

# Surface Water Ambient Monitoring Program (SWAMP) Monitoring Plan for Region 9

## Pilot Study on Pharmaceutical and Personal Care Products in the San Diego Region

Fiscal Year 2008/2009  
And  
Fiscal Year 2009/10



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## **1 Summary Sheet**

### **Beneficial Uses**

This proposed monitoring plan for the Surface Water Ambient Monitoring Program (SWAMP) addresses contaminants of emerging concern in the San Diego region. It addresses several beneficial uses that exist throughout the San Diego watersheds.

### **Assessment Questions**

The following assessment questions will be addressed by the San Diego Regional Water Quality Control Board (SDRWQCB) for the proposed monitoring plan:

1. What is the occurrence and extent of pharmaceuticals and personal care products (PPCPs) in areas with discharge of treated wastewater, with septic tanks, with untreated human waste water, and at reference sites in the San Diego region?
2. Are PPCP levels causes for concern?

To answer the questions, the following steps have to be taken:

1. Sample for PPCPs in different water bodies.
2. Analyze samples for PPCPs.
3. Analyze data for PPCPs.

### **Link to Statewide Monitoring Framework**

The statewide SWAMP program assesses the protection of beneficial uses with its monitoring strategy. Large monitoring programs funded by SWAMP on a statewide and on a regional basis are conducted to assess the health of the watersheds in California. This proposed monitoring plan focuses on contaminants of emerging concern (PPCPs) which are not included in SWAMP statewide and regional monitoring plans.

### **Clean Water Act Sections 305(b)/303(d)**

The data produced by this monitoring plan will be used in water body assessments required under Clean Water Act (CWA) sections 305(b) and 303(d).

## **2 Background**

### **2.1 *Introduction***

#### **Contaminants of Emerging Concern (CECs)**

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 chemical 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 Southern California Coastal Water Research Project (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 address 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.

### **Pharmaceutical and Personal Care Products (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 and non-point sources. PPCPs have recently emerged as environmental contaminants with the potential of 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 (SWRBC, 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.

## **2.2 Past and Current SWAMP Monitoring**

During the first five years of the Surface Water Ambient Monitoring Program (SWAMP), the SDRWQCB focused on monitoring watersheds throughout the Region on a rotational basis to assess whether aquatic life was protected in wadeable streams and to assess the general condition of these streams in the San Diego region. The following measurements were taken at most of the sites: conventional water chemistry, water chemistry for heavy metals and pesticides, sediment and water toxicity, fish tissue (not all sites), benthic macroinvertebrates (not all sites), and physical habitat assessment (not all sites). The five-year cycle was completed in Fiscal Year 2004-05. Assessment reports for each of the eleven watersheds and a synthesis report were produced with FY 2005-2006 funding by SCCWRP.

In 2007 and 2008, sampling throughout the San Diego region has focused to assess the ecological health and to protect aquatic health beneficial uses; bioassessment samples were collected at approximately 42 sites throughout the San Diego region. In addition, bioassessment samples were collected at 11 Reference sites throughout the San Diego region. In 2008, algae as an additional bioindicator were added to the sampling plan.

The Stormwater Monitoring Coalition Regional Watershed Monitoring Program ("SMC study"), which is based on a probabilistic design, but does include some targeted sites for trend analysis, began in 2009. This program is being implemented throughout southern California. For the San Diego Region only, this program includes 24 randomly located sites in San Diego County, 6 sites in Orange County, and 3 sites in Riverside County. SWAMP is funding one-third of the sites in San Diego County, Orange County, and Riverside County. The rest of the sites are funded by the stormwater copermittees. The following indicators were collected on 122 sites throughout southern California: (1) Bioassessment (benthic macroinvertebrates and algae); (2) Riparian wetlands; (3) Water chemistry; (4) Water toxicity, and (5) Physical habitat. Sampling for the program will continue for the next four years with new sites sampled every year.

Since 2008, caffeine measurements were taken at all sites where bioassessment was conducted. Because caffeine is mostly of anthropogenic origin, the objective of the measurement was that caffeine can distinguish between human and non-human sources of surface water contamination.

Starting 2010, the SWAMP R9 monitoring program will continue to fund the SMC study, but will also a program on watershed monitoring coordination in the San Diego region (see monitoring plan for watershed monitoring coordination). Funding is also allocated to support the study proposed in this monitoring plan.

