2012 Sampling Report for Emerging Constituents in the Santa Ana Region

Coordinated by:

Santa Ana Watershed Project Authority

SAWPA

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Section 1: Executive Summary

"Emerging Constituents" (EC) is a phrase used to describe a large number of pharmaceuticals, personal care products, food additives, pesticides and other common household chemicals for which federal and state authorities have not yet established an official water quality standard, approved a standard analytical method or required routine monitoring and reporting. In 2009, water and wastewater agencies in the Santa Ana River region developed a voluntary program to characterize "Emerging Constituents" in 22 municipal wastewater effluents, two sites along the Santa Ana River, and in the two man-made aqueducts used to import water to the area.[1]

The first round of samples was collected and analyzed in June of 2010.[2] The second round of samples was collected and analyzed in June of 2011.[3] And, the third round of samples was collected and analyzed in June of 2012. The final results for 2012 are summarized in Table 1 and discussed in this report.

Table 1: Summary of Analytical Results for 26 Sampling Sites in 2012

Compound	Primary Use	Frequency of Detection	Reported Range[4]	Common Dose
Acetaminophen	Analgesic	12% (3 of 26)	ND – 0.000030 mg/L	500 mg
Bisphenol A (BPA)	Plastic Coating	12% (3 of 26)	ND – 0.000045 mg/L	n/a
Caffeine	Food Additive	73% (19 of 26)	ND – 0.000210 mg/L	100 mg
Carbamazepine	Anti-Convulsant	88% (23 of 26)	ND – 0.000390 mg/L	200 mg
DEET[5]	Insecticide	92% (24 of 26)	ND – 0.001300 mg/L	270 mg
Diuron[6]	Herbicide	81% (21 of 26)	ND – 0.000220 mg/L	n/a
17α Ethinyl Estradiol	Synthetic Hormone	0% (0 of 26)	Never Detected	1 mg
17β Estradiol	Natural Hormone	0% (0 of 26)	Never Detected	1 mg
Gemfibrozil	Anti-cholesterol	77% (20 of 26)	ND – 0.000970 mg/L	600 mg
Ibuprofen	Analgesic	46% (12 of 26)	ND – 0.000110 mg/L	300 mg
Iopromide*	Xray Contrast Agent	65% (17 of 26)	ND – 0.000860 mg/L	500 mg
Naproxen*	Analgesic	23% (6 of 26)	ND – 0.000140 mg/L	200 mg
Sulfamethoxazole	Antibiotic	69% (18 of 26)	ND – 0.002900 mg/L	800 mg
TCEP[7]	Flame Retardant	92% (24 of 26)	ND – 0.000930 mg/L	n/a
Triclosan	Antiseptic	58% (15 of 26)	ND – 0.001000 mg/L	1 mg

Note: "mg/L" = milligram per Liter; 1 mg/L is one part per million. "ND" = Not Detected.

*New compound added to the Santa Ana study in 2012; not previously analyzed in 2010 or 2011.

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[1] The proposed program was reviewed and endorsed by the Santa Ana Regional Water Quality Control Board in Res. No. R8-2009-0071 (Dec. 10, 2009). Task Force members are listed on page 7 of this report.

[2] Santa Ana Watershed Project Authority. 2010 Emerging Constituents Sampling Report of the Emerging Constituents Program Task Force. December, 2010.

[3] Santa Ana Watershed Project Authority. 2011 Emerging Constituents Sampling Report of the Emerging Constituents Program Task Force. December, 2011.

[4] The study imposed a mandatory reporting limit of 0.000010 mg/L (10 nanograms per liter). In some cases, a laboratory may have reported a value less than this level.

[5] DEET is the commonly used abbreviation for *N,N*-Diethyl-*meta*-toluamide; DEET is applied topically not orally.

[6] Diuron is Bayer's registered trade name for DCMU [3-(3,4-dichloropheynl)-1,1-dimethylurea] No endorsement or criticism is implied by this or any other trade name used in this document.

[7] TCEP is the commonly used abbreviation for *tris*(2-carboxyethyl)phosphine.

Although ECs were detected at many of the sampling sites, the concentrations were extremely low. And, where detected, EC concentrations fell well within the range where other studies have shown that "no adverse health effects would be expected."[8, 9] For example, acetaminophen (the active ingredient in Tylenol) was detected at 3 (12%) of the 26 sampling sites. However, the highest reported concentration was less than three-one hundred-thousandths of a milligram. By comparison, one extra strength Tylenol capsule contains 500 milligrams of acetaminophen. Thus, a person would have to swallow more than 4.4 million gallons of treated municipal effluent to accidentally ingest the equivalent of one over-the-counter headache tablet. Similarly, one would have to deliberately drink at least 539,000 gallons from the Santa Ana River (all at once) in order to consume the amount of caffeine normally found in one can of soda.

Section 2: Background & Purpose of Study

Water quality is routinely analyzed at thousands of locations all across the country. Samples are collected from rain water, storm water runoff, freshwater streams, lakes and reservoirs, groundwater wells and tap water to characterize the quality of these various sources. Additional samples from the sewage systems are analyzed to ensure pollution prevention programs and wastewater treatment plants are meeting all federal and state water quality standards.

Recent improvements in analytical laboratory technology have dramatically improved our ability to detect a wider range of chemicals at much lower concentrations.[10] Today, we are able to identify and quantify these emerging constituents in the range of one part-per-trillion (ppt or nanogram per liter).[11] One part per trillion is equal to just one second in 31,546 years. One nanogram per liter is equivalent to a single drop in a volume of water equal to twenty Olympic-sized swimming pools.

Trace levels (approx. 1ppt to 100 ppt) of many different man-made chemicals (including pesticides, pharmaceuticals and personal care products) have been found in waters across the United States.[12] Collectively, these compounds are referred to as "Emerging Constituents" not because they are new but, rather, because their presence can now be detected by more sensitive analytical technology.

