

## C-11-VII.0 QUALITY ASSURANCE / QUALITY CONTROL

### C-11-VII.1 Core Program

Monitoring and reporting is supported by a quality assurance/quality control (QA/QC) program developed and implemented by the Principal Permittee. Laboratory analyses are independently validated through quality control check samples in addition to the quality assurance requirements established by USEPA and Standard Method procedures. The QA/QC program evaluates data for accuracy, precision, and contamination using certified reference materials (CRMs) and laboratory control standards for common analyses, duplicate field samples, and equipment/trip blanks, respectively.

The proportion of quality assurance samples submitted this year was approximately 10% of the total NPDES and TMDL field samples submitted to the contracted laboratories for key analyses referenced in **Table C-11-VII.1**. The annual QA/QC Summary which describes the analysis type and percent breakdown is presented at the following link: <https://ocgov.box.com/v/2016-17-SAR-PEA-C-11-Datasets>.

A designated QA/QC officer oversaw preparation and submittal of multiple types of QA/QC samples from the Principal Permittee's water quality laboratory at the County to evaluate the quality of data produced by the contracted laboratories and the Orange County Health Care Agency Water Quality Laboratory (for bacteria samples). In house synthetic samples were prepared using aliquots of prepared standard solutions in ultra-pure (Nanopure) water matrices for the assurance of the laboratory analytical accuracy. Certified reference materials (CRMs) have also been used to evaluate the accuracy of the contracted laboratories along with the in house synthetic samples. Duplicates of the environmental samples have been submitted to evaluate analytical precision of the submitted sample analyses. Equipment blanks and trip blank samples are prepared and tested to rule out errors or cross contamination in the method setup, equipment used, and / or sample handling procedures.

Along with the previously described QA/QC regime, the Dry Weather Reconnaissance Monitoring program staff routinely analyzed samples that have been prepared by the in house QA/QC officer in order to assess the quality of mobile laboratory field measurements. Additionally, contracted laboratories supplied QA/QC data relating to their respective internal quality control programs utilizing CRMs, spiked, and duplicate samples analyzed along with County environmental sample batches.

Figures and charts were created to present the performance of the laboratories regarding the quality of the sample analyses over the course of 2016-17. Accuracy charts (**Figure C-11-VII.1**) show each analysis and the percent of samples that were within acceptable result boundaries for the constituent of concern. These boundaries have been obtained from the certified reference materials (CRM) documentation for each parameter and used in our accuracy analysis; if no boundary is provided with the CRM, a +/- 25% boundary is used. The precision charts (**Table C-11-VII.2**) show the median and mean of the percent errors of all samples within the respective analysis groups. The blanks charts (**Table C-11-VII.3**) highlight any spikes above reporting limits. **Figure C-11-VII.1**, **Table C-11-VII.2**, and **Table C-11-VII.3** are available at the following link: <https://ocgov.box.com/v/2016-17-SAR-PEA-C-11-Datasets>.

Routine evaluations of the QA/QC data collected are conducted to follow possible trends and concerns more closely. The Permittees have three internal dashboards that help track synthetic samples, duplicates, and blanks, respectively, as the data is reported by contracted laboratories. The dashboards are similar to the accuracy charts (**Figure C-11-VII.1**) used to present the data, and they include interactive filters for the different laboratories, analyses, parameters, water matrices, sample dates, and results to allow users to visualize trends and investigate results more easily and efficiently. As issues are identified, comparative QC studies and investigations are initiated to resolve potential errors or concerns. Analyses from the 2016-17 QA/QC program indicate the following results:

