

Sampling and Laboratory Analysis Plan (SLAP) for the 2010-11 Emerging Constituents Characterization Study in the Santa Ana Watershed

The Santa Ana Watershed Project Authority's (SAWPA) Emerging Constituents (EC) Workgroup submitted a water quality investigation workplan to the Santa Ana Regional Water Quality Control Board (RWQCB) to characterize selected ECs in surface waters and imported waters for calendar year 2010¹. The selected ECs include pharmaceuticals & personal care products (PPCPs), pesticides, herbicides, and industrial indicators of wastewater origin. The analytical laboratories supporting this effort will be able to follow the criteria presented within this Sampling and Laboratory Analysis Plan (SLAP), which is a required element of the workplan.

1. Sample Collection, Preservation, Storage and Holding Times

Sampling and laboratory analysis will be scheduled to meet the deadlines specified in Section 5E of the workplan described in the Phase-II report. Specifically, the results from all POTW (publicly owned treatment works) effluent samples, the State Water Project (SWP) and Colorado River samples from Metropolitan Water District of Southern California (MWDSC), and the first SAR sampling event (two sites) conducted by Orange County Water District (OCWD) are due to SAWPA by July 31st, 2010. These data will be included in the Annual Report that is due to the RWQCB by December 31, 2010. The second set of SAR samples are to be collected and analyzed by OCWD by September 30th, 2010, with these data to be included in the subsequent 2011 Annual Report.

Each designated lab will provide their own sample bottles (pre-cleaned amber glass) preserved with ascorbic acid (50 mg/L) and sodium azide (1 g/L) added to sample bottles before shipment to the sites. Samples bottles can be pre-labeled with site information, and will include date, sampling time, sampler, site location, and required testing. Bottles should include a label with the method's chemical preservatives.

Samplers and laboratory staff will be warned of low-level detection of ECs and potential background sources caused by the sampling process. These personnel should be aware of the potential for interference from the use of target compounds monitored within this investigation (prescription drugs, coffee, ibuprofen, acetaminophen, etc.). Specifically, they will be requested not to consume any caffeinated drinks while at the sample site, nor during the time of sample collection or laboratory analysis. Each designated agency will insure that these sampling guidelines are followed, and that qualified sampling staff are assigned to this investigation. Samplers will wear clean nitrile gloves at each site, and will follow the standard operating procedures outlined within their sampling programs.

¹ Phase-II Report of the Emerging Constituents Workgroup, approved by the Santa Ana Regional Water Quality Control Board on December 10th, 2009

Field Blanks will be taken at each site where a similar sample volume of laboratory reagent water is transferred into a labeled FIELD BLANK sample bottle (preserved). Each laboratory will provide the laboratory reagent water for their field blanks, and any other additional quality control samples required within their laboratory's analysis.

At least one site within each matrix group will be sampled as a duplicate, and noted within the chain of custody (COC) form. Field parameters will be measured and noted onto the COC – electrical conductivity, pH, temperature, dissolved oxygen, etc. Also, enough samples will be taken to ensure that matrix spike and matrix spike duplicates (25-200 ng/L) can be performed on at least 10% of the total samples collected.

Sample extraction holding time is 14 days and the extract analysis holding time 14 days. The laboratory should try and extract and process the EC method as soon as possible after delivery. Samples should be transported in ice (bagged or blue ice) and delivered to the lab at <10°C. Samples are to be kept refrigerated until ready to be extracted (<6°C).

One site location will be identified as a “split sample” and processed by all participating labs. We recommend the *SAR at Prado Dam* site for the split sample. This will represent the matrix split sample within the study. OCWD will collect, split, and distribute this sample to all participating laboratories.

2. Target Analytes

The SAWPA's EC team developed a listing of eleven target compounds to be monitored within this study (see Table 1). The selection criteria are based on detection within previous national studies and recommendations as surrogates for wastewater indicators.

All labs have different EC target lists, and therefore will generate specific information on the samples analyzed. Targets lists will continue to evolve and the reportable levels can also vary. For the purposes of this study, each lab will report to SAWPA the results and related QA/QC data for the eleven target compounds.

All targets will be analyzed using the isotope dilution technique, with the exception of TCEP, as its required labeled standard is cost-prohibitive at the present time.