Emerging Constituents is one of several similar phrases used to describe the same phenomena. Synonyms include: chemicals of emerging concern (CEC), micro-constituents, micro-pollutants, trace organics, etc. However, such phrases may mistakenly imply that it is the concern that is "emerging" rather than the technology to detect these compounds in a water sample. Similarly, referring to such compounds as "Emerging Pollutants" or "Emerging Contaminants" may unintentionally and improperly suggest that the levels detected pose a known hazard to people or the environment when the true risk, if any, has not yet been established by federal or state authorities.

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[8] Intertox, Inc. Comparison of Analytical Results for Trace Organics in the Santa Ana River at the Imperial Highway to Health Risk-based Screening Levels. Seattle, WA. June 25, 2009. This report did not develop or evaluate health based screening levels for BPA, 17α-Ethinyl Estradiol, 17β-Estradiol, Iopromide or Naproxen.

[9] World Health Organization. Pharmaceuticals in Drinking Water (Ch. 2: Human health risk assessment); 2012. http://www.who.int/water_sanitation_health/publications/2012/pharmaceuticals/en/index.html

[10] Vanderford, B.J., et al. "Analysis of Endocrine Disrupters and Personal Care Products in Water Using Liquid Chromatography and Tandem Mass Spectrometry." Analytical Chemistry. 2003 (75:6265-6274)

[11] Vanderford, B.J. and Shane Snyder. "Analysis of Pharmaceuticals in Water by Isotope Dilution Liquid Chromatography/Tandem Mass Spectrometry." Environmental Science and Technology. 2006 (p. 7312-7320).

[12] New York City Environmental Protection. 2010 Occurrence of Pharmaceutical and Personal Care Products (PPCPs) in Source Water of the New York City Water Supply. August 19, 2011.

In general, chemical compounds can be divided into two categories: regulated and unregulated. Regulated chemicals include those for which formal water quality standards or state notification levels have been established. State and federal authorities may issue permits and orders governing the release of such compounds into the environment. These regulations may range from relatively simple monitoring and reporting requirements to strict discharge prohibitions.

By contrast, ECs are usually unregulated chemicals. However, regulatory requirements will change as new information is developed. To that end, additional data are needed to characterize the presence and persistence of ECs in various water sources. This information, along with epidemiological and toxicological data, is used to set priorities for developing new drinking water standards, new water quality standards, new state notification levels and new monitoring requirements. [13]

Once ECs have been detected, the question naturally arises as to what effect, if any, these compounds may have on people and the environment.[14] Several different regulatory agencies share responsibility for determining the acceptable concentration of these chemicals. This is a formidable task as there are tens of thousands of chemical compounds in common use.[15] Consequently, state and federal authorities rely on sales/usage information and monitoring data (from studies such as this one) to help determine appropriate research and regulatory priorities. [16]

The California Office of Environmental Health Hazard Assessment and U.S. EPA have primary legal responsibility for making the necessary risk assessments and recommending appropriate water quality standards for all chemicals including ECs. The Regional Water Quality Control Boards and the California Department of Public Health (DPH) have primary responsibility for implementing these standards.[17]

DPH has suggested that periodic monitoring for trace organic chemicals, including some previously unregulated ECs, may serve as a useful surrogate indictors to evaluate treatment performance and effectiveness for recycled water projects. Therefore, as part of the proposed Groundwater Recharge Reuse Regulations, DPH prepared a draft list of ECs to guide planning and permitting efforts for recycled water recharge projects.[18] DPH recommends monitoring for at least one compound in 5 of the 9 different functional groups (chemical classes).[19] These functional groups represent distinct categories of ECs with different chemical properties. The Santa Ana EC study evaluated at least one compound in 8 of the 9 functional groups. DPH is now in the process of finalizing the new regulation.[20]

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[13] Additional information on the regulatory process governing Emerging Constituents is available at U.S. EPA"s official website: http://www.epa.gov/oppt/existingchemicals/

[14] See, for example, "How Safe is Our Water?" Reader's Digest. Aug., 2011; pg. 102.

[15] U.S. Senate Oversight Hearing on EPA's Unregulated Drinking Water Contaminants Program. July 12, 2011. http://epw.senate.gov/public/index.cfm?FuseAction=Hearings.Hearings&Hearing ID=fc5a8756-8021-23ad-454a-b9eeb7bf1c36

[16] U.S. Government Accountability Office. Environmental Health: Action Needed to Sustain Agencies' Collaboration on Pharmaceuticals in Drinking Water. GAO-11-346. August, 2011.

[17] DPH serves several different regulatory roles with respect to groundwater recharge projects. DPH is responsible, under statute, for establishing water quality criteria for groundwater recharge projects. DPH also acts as a consultant to the Regional Boards on the permit requirements for specific groundwater recharge projects. And, DPH has a co-equal role with the Regional Boards in establishing appropriate permit requirements for groundwater recharge projects that rely on direct injection rather than surface percolation.

[18] California Department of Public Health. Draft Regulations for Groundwater Replenishment with Recycled Water. Proposed revisions published and posted to DPH website on November 21, 2011.

[19] See Section 60320.201(c)(1) of the draft regulation.

[20] See: http://www.cdph.ca.gov/HealthInfo/environhealth/water/Pages/Waterrecycling.aspx

In early 2009, the California State Water Resources Control Board ("State Board') adopted a new Recycled Water Policy (RWP).[21] As part of that Policy, the State Board convened a Blue Ribbon Panel of Experts to recommend appropriate water quality monitoring strategies for ECs in recycled water based on the best available pharmacological and toxicological information taking into consideration the fate and transport of such chemicals through advanced treatments systems and the natural environment. The Blue Ribbon Panel published their report in mid-2010.[22] The State Board has developed an EC monitoring policy based largely on the Blue Ribbon Panel's recommendations.[23] A public hearing was held in October of 2012 and the State Board finalized the new policy in January of 2013.[24]

Section 3: Study Approach and Methods

Relying on results reported in several previous studies, the EC Task Force selected fifteen compounds for further investigation in 2012. These particular chemicals are believed to pose no known health threat at the levels routinely found in the environment. However, these chemicals are considered to be reliable surrogate indicators to evaluate the efficiency and effectiveness of advanced wastewater treatment processes used to produce recycled water.