- The majority of nutrient accuracies were within boundaries. The precision of the nutrients analysis was generally acceptable with the median of percent errors at 0% error and the mean at 7% error.
- The four sample results for toxicity accuracy were within boundaries.
- The precision of the General Minerals, Hardness, and Triclopyr analyses were generally acceptable with low percent errors.
- The majority of pathogen indicator bacteria accuracies were within boundaries. Due to inconsistencies with indicator bacteria precision results, Permittees are conducting an evaluation of the sampling methods for the duplicates and investigating possible improvements that can be made.
- One synthetic sample was created for Methylene Blue Active Substances (MBAS). Two duplicate samples of MBAS were collected; both had a percent error of 0% due to the results being below the reporting limit. The Permittees plan to increase the amount of synthetic and duplicate samples next year to draw better conclusions about contracted laboratory accuracy and precision with the MBAS analysis.
- The accuracy evaluation for the oil and grease analysis showed that the QC results are consistently below their boundaries. This is due to low recoveries in synthetic samples that are related to limitation in the EPA method for this analysis. All duplicate results had a percent error of 0% in the precision analysis due to being less than the reporting limit (<5 mg/L).
- All three saltwater synthetic sample results for total organic carbon (TOC) were within boundaries. However, 9 out of 11 TOC freshwater synthetic sample results were out of boundaries. Because of this, comparative QC studies as well as QC investigations are being evaluated. With regards to duplicate samples and precision, 91% of TOC samples had a percent error less than 10% (the two samples outside this range had percent errors of 10% and 18%). Dissolved organic carbon (DOC) results all had a percent error less than 10%.
- Accuracy results for organophosphorus pesticides (OPP) analyses, also referred to as organophosphate pesticides, trended low throughout the year for some of the analytes. 7 out of 11 of the analytes had less than 50% of samples fall within boundaries. The analytes with the least number of samples within boundaries were Diazinon, Disulfoton, and Phorate. Regarding the precision analyses for OPP analyses, almost all duplicate results had a percent error of 0% because the results were less than the reporting limits. As a consequence of the accuracy and precision results, the Permittees consulted the producer of the Certified Reference Material for this analysis and ordered a synthetic solution to be sent to our contracted laboratory without the usual dilutions conducted at the Principal

Permittee's laboratory. Preliminary data show more accurate results, however some accuracy boundaries were below reporting limits. Additional studies are planned with elevated concentrations, and the Permittees will compare results from ampules used for the first time versus the ampules used for a consecutive time two weeks later. To evaluate the precision of the analysis, duplicates of these synthetics will be evaluated as well.

- Trace metal accuracy results were generally within boundaries. For seawater trace metal accuracies, all elements except for Silver (Ag), Arsenic (As), Mercury (Hg), and Selenium (Se) were within boundaries. Those four constituents were consistently out of boundaries in seawater samples, but they did not present the same problems in the freshwater trace metal accuracy analysis. Because of this, comparative QC studies as well as QC investigations are being evaluated. The precision of freshwater and seawater trace metal analyses have been generally acceptable. For freshwater, the median of percent errors was 0% error and the mean was 7% error. For seawater, the median of percent errors was 3% error and the mean was 7% error. There appeared to be outliers of some metal precision tests in both freshwater and seawater matrices affecting the percent error statistics.
- The precision for TSS had a median of percent errors at 11% error and a mean at 21% error. Because of this, comparative QC studies as well as QC investigations are being evaluated.
- Due to low duplicate sample counts, the Permittees plan to increase the amount of duplicate samples next year in order to draw better conclusions about contracted laboratory precision for the following analyses: Chloride, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and Sulfate (SO<sub>4</sub>).
- Many of the precision results had a percent error of 0% due to results being below reporting limits. The Permittees plan to evaluate this issue further, including potentially obtaining CRM and evaluating duplicate synthetics (with accuracy boundaries above the reporting limit) for the following analyses: Glyphosate, Nonylphenol, Organophosphorous Pesticides (OPPs), Organochlorine Pesticides (OCPs), Pyrethroid Pesticides (PPs), and Polychlorinated Biphenyls (PCBs).
- Trip blanks and equipment blanks for Total Organic Carbon (TOC) had an increased number of samples that were above the reporting limits. Trip blanks and equipment blanks for nutrients and trace metals were generally below the reporting limits, with the majority of the trace metal spikes being Copper blanks. In response to these results, a Quality Assurance Investigation has been implemented with the following activities:
  - The Nanopure source water for these blanks was assessed, and the CASCADA system was replaced with new ELGA systems. The new Nanopure system will be undergoing regular disinfection cycles, and contractor support is being regularly obtained to service and calibrate the system. A trace metals blanks analysis conducted with the new Nanopure system showed QA/QC results below the reporting limits. A nutrient and TOC blanks analysis is also being evaluated.
  - The equipment used for the Dry Weather Reconnaissance Monitoring program will be completely replaced with new acid-washed Nanopure containers, and, if need be, the tubing in pumps and automatic sampling devices will be assessed.