

# Phase-I Report

of the

## Emerging Constituents Workgroup



April, 2009

# Phase I Report of the Emerging Constituents Work Group

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## I. Background

In April, 2006 the Santa Ana Regional Water Quality Control Board ("Regional Board") proposed general waste discharge requirements ("WDRs") to govern the injection or percolation of water from the State Water Project or Colorado River to local aquifers.<sup>1</sup> Although there was widespread agreement on the value of safeguarding groundwater quality, there was no consensus on whether formal discharge permits were the best way to accomplish this objective. Consequently, the Santa Ana Watershed Project Authority ("SAWPA") convened a series of stakeholder meetings to evaluate alternative implementation strategies.

Over the next year, a large group of water and wastewater agencies worked closely with Regional Board staff to develop an effective non-regulatory approach for controlling salinity in groundwater. In January 2008, the Regional Board endorsed the workgroup's recommendation to manage recharge projects through a contractual Cooperative Agreement.<sup>2</sup>

The Cooperative Agreement obligates agencies recharging local aquifers with imported water to evaluate the impact on groundwater quality both before and after such projects go on-line. The California Environmental Quality Act ("CEQA") already requires project operators to mitigate or offset any potential adverse impacts on water quality. Therefore, a combination of more extensive salinity monitoring and modeling, together with existing CEQA regulations, provides water quality protection that is functionally-equivalent to that sought from the proposed general permit.

The draft WDRs also included a specific requirement to analyze samples of imported water for a number of different regulated and unregulated chemicals (aka "emerging constituents").<sup>3</sup> Similar monitoring provisions had been included in a few other permits previously issued by the Regional Board to control the recharge of recycled water.<sup>4</sup> Whether such monitoring was useful or appropriate for projects recharging State Project water or Colorado River water was the subject of considerable debate among stakeholders and regulatory authorities. As a result, SAWPA elected to establish a separate discussion process to address the many issues related to emerging constituents ("EC").

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<sup>1</sup> See tentative resolution No. R8-2006-0005. Attached as Appendix A.

<sup>2</sup> See Santa Ana Regional Water Quality Control Board Resolution No. R8-2008-0019. Attached as Appendix B.

<sup>3</sup> Unregulated chemicals are those man-made pollutants for which there is no recommended 304(a) water quality criteria, no established water quality objective, and no identified Maximum Contaminant Level (MCL) or State Notification Level. Consequently, there is no numeric limit specified in the permit to govern the allowable concentration of the pollutant.

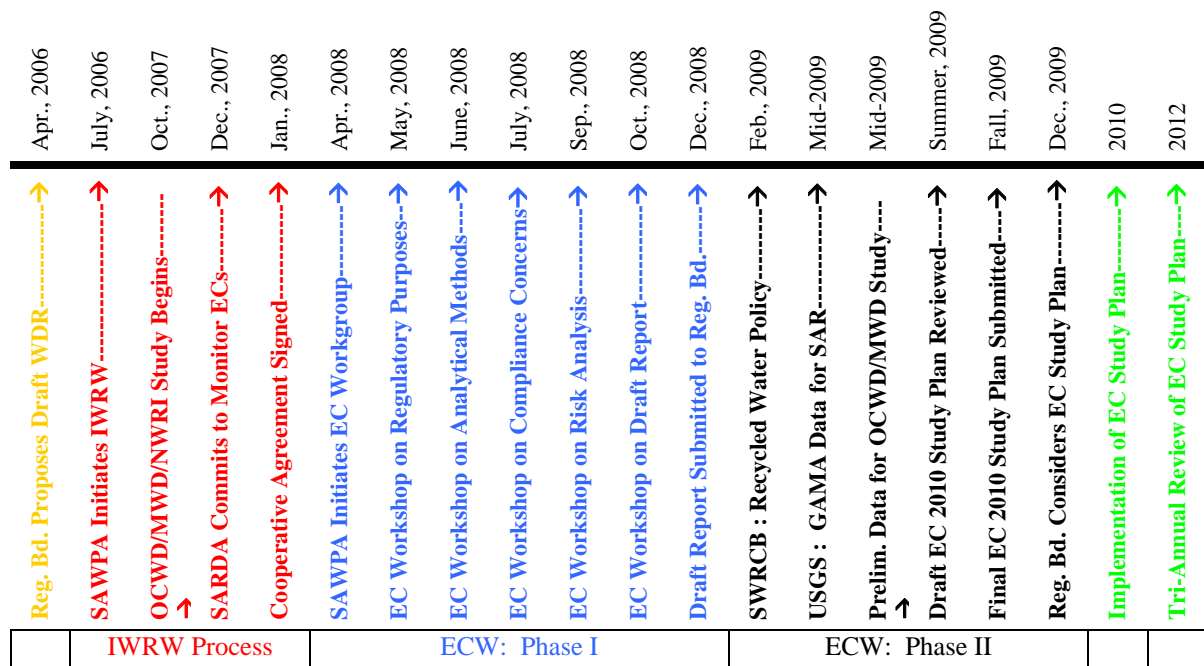
<sup>4</sup> See, for example, the Monitoring and Reporting Program for Regional Board Order No. R8-2005-0033 for Phase I of the Chino Basin Recycled Water Groundwater Recharge Project. Attached as Appendix C. Another example from a similar permit issued to Orange County Water District is presented in Appendix Z.

The Regional Board agreed to support the separate Workgroup provided that, in the interim, one or more agencies agreed to analyze an annual sample of State Project water for a specific list of emerging constituents. The Orange County Water District ("OCWD"), Metropolitan Water District of Southern California ("MWD") and the National Water Research Institute ("NWRI") agreed to analyze several samples over a 12 month period and report their findings in 2009.<sup>5</sup> The Santa Ana River Dischargers Association ("SARDA") agreed to accept the responsibility beginning in 2010 unless the Emerging Constituents Workgroup ("ECW") is able to recommend an alternative sampling and investigation program before then.<sup>6</sup>

The ECW structured its effort into two phases. During Phase I, the Workgroup met regularly to define the purpose of an EC monitoring program, to review the lessons learned from past and present EC monitoring programs, to survey the technical capability of well-qualified commercial laboratories to analyze for ECs, and to identify the potential regulatory issues that may arise as a result of collecting and publishing EC data. Phase I was completed in 2008 and this report summarizes the results of that effort.