Table 2: Emerging Constituents Analyzed in 2012

Compound	Category	Common Use
Acetaminophen	Pharmaceutical	Over-the Counter Analgesic
Bisphenol-A (BPA)	Industrial	Plastic Manufacturing
Caffeine	Food Additive	Non-Prescription Stimulant
Carbamazepine	Pharmaceutical	Prescription Anti-Convulsant
DEET	Pesticide	Insect Repellent
Diuron	Pesticide	Weed Control
17α Ethinyl Estradiol	Pharmaceutical	Prescription Hormone (synthetic)
17β-Estradiol	Pharmaceutical	Prescription Hormone (natural)
Gemfibrozil	Pharmaceutical	Prescription Anti-Cholesterol
Ibuprofen	Pharmaceutical	Over-the-Counter Analgesic
Iopromide	Pharmaceutical	X-ray Contrast Agent
Naproxen	Pharmaceutical	Over-the-Counter Analgesic
Sulfamethoxazole	Pharmaceutical	Prescription Antibiotic
TCEP	Industrial	Flame Retardant
Triclosan	Antiseptic	Commercial Antiseptic

[21] SWRCB. Recycled Water Policy. Resolution No. 2009-0011 (adopted 2/3/09).

[22] Drewes, J.E., P. Anderson, N. Denslow, A. Olivieri, D. Schlenk & S. Snyder. Monitoring Strategies for Chemicals of Emerging Concern (CECs) in Recycled Water. Final Report and Recommendations of a Science Advisory Panel convened by the State Water Resources Control Board. Sacramento, CA. June 25, 2010.

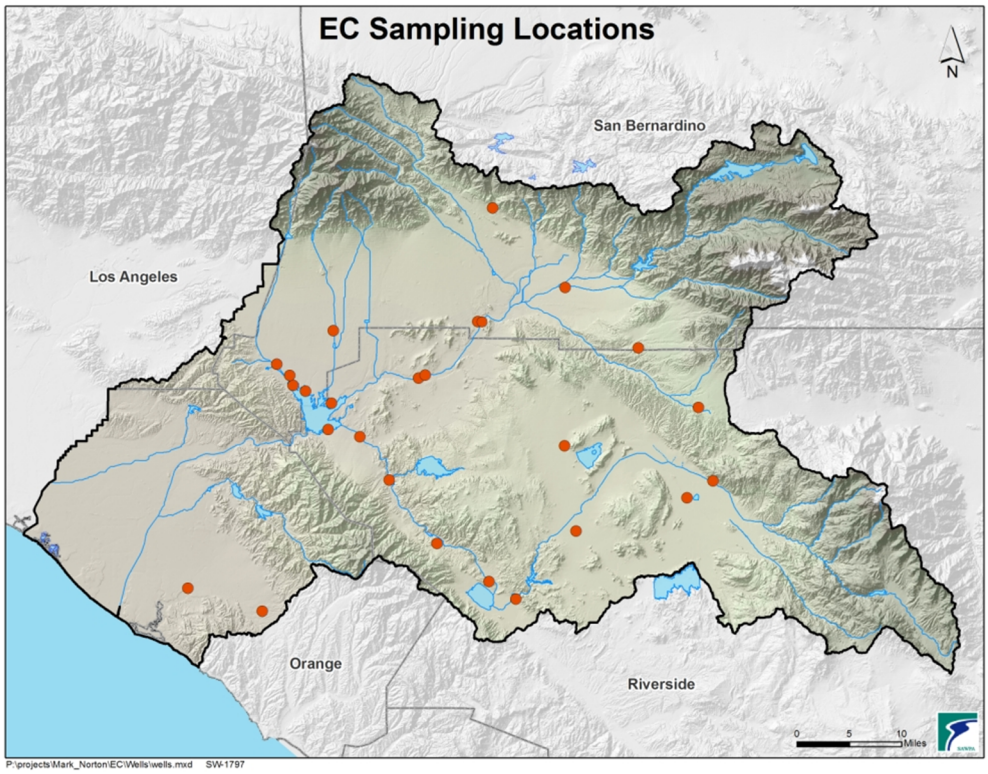
[23] State Water Resources Control Board. Attachment A: Requirements for Monitoring Constituents of Emerging Concern for Recycled Water. Jan. 22, 2013 [SWRCB Resolution No. 2013-0003].

[24] Additional information regarding the SWRCB's proposed monitoring program for ECs is available at: http://www.waterboards.ca.gov/water_issues/programs/water_recycling_policy/draft_amendment_to_policy.shtml

Samples were collected from 22 different wastewater treatment plants operating in the region (see Fig. 1).[25] All 22 POTWs met Title-22 requirements for tertiary filtration prior to discharge. Samples were also collected from two locations along the Santa Ana River (MWD crossing and Prado Dam), one location in the State Water Project (Devil Canyon) and one location near the terminus of the Colorado River Aqueduct (San Jacinto West Portal). Tabular data for all 26 locations in the Santa Ana region are presented in Section 4. The results are consistent with those reported for a similar analysis recently conducted in the Los Angeles Region.[26]

All of the samples were evaluated with the best analytical technology commercially available: Liquid Chromatography/Tandem Mass Spectrometry using the isotope dilution method. This technique is capable of detecting select ECs in de-ionized laboratory water at concentrations in the range of 1 to 10 ng/L. However, the specific laboratory reporting level (LRL) for more complex water matrices varies over time and between laboratories. Therefore the mandatory reporting level for samples in this study was set to a minimum of 10 ng/L for all laboratories. Quality control and assurance data are presented in Sections 5, 6 and 7. The EC Task Force's 2012 sampling program was performed in accordance with the approved study plan and the reported results indicate a high level of quality control at all of the contract laboratories.[27]

Figure 1: 2012 Sampling Locations for ECs in the Santa Ana River Watershed



[25] IEUA-RP5, one of the 23 POTW facilities previously sampled in 2010 and 2011, was not discharging treated wastewater in June of 2012.

