1. Title and Approval Sheet

Quality Assurance Project Plan for the Pilot Study of Pharmaceuticals and Personal Care Products in the San Diego Region.

June 22, 2010

Approvals

Project Manager _____Date_06/22/2010
Lilian Busse

Regional Board QA Officer _____Date_____
Lisa Honma

June 2010

Prepared by:
Cynthia Gorham
San Diego Regional Water Quality Control Board

Contact Information:

California Regional Water Quality Control Board
San Diego Region
9174 Sky Park Court, Suite 100
San Diego, CA 92121-4340
Lilian Busse, Environmental Scientist
(858) 467-2971, LBusse@waterboards.ca.gov

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3. Distribution List

Title:	No of copies:	Name (Affiliation):	Tel. No.:
Project Manager	1	Lilian Busse, RWQCB	(858) 467-2971
QA Officer	1	Lisa Honma, RWQCB	(858) 467-2960
Contract Manager	1	Marco Sigala, Moss Landing	(831) 771-4173
	1	Rusty Fairey, Moss Landing	(831) 771-4161
Laboratory Contact	1	Gail Cho Water Pollution Control Lab, Department of Fish & Game Rancho Cordova, CA	(916) 358-2840

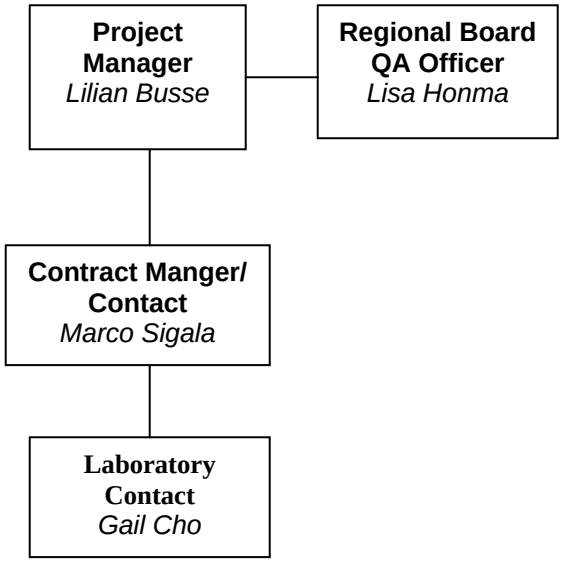
4. Project/Task Organization

The Project Manager, Lilian Busse, will be responsible for general oversight of the project, will serve as the main point of contact, and will hold the original version of the Quality Assurance Project Plan (QAPP). A field crew will be assigned to the project.

The Quality Assurance Officer for the California Regional Water Quality Control Board, San Diego Region (Regional Board) will ensure that all aspects of this Quality Assurance Project Plan (QAPP) are adhered to by those individuals taking and handling samples for the Regional Board. Lisa Honma will serve in this capacity and is not part of the Project Team.

Marco Sigala and Rusty Fairey will serve as the Contract Managers and ensure that the sample handling and analysis of the project samples by the Department of Fish & Game Water Pollution Control Laboratory in Rancho Cordova, CA (WPCL) are performed in accordance with the contractual obligations. Gail Cho will be the laboratory contact for the DFG WPCL.

Figure 1: Organization Chart



5. Problem Definition/Background

Problem Statement

Contaminants of Emerging Concern

Contaminants of emerging concern (CECs) are a diverse group of relatively unmonitored and unregulated chemicals that have been shown to occur at trace levels in wastewater discharges, ambient receiving waters, and drinking water supplies. CECs include pharmaceuticals, personal care products, and other commercial and industrial compounds. There are 129 priority chemicals currently regulated by the USEPA under the Safe Drinking Water Act and Clean Water Act, but there is no regulation of tens of thousands of CECs. An increasing number of studies report the occurrence of CECs in drinking water sources and in the aquatic environments.

Current monitoring programs focus on a small list of contaminants that were identified as priority pollutants decades ago. However, thousands of additional chemical in common use by industry, agriculture, and households are eventually discharged in the environment. Some of these chemicals persist in the environment, accumulate in tissues, and are toxic to aquatic life or impact aquatic life in some other way. Because the production of these new contaminants is likely to continue and/or increase in the future, while behavior, fate and effects are largely unknown, monitoring of those contaminants is important.

For most emerging contaminants, insufficient information is available to determine whether chemical concentrations measured in the environment are likely to have ecologically significant effects.

A workshop about the management of contaminants of emerging concern in California was held at SCCWRP on April 28-29, 2009, in Costa Mesa, California. The findings of the workshop are summarized in a technical report (SCCWRP 2009). State, local health and regulatory agencies are aware of the presence of CECs in the environment, but they have not developed a comprehensive strategy for addressing the monitoring and regulatory actions regarding CECs. The workshop recommended the development of a flexible, multi-element prioritization framework to identify those compounds of highest concern.