In Phase II, the ECW will work to develop a long-term strategy to address emerging constituents in the Santa Ana region. One of the first tasks will be to determine what sort of water quality characterization program would be most appropriate. The ECW has committed to making a formal recommendation to the Regional Board by the fall of 2009. If the ECW is unable to establish a working consensus, then SARDA will continue to analyze and report the same EC data now being collected by OCWD and MWD.

**Figure 1: ECW Timeline**



<sup>5</sup> See study plan entitled "Source, Fate and Transport of Endocrine Disruptors, Pharmaceuticals and Personal Care Products in Drinking Water Sources in California." May 31, 2007. Attached as Appendix D.

<sup>6</sup> See Letter from Santa Ana River Dischargers Association (SARDA) to California Regional Water Quality Control Board – Santa Ana Region. "SARDA Commitment to Analyze State Project Water for Emerging Contaminants." January 18, 2008. Attached as Appendix E.

## II. Regulatory Rationale for Monitoring Emerging Constituents

Chemical monitoring is routinely required to determine whether existing water quality meets the state and federal standards established to protect human health and the environment. On occasion, additional monitoring of other unregulated chemicals<sup>7</sup> is also performed. Since EC monitoring is not currently used to assess compliance with existing water quality standards, there are other reasons given to justify such data collection.<sup>8</sup>

A review of the historical record indicates that EC monitoring was initially recommended by the California Department of Public Health (CDPH) as one possible means of for determining whether drinking water supplies may be contaminated. In 1990, CDPH<sup>9</sup> first proposed revisions to the statewide regulations governing the use or recycled water. In particular, CDPH recommended that reclaimed water should comprise no more than 50% of the water in wells used for human consumption.<sup>10</sup> CDPH also suggested using Total Organic Carbon (TOC) data or Total Dissolved Solids (TDS) data or "other tracer chemicals" to ascertain compliance with the proposed regulations.

During the past 18 years, the Draft Groundwater Recharge Reuse Regulation has been revised many times in response to public comments and new information. Recently, CDPH proposed to specify a number of endocrine disrupting chemicals, pharmaceuticals, personal care products and other "indicator" chemicals for monitoring.<sup>11</sup>

Because the revised Draft Groundwater Recharge Reuse Regulation has not yet been enacted, increased regulatory uncertainty has arisen over the use of reclaimed water. Some state permitting authorities elect to rely on CDPH's proposed regulation to establish EC monitoring requirements for any discharge project where recycled water was likely to percolate to groundwater basins.<sup>12</sup> CDPH describes the rationale for such monitoring:

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<sup>7</sup> Other words are often used to describe unregulated chemicals, including: "emerging contaminants," "pharmaceuticals and personal care products (PPCPs)," "endocrine disruptors," etc. The term "emerging constituents" (or ECs) is used in this report to represent the aforementioned unregulated chemicals and is intended to be synonymous with other similar phrases.

<sup>8</sup> This report uses the terms "monitoring," "sampling," and "investigation" interchangeable to refer to the collection of data relating to the presence and concentration of ECs. Such data are not collected for the purpose of assessing compliance with state or federal water quality objectives because, by definition, there are no such standards for these compounds.

<sup>9</sup> Prior to 2007, the California Department of Public Health was known as the California Department of Health Services ("DHS").

<sup>10</sup> California Department of Public Health. Groundwater Recharge Reuse Draft Regulation. 1990.

<sup>11</sup> California Department of Public Health. Groundwater Recharge Reuse Draft Regulation. January 4, 2007; pp. 22 of 24. (aka "Endnote 5") Attached as Appendix G.

<sup>12</sup> See, for example, the permit issued to Donald C. Tillman Water Reclamation Plant (NPDES No. CA0056227) Attached as Appendix H.

*"Monitoring for these chemicals - or categories of chemicals - is a diligent way of assessing and verifying recycled water characteristics, which can be useful in addressing issues of public perception about the safety of recharge projects. Further, should there be positive findings of these types of chemicals, the recharge agency and the CDPH can give the results due consideration as to whether it is of concern or not. Just what such consideration might entail would depend on what is known and what is not known about the particular chemical, including its potential health effects at the given concentration, the source of the chemical, as well as possible means of better control to limit its presence, treatment strategies if necessary, and other appropriate actions. **Such monitoring is not for compliance purposes, but for informational use only.**"<sup>13</sup> (emphasis in original)*

Subsequent presentations by CDPH staff reveal that the agency's EC monitoring recommendations were meant to be suggestive not prescriptive. Unfortunately, earlier versions of the Draft Groundwater Recharge Reuse Regulation did not make this distinction clear and most permit writers assumed CDPH's list of additional constituents was "THE" list for EC monitoring.<sup>14</sup> Moreover, many permit writers mistakenly concluded that the chemicals identified on CDPH's list were included because each of these chemicals represented a potential health threat.

After becoming aware that parts of the Draft Groundwater Recharge Reuse Regulation were being misinterpreted and misapplied, CDPH revised the proposed text again in August of 2008. The agency emphasized that while it supports the value of EC monitoring, it does not recommend any specific chemicals be analyzed. Rather, it is up to those operating the recharge project to propose chemical tracers that would serve as good indicators of wastewater in recharge water. CDPH warned that:

*"There are no drinking water standards for the [emerging] contaminants listed above and no standards are anticipated. In addition, analytical methods may not be widely available."<sup>15</sup>*

Nevertheless, CDPH also suggested some sort of ongoing EC monitoring program may be useful to address rising public concern. This concern is best illustrated by the recent news reports of trace pharmaceutical chemicals detected in municipal water supplies.<sup>16</sup> Public anxiety over the purity of their drinking water is not new. In the mid-20<sup>th</sup> century, similar apprehension was created even when authorities proposed to add beneficial chemicals, such as fluoride and chlorine, to the water supply. Strong education programs helped overcome these fears.

