatment. ConocoPhillips and Shell refineries utilize dedicated equalization tanks while Valero, Tesoro, and Chevron refineries pipe their effluent to biological treatment units. The Tesoro refinery pre-treats the wastewater (after dissolved gas flotation) by processing it through an air stripper to reduce hydrocarbon and volatile concentrations.

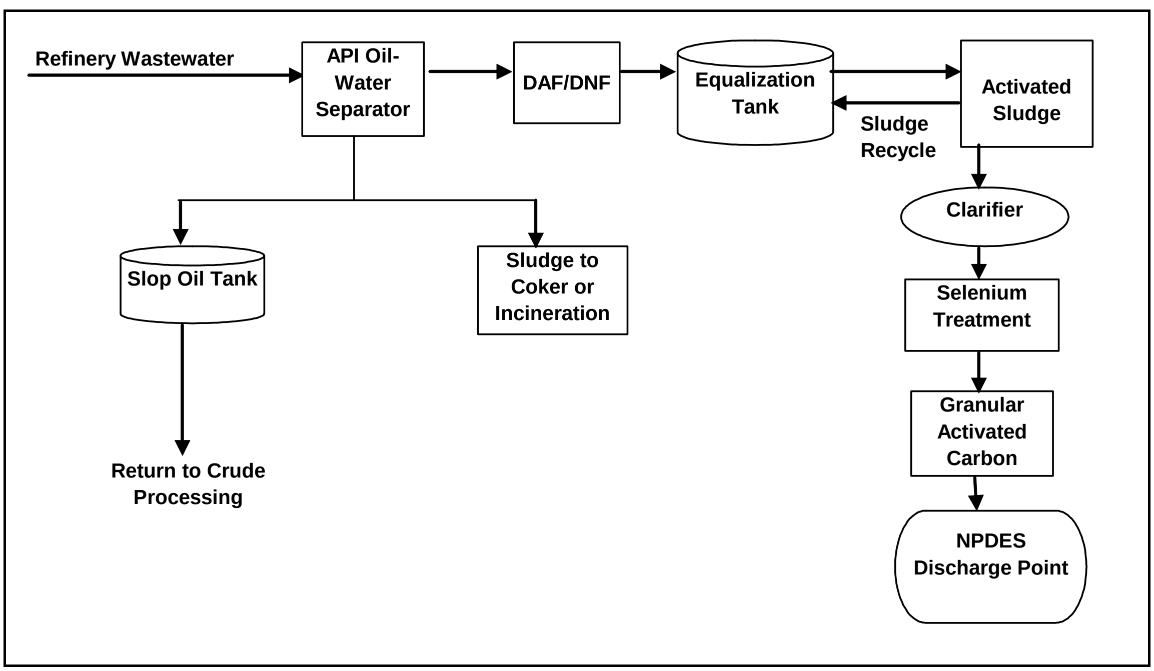
Biological treatment is the traditional method to remove dissolved and/or suspended organic and inorganic compounds from wastewater. Microorganisms used in the treatment feed on, and remove, the majority of the organic materials from the wastewater. Chevron and Tesoro biologically treat their wastewater in large, open and aerated, uncontrolled bermed ponds and lagoons that also act as equalization ponds. The ConocoPhillips and Valero refineries utilize activated sludge as their biological treatment process, which occurs in constructed tanks. Shell refinery's biological treatment includes activated sludge in an open, uncontrolled tank, as well as an aerated pond open to the atmosphere.

All of the Bay Area refineries utilize a combination of additional secondary processes to treat the effluent prior to discharge. Such processes include: flow controls; pH balancing; the addition of nutrients to protect the microorganisms; selenium removal; carbon filtration; and water-enhanced wetland treatment. The treated effluent must meet all applicable California Regional Water Quality

Control Board standards prior to discharge into San Francisco Bay Area waters.

During primary and secondary wastewater treatment operations, most VOC emissions occur as a result of volatilization through passive or active systems. Passive volatilization (i.e., diffusion) of VOCs occurs in open tanks, ponds, lagoons, and channels without aerators, where petroleum or partially-processed petroleum products in wastewater are much higher than ambient concentrations in air and thus, organics volatilize into air in an attempt to reach equilibrium between liquid and vapor phases. Active volatilization (i.e., convection) occurs when air flows or is injected into the water surface through mechanical energy, sweeping organic vapors from the water surface into the air. Active volatilization occurs in aerated portions of the biological treatment units and in the activated sludge tanks. Factors that affect the extent of volatilization include the physical properties of the contaminants (such as vapor pressure, Henry's Law Constant, solubility, and the gas/liquid partition coefficient), temperature of the wastewater, and the design and operation of the treatment units (such as the surface area, presence of foam, and turbulence).

Figure 1: Simplified Refinery Wastewater Treatment System



Source: U.S. EPA

B. Regulation 8, Rule 8

The District regulates emissions from wastewater collection and separation systems in Regulation 8, Rule 8: Wastewater Collection and Separation Systems. The regulation requires refineries to enclose and control emissions from all wastewater collection system components: wastewater separators, wastewater separator forebays and oil-water separator effluent channels; air flotation units; and sludge-dewatering units. These units must have a solid, gasketed, fixed cover; a floating vapor-tight cover; or abatement by a vapor recovery system that emits less than 1,000 parts per million (ppm) (expressed as methane).

The District amended Regulation 8, Rule 8 in September 2004, following completion of the CARB and District study of emissions from wastewater collection systems (drains, manholes, and junction boxes). The study, part one of a two-part study, determined that potentially significant emission reductions could be achieved from installing controls on refinery wastewater collection systems. Accordingly, the District amended Regulation 8, Rule 8 to require petroleum refineries to either install controls on, or institute a rigorous inspection and maintenance plan for, all wastewater collection systems components (drains, manholes, and junction boxes). Controls include installation of water seals or equivalent control measures. The inspection and maintenance plan requires that any uncontrolled wastewater collection component that is found not to be vapor-tight during three inspections within a five-year period must be equipped with a water seal or equivalent control. The District also amended the definition of "vapor-tight" to describe leaks of less than 500 ppm (expressed as methane) above background measured at the interface of the component.