According to the technical report from the workshop, the next step is to formulate preliminary lists of priority CECs, indicator compounds, and surrogate parameters that will be addressed in monitoring including drinking water, recycled water, wastewater discharges, and ambient receiving waters. These preliminary lists could then be incorporated into existing and planned collaborative studies that are organized at the watershed or regional scale. Results from these pilot studies will be used to fill key data gaps and initiate the iterative process formulated during the workshop for prioritizing those CECs in need of regulatory review.

PPCPs

Pharmaceuticals and personal care products (PPCPs) are substances used by individuals for personal health or cosmetic reasons and the products used to increase the growth or improve the health of livestock. PPCPs can enter the aquatic environment both from point and non-point sources. PPCPs have recently emerged as environmental contaminants with adverse impacts on various organisms and on human health. A variety of PPCPs for human use are discharged on a continual basis into wastewater treatment plants via excretion with urine and feces, and through direct disposal. During the wastewater treatment process, the PCPPs can remain unchanged or undergo transformation before being discharged into the environment. Numerous PPCPs and their metabolites have been detected in a variety of water samples, sediment samples, and biological samples (SWRCB, 2010). In southern California, several studies on PPCPs were conducted in specific areas, or on specific samples. Kwon et al. (2009) showed that certain PPCPs are found in fish liver from samples taken near waste water outfalls in southern California. Loraine and Pettigrove (2006) found several PPCPs in raw and treated drinking water in San Diego County.

Decisions or Outcomes

This project will assess the ambient water quality in the San Diego Region streams with respect to whether there are measurable concentrations of PPCPs. Results from nationwide, statewide, and regional studies indicate that PPCPs occur in water bodies in the San Diego region. Monitoring to address PPCPs is currently not being conducted in the San Diego region. The CEC Workshop held in southern

California in April of 2009 recommends, as the next steps, to initiate investigative monitoring rather than regulatory monitoring for CECs. Before starting required regulatory monitoring, the investigative monitoring needs to find the high priority CECs. In addition, the workshop recommended monitoring indicator groups rather than individual contaminants. The proposed study will address both recommendations.

After sampling, the data will be compiled and evaluated. After compilation of the data, a report will be written which will include findings and recommendations for future action from the data evaluation.

6. Project Task/Description

Work Statement and Produced Products

This project addresses contaminants of emerging, specifically PCPPs including surfactants, in the San Diego Region freshwater systems.

Assessment Questions
The following assessment questions will be addressed by the Regional Board for the proposed monitoring plan:

1. What are the occurrence and extent of pharmaceuticals and personal care products (PPCPs) in drinking water, treated wastewater, stormwater, and ambient surface waters in the San Diego region?
2. Are PPCP levels in water cause for concern?

To answer the questions, the following steps must be taken:
1. Collect PPCP samples.
2. Analyze PPCP samples.
3. Analyze PPCP data.

Study Design
Two types of data will be collected for this study: water quality field data collected using an electronic multi-probe, and specific PCPPs analyzed in a lab. PPCPs will be sampled in areas: (1) with a high accumulations of septic tanks; (2) with discharge of an inland waste water treatment plant; (3) with a high accumulation of untreated human waste, and (4) with no obvious discharge of treated or untreated human waste. A targeted sampling design will be used.

The study will focus on three watersheds: the San Diego River, Santa Margarita River, and Tijuana River watersheds. The San Diego River watershed will be sampled because of the Padre Dam Water Recycling Facility. The Santa Margarita River watershed will be sampled because it has a large number of on-site sewage treatment systems (septic systems). The Tijuana watershed will be sampled because of large amounts of untreated human waste. All three

watersheds also have minimally impacted sites (reference sites, no obvious human impact) in the upper watershed.

Samples will be collected at: 1) two reference sites, 2) two sites close to the outfall of the Padre Dam Water Recycling Facility, 3) two sites within watersheds known to have high concentrations of septic systems, 4) two sites within watersheds known to have high concentration of untreated human water.

The monitoring event will be conducted four times in FY 2010-2011 at the locations that will be listed in Table 6-1 when those sites are chosen. Monitoring will occur in 1) early fall, before the first rain event, 2) in winter, during the wet season, and 3) spring after the wet season, and 4) in summer.

Sampling Constraints

A constraint for sampling in the San Diego Region is that few streams truly have perennial flow. The sampling crew may have difficulty collecting samples in early fall before the first rainfall events of the wet season. This constraint can be minimized by extensive site reconnaissance and review of the total drainage area above the sampling site. The amount of rainfall received during the wet season will dictate when samples should be collected in the summer. Low rainfall may require that samples are collected relatively early in the summer season to ensure that sufficient flow is available in the stream.