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<sup>13</sup> California Department of Public Health. Draft Endnotes for Draft Recharge Regulations. Draft dated September 18, 2007; pp. 3 of 6 (Attached as Appendix J).

<sup>14</sup> Brian Bernardos, P.E., California Department of Public Health. California's Draft Criteria for Groundwater Recharge with Reclaimed Water and Emerging Contaminant Control. Presentation to SAWPA's Emerging Constituents Workgroup. May 22, 2008. Attached as Appendix K.

<sup>15</sup> California Department of Public Health. Groundwater Recharge Reuse Draft Regulation. August 5, 2008; pp. 30-32. Attached as Appendix L.

<sup>16</sup> Jeff Donn, Martha Mendoza and Justin Pritchard, Associated Press. "AP Probe Finds Drugs in Drinking Water." March 10, 2008. AP Release. Attached as Appendix M.

Responding to the public's increasing apprehension, Congress held hearings in the spring of 2008 to investigate the EC issue. At those hearings, the Senators received testimony that virtually all of the chemicals detected were less than one part-per-billion and that such concentrations were as much as 5 million times lower than the therapeutic doses approved for human use. One of the foremost experts on the analysis of ECs testified that, at the EC concentrations currently being detected, a person would have to consume approximately 50,000 eight-ounce glasses of water to consume the equivalent of a single Tylenol capsule.<sup>17</sup> Similar estimates have been published by federal authorities from the Environmental Protection Agency (EPA), the Food and Drug Administration (FDA) and the U.S. Geological Survey (USGS). The growing public awareness of ECs in drinking water is less related to new scientific information about potential health threats and more a function of our improving ability to detect chemicals at extremely low concentrations. Therefore, just as with chlorine and fluoride, comprehensive education programs will be necessary to inform the public about the relative risks and benefits.

### **III. Current Water Quality Monitoring Programs for Emerging Constituents**

In 2005, the American Water Works Association Research Foundation (AWWARF) initiated a study to characterize the level of several common pharmaceuticals in city tap water.<sup>18</sup> Many municipal water agencies agreed to participate in and co-sponsor the research project. In fact, it was at a national conference where the results were being reported that the reporters who wrote the AP story in March of 2008 first learned of the issue.

Similar studies to investigate emerging constituents are actually quite common. The USGS is engaged in two large-scale efforts to characterize water quality in both surface and groundwaters. As part of its National Ambient Water Quality Assessment (NAWQA) and Groundwater Ambient Monitoring Assessment (GAMA), USGS has collected and analyzed samples from throughout the Santa Ana River watershed.<sup>19</sup> Some of the results have already been reported. Other data is still being reviewed for quality assurance and quality control (QA/QC). The USGS is cautious about publishing data on emerging constituents where there are no water quality standards established to reassure the public that the detected concentrations are safe. Consequently, rigorous QA/QC procedures are essential given the new analytical methods employed, the exceptionally low detection thresholds, and the potential to undermine public confidence by the mere presence of some emerging constituents in the water supply. Strict QA/QC must be imposed throughout the entire investigation process: sampling, transport, analysis, data storage, reporting and interpretation.

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<sup>17</sup> Dr. Shane Snyder, Research and Development Manager for the Southern Nevada Water Authority. Testimony before the Senate Subcommittee on Transportation Safety, Infrastructure Security and Water Quality on Pharmaceuticals in the Nation's Water: Assessing Potential Risks and Actions to Address the Issue. April 15, 2008 (Attached as Appendix N).

<sup>18</sup> American Water Works Research Foundation. Toxicological Relevance of EDCs and Pharmaceuticals in Drinking Water. Report #3085. March, 2009.

<sup>19</sup> U.S. Geological Survey. Ground-Water Quality in the Santa Ana Watershed, California: Overview and Data Summary. Water-Resources Investigations Report 02-4243. 2002

U.S. EPA has also enacted water quality monitoring requirements for certain unregulated contaminants.<sup>20</sup> In addition, the Unregulated Contaminants Monitoring Rule (UCMR) requires sampling for drinking water systems at the point of entry into the distribution system. The agency uses the resulting data to determine whether additional regulations may be needed under the Safe Drinking Water Act. The UCMR data is also used to help establish priorities for developing new water quality criteria through the Contaminant Candidate List (CCL). Those chemicals found to be most ubiquitous and most abundant will more likely be ranked higher in the agency's risk analysis and resource allocation process.

In 2007, OCWD, MWD and NWRI joined together to characterize EC concentrations from various sources recharging groundwater basins in the Santa Ana region. The sources sampled include municipal effluent discharges, the Santa Ana River, imported water from the State Project, Colorado River water, and storm water runoff. The study was initiated in 2008 and will be finished in 2009. Some samples have already been collected and analyzed, but the results have not yet been reported. Once again, this is due to the extraordinary level of QA/QC required when seeking to identify chemicals in the parts-per-trillion range.<sup>21</sup>

Similar EC data is also being collected and reported pursuant to monitoring conditions established in permits issued to Inland Empire Utilities Agency (IEUA) and the Orange County Water District. Table 1 shows some of the ECs presently being evaluated in the Santa Ana River watershed. Although quite comprehensive, the list is not intended to be exhaustive. Many additional chemicals are evaluated voluntarily by various agencies as part of their routine in-house monitoring programs.

Information gleaned from all of these local monitoring programs is especially important to the ECW. The data will be useful for designing an appropriate long-term monitoring strategy for ECs. In particular, the ECW is hopeful that the results will indicate which chemicals will serve as the most robust and accurate indicators of potential wastewater influence on groundwater supplies. It is also useful to learn how these chemical indicators change in response to environmental conditions and normal drinking water treatment processes.