The District estimates the September 2004 amendments to Regulation 8-8 will reduce VOC emissions by 2.1 tons per day (tpd).

C. Applicable Federal Regulations

The federal New Source Performance Standards (NSPS) for VOC Emissions from Petroleum Wastewater Systems (40 C.F.R. Part 60, Subpart QQQ) and the National Emission Standards for Hazardous Air Pollutants (NESHAP) for Benzene Waste Operations (40 C.F.R. Part 61, Subpart FF) regulate the emissions of VOCs and toxic compounds from petroleum refinery wastewater systems.

The above-referenced New Source Performance Standards established performance standards for oil-water separators, individual wastewater collection drain systems, closed vent systems and control devices. Petroleum refineries must inspect and maintain their wastewater systems regularly. Any control device shall operate with an efficiency of 95 percent or greater to reduce VOC emissions vented to them. These standards apply to the five Bay Area petroleum refineries.

The Benzene NESHAP regulations apply to refineries that emit 10 tons per year (tpy) of any one hazardous air pollutant (HAP), or 25 tpy or more of total HAPs. All of the Bay Area refineries are subject to the Benzene NESHAP regulations. The regulations require petroleum refineries to use maximum achievable control technology (MACT) to control emissions of benzene from waste operations, including certain wastewater systems. The five Bay Area refineries use either carbon adsorption or the collection and venting of wastewater gases to the refinery flare system (vent flap system) as their MACT to control benzene emissions from wastewater systems. Biological treatment units are not subject to these requirements if the benzene concentration in the influent entering the unit is less than 10 ppm by weight. District inspectors conduct unannounced inspections of the refineries' wastewater systems to ensure compliance with the Benzene NESHAP regulations.

III. SUMMARY OF TECHNICAL REVIEW

The goal of phase two of the study was to determine whether there were significant potential VOC emissions from the petroleum refineries' wastewater treatment systems. The unique design of each refinery presented a challenge to District and CARB staff in conducting this study. It was infeasible to collect samples at each refinery to fully characterize emissions from the individual process units because they are large and open to the atmosphere. Instead, District and CARB staff modeled the emissions from each process unit by replicating each refinery's treatment system and calibrating the emissions based on direct vapor measurements.

Set forth below is a summary of the District and CARB modeling approach, the quantification of VOC emissions from the refineries' wastewater treatment operations, and the evaluation of the effectiveness of selected, known control measures to reduce emissions from wastewater streams at the five refineries.

A. Evaluation and Quantification of Emissions

1. TOXCHEM+ Emissions Modeling

Measuring air emissions from large and open treatment units is extremely difficult, if not impossible. Standard source test methods are infeasible because these units are not enclosed and the emission "points" can be several acres in area. In addition to the sampling constraints, the lack of sufficient walkways and piers along the perimeter of the lagoons and ponds limited accessibility and precluded the possibility of collecting samples from the shoreline. An alternative method was to estimate VOC emissions from treatment units by using modeling techniques that incorporate a set of complex mathematic equations to simulate real-life conditions. The advantage of modeling is that a user can develop refinery-specific treatment systems utilizing a combination of site-specific process conditions and default parameters based on studies conducted on similar systems.

District and CARB staff selected the state-of-the-art TOXCHEM+ empirical model to estimate VOC emissions from each refinery's wastewater treatment system. The TOXCHEM+ model is an EPA-approved model designed to quantify emissions from wastewater treatment systems and provides a method to comprehensively evaluate the fate and transport of multiple organic compounds in wastewater during treatment.

To improve the accuracy of the modeling, District and CARB staff collected a representative subset of direct vapor measurements from treatment units at two of the refineries (Valero and ConocoPhillips) that the staff determined were the probable sources of a refinery's highest VOC emissions. Vapor measurements were collected in accordance with EPA's surface isolation emission flux chamber technology. The flux chamber technology is a validated EPA sampling approach for measuring the mass of contaminants that volatilizes from a surface area over time.

In addition to the vapor measurements, the District collected wastewater grab samples at the same locations as that of the flux chamber sampling, the purpose of which was to estimate the mass transfer of hydrocarbons that volatilize into the atmosphere from wastewater.

The District also collected influent wastewater samples at the entry to the biological treatment units and at the point of discharge into San Francisco Bay Area waters and used the sampling data as inputs into the TOXCHEM+ model runs for each refinery's process units. The model calculated potential emissions from each process unit, using a single gasoline range compound that was representative of each refinery's wastewater stream component.

Finally, the District measured emissions from the ConocoPhillips DAF vents. The District conducted a source test on the four DAF vents at ConocoPhillips by measuring the volumetric flow rate and individual chemical concentration emitted from each vent. The vent-specific VOC emissions were estimated by multiplying the sum of the individual non-methane hydrocarbon concentrations by the vent flow rates.

2. Emissions Estimates

The District has estimated that the uncontrolled secondary treatment units at all of the refineries and the uncontrolled primary units located at ConocoPhillips (i.e., DAF vents, channel/weir) emit a total of 0.24 tons per day (tpd) of VOCs (see Table 1). Of that total, ConocoPhillips contributes approximately 0.11 tpd. At four of the refineries, most VOC emissions occurred in the biological treatment units, which include activated sludge tanks. The District attributes the emissions to the volatilization that results from turbulent conditions. The open equalization ponds and clarifiers at all of the refineries had negligible emissions.

It is known that modeling emission estimates have some inherent uncertainties because mathematic equations approximate real life conditions. For example, a model computes a single concentration value for a component, but actual emissions of a component in the system can vary temporally, spatially, and seasonally. Indeed, the District calibrated the TOXCHEM+ model based on direct vapor measurements collected on a single day of sampling at ConocoPhillips and Valero to estimate the VOC emissions from the biological treatment units and clarifiers at the Shell, Tesoro, and Chevron refineries. However, the District verified the estimations, by comparing the wastewater sample results collected from the point of discharge at these three refineries to the predicted discharge concentrations from TOXCHEM+. Using actual vapor emissions measured from ConocoPhillips and Valero refineries improved the accuracy of the estimated emissions. Actual VOC emissions are likely to be even lower than estimated emissions from the TOXCHEM+ model as calibrated for the specific refineries.