Site Selection and Reconnaissance

A targeted sampling design will be used. Established SWAMP sampling sites and reference sites will be considered for this project. Each new site will be evaluated prior to sampling through a reconnaissance process that determines site access and suitability.

Criteria for rejecting sites include:

Safety: Crews may reject a site if it is unsafe to access

Accessibility: Crews must be able to leave the office, access the site within from the nearest road, complete sample collection, and return to the office within eight hours. Landowner permission: Crews may not enter private property without express permission of the landowner. At a minimum, crews should make two attempts to contact non-responsive landowners, after which permission is considered denied.

Target status: Crews must reject sites that do not fit the definition of target status, i.e., perennial, wadeable streams. In the San Diego region, perennial streams are defined as those that flow until the onset of the next rainy season in years with typical rainfall (i.e., September).

All reasons for rejection will be documented and submitted to the QA Officer using Recon Reporting Forms. These forms will be turned over to the project manager at the end of this project to be kept on file with the SWAMP reconnaissance files for future reference.

Constituents to be Monitored and Sample Costs

Water Quality Field Data. In-situ field measurements (dissolved oxygen, water temperature, conductivity, and pH) will be collected at each station. All measurements will be conducted as required by SWAMP protocols.

PPCPs. PPCP samples will be collected at all stations. PCPPs (including three surfactants) for lab analysis are listed in Table 6-2. All samples will be collected following SWAMP sampling protocols for collecting organic chemicals in water.

Table 6-2. PCPP Compounds to be sampled.

Caffeine	Roxithromycin
Carbadox	Erythromycin hydrate
Sulfathiazole	Gemfibrozil
Lincomycin	Triclosan
Sulfamerazine	Chlorotetracycline
Sulfamethizole	Doxycycline
Sulfamethazine	Oxytetracycline
Trimethoprim	Tetracycline
Sulfachloropyridazine	Carbamazepine
Sulfamethoxazole	Fluoxetine
Sulfamethoxine	
Tylosin	Nonylphenol
Ibuprofen	Nonylphenolethoxylate
17β-estradiol	Trimethylphenol-2,4,6

Table 6-3 summarizes the sampling and analysis plan and provides the estimated costs for analysis of the PCPP suite. The total cost for the project, not including labor, is $18,900 for four sampling periods.

Table 6-3: Water/Wastewater Sampling and Laboratory Analysis Plan and Budget Estimation

Analysis	Method	Reference	Septic Tanks	Wastewater discharge	Untreated waste	Field Blank/ duplicate	X	Unit Cost	=	Sub-totals
Personal Care Products/ Pharmaceuticals (by LC-MSMS) - water	EPA 1694	2	2	2	2	1	x	$525	=	$4,725
Surfactants	JACR97_3247-3272	2	2	2	2	1	x	Incl. in PPCPs	=	$ 0
Total x 4 sampling periods									=	**$18,900**

Project Schedule

Table 6-4 outlines the anticipated project schedule and completion dates and includes a timeline for the following tasks and deliverables:
1. List of sites for PPCP study with GPS locations, deliverable date: 9/30/2010.
2. Sampling of sites for PPCP study, and submitting field data to SWAMP database.
3. Analysis of samples, submission of data to SWAMP database, and report for PPCP study to SWAMP database: 3/31/2012

Table 6-4. Project Timeline.

	9/ 10	10/ 10	11/ 10	12/ 10	1/ 11	2/ 11	3/ 11	4/ 11	5/ 11	6/ 11	7/ 11	8/ 11	9/ 11	10/ 11	11/ 11	12/ 11	1/ 12	2/ 12	3/ 12
List of sampling sites, PPCP																			
Sampling and field data in database PPCP																			
Analysis and data in database, PPCP																			

7. Quality Objectives and Criteria for Measurement Data

Data Quality Objectives

Data quality objectives (DQOs) are generally used to determine the level of error considered to be acceptable in the data produced by the sampling program. The DQOs are used to specify acceptable ranges of field sampling and laboratory performances. Data quality objectives for all variables measured in this project will consist of the following data quality objectives found in Table 7-1.

Table 7-1: Data Quality Objectives for Sampling Program.

Measurement or Analysis Type	Applicable Data Quality Objectives
Field sampling for water samples	Completeness, Representativeness, Comparability
Field testing for dissolved oxygen, pH, conductivity, temperature	Accuracy, Precision, Completeness, Representativeness, Comparability
Laboratory Testing, conventional water chemistry	Accuracy, Precision, Completeness, Comparability
Laboratory Testing, trace metal chemistry	Accuracy, Precision, Completeness, Comparability

Representativeness

The representativeness of the data is mainly dependent on the sampling locations and the sampling procedures adequately representing the true condition of the sample site. Sample sites, sampling of relevant media (water, sediment and biota), and use of only approved/documented analytical methods will determine that the measurement data represents the conditions at the investigation site, to the extent possible.