### **2.3 Other Monitoring in the San Diego region**

In addition to the regional SWAMP program, a number of different monitoring and assessment programs are conducted by and for a number of different entities. Some of these programs are controlled by the SDRWQCB; some are controlled by other entities. SDRWQCB-directed programs are conducted by or for the SDRWQCB using funds in the SDRWQCB budget. Currently, funds for SDRWQCB-directed programs consist of (a) SDRWQCB laboratory contract funds (approximately \$50,000/year) and (b) SDRWQCB Surface Water Ambient Monitoring Program (SWAMP) funds (approximately \$250,000/year). SDRWQCB-required programs are conducted by or for dischargers pursuant to SDRWQCB requirements. To a large extent, SDRWQCB-required programs are devoted to producing information about discharges. The costs of the SDRWQCB-required programs exceed by the far the costs for the SDRWQCB-directed programs. Other programs include citizen monitoring groups that monitor the watersheds on a voluntary basis. Some citizen monitoring groups cover the entire San Diego region (e.g. San Diego Coastkeeper, and the San Diego Stream Team), while other groups focus on a single watershed (e.g. San Diego River Park Foundation). None of the SDRWQCB-directed programs or the SDRWQCB-required programs includes monitoring of contaminants of emerging concern.

A large-scale regional monitoring program (Southern California Bight Regional Monitoring (Bight) program) is conducted periodically since 1994. The Bight program is a partnership of more than sixty organizations collaborating to address management questions of regional importance in offshore, nearshore, and enclosed waters of the southern California Bight. The Bight program is organized by the SCCWRP. The Bight program is one of the few programs that address contaminants of emerging concern in southern California. In the Bight 2003 and 2008 survey, measurements of endocrine disruption of fish in the near shore environment were conducted. Results from this study shows that several indicators for endocrine disruption were found in male fish. Also, the Bight 2008 program includes monitoring for harmful algae blooms (both marine, and estuarine).

Also, SCCWRP is currently collaborating with multiple institutions to characterize the occurrence of emerging contaminants and the potential for effects in the southern California coastal environment.

The U.S. Geological Survey has implemented a study to provide baseline information on the environmental occurrence of emerging contaminants such as human and veterinary, industrial and household wastewater products, and reproductive and steroidal in water resources. During 1999 and 2000, 142 streams, 55 wells, and 7 effluent samples were collected across 36 states as part of this national reconnaissance effort. This national reconnaissance of emerging contaminants is the first of its kind in the United States. One or more chemicals were detected in 80 percent of the sites at generally very low concentrations.

#### ***2.4 Proposed SWAMP Sampling for Pharmaceuticals and Personal Care Products in 2010 and 2011***

Results from nationwide, statewide, and regional studies indicate that PPCPs occur in water bodies in the San Diego region. However, there is no monitoring program conducted in the San Diego region which addresses this pollutant group. The CEC Workshop held in southern California in April 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 characterize the occurrence and distribution of high priority CECs. In addition, the workshop recommended monitoring indicator groups rather than individual contaminants. The proposed study will address both recommendations.

PPCPs can occur in: (1) Drinking water; (2) Recycled water for indirect potable reuse and recycled water for non-potable reuse, (3) Treated wastewater (effluent); (4) Stormwater, (5) Surface water; and (6) Groundwater. The proposed study will only address PPCPs in areas with discharge of treated wastewater, with septic tanks, with untreated human water, and at reference sites. PPCPs in recycled water are addressed through the Recycled Water Policy

of the State Water Resources Control Board. Drinking water, stormwater, and groundwater are not addressed due the limited funding for this study.

The proposed work will be a pilot study for the occurrence and extent of PPCPs in the San Diego region. The proposed project will not study the effects of PPCPs on human or ecological health. It will also not address the biological responses in animals to the contaminants groups. This will be done at a later date and on locations where PPCPs was found.

Results from this study will provide evidence if the PPCPs are of major concern in the San Diego region. The new information will be shared and communicated among diverse stakeholder groups. The information will assist managers in planning management strategies for CECs.

## **2.5 Objectives and Monitoring Questions**

The following objectives have been defined for the proposed study:

1. To address the status of the beneficial uses in regard to the PPCPs.
2. To compare measured levels with available effects-based thresholds.
3. To recommend future monitoring and management strategies for PPCPs.