Table 1: VOC Emission Estimates for Refinery Wastewater Treatment Units

Refinery	DAF Vents (tpd)	Effluent Channels/ Weir (tpd)	Biological Treatment Units (tpd)	Equalization Ponds and Clarifiers (tpd)	Total Estimated VOC Emissions (tpd)
ConocoPhillips	0.083	0.022	0.0026	*	0.108
Shell	n/a	n/a	0.023	0.0004	0.023
Tesoro	n/a	n/a	0.049	*	0.049
Valero	n/a	n/a	0.023	*	0.023
Chevron	n/a	n/a	0.033	*	0.033
TOTAL	**0.083**	**0.022**	**0.131**	**0.0004**	**0.236**

Note:
n/a: not applicable, these units are not presented at the refinery
*: the model estimated that emissions from these process units were negligible (less than 5×10^{-10} tpd)

EPA has determined that the accuracy of the flux chamber sampling test method to measure vapor emissions is +/- 30%. The model could be refined even further by using other gasoline range compounds or using an alternative fate and transport model. However, District and CARB staff anticipates that such refinements would only increase the accuracy of the total estimated emissions to within a range of less than +/- 15%, which falls within the range of accuracy of the flux chamber test method. Moreover, further refinements introduce additional, unquantifiable uncertainties to the emission estimates.

B. Identification and Evaluation of Potential Controls

As shown above, biological treatment units and the ConocoPhillips DAF vents generate the majority of VOC emissions during secondary treatment. In general, petroleum refineries can reduce VOC emissions from their secondary treatment processes either by removing VOCs from the wastewater stream prior to secondary treatment or by reducing the stream's exposure to the atmosphere during secondary treatment. Accordingly, District staff investigated several control measures that are designed to achieve one or the other results. The District reviewed reports and studies on wastewater treatment operations and found that steam stripping and liquid phase carbon adsorption were the most reliable, proven, and commonly-used methods to reduce VOCs from wastewater streams. These controls could also reduce VOC emissions from the ConocoPhillips channel/weir depending on their placement. The District evaluated these two control technologies, the results of which are provided in this Staff Report.

The District also evaluated the use of membrane separation and chemical oxidation to reduce VOCs concentrations in the wastewater stream prior to, or during, biological treatment. The District determined that both of these measures were ineffective. Membrane separation is sensitive to fluctuations in the VOC content in the wastewater stream and hydrocarbons in the wastewater would de-activate particular catalysts used in chemical oxidation. The District also evaluated the installation of high-efficiency oil-water separators to reduce a stream's VOC content prior to secondary treatment. The results of that evaluation are also included in this Staff Report.

Last, the District identified installation of aluminum dome covers on activated sludge tanks as a method to reduce exposure of VOCs to atmosphere during biological treatment. This option is technically feasible at the ConocoPhillips and Valero refineries, which utilize activated sludge treatment in constructed tanks, and it is evaluated in this Staff Report.

Steam Stripping

Steam stripping is a proven technology that removes volatile organic compounds from the wastewater stream prior to secondary treatment. Steam stripping removes organic compounds by placing the steam in direct contact with the wastewater. A typical steam stripping system is shown in Figure 2. Wastewater flowing down the steam stripper column comes into contact with the steam flowing up the column. The steam's heat vaporizes organic compounds in the stream. The vaporized organic compounds and uncondensed steam flow out the top of the column and are converted to liquid in an overhead condenser. That liquid flows to a decanter, where the organic compounds are captured on the liquid's surface and are either recycled or incinerated for heat recovery. The treated wastewater is transported from the bottom of the steam stripper to the secondary treatment system.

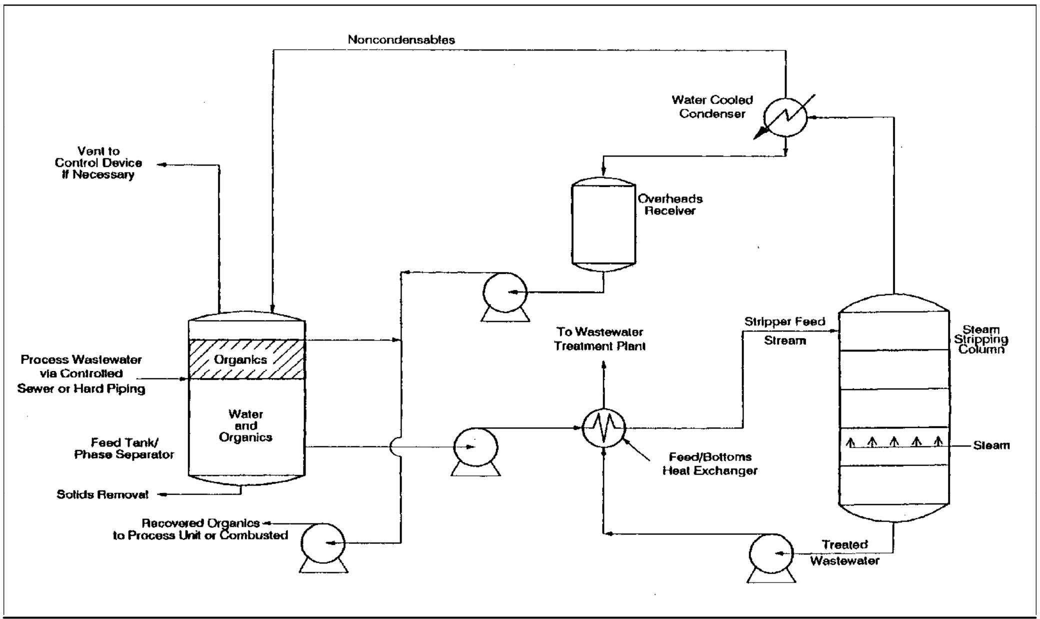
The efficiency of a steam stripper to remove VOCs ranges from 90 to 99 percent[1]. The VOC removal efficiency varies based upon the volatility and solubility of the particular volatile organic compounds in the stream. Steam

[1] Highly volatile compounds that have Henry's Law Constant greater than 1×10^{-3} atm-m^3/mole are reduced by 95 to 99 percent. Removal efficiencies decrease to 90 to 95 percent for medium volatility compounds that have Henry's Law Constant between 1×10^{-5} and 1×10^{-3} atm-m^3/mole.

strippers require proper venting to a secondary control device to ensure optimal operation. Steam stripping is effective at removing the majority of petroleum-related volatile compounds, including benzene, ethylbenzene, toluene, and xylenes, from a refinery's wastewater stream.