In its Draft Groundwater Recharge Reuse Regulation, CDPH stated that it is not necessary to continue monitoring for all, or even most, of the emerging constituents over the long term. Instead, a relative few chemicals can be selected as surrogates for a much broader class or category of potential contaminants. A selective approach is also more appropriate given the existing limitations on analytical methods.

Several experts provided detailed presentations to the ECW summarizing the current state-of-the-art for detecting ECs in a well-qualified commercial laboratory (see Table 2). These scientists were unanimous in their conclusions and recommendations. First, the Liquid Chromatography/Mass Spectrometry (LC/MS) method requires supplemental isotope dilution procedures to reliably measure ECs in the parts-per-trillion range. At present, validated isotope dilution methods are available for fewer than two dozen chemicals.

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<sup>20</sup> U.S. EPA. Unregulated Contaminants Monitoring Rule. Attached as Appendix O. (<http://www.epa.gov/safewater/ucmr/ucmr2/basicinformation.html>)

<sup>21</sup> To place the scientific challenges in more meaningful perspective, it is useful to understand that one part-per-trillion is piece of land the size of a postage stamp in an area the size of Texas.



**Table 1: Current Water Quality Monitoring for Emerging Constituents**

Constituent	Primary Use or Source	M-O-N	UCMR	IEUA	GAMA
Acetaminophen	Pharmaceutical-Analgesic	X		X	X
Amoxicillin	Pharmaceutical-Antibiotic	X		X	
Anthracene	Industrial	X			
Atrazine	Herbicide	X			X
Azithromycin	Pharmaceutical-Antibiotic	X		X	X
Benzo[a]pyrene	Industrial	X			X
a-BHC	Pesticide	X			
b-BHC	Pesticide	X			
d-BHC	Pesticide	X			
g-BHC (Lindane)	Pesticide	X			
Bisphenol A	Plasticizer	X		X	X
Caffeine	Stimulant	X		X	X
Carbamazepine	Pharmaceutical-Anticonvulsant	X		X	X
Ciprofloxacin	Pharmaceutical-Antibiotic	X		X	
DDD	Pesticide	X			
DEET (N,N-diethyl-m-toluamide)	Insect Repellant	X			X
Diethylstilbestrol	Pharmaceutical-Synth. Hormone	X			
Erythromycin	Pharmaceutical-Antibiotic	X			X
Epitestosterone	Pharmaceutical-Hormone	X			
Estradiol (17-b)	Pharmaceutical-Hormone	X		X	
Estriol	Pharmaceutical-Hormone	X			
Estrone	Pharmaceutical-Hormone	X		X	
Ethinylestradiol (17-a)	Pharmaceutical-Hormone	X		X	
Gemfibrozil	Pharmaceutical-Anticholesterol	X		X	X
Ibuprofen	Pharmaceutical-Analgesic	X		X	X
Methoxychlor	Pesticide	X			
4-Nonylphenol	Detergent Metabolite	X		X	
Nonylphenol (Poly) Ethoxylates	Detergent Metabolite	X		X	
4-n-Octylphenol	Detergent Metabolite	X		X	X
4-tert-Octylphenol	Detergent Metabolite	X		X	X
Pentachlorophenol	Fungicide	X			
4-Phenylphenol	Fungicide	X			
Primidone	Pharmaceutical-Anticonvulsant	X			
Progesterone	Pharmaceutical-Hormone	X			
Salicylic Acid	Pharmaceutical-Skin Treatment	X		X	
Sulfamethoxazole	Pharmaceutical-Antibiotic	X			X
Tris(2-chloroethyl) phosphate (TCEP)	Flame Retardant	X			X
Testosterone	Pharmaceutical-Hormone	X			
Tetrabromobisphenol A	Flame Retardant	X			
Trichlorophenol	Fungicide	X			
Triclosan	Pharmaceutical-Antibiotic	X		X	
1-4 Dioxane	Deodorant, Toothpaste, Mouthwash			X	X
Perchlorate	Fertilizer and Rocket Fuel				X
Ethylenediamine tetra-acetic acid (EDTA)	Industrial			X	
Iodinated contrast media	Medical Imaging			X	
Lipitor	Pharmaceutical-Anticholesterol			X	
Methadone	Pharmaceutical			X	
Morphine	Pharmaceutical			X	
Ethylenediamine	Industrial & Pharmaceutical			X	

M-O-N = The special EC characterization study presently being conducted by MWD, OCWD, and NWRI.

UCMR = The chemicals identified in EPA's Unregulated Contaminant Monitoring Rule.

IEUA = The special monitoring requirements in Inland Empire Utilities Agency's NPDES permit.

GAMA = The USGS's Groundwater Ambient Monitoring Assessment program.

Note: the colored shading is only provided to help the reader easily distinguish between columns.