Table 1: Chemicals to be Analyzed in 2010-11 EC Characterization Study

Analyte	CAS#	Category
Acetaminophen	103-90-2	Pharmaceutical
Diuron	330-54-1	Herbicide
Bisphenol-A	80-05-7	Industrial
Caffeine	58-08-2	Food Additive
Carbamazepine	298-46-4	Pharmaceutical
DEET	134-62-3	Pesticide
17 α Ethynylestradiol	57-63-6	Pharmaceutical
Gemfibrozil	25812-30-0	Pharmaceutical
Ibuprofen	15687-27-1	Pharmaceutical
Sulfamethoxazole	723-46-6	Pharmaceutical
TCEP	115-96-8	Industrial

3. QA/QC Procedures

Each lab will operate their method according to their Standard Operating Procedure (SOP), and therefore have associated Quality Assurance/Quality Control (QA/QC) samples analyzed within their procedure to help confirm the reported values. However, general data quality objectives can be developed within this investigation. All laboratories should be able to meet the criteria listed below. In an effort to facilitate the comparison of data produced by multiple laboratories and to minimize the effects of sample interference, the study's minimum reporting level (S-MRL) will be set at 10 ng/L. SAWPA's EC study report will use the S-MRL for final reporting purposes. Each lab will provide their most recent method detection limit (MDL) value for each target reported.

Two "Blind QA Samples" prepared by Environmental Resource Associates (ERA) will be sent directly to each participating lab. The first blind sample will be a mid-level check, where each target compound from SAWPA's target list spiked between 25-200 ng/L in a clean water matrix. The second blind sample will be a low-level check S-MRL Verification, where seven or eight of the eleven target compounds are spiked at a 10-15 ng/L level. These QA samples will be processed along with all received study sites by each laboratory.

Table 2: Method Performance Checks for EC Characterization Study

<u>Sample Description</u>	<u>Specification & Frequency</u>	<u>Acceptance Criteria</u>	<u>Remedial Action</u>
Low-Level CCC at the MRL (RDL)	Each Analysis Run	50-150% target recovery	Instrument Maintenance and Check Standards
Mid-Level CCC	Each Analysis Run	70-130% target recovery	Instrument Maintenance and Check Standards
“RB” Reagent Blank	Each Extraction Set	All targets must be less than 1/3 of the MRL (RDL)	Isolate Source of Contamination and Re-Extract
Low LFB Spiked Reagent Water at the MRL	Each Analysis Run	50-150% target recovery	Check SPE Cartridge Lots Verify Extraction Procedures and Re-extract
LFB – mid level	Each Analysis Run	70-130% target recovery	Check SPE Cartridge Lots Verify Extraction Procedures and Re-extract
Matrix Spikes Matrix Spike Duplicates Spike/Spike Dup (e.g. 200 ng/L - SARMON)	Each Analysis Run 10% minimum of total sample load	60-140% recovery <30% RPD If MS/MSD spike level is <50% of the ambient concentration acceptance limits are not relevant	Investigate Matrix Issues Check Standards and Re-Extract
Field Sample	Run Analysis	Check Internal (Isotope) Recovery (compound independent)	Investigate Matrix Issues Check Standards and Re-Extract
Back Standards	Each Analysis Run Every 10 samples must be bracketed with a CCC std	70-130% target recovery	Instrument Maintenance and Check Standards
Initial Calibration	Started Before Each Analysis Run	Must use at least a 5-point calibration curve Lowest Standard must be at or below reportable detection level (RDL) Calib. Curve <20% RSD	Check Standard Lots and QC Re-shoot or Open New Standards Instrument Maintenance
SAWPA Project Sample Duplicates	Each Analysis Run 10% minimum of total sample load	<30% RPD	Results Reported Re-Extract to confirm if possible
MDLs	Each New SPE Lot or Major Instrument Maintenance	The goal is for the calculated MDL to be 1/3 the RDL. The MDL must be lower than the RDL.	Instrument Maintenance, Extraction Procedures and Check Standards

4. Data Assessment and Reporting

Data will be reviewed by each laboratory's procedure and potential re-extractions or analysis conducted. Any samples that fail specific QA/QC criteria, which require a re-sampling request, will be done and evaluated at each participating lab. A detailed description of the cause(s) of the request will be reviewed.

Laboratories will provide a copy of their detailed SOP within the support of this investigation. Final reports will provide all QA/QC information including spike recovery information, LFB recoveries, blanks, calibration check information, MDLs, and applied method techniques. Blanks and MRL criteria referenced in Table 3 will be followed by all laboratories.