The purpose of this study is to collect data to answer the following monitoring questions:

1. What is the occurrence and extent of PPCPs in areas with discharge of treated wastewater, with septic tanks, with untreated human waste water, and at reference sites in the San Diego region?
2. Are PPCPs levels in receiving waters cause for concern?

## **3 Study Methods**

### **3.1 Monitoring Design**

#### **3.1.1 Site Selection**

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. Also, sites might be chosen based on a previous study on caffeine in San Diego watersheds. Caffeine was found on several sites indicating human waste. Those sites might be targeted for this proposed study.

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.

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.

Locations of monitoring sites are subject to revision. Alternate sites will be identified and will be sampled in order to ensure a full complement of samples is collected throughout the San Diego region. The alternate sites will be selected using the same criteria discussed above.

### 3.1.2 Site Reconnaissance

Site reconnaissance will be used to determine site selection, including alternate sites. The SDRWQCB staff will conduct sample site reconnaissance that will:

- a. Document local watershed characteristics and features;
- b. Measure and characterize flow regime;
- c. Identify land ownership and access issues;
- d. Provide photo-documentation of the site;
- e. Record on the ground GPS coordinates (WGS 84, decimal degrees) for the site;
- f. Map the site on both a watershed and reach scale; and
- g. Identify and prioritize nearby alternate sites for contingency or follow-up monitoring.

### 3.1.3 Field location of sample collection sites

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.

### 3.1.4 Sampling Frequency

The monitoring will be conducted four times starting summer/fall of 2010 at the sampling locations. 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.

## **3.2 Selected Analytes**

The PPCPs are divided into pharmaceuticals and surfactants. Surfactants are usually organic compounds that are amphiphilic, and therefore they are soluble in both organic solvents and water. The following pharmaceuticals are the common pharmaceuticals and will be measured for the proposed study: (1)Caffeine; (2) Carbadox; (3) Sulfathiazole; (4) Lincomycin; (5) Sulfamerazine; (6) Sulfamethizole; (7) Sulfamethazine; (8) Trimethoprim; (9) Sulfachloropyridazine; (10) Sulfamethoxazole; (11) Sulfadimethoxine; (12) Tylosin; (13) Roxithromycin; (14) Erythromycin hydrate; (15) Gemfibrozil; (16) Ibuprofen; (17) Triclosan; (18) Chlorotetracycline; (19) Doxycycline; (20) Oxytetracycline; (21) Tetracycline; (22) 17 $\beta$ -estradiol; (23) Carbamazepine; and (24) Fluoxetine. Surfactants can be found in personal care products like shampoo, and the following surfactants will be measured: (1) Nonylphenol; (2) Nonylphenolethoxylate; and (3) Trimethylphenol-2, 3, 4.

### **3.2.1 Sampling and Lab Analyses**

Staff from the SDRWQCB will collect the samples for the proposed study. The samples will be shipped to the Water Pollution Control Laboratory (WPLC) of the Department of Fish and Game (CDFG) in Rancho Cordova. Replicate samples will be taken at 5 percent of the sites to assure QA/QC in the field.

All samples will be performed under the State Water Board statewide master contract with CDFG. This arrangement will make use of the expertise of the CDFG in the analysis of PPCPs. Sample collection and sample analysis will be performed according to the most recent version of the SWAMP QAPrP (2008) and the QAPP for the Pilot Study of Pharmaceuticals and Personal Care Products in the San Diego Region (2010). Laboratory analyses will be conducted in accordance with standard methods specified in the State Water Board statewide master contract with the CDFG.

## **3.3 Data**

### **3.3.1 Data Quality Evaluation and Data Reporting**

Data quality evaluation and data reporting will be as specified in the SWAMP QAPrP (2008) and the QAPP for the Pilot Study of Pharmaceuticals and Personal Care Products in the San Diego Region (2010). We do not anticipate needing additional special data quality evaluation or data reporting procedures.

### 3.3.2 Data Analysis

Data will be compared to applicable water quality objectives and other relevant thresholds if available. For parameters where no objectives or thresholds are available, data will be compared to other data in California, and the U.S.

