Western States Petroleum Association
Credible Solutions • Responsive Service • Since 1907

Kevin Buchan
Senior Coordinator, Bay Area and State Water Issues

VIA ELECTRONIC MAIL

May 23, 2012

Bruce Wolfe
Executive Officer
San Francisco Regional Water Quality Control Board
1515 Clay Street, 14th Floor
Oakland, CA 94612

RE: Revised Nutrients 13267 Sampling and Analysis Plan for the Five Bay Area Refineries

Dear Mr. Wolfe,
The Western States Petroleum Association (WSPA) is a non-profit trade association representing twenty-six companies that explore for, produce, refine, transport and market petroleum, petroleum products, natural gas and other energy supplies in California, Arizona, Nevada, Oregon, Washington and Hawaii.

WSPA submits the attached revised Sampling and Analysis Plan (SAP) for your approval on behalf of the Chevron Richmond, ConocoPhillips Rodeo, Shell Martinez, Tesoro Golden Eagle, and Valero Benicia refineries. WSPA and the five refineries held consultation with Board staff and incorporated amendments per their direction into this revision. We appreciate the efforts by Board staff to work collaboratively with WSPA and the refineries on this important project. Please feel free to contact me at your convenience should the need arise.

Sincerely,

Kevin Buchan

1415 "L" Street, Suite 600, Sacramento, California 95814
(916) 498-7755 • FAX: (916) 444-5745 • Kevin@wspa.org • www.wspa.org

Enclosure: Sampling and Analysis Plan for Bay Area Refineries

Cc: Naomi Feger/SFRWQCB
Tong Yin/SFRWQCB

1415 “L” Street, Suite 600, Sacramento, California 95814
(916) 498-7755 ● FAX: (916) 444-5745 ● Kevin@wspa.org ● www.wspa.org

SAMPLING AND ANALYSIS PLAN for BAY AREA REFINERIES

Pursuant to March 8, 2012 Water Code Section 13267 Technical Report Order Requiring
Submittal of Information on Nutrients in Refinery Wastewater Discharges - Revised May 2012

Requirements: A Sampling and Analysis Plan (SAP) for collecting nutrient information from treated process wastewater discharges was submitted to the RWQCB by April 30, 2012. Required SAP elements include: 1) a sampling schedule, 2) contract labs to be used, 3) analytical methods to be used, and 4) detection limits of the methods. Per RWQCB staff direction, this SAP was revised and is being submitted collectively by the five (5) Bay Area refineries noted in the Permitted Refineries Mailing List attached to the Technical Report Order, as follows:

- Chevron Products Company, 841 Chevron Way, Richmond, CA 94801
- ConocoPhillips Company, 1380 San Pablo Avenue, Rodeo, CA 94572-1354
- Shell Oil Products US and Equilon Enterprises LLC, 3485 Pacheco Blvd, Martinez, CA 94553
- Tesoro Refining & Marketing Co., 150 Solano Way, Martinez, CA 94553
- Valero Refining Company, 3400 East Second Street, Benicia, CA 94510-1005

If Regional Board staff wishes to provide additional comments on this SAP, please respond to:

Kevin Buchan c/o Western States Petroleum Association
1415 L Street, Suite 600, Sacramento, CA 95814 or Kevin@wspa.org