Table 3: Blanks and MRL Criteria for Preliminary EC Characterization Study

Batch QC	QC result	Secondary check	Reporting qualifiers
Method Blank	<MRL		OK to report - not clear that 1/3 MRL is always feasible (e.g. caffeine)
	>MRL	Samples ND	OK to report
	>MRL	Samples positive	Reprocess all positive samples
MRL - Check	<50%		Reprocess entire batch
	50-150%		Proceed
	>150%		Report if samples ND & note qualifier
LCS (spike must be <10x the MRL and should be representative of samples)	<70%		Reprocess entire batch
	70-130%		Proceed
	>130%		Report if samples ND & note qualifier
Field QC			
Field QC	QC result	Secondary check	Reporting qualifiers
Field Blank	< MRL		Proceed
	1-2x MRL		
	1-2x MRL	Samples ND	Report
	1-2x MRL	samples >2x field blank	Report value with flag (field blank contains target analyte but sample >2X field blank level)
	1-2x MRL	samples <2x field blank	Report ND with flag (field blank contains similar levels to sample)
	>2x MRL		
	>2x MRL	samples <10x Field Blank	Field Contamination (Resample required)
	>2x MRL	samples >10x field blank	Report value with flag (field blank contains target analyte but sample >10X field blank level)

5. Data Interpretation and Application

Because the analytical techniques used to support EC characterization studies are still in the early stages of development, great care must be exercised when using the results of such studies. To ensure that water quality monitoring data is used appropriately, EPA has established formal Data Quality Assurance requirements:

*"EPA has developed a mandatory Agency-wide Quality System (or QA program) that requires all organizations performing work for EPA to assure that: environmental data collected are of the appropriate type and quality for their intended use...."*²

*"Data Quality Objectives (DQOs) are statements of the level of uncertainty that a decision maker is willing to accept in results derived from environmental data, when the results are going to be used in a regulatory or programmatic decision (e.g., setting or revising a standard, or determining compliance). They are a tool that the permit writer may use to ensure that resources are being expended in the most efficient way, and that data collected are sufficient to support the decision making process and not extraneous to that process. To be complete, these quantitative DQOs must be accompanied by clear statements of: decisions to be made; why environmental data are needed and how they will be used; time and resource constraints on data collection; descriptions of the environmental data to be collected; specifications regarding the domain of the decision; calculations, statistical or otherwise, that will be performed on the data in order to arrive at a result. Without first developing DQOs, a QA program can only be used to document the quality of obtained data, rather than to ensure that the data quality obtained will be sufficient to support a permitting decision."*³

The most common use of water quality monitoring data is to evaluate compliance with relevant water quality standards. Therefore, DQOs are usually established in order to ensure that the resulting information is suitable for that intended regulatory purpose. The data quality criteria established in conjunction with California's 303(d) listing guidance is an example of such DQOs.⁴

² U.S. EPA. EPA Requirements for Quality Management Plans; EPA QA/R-2; Nov., 1999.

³ U.S. EPA. NPDES Permit Writer's Guide to Data Quality Objectives; Nov., 1990; p. 1-4 & 1-5.

⁴ State Water Resources Control Board. Water Quality Control Policy for Developing California's Clean Water Act Section 303(d) List. Sept. 30, 2005; Section 6.1 @ pgs. 17-26. See also Final Functional Equivalent Document for Water Quality Control Policy for Developing California's Clean Water Act Section 303(d) List. Sept., 2004. Pgs. 232-235.

However, since there are no federal or state water quality standards for the ECs analyzed during this characterization study, it is not possible to establish appropriate DQOs for evaluating compliance with such standards.⁵ Therefore, until EPA approves standard analytical methods, the data collected as part of this preliminary EC characterization study should be considered "provisional."⁶ This is consistent with EPA's guidance:

*...methods which will be used extensively for regulatory purposes or where significant decision must be based on the quality of the analytical data normally require more extensive validation and standardization than methods developed to collect preliminary baseline data.*⁷

The data quality objectives established in this Sampling and Analysis Plan are suitable for supporting an early effort to characterize EC concentrations in the Santa Ana watershed. However, a more rigorous data quality review will be necessary before the new information can be deemed suitable to support some regulatory applications, such as: 303(d) listing decisions, antidegradation analyses or translating narrative criteria into numeric TMDL targets or effluent limits. This issue is best addressed by the State Board, through the normal public hearing process, after the Blue Ribbon Panel on Emerging Constituents submits its recommendations.