[26] Southern California Coastal Water Research Project (SCCWRP). Screening Study for Constituents of Emerging Concern (CECs) in Selected Freshwater Rivers in the Los Angeles Region. June 22, 2012.

[27] A detailed quality assurance and quality control program was developed and submitted to the Regional Board staff for review in March of 2010. The Executive Officer approved that plan prior to collecting or analyzing any samples. A updated copy of the Sampling and Laboratory Analysis Plan (SLAP) is attached as Appendix A.

Because the analytical techniques used to analyze for ECs have not yet been formally approved by federal or state authorities, great care must be exercised when interpreting and reporting the results of such studies.[28] The data generated from the non-standard methods employed during this preliminary characterization study have not been certified for regulatory purposes such as: 303(d) listing decisions, antidegradation analyses, or translating narrative criteria into numeric effluent limits. These legal determinations depend on detailed risk assessments that are not yet available.

Nevertheless, data from studies such as this one are useful for determining which ECs, if any, should be prioritized for additional method development or more routine monitoring.[29] In fact, two of the ECs voluntarily analyzed by the EC Task Force during the past three years have already been added to EPA's Unregulated Contaminant Monitoring Rule (UCMR-3).[30] And, six are included in the mandatory EC monitoring program recently enacted by the SWRCB for recycled water projects.[31]

In January of 2013, the State Water Resources Control Board approved amendments to the Recycled Water Policy that describe future monitoring requirements related to Emerging Contaminants. Although these requirements apply only to project that intentionally recharge recycled water, the EC Task Force has decided to perform one more round of voluntary EC analyses during the coming year. Samples will be collected from all of the same locations as were investigated in 2012. However, in 2013, the Task Force will focus exclusively on seven EC analytes identified by the SWRCB.[32] The Sampling and Laboratory Analysis Plan (SLAP) will be updated accordingly. Following the final round of voluntary sampling in 2013, future EC monitoring will be governed by the regulatory requirements set forth in the Recycled Water Policy (as amended by SWRCB Resolution No. 2013-0003).

Table 3: Members of SAWPA's Emerging Constituents Task Force:

Eastern Municipal Water District	City of Beaumont
Inland Empire Utilities Agency	City of Redlands
Orange County Water District	City of Corona
San Bernardino Valley Muni. Water Dist.	City of Rialto
Western Municipal Water District	City of Riverside
Irvine Ranch Water District	Yucaipa Valley Water District
Metropolitan Water District of So. Calif.	Lee Lake Water District
San Gorgonio Pass Water Agency	Jurupa Community Services District
Elsinore Valley Municipal Water District	Chino Basin Watermaster
Western Riverside County Regional Wastewater Authority	Colton/San Bernardino Regional Tertiary and Wastewater Reclamation Authority

[28] Federally-approved standard methods are promulgated in accordance with and identified within 40 CFR Part 136 and 40 CFR Part 141..

[29] U.S. Government Accountability Office. Environmental Health: Action Needed to Sustain Agencies' Collaboration on Pharmaceuticals in Drinking Water. GAO-11-346. August, 2011.

[30] 17α Ethinyl Estradiol and 17β Estradiol (see 77 FR 85, 26099; May 2, 2012).

[31] Caffeine, DEET, Gemfibrozil, Iopromide, Triclosan and 17β Estradiol

[32] The 2013 EC characterization study will include: 17β-estradiol, Caffiene, Triclosan, Gemfibrozil, Iopromide, DEET & Sucralose. NDMA will be excluded because it is already addressed by other regulatory water quality monitoring programs. And, the reporting limit for 17β-estradiol will be revised to 1 ng/L.

Please direct all comments and questions to:

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Section 4: EC Sampling Results (ng/L) for 2012