### 3.3.3 Data Management

Data will be stored in the SWAMP database. The data produced by this monitoring plan will be used for a future cycle of water quality assessments under the Clean Water Act (CWA), sections 305(b) and 303(d).

## **4 Coordination and Collaboration**

The SDRWQCB will collaborate with other agencies, non-governmental organizations, non-profit organizations (e.g. San Diego Coastkeepers), and/or Tribal Nations to expand the planned monitoring in the watersheds. The data from this proposed study will be shared with a diverse group of stakeholders.

SWAMP regional allocations will be also spent to coordinate watershed monitoring in the San Diego River watershed. Information from this study will be included into the watershed monitoring coordination. Data will be also included into the San Diego Data Portal from EcoLayers and data will therefore be available to all stakeholders.

We are also planning to coordinate and integrate this SWAMP monitoring effort with other monitoring efforts that include PPCPs. This study will be closely coordinated with a monitoring study on contaminants of emerging concern that is conducted by SCCWRP.

## **5 Quality Assurance**

The SWAMP QAPrP (2008) and the QAPP for the Pilot Study of Pharmaceuticals and Personal Care Products in the San Diego Region (2010) will be followed throughout this project. The QA Officer for the project will be Lilian Busse, project manager and SWAMP Region 9 coordinator. The collection of field samples will follow the following standard operating procedures: "Marine Pollution Studies Laboratory – Department of Fish and Game (MPSL-DFG) Standard Operating Procedures (SOPs) for Conducting Field Measurements and Field Collections of Water and Bed Sediment Samples in the Surface Water Ambient Monitoring Program (SWAMP)". The QA Officer will assure that the SOP will be followed, and staff, that will conduct sampling, will receive training on the SOP. Quality control for field sampling will include a 5 percent field duplicate level for all parameters. The WPCL of the CDFG will follow QA manuals for the analysis of PPCPs. The SWAMP database team will apply SWAMP QA/QC procedures when uploading the data to the SWAMP database.

## 6 Deliverable Products/Reporting

The deliverable product will be a technical report that presents the findings on PPCPS. The report will be available to the public on the SDRWQCB website in March 2012.

## 7 Project Schedule

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, one month after sampling
3. Analysis of samples, submission of data to SWAMP database, and report for PPCP study to SWAMP database: 3/31/2012.

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List of sampling sites, PPCP																			
Sampling and field data in database PPCP																			
Analysis and data in database, PPCP																			

## 8 References

Anderson, M.A. 2009: Water Quality Management in Lake San Marcos: Analysis of Available Data. Draft Report, *Riverside*.

CCoWS 2009: Monitoring and Reporting an Emerging Water Quality Issue: Freshwater Cynaobacteria Toxins. Central Coast Watershed Studies. The Watershed Institute, Division of Science and Environmental Policy, California State University Monterey Bay.

Chorus, I. and Bartum. J. 1999: Toxic cyanobacteria in water: A guide to their public health consequences, monitoring, and management. London and New York, pages 41-111.

Gregory A. Loraine and Mark E. Pettigrove 2006: Seasonal Variations in Concentrations of Pharmaceuticals and Personal Care Products in Drinking Water and Reclaimed Wastewater in Southern California. *Environ. Sci. Technol.* 40, 687-695.

Kwon, J.-W., Armbrust, K.L., Vidal-Dorsch, D.E. m Bay, S.M, and Xia, K. 2009: Determination of 17 $\alpha$ -ethynylestradiol, carbamazpine, diazepam, simvastatin, and oxybenzone in fish livers. ?? (SCCWRP paper)

Quality Assurance Project Plan for the Pilot Study of Pharmaceuticals and Personal Care Products in the San Diego Region 2010.

SCCWRP 2009: Managing Contaminants of Emerging Concern in California: Developing Processes for Prioritizing, Monitoring, and Determining Threshold of Concern. SCCWRP Technical Report 600, produced by: California Ocean Science Trust, National Water Research Institute, San Francisco Estuary Institute, Southern California Coastal Water Research Project, and Urban Water Research Center of the University of California, Irvine.

Stone D. and Bress, W. 2006: Addressing Public Health Risks for Cynaobacteria in Recreational Freshwaters: The Oregon and Vermont Framework. *Integrated Environmental Assessment and Management*, Vol. 3, No. 1, pages 137-143.

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](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.