It is well known that water flowing past a given location on land is constantly changing in response to rainfall, soil saturation, return flows, etc. Sampling schedules will be designed with respect to frequency, locations and methodology in order to maximize representativeness, where possible.

Comparability

The comparability of data produced by and for SWAMP is predetermined by a commitment to use standardized methods, where possible. These methods specify the units in which the results are to be reported.

Measurements are made according to standard procedures, or documented modifications thereof, which provide data of equal or higher quality, using common units such as Celsius, feet, feet/sec, mg/L, mg/kg, etc.

Completeness

The completeness of data is a relationship between how much of the data are available for use compared to the total potential data identified in the monitoring

plan. Ideally, 100% of the data should be available. However, the possibility of data becoming unavailable due to laboratory error, or samples broken in shipping must be expected. Also, unexpected situations may arise where field conditions do not allow for 100% data completeness. Therefore, 90% data completeness is required. Completeness results will be checked; this will allow identifying and correcting problems.

Precision and Accuracy

The precision and accuracy of data are determined by particular actions of the analytical laboratory and field staff. Any doubts of precision and accuracy resulting from data quality observation will be addressed and discussed in the final report. The precision of data is a measure of the reproducibility of the measurement when an analysis is repeated. It is reported in Relative Percent Difference (RPD) or Relative Standard Deviation (RSD). The accuracy of an analysis is a measure of how close a measurement is to the true value. It is measured, where applicable, by adding a known amount of the constituent to a portion of the sample and determining how much of this spike is then measured. It is reported as Percent Recovery. The acceptable percent deviations and the acceptable percent recoveries are dependent on many factors including: analytical method used, laboratory used, media of sample, and constituent being measured.

Laboratory precision measurements will be determined on laboratory replicates. The number of laboratory replicates will be in accordance with the Laboratory's Quality Assurance document. Field duplicates will be collected for the precision of field samples. At least five (5) percent of all samples collected for the project shall be quality control samples. The number of duplicates will be one per sampling event. In situ measurements of dissolved oxygen, pH, conductivity, and temperature will be taken at each location using an YSI multimeter. The YSI multimeter will be calibrated the morning of the sampling, and documentation of the calibration will be provided in the final report.

The evaluation of accuracy for water quality parameters tracked by the laboratory will be conducted by the use of spikes, matrix spikes, and check standards as outlined in the SWAMP QAPrP (2008) and the Standard Operating Procedures (SOP) for the prescribed Method. The data quality objectives for field and laboratory measurements for the projects are provided in Table 7-2. The target reporting limits are in accordance with the SWAMP target reporting limits or lower.

Although the laboratory duplicate and matrix spike duplicate both provide information regarding precision, they are unique measurements. Laboratory duplicates provide information regarding the precision of laboratory procedures. The matrix spike duplicate provides information regarding how the matrix of the sample affects both the precision and bias associated with the results. It also determines whether or not the matrix affects the results in a reproducible manner. Because the two concepts cannot be used interchangeably, it is unacceptable to analyze only an MS/MSD when a laboratory duplicate is required.

Table 7-2: Data Quality Objectives for field and laboratory measurements.

Analyte	Target Reporting Limit	Acceptance Criteria
Temperature	0.5°C	Resolution: 0.01°C* Accuracy: ± 0.15°C*
pH	0.5 units	Resolution: 0.01 units* Accuracy: ± 0.2 units*
Conductivity	2.5 mS/cm	Resolution: 0.001 mS/cm* Accuracy: ± 0.5% of reading or ± 0.001 mS/cm* (whichever is greater)
Dissolved Oxygen	0.5 mg/L	Resolution: 0.1% air saturation/ 0.01 mg/L* Accuracy: ± 2% or reading or 2% air saturation* (whichever is greater) ± 2% or reading or 0.2 mg/L* (whichever is greater)
Caffeine	0.050 ng/L	- Reference Material: measured value <95% confidence intervals, or 80-120% recovery - Matrix spike: 80-120% recovery - Matrix spike duplicate, laboratory duplicate and field duplicates: 25% relative percent difference
Carbadox	0.005 ng/l	
Sulfathiazole	0.020 ng/L	
Lincomycin	0.050 ng/L	
Sulfamerazine	0.010 ng/L	
Sulfamethizole	0.010 ng/L	
Sulfamethazine	0.010 ng/L	
Trimethoprim	0.005 ng/l	
Sulfachloropyridazine	0.010 ng/L	
Sulfamethoxazole	0.010 ng/L	
Sulfadimethoxine	0.005 ng/l	
Tylosin	0.100 ng/L	
Roxithromycin	0.100 ng/L	
Erythromycin hydrate	0.010 ng/L	
Gemfibrozil	0.005 ng/l	
Ibuprofen	0.050 ng/L	
Triclosan	0.050 ng/L	
Chlorotetracycline	0.020 ng/L	
Doxycycline	0.020 ng/L	
Oxytetracycline	0.020 ng/L	
Tetracycline	0.020 ng/L	
17β-estradiol	0.200 ng/L	
Carbamazepine	0.010 ng/L	
Fluoxetine	0.010 ng/L	
Nonylphenol	2.0 ng/L	
Nonylphenolethoxylate	2.0 ng/L	
Trimethylphenol-2,4,6	2.0 ng/L	