Table 4a: June 2012 - POTWs

Sampling Location	Acetaminophen	Bisphenol A	Caffeine	Carbamazepine	DEET	Diuron	17β Estradiol (E2)	17α Ethynylestradiol (EE2)	Gemfibrozil	Ibuprofen	Iopromide	Naproxen	Sulfamethoxazole	TCEP	Triclosan
City of Beaumont WWTP No. 1	<10	<10	43	230	75	21	<10	<10	57	15	<10	<10	200	240	<10
City of Corona WRF 1B	<10	<10	14 BA	150	230	34	<10	<10	<10	69	46	<10	20	370	15
City of Corona WRF 2	<10	<10	190	310	350	110	<10	<10	330	100	210	50	2900	420	180
City of Corona WRF 3	<10	<10	23 BA	68	160	<10	<10	<10	<10	68	26	<10	<10	240	<10
EMWD MV-RWRF	30	<10	200	120	350	42	<10	<10	970	<10	110	<10	400	660	<10
EMWD PV-RWRF	<10	<10	20	<10	180	12	<10	<10	<10	<10	<10	<10	<10	650	<10
EMWD SJV-RWRF	<10	<10	170	190	640	65	<10	<10	930	<10	<10	<10	460	520	66
EMWD TV-RWRF	<10	<10	31	<10	340	<10	<10	<10	<10	<10	<10	<10 R7	<10	510	<10
EVMWD Horsethief Canyon	<10	<10	<10	69	310	<10	<10	<10	<10	<10	<10	<10	<10	780	<10
EVMWD Railroad Canyon WRP	20	<10	11 B4	110	190	<10	<10	<10	250	<10	<10	<10	190	500	<10
EVMWD Regional WRP	30	<10	170	220	280	39	<10	<10	<10	<10	<10	<10	150	580	1000
IEUA CCWRF	<10	<10	13	80	50	220	<10	<10	<10	<10	88	<10	<10	480	<10
IEUA RP1 02	<10	<10	<10	110	400	38	<10	<10	<10	<10	110	<10	<10	550	18
IEUA RP1 1B	<10	<10	<10	88	550	15	<10	<10	<10	<10	120	<10	<10	560	25
IEUA RP5 (no discharge at facility to sample)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
IRWD Los Alisos Plant	<10	45	210 FA	150	520	84	<10	<10	670	55	340	19	1000	330 M2	45
IRWD Michelson Plant	<10	24	26	82	520	18	<10	<10	24	24	<10	<10	<10	360 M2	31
City of Redlands WWTP	<10	<10	<10	390	87	35	<10	<10	<10	<10	<10	<10	<10	460	<10
City of Rialto WWTP	<10	<10	15	160	1300	18	<10	<10	15	<10	27	<10	35	930	<10
City of Riverside RWQCP	<10	<10	12	100	370	31	<10	<10	<10	<10	860	<10	14	660	<10
City of San Bernardino RIX	<10	40	140	340	180	63	<10	<10	350	110	27	140	1200	150	28
WRCWRA Treatment Plant	<10	<10	77	280	420	67	<10	<10	440	97	27	90	1600	370	24
YVWD WRF	<10	<10	33	200	420	81	<10	<10	220	<10	<10	34 E	1300	710	86

Table 4b: June 2012 - River Sites

State Project Water at Devil Canyon (MWD)	<10	<10	18	<10	<10	132	<10	<10	<10	<10	<10	<10	12	<10	<10
Colo River at San Jacinto West Portal (MWD)	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Santa Ana River near MWD crossing (OCWD)	<10	<10	49	90	43	58	<10	<10	49	<10	<10	24	198	79	<10
Santa Ana River near Prado Dam (OCWD)	<10	<10	15	97	100	38	<10	<10	23	<10	42	<10	108	223	<10

Table 4c: September 2011 - River Sites

Santa Ana River near MWD crossing (OCWD)	<10	<10	11	110	<10	47	<10	<10	<10	<10	NA	NA	169	77	<10
Santa Ana River near Prado Dam (OCWD)	<10	68	55	92	43	30	<10	<10	<10	<10	NA	NA	94	198	<10

Notes:

	10 ng/L is the designated Study Reporting Limit (SRL) for this study. The Laboratory Reporting Limits (LRL) are provided in the supporting documentation.
NA	No Sample Available.
B4	Only needed for Elsinore. Detected in FB above MRL, may be false positive.
E	Estimated value. Isotopic analog had multiple peaks.
FA	Field blank contains target analyte but sample >10X field blank level or not detected in sample. (only needed for Los Alisos IRWD)
M2	Matrix spike recovery was low, but the associated blank spike recovery was acceptable. Only applicable to the 2 TCEP samples for IRWD. Possible low bias due to matrix, but spike level also <1/3 of ambient level so may not be meaningful.
R7	LFB/LFBD RPD exceeded the laboratory acceptance limit. Recovery met acceptance criteria.
BA	Analyte was detected at 24 ng/L in the filtered Method Blank associated with the reported samples.

Section 5: QA/QC Field Blank Data (ng/L) for 2012

Table 5a: June 2012 - POTWs

Sampling Location	Acetaminophen	Bisphenol A	Caffeine	Carbamazepine	DEET	Diuron	17β Estradiol (E2)	17α Ethynylestradiol (EE2)	Gemfibrozil	Ibuprofen	Iopromide	Naproxen	Sulfamethoxazole	TCEP	Triclosan
City of Beaumont WWTP No. 1	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
City of Corona WRF 1B	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
City of Corona WRF 2	<10	26	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
City of Corona WRF 3	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
EMWD MV-RWRF	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
EMWD PV-RWRF	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
EMWD SJV-RWRF	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
EMWD TV-RWRF	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
EVMWD Horsethief Canyon	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
EVMWD Railroad Canyon WRP	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
EVMWD Regional WRP	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
IEUA CCWRF	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
IEUA RP1 02	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
IEUA RP1 1B	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
IEUA RP5 (no discharge at facility to sample)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
IRWD Los Alisos Plant	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
IRWD Michelson Plant	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
City of Redlands WWTP	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
City of Rialto WWTP	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
City of Riverside RWQCP	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
City of San Bernardino RIX	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
WRCWRA Treatment Plant	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
YVWD WRF	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10

Table 5b: June 2012 - River Sites

State Project Water at Devil Canyon (MWD)	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Colo River at San Jacinto West Portal (MWD)	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Santa Ana River near MWD crossing (OCWD)	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	10	<10
Santa Ana River near Prado Dam (OCWD)	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10

Table 5c: September 2011 - River Sites

Santa Ana River near MWD crossing (OCWD)	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	NA	NA	<10	<10	<10
Santa Ana River near Prado Dam (OCWD)	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	NA	NA	<10	<10	<10

Notes:

	10 ng/L is the designated Study Reporting Limit (SRL) for this study. The Laboratory Reporting Limits (LRL) are provided in the supporting documentation.