This control technology requires monitoring to assure optimal operation.

Figure 2: Typical Steam Stripper Design



Source: U.S. EPA

Liquid Phase Carbon Adsorption

Liquid phase carbon adsorption may be used as a stand-alone control device and as a secondary control device to reduce VOC emissions from the gas-phase streams from a steam stripper. Liquid phase carbon adsorption utilizes "activated" carbon, i.e. carbon that has been processed to produce a porous structure. As wastewater passes through the activated carbon bed, organic compounds in the stream are adsorbed to the carbon and are removed.

Two types of liquid phase carbon adsorption are the fixed bed and moving bed systems. The fixed-bed system is ideal for low-flow wastewater streams where multiple carbon beds can be taken off-line and regenerated. A moving bed carbon adsorption system is in continuous operation with wastewater entering from the bottom of the column and regenerated carbon introduced from the top. Spent carbon is continuously removed from the bottom of the bed.

As a stand-alone control device, liquid phase carbon adsorption typically treats wastewater streams containing low concentrations of nonvolatile compounds and high concentrations of non-degradable compounds, such as polychlorinated biphenyls (PCBs). The removal efficiency ranges generally from 90 to 99 percent. This device is also suitable as a secondary control device to reduce VOC emissions from the feed tank of the steam stripper.

Refineries must continuously monitor liquid phase adsorption equipment to ensure that the carbon beds are regenerated.

External Roof Tanks

An external floating roof for storage tanks is typically used to reduce volatilization of VOCs from stored organic liquids. A typical floating roof tank consists of an open-topped cylindrical steel shell with a roof floating on the liquid that rises and falls with the liquid level in the tank. Because the tanks used at ConocoPhillips and Valero refineries were originally designed as open tanks, appropriate deck, fittings, and rim seal system are not available to support a floating roof. Instead, a domed (covered) external roof, which consists of a structure typically made of aluminum that is self-supporting from its periphery, may be installed on the constructed activated sludge tanks. The aluminum dome can be built on the ground and placed on top of the tank without removing the tank from service. Domed external roofs are anticipated to be almost maintenance-free.

A domed (covered) external floating roof would accommodate only the activated sludge tanks at the ConocoPhillips and Valero refineries.

The domed roof tanks require the installation of a vapor recovery system or a vapor control system to reduce VOC emissions. Typically, such vapor controls can reduce emissions up to 99 percent.

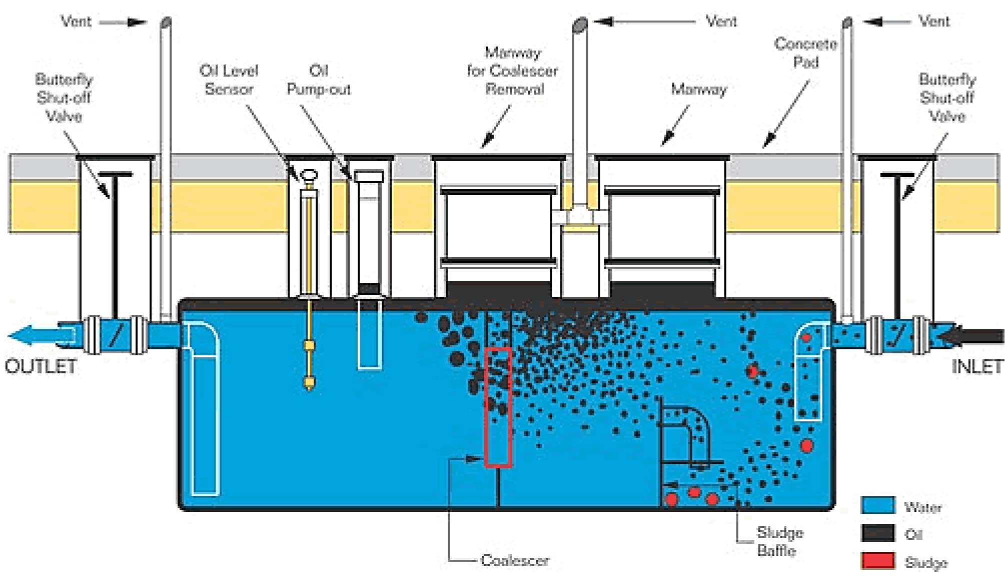
Emerging Technology

The DAF vents at ConocoPhillips are responsible for 35% of the total VOC emissions from all five refineries. Although carbon adsorption canisters may be installed over each vent, the District has encountered problems with the canisters that may affect their long-term performance at reducing VOC emissions. For example, long chain hydrocarbons tend to clog the carbon pores, thus reducing the adsorption capacity of the carbon and requiring continuous regeneration and disposal. Another option is to reduce the VOC content of the wastewater stream prior to entry into the DAF unit through source control or installation of a high efficiency oil-water separation unit.

Petroleum refineries may improve recovery of petroleum products prior to entering the wastewater treatment systems by use of a higher performance oil-water separator that can reduce the hydrocarbon concentration in the effluent. Kleerwater© Oil-Water separators use coalescer balls to separate free-floating oils and greases from water mixtures.