* = no SWAMP requirement available

8. Special Training Needs/Certification

Under this project, Regional Board staff will collect water samples and will send the water samples to the DFG WPCL every day after a sampling event. All staff and any students accompanying a Regional Board staff member in the field must complete the basic 4-hour field safety training provided by the state. At the Regional Board, Brian McDaniel provides access to this test. All staff and students participating in sampling must also attend the Field Sampling Technique Training provided by Cynthia Gorham. This training is designed to teach the proper sampling methods and proper use of other necessary equipment in the field. Furthermore, Regional Board staff will follow sampling guidelines outlined in this QAPP, which is SWAMP comparable. The DFG WPCL will follow the Quality Assurance Project Manual (see Appendix A), which is SWAMP comparable. The Project Manager is responsible for assuring that training requirements are met, and will provide training documentation in the final report.

9. Documents and Records

The Regional Board will collect records of sample collection and field observations. Records will be uploaded to paperless office once reviewed. The DFG WPCL will generate records for sample receipt and storage, analyses, and reporting.

Copies of this QAPP will be made available to all parties involved with the project, including the field sampling crew from the Regional Board. Any future amendments to the QAPP will be held and distributed in the same fashion. All originals of this first and subsequent document will be held at the Regional Board office. Copies of versions, other than the most current, will be discarded so as not to create confusion.

10. Sampling Process Design

Work under this QAPP will be performed at the designated sites within the San Diego Region. Sample sites will be chosen to represent the environments described in Section 6. The sampling team will take field duplicate samples at 5% of the sites and will be randomly collected for each sampling event (four events will be sampled). Sampling teams should not attempt to reach a site that is dangerously inaccessible.

Water samples will be collected by hand at all locations as a grab sample. Samples will be shipped to the WPCL. The results will verify the presence (or absence) and concentration of selected PPCPs in San Diego Region surface waters and in treated water in the Region.

11. Sampling Methods

Collection of Water Samples for PPCPs

Dissolved oxygen, pH, conductivity, and temperature will be measured in situ with at each location using an electronic multimeter at about 0.5-meter depth or one-half the total depth if the total water depth is shallower than 1.0 meters. All sampling instruments will be rinsed with ambient water following use at each site. Care should be taken to prevent disturbing sediment while taking in situ measurements or collecting water samples.

In streams, samples will be collected as grab samples from approximately midstream and at least 0.3 meters from bank and about 0.1-meter depth at the thalweg. All water samples collected will be collected using clean techniques that minimize sample contamination. Samplers will always wear nitrile gloves to prevent contamination of the sample from contamination with products worn by the sample handler, and to protect human health. In addition, smoking and handling or ingesting pharmaceuticals should be avoided shortly before and during sampling for PPCPs. Also, the field collection personnel should avoid the use of lotions, perfumes, and/or insect repellent. Grab samples will be collected into amber glass bottles Special attention must be given to compounds such as fluorochemicals, which are known to be present in Teflon lined bottle caps. Sample bottles should also be cleaned thoroughly with applicable solvents (e.g., water, methanol, acetone, dichloromethane, hexane) to ensure the cleanliness of the bottles prior to sampling. Liquid soaps containing non-ionic organic surfactants should be avoided for cleaning of the equipment. Furthermore, sampling equipment should be composed of materials such as stainless steel that will not leach target PPCPs and should be cleaned with solvent between sample locations to prevent cross contamination (SWRCB, 2010). After collection, field-collected samples will be placed in ice chests with wet ice to bring the samples to 4˚C for storage and transport to the DFG WPCL.

The sample collection method requires that the sample bottle and lid come into contact only with surfaces known to be clean, or with the water sample. If the performance requirements for specific samples are not met, the sample will be re-collected. If contamination of the sample container is suspected, a fresh sample container will be used.

Any problems that occur with the sampling methods should be reported to the project manager (Lilian Busse). The project advisor(s) will assess the problem(s) and is responsible for taking corrective action. Any of these problems will be documented in the Field Log.