Section 6: QA/QC Reference Samples Spiked with Known EC Concentrations

Table 6a: June 2012 - QC Data, MWD

Analyte	Acetaminophen		Bisphenol A		Caffeine		Carbamazepine		DEET		Diuron		17α Ethynylestradiol (EE2)		17β Estradiol (E2)		Gemfibrozil		Ibuprofen		Iopromide		Naproxen		Sulfamethoxazole		TCEP		Triclosan	
MRL (ng/L)	5		10		5		2		2		6		5		5		3		10		5		3		3		4		3	
		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery
Devil Canyon Field Blank	<5		<10		<5		<2		<2		<6		<5		<5		<3		<10		<5		<3		<3		<4		<3	
Devil Canyon	0.1		0.0		18.3		2.8		8.5		132.0		0.0		1.3		0.4		2.6		0.0		0.0		11.6		7.6		0.0	
Devil Canyon_spike 50 ppt	47.3	94%	52.7	105%	60.8	85%	55.9	106%	66.1	115%	186.0	108%	53.1	106%	64.2	126%	58.8	117%	51.2	97%	45.7	91%	64.0	128%	62.4	102%	43.8	72%	58.8	118%
Devil Canyon_spike 50 ppt duplicate	46.9	94%	48.9	98%	59.8	83%	53.0	100%	62.6	108%	182.0	100%	49.8	100%	63.8	125%	59.4	118%	45.7	86%	40.4	81%	64.3	129%	59.4	96%	38.5	62%	61.9	124%
MS/MSD Relative % Diff (RPD)	1.0		7		2		5		5		2		6		1		1		11		12		0		5		13		5	

Table 6b: June 2012 - QC Data, OCWD

Analyte	Acetaminophen		Bisphenol A		Caffeine		Carbamazepine		DEET		Diuron		17α Ethynylestradiol (EE2)		17β Estradiol (E2)		Gemfibrozil		Ibuprofen		Iopromide		Naproxen		Sulfamethoxazole		TCEP		Triclosan	
MRL (ng/L)	5		10		3		1		1		5		2		2		1		1		10		5		1		5		1	
		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery
True Value Low LFB (ng/L)	5		10		3		1		1		5		2		2		1		1		10		5		1		5		1	
Laboratory Result Low LFB	4.1	82%	14.5	145%	1.8	59%	0.90	90%	0.87	87%	4.2	83%	2.5	127%	2.1	103%	0.47	47%	0.53	53%	7.7	77%	4.1	82%	0.78	78%	3.4	68%	0.53	53%
True Value LFB (ng/L)	10		50		30		10		10		10		10		10		10		10		20		10		10		10		10	
Laboratory Result mid-level LFB*	9.5	95%	51.9	104%	30	100%	9.9	99%	9.6	96%	9.9	99%	11.3	113%	9.9	99%	6.3	63%	9.7	97%	17.4	87%	9.0	90%	9.9	99%	12.8	128%	9.0	90%
SAR near Prado Dam (Initial)	5.2		<10		14.5		96.6		100		38.1		<2		<2		23.1		<1		41.6		<5		108		223		2.7	
SAR near Prado Dam Matrix Spike*	191	93%	279	140%	655	107%	292	98%	311	106%	249	105%	183	92%	202	101%	164	71%	219	110%	258	108%	219	110%	317	105%	425	101%	215	106%
SAR near Prado Dam Mat Spk (dup)	196	95%	308	154%	633	103%	292	98%	296	98%	255	108%	190	95%	182	91%	169	73%	215	108%	248	103%	215	108%	307	100%	439	108%	211	104%
MS/MSD Relative % Diff (RPD)	2.6		9.9		3.4		0.00		4.9		2.4		3.8		10.4		3.0		1.8		4.0		1.8		3.2		3.2		1.9	

Note: Spike concentration = 200 ng/L except Caffeine with spike concentration = 600 ng/L

Table 6c: September, 2011 - QC Data, OCWD

Analyte	Acetaminophen		Bisphenol A		Caffeine		Carbamazepine		DEET		Diuron		17α Ethynylestradiol (EE2)		17β Estradiol (E2)		Gemfibrozil		Ibuprofen		Iopromide		Naproxen		Sulfamethoxazole		TCEP		Triclosan	
MRL (ng/L)	5		10		3		1		1		5		2		2		1		1		NA		NA		1		5		1	
		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery		Recovery
True Value Low LFB (ng/L)	5		10		3		1		1		5		2		2		1		1		NA		NA		1		5		1	
Laboratory Result Low LFB	4.7	94%	13.3	133%	4.2	141%	0.71	71%	0.79	79%	5.0	101%	2.2	111%	2.5	123%	0.9	90%	1.2	124%	NA	NA	NA	NA	0.95	95%	4.6	91%	1.5	145%
True Value LFB (ng/L)	10		50		30		10		10		10		10		10		10		10		NA		NA		10		10		10	
Laboratory Result mid-level LFB**	10.2	102%	49.5	99%	31.7	106%	10.6	106%	10.4	104%	9.5	95%	98.3	98%	11.6	116%	9.4	94%	8.5	85%	NA	NA	NA	NA	10.4	104%	10.4	104%	11.8	118%
SAR MWDXING-01 (Initial)	6.5		67.8		55.4		91.9		42.5		29.6		<2		<2		4.0		3.9		NA		NA		94		198		4.4	
SAR MWDXING-01 Matrix Spike**	210	102%	261	96%	657	100%	289	99%	237	97%	233	102%	202	101%	181	91%	194	95%	209	103%	NA	NA	NA	NA	293	100%	421	112%	238	117%
SAR MWDXING-01 Matrix Spike (dup)	214	104%	247	90%	662	101%	292	100%	237	97%	234	102%	197	99%	184	92%	198	97%	205	101%	NA	NA	NA	NA	286	96%	408	105%	243	119%
MS/MSD Relative % Diff (RPD)	1.9		5.5		0.76		1.0		0.00		0.43		2.5		1.6		2.0		1.9		NA		NA		2.4		3.1		2.1	