SAP Elements

1. A total of ten (10) laboratory analytical and three continuously monitored parameters are included in the 13267 Order and presented in Table 1.
2. Effluent nutrient sampling will be at the normal treated process wastewater compliance monitoring locations (point-of-compliance) at each refinery.
3. Nitrogen and phosphorus-containing parameters will be reported as Nitrogen (N) or as Phosphorus (P), respectively. All laboratory-determined parameters will be reported as mg/L and calculated as kg/day.
4. Alternate methods to those specified in the 13267 request are listed to allow for lower detection limits to provide greater flexibility in the choice of certified laboratories or to resolve any analytical difficulties that may occur during the study period.
5. Table 1 in the 13267 Order indicates all nutrient study samples to be 24-hour composites; however, per subsequent discussions, Board staff have specified that:
   - A 24-hour composite sample is preferred for Total Ammonia (as N). Therefore, the NPDES Division directed nutrient study samples collected for Total Ammonia (as N) to be 24-hour composites for any refinery whose MRP requires a grab sample for this parameter. As an alternative, an affected refinery may collect a separate 24-hour composite sample for the purposes of the nutrient study.
   - The study sample collected for dissolved Orthophosphate should be a grab sample that is filtered onsite through a 0.45 micron filter within 15 minutes pursuant to 40 CFR 136.3, Table II. The study sample collected for total Orthophosphate will be a parallel unfiltered grab sample. Both samples will be submitted to a certified laboratory within the 48-hour hold time.
6. Sampling and analysis for the nutrient parameters noted in this proposed SAP will occur monthly. The selected sample date will typically correspond with randomly selected monthly or weekly effluent compliance sampling dates, as specified in the discharger's NPDES permit and as selected by each refinery.
7. Two additional wet season sample dates will be selected, independently, by each refinery based on local rainfall and/or effluent discharge flows to provide data representative of "peak wet-weather flows".
8. Continuous monitoring data (e.g. pH, temperature and flow) will be reported as specified in the 13267 Order.
9. The 13267 Order requests parallel analysis of both soluble and total forms of Total Kjeldahl Nitrogen, Total Phosphorus and Orthophosphate. The solubility of these three study nutrients is maximized in the pH range of refinery effluents and the carbonaceous solids that constitute refinery TSS in tertiary treated effluent are typically found in the integer ppm range (e.g. ~0.0001%). Therefore, the data sets that are generated for each study parameter requiring both soluble & total forms are expected to be nearly identical, subject to sampling, preparation and analytical variability.
10. After the first year of monitoring, the refineries may request the Regional Water Board to:
    - reduce the sampling frequency if monitoring data show little variability or mass loadings are insignificant compared to other dischargers in the region, and/or

- waive the analysis of specific parameters that have been shown to be duplicative or have a non-detect or negligible contribution to nutrient loading in San Francisco Bay.

11. Board staff has also requested that the refineries list all the labs that the refineries may choose from even if each refinery has not decided which lab to use at this time. Each refinery will submit an individual laboratory list indicating the analytical methods to be used and the corresponding RL's and MDL's. At their discretion, each refinery may still choose to:
    - utilize one or more NELAP &/or ELAP Certified Laboratories to conduct the required analytical nutrient testing,
    - send their nutrient study samples to one or more laboratories based on the level of service provided and/or other QA/QC criteria, and
    - perform the laboratory analyses using any of the alternate approved analytical methods listed in Table 1 based on the available analytical options, detection limits and/or other factors that may be unique to a specific refinery.
12. The certified analytical laboratory will run a method blank, a matrix spike and matrix spike duplicate with each batch of nutrient samples, as required by the approved test method. Once during the year, each refinery is encouraged to make arrangements with the analytical laboratory to supply a double sample volume for one or more nutrient parameters or groups. On request, the double-volume(s) will allow the laboratory to perform the matrix spike and matrix spike duplicate testing on the refinery sample and report accordingly. As an option, each refinery may include a field blank (DI water) to provide a measure of sampling variability, and/or a blind duplicate (a split of a study sample identified differently) along with their nutrient study effluent samples.
13. A spreadsheet-based reporting worksheet is being developed for this nutrient study. As an alternative, each refinery may choose to submit an appropriately formatted EDD file for the nutrient parameters.
14. Each refinery will make the necessary sample transportation arrangements with their certified analytical laboratory(s) to ensure that each 24-hour composite or grab nutrient study sample is collected into the appropriate container, preserved with H_2SO_4 (if required), maintained at $\leq 4^oC$ in transit, delivered under chain-of-custody and within the applicable regulatory hold time for further preparation and/or analysis at the certified laboratory.

Table 1: Alternative Methods

Analytical Parameter	Available Analytical Methods
Total Dissolved Nitrogen as N	SM20 4500-N
Total Kjeldahl Nitrogen as N	SM20 4500-NH_3; EPA 350.2
Soluble Kjeldahl Nitrogen as N	SM20 4500-NH_3; EPA 350.2
Nitrate as N	SM20 4500-NO_3; EPA 353.3; 353.2; 353.1; 300; 300.1; 352.1
Nitrite as N	SM20 4500-NO_2; EPA 354.1; EPA 353.3; 353.2; 353.1; 300; 300.1
Total Ammonia as N	SM20 4500-NH_3; EPA 350.2, 350.3
Total Phosphorus as P	SM20 4500-P; EPA 365.1; 365.2; 365.3; 365.4
Total Phosphorus (soluble) as P	SM20 4500-P; EPA 365.1; 365.2; 365.3; 365.4
Orthophosphate (diss./total) as P	SM20 4500-P; EPA 365.1; 365.2; 300; 300.1
TSS	SM20 2540D; EPA 160.2