Note to samplers: Make sure there is enough wet-ice for all samples. Each sample container should be in immediate contact (touching) the ice. Samplers should bring a small ice chest to the sample site containing sufficient ice for each sample container to be in immediate contact with ice. Sampling containers should

be placed on ice without delay. This means not transporting sampling containers without a cooler, and not placing sampling containers on hot asphalt while opening vehicle. Coolers should be placed in vehicle in a closely packed fit to avoid movement of ice chests and samples during transportation. Sample containers should be placed in ice chest upright when possible, and in a closely packed fashion to avoid spillage and movement.

Table 11-1: Collection of Water Quality Variables.

Sampling location	Analytical parameter	Matrix	Depth	Samples	Sampling SOP	Sampling volume
All locations	Dissolved oxygen, pH, conductivity, temperature	Water	0.1m below water surface for streams, 0.5m for reservoirs	1 per site	SWAMP QMP*	N/A
All locations	PPCPs, surfactants	Water	0.5 m below water surface	1 per site with duplicates at 10% sites	SWAMP QMP*	1000 ml

12. Sample Handling and Custody

Sample Handling

In the field, all samples will be packed in wet ice during transport so that they will be kept at approximately 6˚C. All caps and lids will be checked for tightness prior to storing. All samples will be handled, prepared, transported and stored in a manner so as to minimize bulk loss, analyte loss, and contamination or biological degradation. Sample containers will be clearly labeled with an indelible marker. Water samples will be kept in Teflon™, glass, or polyethylene bottles and kept cool at a temperature of 6˚C until analyzed. Maximum holding times for specific analyses are listed in Table 7 below.

DFG WPCL will follow sample custody procedures outlined in their QA plans (Appendix A). The QA Program Manual will be on file in the DFG WPCL.

All samples remaining after successful completion of analyses will be disposed of properly. It is the responsibility of the personnel of the DFG WPCL to ensure that all applicable regulations are followed in the disposal of samples or related chemicals.

Chain-of-custody procedures require that possession of samples be traceable from the time the samples are collected until completion and submittal of analytical results. A complete chain-of-custody form is to accompany the transfer of samples to the DFG WPCL.

Containers supplied by DFG WPCL will be used for sample collection. New sample bottles will be picked up from the laboratory or be delivered to the Regional Board Office at least one week prior to each sampling event.

Laboratory Custody Log

The DFG WPCL shall maintain custody logs sufficient to track each sample submitted and to analyze or preserve each sample within specified holding times. A sample is considered under custody when is in actual possession, in view after a physical possession and it is placed in a secure area (accessible by or under the scrutiny of authorized personnel only after in possession).

Data Sheet

Field crews shall be required to keep a field log for each sampling event. The following items should be recorded in the field log for each sampling event:

- Time of sample collection.
- Sample ID numbers and unique IDs for any duplicate or blank samples.
- Time of arrival and departure from site, and results of any field measurements not written on a data sheet.
- Qualitative descriptions of relevant water conditions (e.g. color, flow level, clarity) or weather (e.g. wind, rain) at the time of sample collection.
- Description of any unusual occurrences associated with the sampling event, particularly those that may affect sample or data quality.

The field crews shall have custody of samples during field sampling. Chain of custody forms will accompany all samples during shipment to the DFG WPCL. All water quality samples will be shipped to the DFG WPCL by someone from the Regional Board Office.

Table 12-1: Summary of Sample Container, Volume, Initial Preservation, and Holding Time Recommendations for Water Samples.

Method	Bottle Type	Initial Field Preservation	Maximum Holding Time
PPCPs – EPA 1694	1000-mL amber glass bottle, with Teflon lid-liner	Cool to 6°C, dark sodium thiosulfate or ascorbic acid required if residual chlorine present	48 hours at 6°C 7 days at -10°C
Surfactants – JACR97_3247-3272	1000-mL I-Chem 200 Series amber glass bottle, with Teflon lid-liner	Cool to 6°C, dark	7 days

*from SWRCB, April 2010, and WPCL. ^from SWAMP QAPrP, Appendix B, 2008

13. Analytical Methods

Laboratories

The Regional Boards established a contract with the DFG WPCL. The DFG WPCL will document the methods they use, the SOPs, and the data acceptability criteria of their analytical capabilities in their Quality Assurance (QA) Manual respectively (Appendix A).

The laboratory supervisor of the DFG WPCL has the primary responsibility for responding to a failure of analytical systems. Solutions which are consistent with the measurement objectives will be reached in consultation with the project manager. The method numbers used by the DFG WPCL for each analytical procedure they perform for SWAMP is available in each laboratory's respective QA Plan on file with that laboratory.