**Table 1: Current Water Quality Monitoring for Emerging Constituents** (continued)

Constituent	Primary Use or Source	M-O-N	UCMR	IEUA	GAMA
Trimethoprin	Pharmaceutical-Antibacterial				X
Diazinon	Pesticide			X	X
Vanadium	Steel Additive				X
Dimethoate	Pesticide		X		X
Terbufos sulfone	Pesticide degradate		X		X
BDE-47	Flame Retardant		X	X	
BDE-99	Flame Retardant		X	X	
HBB	Flame Retardant		X	X	
BDE-153	Flame Retardant		X	X	
BDE-100	Flame Retardant		X	X	
1,3-dinitrobenzene	Explosive		X		
2,4,6-trinitrotoluene (TNT)	Explosive		X		
Hexaydro-1,3,5-trinitro-1,3,5-triazine	Explosive		X		
Acetochlor	Herbicide		X		X
Alachlor	Herbicide		X		X
Metolachlor	Herbicide		X		X
Acetochlor ethane sulfonic acid (ESA)			X		
Acetochlor oxanilic acid (OA)			X		
Alachlor ethane sulfonic acid (ESA)			X		
Alachlor oxanilic acid (OA)			X		
Metolachlor ethane sulfonic acid (ESA)			X		
Metolachlor oxanilic acid (OA)			X		
N-Nitrosodimethylamine (NDMA)			X		X
N-nitroso-diethylamine (NDEA)			X	X	
N-nitroso-di-n-butylamine (NDBA)			X		
N-nitroso-di-n-propylamine (NDPA)			X		
N-nitroso-methylethylamine (NMEA)			X		
N-nitroso-pyrrolidine (NPYR)			X	X	
N-butylbenzene				X	
sec-butylbenzene				X	
tert-butylbenzene				X	
Carbon disulfide	Industrial			X	
Chlorate				X	
2-chlorotoluene				X	
Isopropylbenzene	Industrial			X	
N-propylbenzene				X	
1,2,4-trimethylbenzene				X	
1,3,5-trimethylbenzene				X	
1,7-dimethylxanthine	Pharmaceutical-CNS Stimulant				X
Benzophenone	Sunscreens				X
Cholesterol	Fecal Indicator				X
Cimetidine	Pharmaceutical-Antihistamine				X
Codeine	Pharmaceutical-Analgesic				X
Dehydronifedipine	Pharaceutical (metabolite)				X
Diltiazem	Pharmaceutical-Antiangina				X
Diphenhydramine	Pharmaceutical-Antihistamine				X
Fluoxetine	Pharmaceutical-Antidepressant				X
Furosemide	Pharmaceutical-Diuretic				X
Metformin	Pharmaceutical-Antihyperglycemic				X
Miconazole	Fungicide				X
Ranitidine	Pharmaceutical-Antihistamine				X

M-O-N = The special EC characterization study presently being conducted by MWD, OCWD, and NWRI.

UCMR = The chemicals identified in EPA's Unregulated Contaminant Monitoring Rule.

IEUA = The special monitoring requirements in Inland Empire Utilities Agency's NPDES permit.

GAMA = The USGS's Groundwater Ambient Monitoring Assessment program.

Note: the colored shading is only provided to help the reader easily distinguish between columns.

**Table 1: Current Water Quality Monitoring for Emerging Constituents** (*continued*)

Constituent	Primary Use or Source	M-O-N	UCMR	IEUA	GAMA
Salbutamol	Pharmaceutical-Antiasthmatic				X
Warfarin	Pharmaceutical-Anticoagulant				X
Menthol*	Pharmaceutical				X
Methyl salicylate (Wintergreen Oil)*	Pharmaceutical & Flavorings				X
Camphor*	Pharmaceutical				X
1,4-Dichlorobenzene*	Moth repellent, fumigant, deodorant				X
1-Methylnaphthalene*	Gasoline & diesel fuel				X
2,6-Dimethylnaphthalene*	Diesel fuel & kerosene				X
2-Methylnaphthalene*	Gasoline, diesel fuel, crude oil				X
3-beta-Coprostanol*	Carnivore fecal indicator				X
3-Methyl—1(H)-indole (Skatole)*	Fragrance, stench in feces				X
3-tert-Butyl-4-hydroxy anisole (BHA)*	Antioxidant, preservative				X
4-Cumylphenol*	Detergent metabolite				X
5-Methyl-1H-benzotriazole*	Detergent metabolite				X
Acetophenone*	Fragrance and flavorings				X
AHTN*	Musk Fragrance				X
Anthracene*	Pesticides, paints				X
Antraquinone*	Dyes				X
Beta-Sitosterol*	Plant sterol				X
Beta-Stigmastanol*	Plant sterol				X
Bromacil*	Herbicide				X
Carbaryl*	Pesticide				X
Carbazole*	Pesticide, Dyes, Lubes, Explosives				X
Chlorpyrifos*	Pesticide				X
Cotinine*	Nicotine Metabolite				X
d-Limonene*	Fungicide, Antimicrobial				X
Fluoranthene*	Coal tar and asphalt				X
HHCB*	Musk fragrance				X
Indole*	Feces, Perfumes, Pesticides, Coffee				X
Isoborneol*	Fragrance in perfumes, disinfectants				X
Isoquinoline*	Pharmaceutical				X
Isophorone*	Pesticides, Paint, Ink, Sealant				X
Metalaxyl*	Herbicide, fungicide				X
Naphthalene*	Fumigant, moth repel., gasoline				X
p-Cresol*	Wood preservative				X
Pentachlorophenol*	Herbicide, fumigant, pesticide				X
Phenanthrene*	Explosives, tar, diesel, crude oil				X
Phenol*	Disinfectant				X
Prometon*	Herbicide				X
Pyrene*	Industrial & Pharmaceutical				X
Tributyl phosphate*	Flame retardant, antifoaming agent				X
Triethyl citrate*	Cosmetics & Pharmaceuticals				X
Triphenyl phosphate*	Plasticizer, flame retardant				X
Tris (2-butoxyethyl) phosphate*	Flame retardant				X
Tris (2-chloroethyl) phosphate*	Plasticizer, flame retardant				X
Tris (dichloroisopropyl) phosphate*	Flame retardant				X

M-O-N = The special EC characterization study presently being conducted by MWD, OCWD, and NWRI.<sup>22</sup>

UCMR = The chemicals identified in EPA's Unregulated Contaminant Monitoring Rule.

IEUA = The special monitoring requirements in Inland Empire Utilities Agency's NPDES permit.

GAMA = The USGS's Groundwater Ambient Monitoring Assessment program.

Note: the colored shading is only provided to help the reader easily distinguish between columns.

<sup>22</sup> Each year Metropolitan Water District and Orange County Water District perform many thousands of other chemical analyses, in addition to this preliminary EC characterization study, to assure the safety of municipal water supplies. Comprehensive water quality reports are submitted to state authorities on a regular basis.

Second, relatively few laboratories have the equipment, expertise and experience needed to measure ECs accurately. Evaluating a large number of different ECs will require several different laboratories because no single firm is capable of performing all of the various analytical methods. However, this situation is expected to improve in response to rapidly growing demand for additional EC data.