Continuous Parameter	Units	Frequency	Report As:
Flow	mgd	Continuous	Daily average flow
pH	S.U.	Continuous	Daily minimum, maximum & average
Temperature	Degrees F	Continuous	Daily minimum, maximum & average

Supplemental to

Revised Nutrients 13267 Sampling and Analysis Plan
for the Five Bay Area Refineries, May 23, 2012

Sampling Matrix for

Chevron Richmond Refinery
Phillips 66 San Francisco Refinery
Shell Martinez Refinery
Tesoro Golden Eagle Refinery
Valero Benicia Refinery

Chevron Richmond Refinery

13267 Nutrients Sampling and Analysis Information

Sampling Location	Parameter	Units	Proposed Sample Type	Analytical Method	Lab	Reporting Level* (mg/L)	Method Detection Limit (mg/L)
E-001	Total Dissolved Nitrogen	mg/L as N kg/day as N	24-hour composite	Calculation	Caltest	0.1	N/A
E-001	Total Kjeldahl Nitrogen	mg/L as N kg/day as N	24-hour composite	SM20 4500-NH3 C	Caltest	0.1	0.07
E-001	Soluble Kjeldahl Nitrogen	mg/L as N kg/day as N	24-hour composite	SM20 4500-NH3 C	Caltest	0.1	0.07
E-001	Nitrate	mg/L as N kg/day as N	24-hour composite	EPA 353.2	Caltest	0.1	0.02
E-001	Nitrite	mg/L as N kg/day as N	24-hour composite	SM20 4500-NO2 B	Caltest	0.03	0.002
E-001	Total Ammonia	mg/L as N kg/day as N	24-hour composite	SM20 4500-NH3 D-1997 SM20 4500-NH3 C	On-Site or Caltest	0.1 0.1	0.02 0.06
E-001	Total Phosphorus	mg/L as P kg/day as P	24-hour composite	SM20 4500-P E	Caltest	0.1	0.007
E-001	Total Phosphorus (soluble)	mg/L as P kg/day as P	24-hour composite	SM20 4500-P E	Caltest	0.1	0.007
E-001	Orthophosphate (dissolved)	mg/L as P kg/day as P	Grab	SM20 4500-P E	Caltest	0.1	0.006
E-001	Orthophosphate (total)	mg/L as P kg/day as P	Grab	SM20 4500-P E	Caltest	0.1	0.006
E-001	TSS	mg/L	24-hour composite	SM 2540-D	On-site or Caltest	N/A 3.0	2.0 2.0
E-001	Flow	mgd	Continuous	N/A	N/A	N/A	N/A
E-001	pH	Standard unit	Continuous	N/A	N/A	N/A	N/A
E-001	Temperature	Degree °F	Continuous	N/A	N/A	N/A	N/A

Phillips 66 Company San Francisco Refinery Section 13267 Nutrient Study Facility-Specific Sample Information