Corrective Action for Laboratory Activities:

Failures in field and laboratory measurement systems involve, but are not limited to, instrument malfunctions, failures in calibration, sample jar breakage, blank contamination, and quality control samples outside of the defined limits (Data Acceptability Criteria). In many cases, the field technician or lab analyst will be able to correct the problem. If the problem is resolvable by the field technician or lab analyst, then they will document the problem in their field notes or laboratory record and complete the analysis. If the problem is not resolvable, then it is conveyed to the respective supervisor, who will make the determination if the analytical system failure compromised the sample results and should not be reported. The nature and disposition of the problem is documented in the data report that is sent to the Project Manager. Detection limits may be affected by instrument sensitivity or by bias due to contamination or matrix interferences. Common laboratory practice is to adjust detection limits upward in cases where high instrument precision (i.e., low variability) results in calculated detection limits

that are lower than the absolute sensitivity of the analytical instrument. In these cases, best professional judgment is used to adjust detection limits upward to reduce false positives and values below the detection limit are not reported. In all cases, results cannot be reported for values less than the Method Detection Limit (MDL-see definitions below).

The recommended applications of detection and quantification limits should be followed:

- Values below the Method Detection Limit (MDL, per 40 CFR Part 136) are to be reported as a negative ("-") sign followed by the actual MDL value, and flagged with an ND = not detected.
- Values between the MDL and the Reporting Limit (RL, aka quantification limit, which is the MDL multiplied by a factor of 1-10, as determined by the lab to provide acceptable precision values among replicated measurements) should be reported as the actual measured value (not negative), with a flag that is carried all the way through data storage, handling, and reporting. The flag is DNQ = detected, not quantifiable.
- Values above the RL (or quantification limit) are deemed as acceptable values without reservation, and are shown as the actual measured value, and assigned a QA code of A (Acceptable without reservation).
- Other QA qualification codes may occur if QC criteria are not met or qualification is deemed appropriate during subsequent QA review.

Analytical Methods

Methods used for water quality parameters (see Table 13-1) will follow SWAMP approved SOPs.

Table 13-1: Field testing and laboratory analytical

Analyte	SOP	Modified yes/no
Temperature	SM 2550-B	No
pH	SM 2510-B	No
Conductivity	SM 2510-B	No
Dissolved Oxygen	SM 4500O-G	No
PPCPs	EPA 1694	No
Surfactants	JACR97_3247-3272	No

14. Quality Control

Adherence to SOPs by all data collectors will ensure that all samples are collected, handled, and processed with the maximum level of quality control as summarized in Table 14-1. Quality assurance and quality control activities for sampling include the collection of field duplicates for chemical testing, and the preparation of field blanks.

Field duplicates are used to assess the variability attributable to collection, handling, shipment, storage, and/or laboratory handling and analysis. Procedures for collecting field duplicates should be the same as that used for the collecting field samples. Duplicates of samples will be collected by filling two sample containers at the same time or in rapid sequence at a minimum of 10% of the sites. Sample containers will be labeled separately, but will not be identified as "duplicate" to the laboratory.

Field Blanks are used to determine if field sampling activities are a potential source for contamination. Field blanks will be periodically submitted to verify that sample contamination is not occurring. To collect field blanks, the same equipment used for collection of field samples should be used to pour blank water into blank sampling containers. Analyte free water will be used to fill field blanks.

Analytical quality assurance includes the following: (1) Adherence to documented procedures, U.S. EPA methods, SOPs or other approved methods; (2) adequate calibration of analytical instruments, and (3) complete documentation of sample tracking and analysis.

Laboratory quality control checks will include the use of method blanks, matrix spikes, duplicates, and laboratory control samples.

Corrective actions will be taken when analysis is deemed suspect for some reason. The corrective action n typically involves the following:

- A check of procedures
- A review of documents and calculations to identify possible errors.
- Correction of errors
- A re-analysis of sample if available

Table 14-1: Standard Operating Procedures

QC Check	Information Provided
Field duplicates	
Field samples	Sampling + measurement precision
Field duplicates	Precision of all steps after acquisition
Field blanks	
Bottle blank	Cleanliness
Field Blank	Transport, storage, and field handling bias
Laboratory QA	
Blanks	Minimum detection limit per each analyte
Field splits	Shipping + inter-laboratory precision
Laboratory splits	Inter-laboratory precision
Laboratory replicates	Analytical precision
Analysis replicates	Instrument precision
Matrix spike replicate	Analytical bias and precision
Analysis matrix spike, Instrument bias	80-120% Acceptance limit
Surrogate spike	Analytical bias
Calibration check samples	Following USEPA guidelines and recommendations of instrument manufacturer for Accuracy / Precision
Zero check	Calibration drift and memory effect
Span check	Calibration drift and memory effect
Mid-range check	Calibration drift and memory effect
Replicates, Splits etc.	75-125% Acceptance limit pg 48
Reagent Blank	Contaminated reagent
Rinsate or equipment blank	Contaminated equipment
Method blank	Response of an entire laboratory analytical system
Spikes	Percent recovery will be assessed for 1in 20 samples
Matrix Spike	Analytical (preparation + analysis) bias

15. Instrument/Equipment Testing, Inspection, and Maintenance

The Regional Board staff will test and maintain their field equipment in accordance with its SOPs, which include those specified by the manufacturer and those specified by the method. Before each trip out into the field, the field staff will be responsible for inspecting the YSI multimeter. Any unusual readings or occurrences during inspection will be documented in the YSI multimeter log book and reported to the project manager.