Figure 3 presents a schematic of the Kleerwater technology. Influent enters the separator and passes through an inlet diffuser that reduces the velocity of the influent to facilitate deposition of the heavier matter. Large oil droplets begin to rise toward the oil-water interface. The remaining oil droplets attach to the surface of the coalescer balls which grow larger, release and rise to the oil/water interface. In tests, the separator has reduced hydrocarbon concentrations in effluent to as low as 5 parts per million (ppm). However, none of the Bay Area refineries has installed this technology and there is no certainty that the technology would exhibit the same level of performance at the refineries as demonstrated in the tests.

Figure 3: Kleerwater© Oil Water Separator



Source: US EPA

C. Evaluation of Cost and Cost-Effectiveness of Controls

The District investigated the technical feasibility, potential emission reductions, and costs of installing and operating the control strategies identified in Section II.B. The District estimated the total annual costs of potential control technologies installed at all refineries, where feasible. The total annual costs for a control technology are calculated based on a ten-year period and are comprised of the annualized capital costs and the annual recurring operation and maintenance (O & M) costs.

Capital costs were estimated using the capital recovery method, which accounts for depreciation and interest (i.e., inflation) costs over the useful life of the control.

The District annualized the capital costs using the following equation:

Annualized Cost = (*Capital Recovery Factor*)×(*Capital Expenditure)*

Where:

Capital Expenditure is the equipment and installation costs
Capital Recovery Factor is 14.2% (7% per year over 10 years)

The District estimated the annual recurring O & M costs, which include expenditures for utilities, replacement of adsorption material, and inspections.

District staff estimated a control technology's' cost effectiveness by summing the total annual costs for the control technology installed at all of the refineries and dividing that sum by the total annual VOC emissions reductions to be achieved from all refineries.

Steam Stripper

Capital costs to install a steam stripper at each petroleum refinery were based on EPA (1992) estimated costs that the District adjusted to reflect 2005 U.S. dollars based on the consumer price index. These costs are based also on the number and size of steam strippers needed to treat the average wastewater flow at each of the refineries.

The capital costs to install a steam stripper at each refinery are estimated to be between about $11.7 million and $40.9 million, as shown in Table 2. When annualized over ten years, the total annual costs are between $7.1 million and $24.8 million per year, including annual O&M costs. The costs include equipment and direct installation costs, based on engineering cost estimation techniques. The purchased equipment costs assume a carbon steel construction system that consists of the feed tank and stripper column, auxiliary piping and equipment, and instrumentation, plus freight and taxes. The direct installation costs include engineering design and construction, start-up and testing, electrical wiring, insulation, equipment support, and painting.

The total capital costs do not include the necessary additional costs to install a control device at each refinery to vent emissions from the steam stripper. All of the Bay Area refineries have such controls already. However, the District staff understands that the refineries' existing vapor recovery units operate at or near capacity. Accordingly, the refineries must modify their control systems extensively to accommodate the additional vapor load from a steam stripper to the existing recovery unit or to install additional vapor recovery devices.

In addition, the estimated total capital costs do not include capital equipment expenditures (such as a new boiler to generate steam), installing scrubbers, land acquisition to contain the system, and construction of a structure to house the system. Moreover, the estimated capital costs do not account for system upgrades, expansions or additional systems to treat the refineries' wet weather flow conditions.

Annual recurring costs are comprised of direct and indirect costs. The direct expenses include utility costs to operate the steam stripper, such as electricity, steam, and water, and general maintenance and repair costs. The refineries will have increased recurring costs of periodically monitoring the performance of the stripper. Indirect costs include property taxes, insurance, and administrative costs, estimated based on a percentage of the total capital costs. The annual recurring cost do not account for any benefit derived from the recovery of organic material.

Table 2: Annual Costs for Steam Stripper

Refinery	Capital Cost (Thousand Dollars)	Annualized Capital Cost (Thousand Dollars per Year)	Annual Recurring O&M Costs (Thousand Dollars per Year)	Total Annual Cost (Thousand Dollars per Year over 10 years)
ConocoPhillips	14,320	2,033	6,655	8,689
Shell	29,515	4,191	13,739	17,930
Tesoro	21,164	3,005	9,832	12,837
Valero	11,725	1,665	5,435	7,100
Chevron	40,860	5,802	19,016	24,819
Total	117,584	16,696	54,677	71,375

Based on the estimates of 0.15 tpd of VOC emissions (Table 1) from biological treatment units and channel/weir, it is expected that 0.14 tpd (50.3 tons per year) of emission reductions can be achieved by installing a steam stripper, assuming a 90% removal efficiency. The cost-effectiveness to reduce emissions from all refineries from their biological treatment units and ConocoPhillips' channel/weir is $1.42 million per ton of VOCs reduced. This cost does not include the additional expenses noted above, such as installation or modification of existing vapor recovery systems. This control technology applied to the refineries' current treatment systems does not achieve adequate VOC reductions to warrant the costs.

Carbon Adsorption

Capital costs for installation of liquid phase carbon adsorption units to handle flow rates exceeding 100,000 gallons per day are generally $8.38 per 1,000 gallons of treated wastewater. This cost is based on EPA estimates, adjusted to reflect 2005 dollars. The actual unit construction cost may vary, depending upon the chemical concentrations and flow rates of the particular wastewater stream, the type of contaminants in the stream, mass loading, required effluent concentration, and site/timing requirements. The estimated annual installation and operating costs for a carbon adsorption unit at each refinery are presented in Table 3. The costs are based on the estimated general unit cost of $8.38 per 1,000 gallons of treated wastewater.

The listed costs include neither the additional costs to dispose of spent carbon nor the costs to modify the existing vapor recovery unit to treat the additional vapor load.

The refineries must conduct pilot tests to verify the effectiveness of the control at reducing VOC emissions from their particular wastewater treatment system. The total capital costs do not include the cost of such pilot tests.

The cost-effectiveness of installing a liquid phase carbon adsorption system was estimated assuming that 0.14 tpd of VOCs would be removed based on a 90% removal efficiency. The total annualized costs from all refineries ranged from $6.7 million to $24 million. Therefore, the cost-effectiveness to reduce emissions from the biological treatment units and channel/weir is $1.35 million per ton of VOC reduced. This technology, as applied to the refineries' current treatment systems does not cost-effectively reduce the estimated VOC emissions.