Sample Location [1]	Parameter	Proposed Sample Type	Analytical Method	Certified Lab [2]	RL [3]	MDL	Units
EFF-002	Total Dissolved Nitrogen	24-hour composite	SKN + NO3 + NO2	n/a	n/a		mg/L, kg/day as N
EFF-002	Total Kjeldahl Nitrogen (TKN)	24-hour composite	SM 4500-NH3 C	Delta Environmental	0.08	0.08	mg/L, kg/day as N
EFF-002	Soluble Kjeldahl Nitrogen (SKN)	24-hour composite	SM 4500-NH3 C	Delta Environmental	0.08	0.08	mg/L, kg/day as N
EFF-002	Nitrate	24-hour composite	EPA 300.1	Delta Environmental	0.02	0.002	mg/L, kg/day as N
EFF-002	Nitrite	24-hour composite	EPA 300.1	Delta Environmental	0.02	0.002	mg/L, kg/day as N
EFF-002	Total Ammonia	24-hour composite	SM 4500-NH3 F	Delta Environmental	0.04	0.003	mg/L, kg/day as N
EFF-002	Total Phosphorus	24-hour composite	SM 4500-PB& E	Delta Environmental	0.05	0.006	mg/L, kg/day as P
EFF-002	Total Phosphorus (soluble)	24-hour composite	SM 4500- PB& E	Delta Environmental	0.05	0.006	mg/L, kg/day as P
EFF-002	Orthophosphate (dissolved)	Grab [4]	EPA 300.1	Delta Environmental	0.02	0.005	mg/L, kg/day as P
EFF-002	Orthophosphate (total)	Grab	EPA 300.1	Delta Environmental	0.02	0.005	mg/L, kg/day as P
EFF-002	Flow	Continuous	n/a	n/a	n/a		MGD
EFF-002	pH	Continuous	n/a	n/a	n/a		S.U.
EFF-002	Temperature	Continuous	n/a	n/a	n/a		°F
EFF-002	TSS	24-hour composite	SM 2540-D	Phillips 66	2.0	1.0	mg/L

[1] EFF-002 is the treated process effluent point-of-compliance.

[2] The ELAP Certification Number for Delta Environmental Laboratories is #1857. The Phillips 66 Laboratory ELAP Certification Number is #2544

[3] The 05/11/12 RWQCB comments on SAP requested "minimum level"; Phillips 66 interprets this to mean "minimum reporting level" or RL.

[4] The grab study sample collected for dissolved Orthophosphate will be 0.45 micron filtered pursuant to 40 CFR 136.3, Table II.

Shell Oil Products US and Equilon Enterprises LLC

Nutrients Sampling and Analysis Information

Sampling Location	Parameter	Units	Proposed Sample Type	Analytical Method	Contract Lab	Reporting Level* (mg/L)	Method Detection Limit (mg/L)
E-001	Total Dissolved Nitrogen	mg/L as N kg/day as N	24-hour composite	Calculation	Caltest	0.1	n/a
E-001	Total Kjeldahl Nitrogen	mg/L as N kg/day as N	24-hour composite	SM20 4500-NH3 C	Caltest	0.1	0.07
E-001	Soluble Kjeldahl Nitrogen	mg/L as N kg/day as N	24-hour composite	SM20 4500-NH3 C	Caltest	0.1	0.07
E-001	Nitrate	mg/L as N kg/day as N	24-hour composite	EPA 353.2	Caltest	0.1	0.02
E-001	Nitrite	mg/L as N kg/day as N	24-hour composite	SM20 4500-NO2 B	Caltest	0.03	0.002
E-001	Total Ammonia	mg/L as N kg/day as N	24-hour composite	SM20 4500-NH3 C	Caltest	0.1	0.06
E-001	Total Phosphorus	mg/L as P kg/day as P	24-hour composite	SM20 4500-P E	Caltest	0.1	0.007
E-001	Total Phosphorus (soluble)	mg/L as P kg/day as P	24-hour composite	SM20 4500-P E	Caltest	0.1	0.007
E-001	Orthophosphate (dissolved)	mg/L as P kg/day as P	Grab	SM20 4500-P E	Caltest	0.1	0.006
E-001	Orthophosphate (total)	mg/L as P kg/day as P	Grab	SM20 4500-P E	Caltest	0.1	0.006
E-001	Flow	mgd	Continuous	n/a	n/a	n/a	n/a
E-001	pH	Standard unit	Continuous	n/a	n/a	n/a	n/a
E-001	Temperature	Degree °F	Continuous	n/a	n/a	n/a	n/a
E-001	TSS	mg/L	24-hour composite	SM 2540-D	Shell or Caltest	n/a 3.0	2.0 2.0

*05/11/12 RWQCB comments on SAP requested “minimum level”; Shell interprets this to mean “minimum reporting level”.