Third, the acceptable level of precision for EC methods is expressed as a 30% coefficient-of-variation (CV).<sup>23</sup> CV is a common statistical parameter used to describe data variability. It is calculated by dividing the standard deviation of a dataset by the mean of the same dataset. A 30% CV is not the same as saying that the range of error in the estimate is plus or minus 30%. Instead, a 30% CV means that one would be 95% confident that the range of reported values for identical split samples to fall within plus or minus 60% of the average for all of the samples.

For example, assume that 100 state patrol officers line up along the highway holding identically manufactured and calibrated radar guns. Further assume that all 100 officers point those radar guns at a single car traveling at exactly 55 mile-per-hour. If the radar guns have a relative precision of 30% CV, then 95 of the 100 radar guns will report an estimated speed somewhere between 22 mph and 88 mph. It is likely that one of the radar guns will indicate the car isn't moving and one of the radar guns will show the car traveling in excess of 102 mph. Fortunately for the State Patrol, real radar guns have much better precision than the methods used to measure emerging constituents. By way of comparison, traditional analytical methods used to quantify other common pollutants (ammonia, metals, TDS, etc.) often have a reported CV of less than 5%. However, it this was not always the case.<sup>24</sup> And, the methods used to detect ECs are also expected to improve with time.

**Table 2: Expert Presentations to the Santa Ana EC Work Group in Summer, 2008**

<b>Expert</b>	<b>Affiliation</b>	<b>PowerPoint</b>
Mr. Brian Bernados, P.E.	California Department of Health	See Appendix K
Dr. Jörg Drewes	Colorado School of Mines	See Appendix Q
Dr. Doug Drury	Clark County Water Reclamation District	See Appendix R
Dr. Andrew Eaton	MWH Laboratories	See Appendix S
Ms. Nel Groenveld	Inland Empire Utilities Agency	See Appendix T
Dr. Y. Carrie Guo	Metropolitan Water District of So. California	See Appendix U
Mr. Justin Kulongoski	U.S. Geological Service	See Appendix V
Dr. Shane Snyder	Southern Nevada Water Authority	See Appendix W

<sup>23</sup> Some laboratories prefer to use the phrase "Relative Percent Difference (RPD)" when referring to the Coefficient-of-Variation.

<sup>24</sup> Herbert L. Windom, et al. "Inadequacy of NASQAN Data for Assessing Metal Trends in the Nation's Rivers." Environmental Science Technology. Vol. 25. 1991 pp. 1137-1142.

Fourth, many ECs are significantly reduced by current water and wastewater treatment practices. Others may be changed by sunlight or percolation through the soil column. Therefore, most these chemicals would serve as poor indicators of potential contamination in groundwater. If one desires to use select chemicals as tracers to detect the influence of wastewater in raw water supplies, then it is essential to choose those that are most persistent in the environment and least susceptible to accidental sample contamination.<sup>25</sup> Relatively few ECs meet this criteria.

In sum, there are a number of EC characterization studies already underway. The results of these efforts will be useful to guide development of any long-term monitoring strategy. Any such program should focus on the most robust indicators of wastewater rather than attempting to measure a wide variety of ECs. Success will depend on the availability of accurate and reliable methods and qualified laboratories to perform the tests. Finally, it is important to acknowledge the intrinsic level of scientific uncertainty and imprecision associated with new analytical detection technologies. Great care should be exercised when collecting, interpreting and reporting the data.

#### **IV. Implementation Issues for an Emerging Constituent Monitoring Program**

Most of the current EC characterization efforts, including those sponsored by USGS, AWWARF, Southern Nevada Water Authority, OCWD, MWD and NWRI were undertaken voluntarily. Some of the analyses were initiated in response federal (EPA) mandates or state (CDPH) recommendations. But, in all cases, the data was collected for the expressed purpose of informing future public policy decisions. In each instance, regulatory authorities explicitly renounced using the EC monitoring data for compliance purposes.

When the Santa Ana Regional Water Quality Control Board proposed to require more comprehensive water quality monitoring for groundwater recharge projects, there arose considerable anxiety over how such data might be used in a regulatory context. It is important to note that the Regional Board gave no indication the EC data would be used for anything other than to support CDPH's general inquiries on the subject. However, discussion among the stakeholders revealed that there were four significant regulatory questions that should be addressed.

First, given the absence of EPA-approved standard methods<sup>26</sup> for nearly all of the ECs that may be monitored, how can the data be certified when it is reported? How will the Method Detection Limit (MDL), Practical Quantitation Level (PQL) and/or Laboratory Reporting Level (RLR) be determined? EC values vary greatly between individual test runs and different laboratories; therefore, how will intra- and inter-laboratory accuracy and precision be defined? How will state certification be determined for laboratories performing non-standard methods?

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<sup>25</sup> One expert noted that some methods used to detect caffeine were so sensitive that samples may be inadvertently contaminated by the laboratory technician's breath if he/she drank coffee, tea or cola before conducting the test.

<sup>26</sup> EPA approved standard methods refer to those that have been certified in 40 CFR Part 136.

In general, permittees are required to certify that all data and information submitted to state and federal authorities is "true, accurate and complete."<sup>27</sup> Most permittees rely on the fact that the laboratories use EPA-approved methods and the fact that the state certifies each laboratory to perform such methods as the basis for trusting the reported data. Water and wastewater utilities are justifiably concerned about reporting results to regulators when there is not yet a reliable means to validate the underlying data.

Second, it is uncertain how EC data might be used to evaluate compliance with narrative objectives in the Basin Plan. For example, the Basin Plan states that "all waters of the region shall be maintained free of substances in concentrations which are toxic, or that produce detrimental physiological responses in human, plant, animal or aquatic life."<sup>28</sup> Historically, robust measures such as mortality rates, reproduction rates, or growth rates were used to assess probable toxicity. Now, however, the ability to measure small changes in hormonal activity, enzyme reactions, and other potential histopathologic endpoints greatly complicates the question of what constitutes a "detrimental physiological response." Can the detection of some ECs be cause for including a waterbody on the state's 303(d) list of impaired waterbodies despite the absence of a numeric water quality objective?