Table 3: Annual Costs for Carbon Adsorption Equipment

Refinery	Total Annual Cost of Installing and Operating a Carbon Adsorption Unit (Thousand Dollars per Year)
ConocoPhillips	8,258
Shell	17,126
Tesoro	12,233
Valero	6,728
Chevron	23,733
Total	68,078

Source: Federal Remediation Technology Roundtable (FRTR). Downloaded from www.frtr.gov/matrix2/section4/4-47.html

Moreover, there are several limitations with this control technology that may restrict its effectiveness at removing hydrocarbons from individual refinery wastewater streams and render it less effective than that of a comparably-priced steam stripper. For example, the presence of multiple contaminants can possibly impact the performance of the unit. Influent with high suspended solids and oil and grease may also cause fouling of the carbon and require extensive pretreatment.

External Roof Tanks

District staff also considered the possibility of installing a domed roof on top of the biological treatment units to reduce VOC emissions. Only ConocoPhillips and Valero refineries have activated sludge tanks that can actually sustain an external domed roof. Neither refinery could utilize a floating roof tank. The Tesoro and Chevron refineries would have to replace their existing biological treatment system in bermed, aerated lagoons and ponds with tanks and install foundations/infrastructure to support the domes and tanks. The Shell refinery has a tank and pond treatment system. The District did not estimate the costs to install a dome on the tank because the aerated pond was the major source of emissions.

To evaluate the feasibility of doming the tanks, District staff reviewed the staff report prepared by South Coast Air Quality Management District (SCAQMD) in 2001. That year, SCAQMD adopted Rule 1178 to reduce VOC emissions from storage tanks at petroleum facilities by doming tanks that store high vapor pressure material. The SCAQMD staff report provided costs to install a domed roof on external floating roof tanks containing liquids with vapor pressures greater than or equal to 3 psia. SCAQMD staff contacted three manufacturers and found that tank costs depended on the diameter of the tanks.

For ConocoPhillps and Valero refineries, each tank ranged from 40 to 100 feet in diameter. Based on the costs provided in the SCAQMD report, the capital cost to install a single aluminum dome roof on an existing external floating roof tank would range from $80,000 to $153,000 depending on the diameter of the tank. That cost includes the installation of a fire-suppression system, which requires additional fixed or semi-fixed piping and foam nozzles to dispense fire suppressant foam. Capital costs were estimated assuming that two 100-foot diameter tanks would be domed at the ConocoPhillips refinery and five 50-foot tanks would be covered at the Valero refinery. This cost estimate does not include the additional expenses to modify the existing activated sludge tanks, by installing proper seals and deck fittings and ensuring that a suitable foundation and infrastructure with utility lines are in place to sustain the dome roof.

Annual operation and maintenance costs were estimated as 9% (4% for administrative costs and 5% for maintenance cost) of the capital cost. Table 4 presents the average total annualized cost for doming the activated sludge units.

The estimated emission reductions from doming the tanks at ConocoPhillips and Valero refineries, assuming a 95% removal efficiency, would total 0.025 tpd (nine tons per year) from the biological treatment units. The total annual costs for doming these tanks ranged from $82,600 to $139,000. Therefore, the cost-effectiveness to reduce emissions from biological treatment units is $25,000 per ton of VOCs reduced.

Table 4: Annual Costs for Dome Roof

Refinery	Capital Cost (Thousand Dollars)	Annualized Capital Cost (Thousand Dollars per Year)	Annual Recurring O&M Costs (Thousand Dollars per Year)	Total Annual Cost (Thousand Dollars per Year over 10 years)
ConocoPhillips	365	50	32	83
Valero	600	85	54	139
Total	965	135	86	222

Since issuance of the SCAQMD report, stakeholders in the South Coast region have reviewed SCAQMD cost estimates and concluded that their cost estimates were 30 percent lower than actual costs for installing a dome. In addition, since adoption of Rule 1178, industries at SCAQMD have proposed to dome only tanks less than 95 feet in diameter due to cost effectiveness considerations.

In addition to the structural limitations described above, the Bay Area refineries would need to vent the vapor losses to either an existing vapor recovery system that can handle the additional load or modify or construct an on-site vapor control system. Although the costs to install aluminum domes are substantially lower than the other two control options, the emission reductions are also significantly lower and there are significant uncertainties regarding the feasibility of installing domes on existing tanks that were not originally designed to handle a roof. Overall, this option has many uncertainties that make it an unreliable VOC control measure.

For all the remaining refineries, doming the biological treatment units would be cost prohibitive. The refineries would have to construct tanks to replace the existing lagoons and ponds. One refinery provided a summary of actual capital costs spent on constructing a single activated sludge tank that exceeded $30 million dollars.

IV. SUMMARY OF PUBLIC CONSULTATION PROCESS

District staff has undertaken a comprehensive evaluation of refineries' treatment systems in order to complete Phase Two of the study under Further Study Measure 9. The process involved extensive participation from the public and affected parties. District staff met with its advisory technical working group and held a public workshop prior to a public hearing before the Board of Directors.

A. Technical Working Group

District staff formed a Regulation 8, Rule 8 working group in 2002 to review technical issues concerning wastewater collection and treatment systems during Phases One and Two of the Further Study Measure 9 study. The technical working group was comprised of representatives from CARB, Western States Petroleum Association (WSPA), the five Bay Area Refineries, the California Regional Water Quality Control Board, Communities for a Better Environment (CBE), and District staff. For phase two of the study, District convened four meetings and held conference calls. The group participated in the development of the work plan, the refineries' sampling plans, and modeling approach. The group also discussed the wastewater emission estimates, potential control technologies, costs of emissions controls, and treatment of confidential information. The following is a summary of the meetings:

April 4, 2005 Meeting

The kick-off meeting began with introductions followed by a discussion of the Draft Phase Two Work Plan. The purpose of the Work Plan was to provide a strategy for identifying uncontrolled sources and estimating VOC emissions from refinery wastewater treatment process. The Draft Work Plan included the proposed sampling methodology, sampling approach, overall costs of the project, and proposed schedule. Members discussed potential financial contributions from petroleum refining industry representatives to support the sampling plan and discussed a proposed schedule for refinery site visits.