⁵ EPA publishes recommended federal water quality criteria pursuant to Section 304(a) of the Clean Water Act. State water quality standards are normally documented in the Water Quality Control Plan (aka "Basin Plan") adopted by each of the California Regional Water Quality Control Boards.

⁶ EPA's criteria for certifying a new standard method, pursuant to 40 CFR Part 136, requires a thorough demonstration of accuracy, precision, method detection levels, representativeness, ruggedness, comparability and availability for the proposed analytical procedure. See U.S. EPA. Availability, Adequacy, and Comparability of Testing Procedures for the Analysis of Pollutants Established Under Section 304(h) of the Federal Water Pollution Control Act - Report to Congress; EPA/600/9-87/030; September, 1988 for a more detailed discussion.

⁷ U.S. EPA. Availability, Adequacy, and Comparability of Testing Procedures for the Analysis of Pollutants Established Under Section 304(h) of the Federal Water Pollution Control Act - Report to Congress; EPA/600/9-87/030; September, 1988; pg.3-5S

6. Definitions

- Blind QA Samples** – An unknown quality assurance sample, which is spiked with the study's target compounds in a reagent water matrix. QA samples are provided by a method Performance Evaluation (PE) vendor – Environmental Resource Associates (ERA). Two QA samples are provided within this study – a mid level calibration check (25-200 ng/L) and an S-MRL check (10-15 ng/L). QA samples are sent directly to participating labs by the PE vendor for analysis.
- CCC** – Continuous Calibration Check – a method required standard to verify the calibration curve – most labs will run verification at the mid-level of the calibration – and at the reportable detection level - RDL (minimum reporting level – MRL).
- COC** - Chain of Custody – document that provides field and site information and conditions. COC information is transferred into the lab's database, includes basic field parameters. This is a legally required lab document.
- Field Blank** – A quality control sample used to monitor/verify sampling conditions at the site. The field blank is processed by pouring laboratory reagent water into a preserved sample container for the required method. The process mimics the sampling techniques for the site sample; tested to insure that none of the targets determined within the sample are coming from the process of sampling.
- LFB/LCS (low/high)** -Laboratory Fortified Blank/Laboratory Control Sample – is a laboratory reagent water sample, which is spiked with the method targets, and extracted within each method batch of samples. Processed just like a sample. This quality control sample insures that the method is generating acceptable data. Labs may run both an MRL/RDL level LFB (low) as well as a mid-level LFB (high).
- MBLK / BLK/ RB** – Method Blank/ Blank / Reagent Blank – is a method quality control sample consisting of laboratory reagent water and extracted and analyzed identically to all samples within each analytical batch. It monitors the laboratory method and techniques for any sources of contamination or interference.

- MDLs –** Method Detection Levels – are a statistical calculated value for each target analyzed by the laboratory’s method. MDLs are performed by processing seven or more spiked replicates samples at a low-level, and analyzed over a three or more day period under method conditions. MDLs represent the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDLs goal is to be 3x lower than the laboratory established RDL/MRL.
- MRL/RDL –** Minimum Reporting Limit/ Reportable Detection Level - Represents the minimum quantifiable concentration level for a target analyte within the method. It usually represents the lowest calibration level within the standard curve. The MRL/RDL must be higher than the statistically calculated MDL.
- MS/MSD -** Matrix Spike / Matrix Spike Duplicate – are quality control samples processed within each analytical batch. They represent field samples that have been spiked with a known concentration of target analytes and processed within the entire method along with all samples. These QC samples are used to monitor the impact of sample matrix on the accuracy and precision of the results.
- RPD –** Relative Percent Difference – is a quality control value calculated from the MS/MSD samples (as well as other QC duplicates) as a measure of the precision of the method. $RPD = ((X1-X2) / ((X1+X2)/2))*100$
- S-MRL –** Study’s Minimum Reporting Limit – The lowest concentration level at which each target within this study will be quantified and reported – 10 ng/L.
- SOP –** Standard Operating Procedure – the laboratory document that provides detailed directions as to the steps and procedures within the method of analysis. Procedure followed by laboratory technicians and chemists so as to produce consistent reliable results. SOPs are also used by field staff.
- SPE –** Solid Phase Extraction – analytical technique used within the lab to extract and process samples. Disks and cartridges are used to retain the targets of interest during the extraction process – eluted with appropriate solvents and then concentrated for final analysis.
- Split Sample –** Split Sample – is a quality assurance control, which is an actual field sample that is sent to multiple labs for analysis. The split samples provide a comparison of quality analysis between different labs.