A report issued by the State Water Resources Control Board (SWRCB) in January of 2008 listed "feminized fish, premature spawning and eggshell thinning" as serious threats caused by a wide variety of emerging constituents including pharmaceuticals and personal care products.<sup>29</sup> U.S. EPA's Science Advisory Board went so far as to suggest that it may be time to reverse the traditional burden-of-proof so that all chemicals are assumed to be harmful until proven otherwise.<sup>30</sup> Such statements effectively nullify previous assurances that monitoring data will not be used for compliance purposes. If the mere detection of an EC imposes an obligation to prove that chemical is safe or be subject to enforcement action, then it is likely that all groundwater recharge projects would cease. Few water agencies have the resources to make the necessary scientific demonstrations.

Third, it is unclear how permitting authorities will apply the state and federal antidegradation regulations with respect to emerging constituents. Most of these chemicals are man-made and do not occur naturally in the environment. Therefore, by definition, where such chemicals are detected, it may be argued that the water quality has been degraded. Consequently, it may be necessary to demonstrate that allowing lower water quality provides maximum benefit to the people of California<sup>31</sup> or that lower water quality is necessary to accommodate important social and economic growth in the region.<sup>32</sup>

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<sup>27</sup> 40 CFR 122.22(d)

<sup>28</sup> California Regional Water Quality Control Board - Santa Ana Region. Water Quality Control Plan - Santa Ana River Basin (8). January 24, 1995 (Updated February, 2008); pp. 4-23

<sup>29</sup> California State Water Resources Control Board. Emerging Pollutants of Concern: A Survey of State Activities and Future Needs." January, 2008. (Appendix F)

<sup>30</sup> U.S. EPA. Aquatic Life Criteria for Contaminants of Emerging Concern: Part 1 – General Challenges and Recommendations. June 3, 2008. Internal Working Draft. (Appendix X)

<sup>31</sup> SWRCB Resolution No. 68-16

<sup>32</sup> U.S. EPA. 40 CFR 131.12

The obligation to comply with state and federal antidegradation policies applies even when there is no evidence to indicate that the chemicals in question are impairing beneficial uses. A similar argument was used successfully to disallow a permit for storing potable water in aquifers near Roseville, California. In that case, the measured by-products of chlorine disinfection met all applicable drinking water standards. But, because the concentration of these chemicals was greater than the natural background levels in the receiving water, and there may be some incremental increase in human health risk, antidegradation regulations were found to apply.<sup>33</sup>

Fourth, to what extent (if any) does the detection of emerging constituents trigger any obligations under §13522 of the Porter-Cologne Water Quality Control Act? Section 13522 states:

*"Whenever the State Department of Health Services or any local health officer finds that a contamination exists as a result of the use of recycled water, the department or local health officer shall order the contamination abated in accordance with the procedure provided for in Chapter 6 (commencing with Section 5400) of Part 3 of Division 5 of the Health and Safety Code."*<sup>34</sup>

This issue may be resolved when CDPH adopts the Draft Groundwater Recharge Regulations. The proposed revisions regulate the amount of recycled water that can be recharged in proximity to water supply wells.

It is important to emphasize that neither the Regional Board or CDPH has given any indication that EC data will be used in the manner described by the preceding four points. However, some of the statements published by EPA and the SWRCB have fostered great fear that such regulatory initiatives may be forthcoming. The resulting uncertainty is inhibiting water reclamation and reuse in California. Partly in response to these concerns, and to restore balance between the competing interests, the SWRCB has adopted a new Recycled Water Policy that addresses some of the EC issues.<sup>35</sup>

In particular, the SWRCB intends to establish a Blue Ribbon Advisory Panel comprised of experts in human toxicology, environmental toxicology, epidemiology, biochemistry, civil engineering and laboratory detection technology. The Panel is charged with summarizing the current state of scientific knowledge with regard to the risks associated with emerging constituents. It also appears that the SWRCB intends to rely on the Panel to help establish priorities for developing new water quality objectives.

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<sup>33</sup> California Regional Water Quality Control Board – Central Valley Region. Staff Report on the Regulation of ASR Projects in the Central Valley Region, General Strategy. 2006.

<sup>34</sup> Section 5410 of the Health & Safety Code defines contamination as the risk of poisoning or spreading disease.

<sup>35</sup> State Water Resources Control Board. Recycled Water Policy. February 3, 2009. Attached as Appendix P.

## V. Findings and Recommendations

Because the issue of emerging constituents rests at the cutting edge of science, regulatory efforts should proceed with greater diligence. The SWRCB's commitment to convene a Blue Ribbon Panel to review the emerging science of unregulated chemicals is a good example of proactive caution. In addition, the EC Workgroup makes the following recommendations:

- 1) Some EC monitoring is necessary to implement state health regulations. It may be necessary to analyze for chemicals with State Notification Levels even if there are no water quality objectives established for those chemicals. In addition, if CDPH adopts the proposed revisions to Draft Groundwater Recharge Regulations, some sort of tracer monitoring will be needed to demonstrate that effluent concentrations do not exceed allowable maximums in water supply wells. ECs monitoring may be used to supplement the Total Organic Carbon (TOC) or Total Dissolved Solids (TDS) data currently used to perform fate and transport studies.
- 2) When EC monitoring requirements are included in any discharge permit to satisfy a specific state or federal requirement, the Regional Board should identify the basis for the requirements in the Fact Sheet accompanying the permit.
- 3) Where ECs are used as surrogate indicators to confirm adequate wastewater treatment and/or to identify the potential presence of wastewater in a well, that purpose can be achieved by analyzing for the relatively few chemicals for which robust detection methods are available. There is no additional public health benefit accrued by analyzing for a very large number of ECs. In addition, there may be other metrics that achieve the same purpose at less cost and greater scientific certainty. Such alternatives should also be explored.
- 4) Any effort to characterize EC concentrations in the watershed should rely solely on analytical methods (principally LC/MS with isotope dilution) previously demonstrated to provide the most accurate and precise results. In addition, only well-qualified laboratories with significant previous experience using such methods should be commissioned to perform such studies.
- 5) Determining safe levels for any given chemical is complex and resource-intensive endeavor. Primary responsibility for evaluating the risk each EC may pose to human health or the environment rests with EPA's Office of Science and Technology (EPA-OST), the California Office of Environmental Health Hazard Assessment (OEHHA) and the California Department of Public Health. Neither the Regional Board nor the local water and wastewater agencies have sufficient resources or expertise to perform the sophisticated epidemiological studies needed to establish numeric water quality objectives for emerging constituents.<sup>36</sup> The Workgroup strongly endorses the State Board's decision to convene a Blue Ribbon Panel of Experts to explore such issues.