June 8, 2005 Meeting

The members discussed the draft conceptual sampling plan that outlined the sampling methodologies to be used, laboratory analysis, emission modeling approach, and quality assurance protocol. Based on the modeling completed on the phase one study, the workgroup members agreed, based on consistency, to continue to use the TOXCHEM+ model to estimate emissions from the treatment systems. The members also agreed that the model results would be calibrated using the direct vapor measurements collected from the two refineries.

September 14, 2005

The members discussed the preliminary results of the sampling and modeling at the five Bay Area refineries. They also discussed VOC emissions estimated using the TOXCHEM+ model and calibration of the model using the flux chamber results.

October 20, 2005

The members discussed potential control technologies to reduce VOC emissions and the technical feasibility of installing the technologies. The discussion included a summary of costs for installing and operating the control strategies as well as anticipated emission reductions.

B. Public Workshop

On September 27, 2005, staff published a Workshop Staff Report that presented staff's technical analysis and recommendations not to amend Regulation 8, Rule 8 at this time. Staff held one workshop in Martinez, California on October 27, 2005 to solicit public comments on District staff's recommendation. The District also provided a public comment period from September 27 – November 3, 2005 for interested parties to submit written comments to the District. Discussions and responses to comments received during the public comment period are presented in Attachment A.

V. REASONS FOR NOT PROPOSING FURTHER AMENDMENTS TO REGULATION 8, RULE 8 AT THIS TIME

The District staff has determined that significant VOC emission reductions from existing secondary treatment systems would not be obtained at this time at a reasonable cost. Staff has estimated that conservatively, the five refineries emit up to a total of 0.24 tpd of VOCs into the atmosphere. Control of the wastewater treatment systems will not produce significant reductions of VOC emissions in the Bay Area. The imposition of controls will reduce VOC emissions by 0.14 tpd. At this time, further amendments to Regulation 8, Rule 8 are not viable options to reduce VOC emissions.

If the District determines to adopt or amend a District regulation, it must consider the cost to implement the rule and achieve air quality improvements. There is no such requirement where the District investigates whether, and determines not to adopt or amend a District regulation. That said, District staff have considered the cost-effectiveness of potential further controls in phase two of its Further Study Measure 9 study as one factor in its determination not to propose further controls on refinery wastewater treatment systems. The District staff identified, and estimated the costs to install, the three most reliable, proven technologies to control VOCs in refinery wastewater treatment systems, either by removing VOC emissions from the wastewater streams prior to secondary treatment or by controlling VOCs during treatment. Staff estimated the direct capital costs and limited O & M costs to install these control technologies, conservatively excluding the necessary appurtenant costs to install new control devices at the existing facilities. For example, the costs did not include the construction expenses to contain open bermed ponds. Similarly, the capital costs did not cover installation of additional control devices to treat high wastewater flows during wet weather conditions. Under the District's traditional cost-effectiveness analysis for proposed rule amendments, the District found that even the most reliable measures to control VOC emissions in wastewater treatment systems were not cost-effective measures at the refineries for addressing ozone.

Moreover, District staff could not confirm that these technologies, while proven generally, are feasible to install at the any of the Bay Area refineries or are compatible with the refineries' current treatment systems. For example, each of the refineries must conduct pilot testing of a carbon adsorption system to confirm its efficiency to remove hydrocarbons from that refinery's wastewater stream.

VI. CONCLUSION

The District and CARB committed in the 2001 Ozone Plan to assess whether there are potential significant VOC emissions from refinery wastewater collection and treatment systems as a measure to reduce ozone. Last year, the District adopted requirements that impose stringent controls on the collection systems. This year, District staff has evaluated refinery wastewater treatment systems. Based on emission estimates developed from field tests and modeling techniques, staff estimated that a total of 0.24 tpd of VOCs are emitted to the atmosphere from the treatment process from all five refineries. During secondary treatment, the majority of emissions are produced from biological treatment units, where the wastewater is exposed to the atmosphere. District staff has determined that the imposition of even the most reliable, proven technologies will reduce VOC emissions by 0.14 tpd.

The District staff has determined that significant VOC emission reductions from existing secondary treatment systems would not be obtained at this time at a reasonable cost. Further, there is a potential incompatibility of installing of these proven control technologies at these refineries.

Accordingly, controlling emissions from wastewater treatment systems is not a viable measure to address ozone at this time. District staff does not find that further amendments of Regulation 8, Rule 8 are warranted.

VII. REFERENCES

1. California Air Resources Board Draft Technical Assessment Document (TAD) “Potential Control Strategies to Reduce Emissions for Refinery wastewater Collection and Treatment Systems.” January 2003.

2. South Coast Air Quality Management District, “Draft Staff Report Proposed Rule 1178 – Further Reductions of VOC Emissions from Storage Tanks at Petroleum Facilities,” October 26, 2001.

3. The TGB Partnership. Letter submitted from Rob Ferry to the BAAQMD entitled, “Commentary on the WSPA Cost-Effectiveness Analysis of Requiring Domes for EFRTs at Bay Area Refineries.” Dated October 27, 2004.

4. United States Environmental Protection Agency, AP-42 “Waste Water Collection, Treatment And Storage,” January 1995.

5. United States Environmental Protection Agency, 1989 “Hazardous Air Pollutant Emissions from Process Units in the Synthetic Organic Chemical Manufacturing Industry – Background Information for Proposed Standards. Volume 1B, Control Technologies,” November 1992.

ATTACHMENT A: RESPONSES TO PUBLIC COMMENTS

This section presents a summary of public comments that were received during the workgroup meeting, public workshop, or as part of the public consultation process.