Note: Spike concentration = 200 ng/L except Caffeine with spike concentration = 600 ng/L

Section 7: QA/QC Identical Split Sample Data for June 2012

Table 7a: ERA - QC Low-Level Check

Analyte	%RSD	Assigned Value	Mean Recovery	Median Recovery	OCWD Result (ng/L)	MWD Result (ng/L)	E.S.Babcock Result (ng/L)	MWH Result (ng/L)	CSM Result (ng/L)	OCWD % Recovery	MWD % Recovery	E.S.Babcock % Recovery	MWH % Recovery	CSM % Recovery
Acetaminophen	11.4	**13.5**	93.6	94.1	**12.7**	**13.0**	**12.2**	**9.98**	**7.71**	**94.1**	**96.3**	**90.4**	**73.9**	**57.1**
Bisphenol A	9.1	**13.9**	90.6	91.4	**13.1**	**12.0**	**12.7**	**10.6**	**21.3**	**94.2**	**86.3**	**91.4**	**76.3**	**153.2**
Caffeine	13.9	**13.0**	114.6	116.9	**13.5**	**16.0**	**15.2**	**11.6**	**16.1**	**103.8**	**123.1**	**116.9**	**89.2**	**123.8**
Carbamazepine	13.0	**12.0**	104.4	108.3	**13.1**	**13.0**	**11.5**	**9.81**	**12.1**	**109.2**	**108.3**	**95.8**	**81.8**	**100.8**
DEET	------	**-----**	------	------	**<1**	**<2**	**<10**	**<10**	**<10**	------	------	------	------	------
Diuron	------	**-----**	------	------	**<5**	**<6**	**<10**	**<10**	**NA**	------	------	------	------	**NA**
17a-Ethynylestradiol	------	**-----**	------	------	**<2**	**<5**	**<10**	**<10**	**NA**	------	------	------	------	**NA**
17b-Estradiol	6.99	**14.0**	99.5	101.4	**14.6**	**13.0**	**14.2**	**15.4**	**NA**	**104.3**	**92.9**	**101.4**	**110.0**	**NA**
Gemfibrozil	13.1	**12.0**	91.9	99.2	**12.2**	**9.00**	**11.9**	**10.9**	**<10**	**101.7**	**75.0**	**99.2**	**90.8**	**------**
Ibuprofen	10.5	**13.5**	101.0	97.8	**12.7**	**15.0**	**13.2**	**11.7**	**14.8**	**94.1**	**111.1**	**97.8**	**86.7**	**109.6**
Sulfamethoxazole	------	**-----**	---	---	**<1**	**<3**	**<10**	**<10**	**<1**	------	------	------	------	------
TCEP	------	**-----**	---	---	**<5**	**<5**	**<10**	**<10**	**<5**	------	------	------	------	------
Triclosan	------	**-----**	---	---	**3.68**	**4.00**	**<10**	**<10**	**4.82**	------	------	------	------	------
Iopromide	------	**-----**	---	---	**<10**	**<5**	**<10**	**<10**	**NA**	------	------	------	------	**NA**
Naproxen	13.8	**13.0**	83.1	76.9	**9.99**	**10.0**	**12.4**	**9.05**	**13.0**	**76.8**	**76.9**	**95.4**	**69.6**	**100.0**

Table 7b: ERA - QC Mid-Level Check

Analyte	%RSD	Assigned Value	Mean Recovery	Median Recovery	OCWD Result (ng/L)	MWD Result (ng/L)	E.S.Babcock Result (ng/L)	MWH Result (ng/L)	CSM Result (ng/L)	OCWD % Recovery	MWD % Recovery	E.S.Babcock % Recovery	MWH % Recovery	CSM % Recovery
Acetaminophen	7.00	**175**	88.7	90.6	**164**	**155**	**162**	**140**	**169**	**93.7**	**88.6**	**92.6**	**80.0**	**96.6**
Bisphenol A	6.20	**72.4**	88.7	90.8	**65.5**	**66.0**	**67.0**	**58.3**	**66.9**	**90.5**	**91.2**	**92.5**	**80.5**	**92.4**
Caffeine	15.0	**90.0**	95.0	93.1	**92.5**	**100**	**75.0**	**74.5**	**97**	**102.8**	**111**	**83.3**	**82.8**	**107.8**
Carbamazepine	8.61	**194**	94.7	97.7	**194**	**195**	**185**	**161**	**180**	**100.0**	**101**	**95.4**	**83.0**	**92.8**
DEET	8.36	**112**	94.3	96.0	**106**	**109**	**114**	**93.3**	**134**	**94.6**	**97.3**	**101.8**	**83.3**	**119.6**
Diuron	10.8	**180**	94.7	98.1	**185**	**173**	**180**	**144**	**NA**	**102.8**	**96.1**	**100.0**	**80.0**	**NA**
17a-Ethynylestradiol	9.43	**87.5**	91.4	89.8	**81.2**	**90.0**	**76.0**	**72.7**	**NA**	**92.8**	**103**	**86.9**	**83.1**	**NA**
17b-Estradiol	11.5	**165**	93.9	97.0	**165**	**170**	**155**	**130**	**NA**	**100.0**	**103**	**93.9**	**78.8**	**NA**
Gemfibrozil	16.8	**130**	85.7	83.7	**133**	**95.0**	**121**	**96.5**	**116**	**102.3**	**73.1**	**93.1**	**74.2**	**89.2**
Ibuprofen	15.1	**100**	88.5	86.9	**89.7**	**106**	**84.0**	**74.1**	**90.3**	**89.7**	**106**	**84.0**	**74.1**	**90.3**
Sulfamethoxazole	16.5	**175**	93.1	100.0	**179**	**171**	**179**	**123**	**197**	**102.3**	**97.7**	**102.3**	**70.3**	**112.6**
TCEP	18.5	**176**	86.4	88.9	**180**	**166**	**115**	**147**	**178**	**102.3**	**94.3**	**65.3**	**83.5**	**101.1**
Triclosan	14.3	**146**	98.6	103.8	**147**	**159**	**114**	**156**	**135**	**100.7**	**109**	**78.1**	**106.8**	**92.5**
Iopromide *	98.64	**15**	133.7	85.4	**5.56**	**16**	**49**	**9.63**	**NA**	**37.1**	**106.7**	**326.7**	**64.2**	**NA**
Naproxen	8.34	**135**	87.8	85.2	**114**	**116**	**133**	**111**	**124**	**84.4**	**85.9**	**98.5**	**82.2**	**91.9**