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<sup>36</sup> Memorandum of Agreement Between the Department of Health Services and the State Water Resources Control Board on Use of Reclaimed Water. 1996 (Appendix I)



- 6) EC monitoring programs will vary in relation to a number of important factors, including: the nature of the source water (e.g. municipal effluent, urban runoff), the nature of the receiving water (e.g. surface water or groundwater), the nature of the potential threat (e.g. human health or aquatic toxicity), and the nature of the recharge project (e.g. managed recharge basins or incidental percolation from a flowing river). Therefore, it is appropriate to encourage site-specific investigations in lieu of broad generic EC monitoring.
- 7) Existing state and federal law provides adequate authority to protect people and the environment from any adverse impacts of emerging constituents when such impacts are known.<sup>37</sup> It is not necessary to adopt a numeric water quality objective before the Regional Board can take appropriate action.<sup>38</sup> The Basin Plan already prohibits nuisance pollution and the discharge of any substance in concentrations that may be harmful to humans, plants, animals, or aquatic organisms. The Triennial Review process requires the Regional Board to reassess and update the Basin Plan every three years to ensure that the best available science is used to beneficial uses. Separately, the California Environmental Quality Act requires those proposing to implement groundwater recharge projects to mitigate any significant adverse effects on water quality.
- 8) EC monitoring efforts should be managed to assure uniform quality, consistent data interpretation, and eliminate redundant expenditures. By necessity, such investigations must be reviewed and updated regularly, through an adaptive management process, to assure scarce resources are providing measurable protection to human health and the environment and that the best available science is used to guide water quality analyses and regulatory policy.
- 9) All EC monitoring programs should include a substantial public education component to explain the meaning and significance of reported data. The fact that these chemicals are "unregulated" and that there are no applicable water quality standards does not engender a sense of safety and security. Rather, it creates additional uncertainty which tends to increase the general sense of vulnerability in the public. Great care must be exercised in communicating the new data in order to avoid misinterpretation of the implied threat and misunderstanding of the actual health risks.
- 10) There is a shared commitment among both the regulatory authorities and the local water agencies to provide adequate supplies of safe and affordable water to the community. Therefore, it is possible to safeguard water quality through the use of contractual cooperative agreements. Such agreements should be preferred until it becomes evident that a genuine threat to human health or the environment is not being properly addressed.

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<sup>37</sup> See, for example, U.S. EPA. Agency Information Collection Activities: Proposed Collection; Comment Request; Study of Unused Pharmaceuticals from Medical and Veterinary Facilities (New), EPA ICR Number 2316.01, OMB Control No. 2040-NEW. 73 Fed. Reg. 156, 46903. August 12, 2008. See also U.S. EPA. Data Requirements for Antimicrobial Pesticides; Proposed Rule. 73 Fed. Reg. 196, 59382. October 8, 2008.

<sup>38</sup> One example of proactive efforts to reduce the amount of pharmaceuticals in wastewater effluent is California's statewide "No Drugs Down the Drain" campaign – a joint effort of the SWRCB, U.S. EPA and the California Association of Sanitation Agencies (CASA). October 4-11, 2008.

- 11) It would be more cost-effective and productive for water and wastewater agencies to continue working collaboratively in Phase II rather than to initiate separate efforts to recommend future EC monitoring programs.
- 12) Phase I of SAWPA's Emerging Constituents Workgroup successfully achieved its stated objectives. Stakeholders have a more thorough understanding of the regulatory purpose for requiring EC monitoring, the current ability of laboratories to detect ECs, and the various efforts already underway to characterize EC concentrations in the watershed.
- 13) Permitting authorities are aware of the unintended regulatory consequences that may ensue as additional EC data is gathered and reported. Therefore, in order to encourage proactive water quality monitoring, it is appropriate to acknowledge that the data are being collected for informational purposes only and is not intended to be used to determine compliance with narrative or numeric water quality objectives until such time as the appropriate state and/or federal agencies have concluded that one or more of the ECs pose a significant risk to human health or the environment.
- 14) There is general consensus that the ECW should proceed to Phase II in 2009.

## **VI. Conclusion**

The primary purpose of Phase II is to develop a long-term strategy for investigating emerging constituents in the Santa Ana River watershed. That strategy may include developing a revised plan for EC monitoring to begin in 2010. Or, it may recommend that local stakeholders follow the SWRCB's lead as described in the newly adopted Reclaimed Water Policy. Much depends on the results of EC studies currently underway in the region.

If additional EC monitoring is to occur after 2009, then a large number of details must be addressed. What ECs should be monitored? Where should samples be collected? How often should samples be analyzed? What methods will be used? How will quality control be assured? How will results be certified and reported? What level of evaluation and interpretation should attend the data? How can the scientific and technical information best be explained to the public? In addition, all of the regulatory implementation issues identified in Section IV of this report must also be tackled.

Perhaps it is impossible to achieve so much in only the next 12 months. However, as noted earlier, the management process for Phase II is intended to be adaptive. There is no expectation that all outstanding issues will be permanently resolved; only that these concerns will be considered in good faith. The work products developed during the coming year are intended to begin the effort in earnest.

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