Workgroup Meeting

Following the October 20, 2005 workgroup meeting, WSPA submitted written comments on the Workshop Staff Report. First, WSPA noted that the costs listed in the Workshop Staff Report to implement the control technology for steam strippers were inconsistent with the cost analysis provided during the October 20 technical working group meeting. Second, WSPA noted that the District did not estimate the cost of installing the steam stripper and liquid phase carbon adsorption unit based on maximum flow rates, which occur during wet weather conditions, thereby affecting the size of the particular controls required for each refinery. Also, WSPA stated that a liquid phase carbon adsorption unit is not a reliable control for treating wastewater influent. Last, WSPA stated that the costs to install and operate many of the controls were under-estimated because the District did not include the costs for installing supporting units and infrastructure in its cost analysis. Staff has corrected the cost analysis and included an itemization of probable additional capital expenses into Section III C.

Public Workshop

During the public workshop on October 27, 2005, CBE proposed that the District amend Regulation 8, Rule 8 to require monitoring of the wastewater entering the wastewater treatment systems to determine whether the new controls required on upstream collection components by the September 2004 amendments will increase hydrocarbon concentrations in the downstream treatment systems. District and CARB staff have estimated that less than 1 part per million (ppm) to 26 ppm of additional hydrocarbon would be introduced into the separation system, depending on the refinery, based on refinery-specific wastewater concentrations and flow rates. The hydrocarbon concentration at the separator is anticipated to incrementally increase by less than <0.5% to 16%. Although the hydrocarbon concentration would significantly decrease once it is processed through the oil-water separators and dissolved gas flotation units, the incremental increase in hydrocarbon concentrations is within the natural variation seen during normal operations and within the boundaries of wet weather seasonal variations. Moreover, increased hydrocarbon concentrations do not correlate directly to more VOC emissions. District staff does not expect VOC emissions from the treatment system to increase beyond levels typical of seasonal and wet weather flow conditions. Therefore, additional monitoring of the effluent into the biological treatment units is not warranted.

CBE also suggested that the District's review of Regulation 8, Rule 8 should include an evaluation of the toxicity of the volatile organic compounds released from wastewater treatment systems and the impact of those releases on refinery workers and nearby communities. CBE noted the potential impact in particular upon the working and residential communities adjacent to ConocoPhillips, which the District has estimated is the refinery with the highest uncontrolled VOC emissions from its wastewater treatment system.

The District has conducted a preliminary risk evaluation of potential health risks from VOC emissions from the ConocoPhillips wastewater treatment system to the refinery's nearest resident and to workers in the nearby community. District staff estimated downwind annual air concentrations for off-site workers and the nearest resident (using EPA's air dispersion model, SCREEN) and compared the estimated air concentrations to acceptable, health-protective concentration limits promulgated by EPA Region 9 for which an individual may be exposed to VOC compounds over their lifetime. District staff determined that under these worst-case conditions, the predicted annual air concentrations of residents and off-site workers were below EPA limits[2], applying EPA's risk assessment methodology.

District staff also conducted a similar preliminary risk evaluation for on-site workers in the vicinity of the wastewater treatment system. The American Conference of Government Industrial Hygienists (ACGIH) sets limits of air concentrations for which workers may be repeatedly exposed daily without adverse effect (based on an 8-hour day, 40-hour workweek). Staff estimates that the on-site workers' exposures to air concentrations are significantly below the ACGIH time-weighted average threshold limits[3].

The District staff's preliminary risk evaluation does not identify adverse effects overall to off-site residents, off-site workers, or on-site workers from uncontrolled VOC emissions from ConocoPhillips' wastewater treatment system. Because emissions from the other refineries' wastewater treatment systems are much lower, the worker and off-site exposures would be much lower as well. The results of this evaluation further support the District staff's recommendation not to amend Regulation 8 Rule 8 at this time as an ozone measure.

<u>Public Comment Period</u>

During the public comment period, the District received one comment letter from CBE dated November 3, 2005. First, CBE commented that the District staff did not evaluate the feasibility and cost-effectiveness of reducing VOC emissions through operational changes by implementing pollution prevention controls. Potential pollution prevention strategies designed to reduce the VOC concentrations entering the collection systems were discussed in the phase one staff report. The District staff has included the option of implementing pollution prevention strategies to the refineries for controlling wastewater collection system

[2] US EPA Region 9 Preliminary Remediation Goals (PRGs) 2004 Table. http://www.epa.gov/region09/waste/sfund/prg/

[3] American Conference of Governmental Industrial Hygienists (2004), 2004 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices.

components in the phase one staff report and as noted by CBE, some of the refineries have implemented such programs in order to comply with the September 15, 2004 amendments to Regulation 8, Rule 8. Any reductions of VOCs in the wastewater stream will reduce VOCs at the treatment systems. No additional pollution prevention strategies are available that would solely be applicable to the treatment systems without impacting, at the outset, the collection and separation systems. Consequently, no additional pollution prevention programs were discussed in the phase two staff report.

Second, CBE commented that the feasibility of implementing controls has not been evaluated adequately for ConocoPhillips which is responsible for over 45% of all emissions from wastewater treatment systems. CBE adds that the District ignores factors such as hot spots emissions, toxicity risk, and outdated technology and environmental justice in its feasibility analysis. As stated in response to the CBE comments on the public workshop, the District staff took into account many factors in considering its recommendation not to amend Regulation 8, Rule 8. ConocoPhillips is cooperating with the District to evaluate options to reduce emissions from the channel/weir and DAF vents.

Lastly, CBE recommends that additional monitoring of VOC inputs to the refinery wastewater treatment systems is required. As discussed in the response to CBE comments on the public workshop, VOC concentrations in the wastewater stream are not anticipated to increase by more than 16% due to controls placed on upstream collection systems. This incremental increase is within the natural variation seen during normal operations and within the boundaries of wet weather seasonal variations. Consequently, a requirement for additional monitoring of the effluent into the biological treatment units is not warranted. However, the District may use its existing authority to sample, source test, or periodically monitor hydrocarbon concentrations at any of refineries' wastewater systems.