Tesoro Golden Eagle Refinery, Martinez, CA

Nutrients Sampling and Analysis Information
Pursuant to March 8, 2012 Water Code Section 13267 Technical Report Order – Nutrients in Refinery Wastewater Discharges

Sampling Location	Parameter	Unit	Proposed Sample Type	Analytical Method	Contract Lab	Reporting Level* (mg/L)	Method Detection Limit (mg/L)
E-001	Total Dissolved Nitrogen	mg/L as N, kg/day as N	24-hour composite	Calculation	Caltest	0.1	n/a
E-001	Total Kjeldahl Nitrogen	mg/L as N, kg/day as N	24-hour composite	SM20 4500-NH3 C	Caltest	0.1	0.07
E-001	Soluble Kjeldahl Nitrogen	mg/L as N, kg/day as N	24-hour composite	SM20 4500-NH3 C	Caltest	0.1	0.07
E-001	Nitrate	mg/L as N, kg/day as N	24-hour composite	EPA 353.2	Caltest	0.1	0.02
E-001	Nitrite	mg/L as N, kg/day as N	24-hour composite	SM20 4500-NO2 B	Caltest	0.03	0.002
E-001	Total Ammonia	mg/L as N, kg/day as N	24-hour composite	SM20 4500-NH3 C	Caltest	0.1	0.06
E-001	Total Phosphorus	mg/L as P, kg/day as P	24-hour composite	SM20 4500-P E	Caltest	0.1	0.007
E-001	Total Phosphorus (soluble)	mg/L as P, kg/day as P	24-hour composite	SM20 4500-P E	Caltest	0.1	0.007
E-001	Orthophosphate (dissolved)	mg/L as P, kg/day as P	Grab (filtered on-site within 15 minutes)	SM20 4500-P E	Caltest	0.1	0.006
E-001	Orthophosphate (total)	24-hour composite	Grab	SM20 4500-P E	Caltest	0.1	0.006
E-001	TSS	mg/L	24-hour composite	SM 2540-D	Caltest	3	1
E-001	Flow	mgd	Continuous	n/a	n/a	n/a	n/a
E-001	pH	Standard units	Continuous	n/a	n/a	n/a	n/a
E-001	Temperature	Degree F	Continuous	n/a	n/a	n/a	n/a

*05/11/12 RWQCB comments on the SAP for Bay Area Refineries requested “minimum level”; Tesoro interprets this to mean “minimum reporting level”.

Valero Refining Company – CA, Benicia Refinery
Nutrients Sampling and Analysis Information

Sampling Location	Parameter	Unit	Sample Type	Analytical Method	Contract Lab	Reporting Level* (mg/L)	Method Detection Limit (mg/L)
E-001	Total Dissolved Nitrogen	mg/L as N, kg/day as N	24-hour composite	Calculation	Caltest	0.1	n/a
E-001	Total Kjeldahl Nitrogen	mg/L as N, kg/day as N	24-hour composite	SM20 4500-NH3 C	Caltest	0.1	0.07
E-001	Soluble Kjeldahl Nitrogen	mg/L as N, kg/day as N	24-hour composite	SM20 4500-NH3 C	Caltest	0.1	0.07
E-001	Nitrate	mg/L as N, kg/day as N	24-hour composite	EPA 353.2	Caltest	0.1	0.02
E-001	Nitrite	mg/L as N, kg/day as N	24-hour composite	SM20 4500-NO2 B	Caltest	0.03	0.002
E-001	Total Ammonia	mg/L as N, kg/day as N	24-hour composite	SM20 4500-NH3 C	Caltest	0.1	0.06
E-001	Total Phosphorus	mg/L as P, kg/day as P	24-hour composite	SM20 4500-P E	Caltest	0.1	0.007
E-001	Total Phosphorus (soluble)	mg/L as P, kg/day as P	24-hour composite	SM20 4500-P E	Caltest	0.1	0.007
E-001	Orthophosphate (dissolved)	mg/L as P, kg/day as P	Grab (filtered onsite)	SM20 4500-P E	Caltest	0.1	0.006
E-001	Orthophosphate (total)	mg/L as P, kg/day as P	Grab (filtered onsite)	SM20 4500-P E	Caltest	0.1	0.006
E-001	Flow	MGD	Continuous	n/a	n/a	n/a	n/a
E-001	pH	SU	Continuous	n/a	n/a	n/a	n/a
E-001	Temperature	degree C	Continuous	n/a	n/a	n/a	n/a
E-001	TSS	mg/L	24-hour composite	SM 2540-D	Valero	n/a	2.0

*05/11/12 RWQCB comments on SAP requested “minimum level”; Valero interprets this to mean “minimum reporting level”.