The DFG WPCL maintains their equipment in accordance with their SOPs, which include those specified by the manufacturer and those specified by the method.

16. Instrument/Equipment Calibration and Frequency

The Regional Board staff will calibrate their field equipment based in accordance with its SOPs, which include those specified by the manufacturer and those specified by the method. The project manager is responsible for appointing a field crew member to properly calibrate and document calibration of the YSI multimeter before each sampling trip. Any unusual readings or occurrences during calibration will be documented in the YSI multimeter log book by the project manager.

The DFG WPCL will perform their calibration for their instruments according to their SOPs.

17. Inspection/Acceptance for Supplies and Consumables

Laboratory supplies and sample containers will be inspected by the DFG WPCL according to their SOPs. All other supplies and consumables will be inspected by field staff and by the project manager prior to use, and examined for any damage. Any unusual concerns will be documented by the project manager.

18. Non-direct Measurements (Data Acquisition)

The 2007 SWAMP Report on the Santa Margarita Hydrologic Unit, the 2008 SWAMP Report on the San Diego Hydrologic Unit, and the 2008 SWAMP Report on the Tijuana Hydrologic Unit have surface water data for each of these watersheds, however, these data do not address PCPPs. These data will be referenced in the final report, as many of the constituents in the past SWAMP data will share common sources with the different PCPPs, and a common fate and transport.

19. Data Management

The project manager will be responsible for proper data management. Lab analyses received from the DFG WPCL will be maintained in a file of data records and be uploaded to paperless office. Field measurements from all sites will also be maintained in various files in accordance to specific sites and will be uploaded to paperless office. The DFG WPCL will follow their SOPs for data management, including record keeping and tracking, document control, and data handling.

20. Assessment and Response Actions

The DFG WPCL will be routinely monitored by the SWAMP QA team. Any inadequacy will be noted in a response letter, and the field crews and the contract laboratory is responsible for making any corrections needed and to report those corrections to the SWAMP QA team.

21. Reports to Management

After receiving analytical results from the sampling, a draft report will be prepared by the project manager. A final report will be prepared by the project manager the due date will be dependent upon the availability of the data but latest by December 2012. The project manager will provide an analysis of the results under special study and make recommendations to management. An evaluation of the QA results will be included in the final report along with a discussion on whether the calibration records for the YSI multimeter support quality data of the reported results.

22. Data Review, Verification, and Validation

Data generated by project activities will be reviewed against the DQOs and the quality assurance/quality control practices cited in this document. Data will be separated into three categories: data meeting all data quality objectives, data meeting failing precision or recovery criteria, and data failing to meet accuracy criteria. Data meeting all data quality objectives, but with failures of quality assurance/quality control practices, will be set aside until the impact of the failure on data quality is determined. Once determined, the data will be moved into either the first category or the last category.

Data falling into the first category is considered usable by the project. Data falling into the last category is considered not usable. Data falling in the second category will have all aspects assessed. If sufficient evidence is found supporting data quality for use in this project, the data will be moved to the first category, but will be flagged with a “J” as per U.S. EPA specifications.

23. Verification and Validation Methods

Data will be verified and validated by the project manager. This will be done by reviewing chain of custody forms, receipt logs and calibration information, and also by following all SOPs. The DFG WPCL will perform checks on data, and any issues will be noted. Any corrections require an agreement with the Regional Board that the correction is appropriate.

24. Reconciliation with User

The goal of the study is to determine the presence (or absence) and concentration of PPCPs in the San Diego Region of California. Any limitations from data quality on data use will be mentioned and discussed in the final report.

25. References

SWAMP. 2002. Quality Assurance Management Plan v1.0. State Water Resources Control Board. Sacramento, CA. http://www.waterboards.ca.gov/water_issues/programs/swamp/qamp.shtml

SWAMP. 2008. Quality Assurance Program Plan. State Water Resources Control Board. Sacramento, CA. http://www.waterboards.ca.gov/water_issues/programs/swamp/docs/qapp/swamp_qapp_master090108a.pdf

SWRCB. 2010. Final Report: Monitoring Strategies for Chemicals of Emerging Concern (CECs) in Recycled Water. Ca. State Water Resources Control Board, April, 15, 2010. Sacramento, CA.

26. Appendix A: Quality Assurance Program Manual, Department of Fish & Game Water Pollution Control Laboratory – available at