* ERA Estimated Values only

Table 7c: SAR-BELOWDAM-01 (Matrix Split)

Analyte	%RSD		Mean Result (ng/L)	Median Result (ng/L)	OCWD Result (ng/L)	MWD Result (ng/L)	E.S.Babcock Result (ng/L)	MWH Result (ng/L)	CSM Result (ng/L)
Acetaminophen	---	---	---	---	**5.15**	**<5**	**<10**	**<10**	**<10**
Bisphenol A	---	---	---	---	**<10**	**<10**	**20.0**	**<10**	**<25**
Caffeine	57.8	---	22.1	16.75	**14.5**	**19.0**	**41.0**	**14.0**	**17.1**
Carbamazepine	11.5	---	95.9	96.3	**96.6**	**109**	**96.0**	**82.0**	**97.7**
DEET	10.3	---	104.8	105.5	**100**	**111**	**116**	**92.0**	**135**
Diuron	18.8	---	38.8	37.1	**38.1**	**36.0**	**49.0**	**32.0**	**NA**
17a-Ethynylestradiol	---	---	---	---	**<2**	**<5**	**<10**	**<10**	**NA**
17b-Estradiol	---	---	---	---	**<2**	**<5**	**<10**	**<10**	**NA**
Gemfibrozil	10.3	---	20.7	20	**23.1**	**19.0**	**20.0**	**<10**	**16.5**
Ibuprofen	---	---	---	---	**<1**	**<10**	**<10**	**<15**	**<10**
Sulfamethoxazole	8.75	---	102.8	103.5	**108**	**99.0**	**112**	**92.0**	**127**
TCEP	28.2	---	216	231.5	**223**	**240**	**129**	**270**	**229**
Triclosan	---	---	---	---	**2.70**	**6.00**	**<10**	**<10**	**<5**
Iopromide	91.5	---	82	51.8	**41.6**	**62**	**192**	**31.0**	**NA**
Naproxen	---	---	---	---	**<5**	**<3**	**<10**	**<10**	**3.41**

Site Blank	OCWD Result (ng/L)	MWD Result (ng/L)	E.S.Babcock Result (ng/L)	MWH Result (ng/L)
TCEP	**<5**	**15**	**11.7**	**<10**

APPENDIX A:

Sampling and Laboratory Analysis Plan (SLAP) for the

Emerging Constituents Sampling Program in the Santa Ana Watershed

The Santa Ana Watershed Project Authority's (SAWPA) Emerging Constituents (EC) Program Task Force submitted a water quality investigation workplan to the Santa Ana RegionalWater Quality Control Board (RWQCB) to characterize selected ECs in surface waters and imported waters for calendar year 2010[1].The selected ECs include pharmaceuticals & personal care products (PPCPs), pesticides, herbicides, and industrial indicators of wastewater origin. The analytical laboratories supporting this effort follow the criteria presented within this Sampling and Laboratory Analysis Plan (SLAP), which is a required element of the workplan. This SLAP was updated in 2012 to reflect the inclusion of four additional ECs.

1. Sample Collection, Preservation, Storage and Holding Times

Sampling and laboratory analysis follows annual 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, of each year. These data will be included in the Annual Report that is due to the RWQCB by December 31 of each year. The second set of SAR samples is to be collected and analyzed by OCWD by September 30th each year, with these data to be included in the subsequent 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, using bottles provided by each laboratory.

2. Target Analytes

In 2009, the SAWPA's EC team developed a listing of eleven target compounds to be monitored within this study. In 2011, Triclosan and 17b-Estradiol were added to the list followed by Naproxen and Iopromide added in 2012. (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 may generate specific information on the samples analyzed that may go beyond the SAWPA required list. 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 fifteen 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 2010-12 EC Characterization Study

2010	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
	17αEthynylestradiol	57-63-6	Pharmaceutical
	Gemfibrozil	25812-30-0	Pharmaceutical
	Ibuprofen	15687-27-1	Pharmaceutical
	Sulfamethoxazole	723-46-6	Pharmaceutical
	TCEP	115-96-8	Industrial
Added 2011	17b-Estradiol	50-28-2	Hormone
Added 2011	Triclosan	3380-34-5	Pharmaceutical
Added 2012	Naproxen	22204-53-1	Pharmaceutical
Added 2012	Iopromide	73334-07-3	Contrast Medium

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 for each compound. SAWPA's EC sampling 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 to verify that they can determine results at the S-MRL level.

Two “Blind QC 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 is 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 in a similar manner to all received study sites by each laboratory.

Table 2: Method Performance Checks for EC Characterization Study

Sample Description	Specification &Frequency	Acceptance Criteria	Remedial Action
Low-Level CCCat 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 re-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 QC 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	**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]

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[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 may 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 recommendations are finalized and adopted.

[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 QC Samples – An unknown quality control sample, which is spiked with the study's target compounds in a reagent water matrix. QC samples are provided by a method Proficiency Testing (PT) vendor – Environmental Resource Associates (ERA). Two QC samples are provided within this study – a mid level calibration check (25-200 ng/L) and an S-MRL check (10-15 ng/L). QC 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.