November 8, 2010

STAFF REPORT

CONSTITUENTS OF EMERGING CONCERN (CEC) MONITORING FOR RECYCLED WATER

This staff report provides recommendations for monitoring CECs in municipal recycled water used for groundwater recharge/reuse and landscape irrigation and for additional research on CEC monitoring. It relies on the recommendations presented in the CEC Advisory Panel report, *Monitoring Strategies for Chemicals of Emerging Concern (CECs) in Recycled Water – Recommendations of a Scientific Advisory Panel*, dated June 25, 2010. It also incorporates recommendations provided by the California Department of Public Health (CDPH)[1].

Background

On February 3, 2009, the State Water Resources Control Board (State Water Board) adopted the Policy for Water Quality Control for Recycled Water (Recycled Water Policy) (Resolution 2009-0011); the Recycled Water Policy became effective on May 14, 2009. The Recycled Water Policy presents several provisions that mandate the monitoring of CECs in municipal recycled water[2]. The Recycled Water Policy, however, recognized that the knowledge regarding CECs is incomplete and guidance would be needed to establish requirements for CEC monitoring. Therefore, the Recycled Water Policy also directed that the State Water Board, in consultation with the CDPH, convene a "blue-ribbon" advisory panel to guide future actions relating to CECs in municipal recycled water[3].

In accordance with the provision of the Recycled Water Policy, the State Water Board staff contracted the Southern California Coastal Water Research Project (SCCWRP) to convene an advisory panel on CECs in municipal recycled water. The CEC Advisory Panel (Panel) was charged with reviewing the scientific literature regarding CECs in recycled water, describing the current state of scientific knowledge regarding the risks of CECs to public health and the environment, and providing recommendations on monitoring CECs for various water recycling practices, including groundwater recharge/reuse to augment groundwater via surface spreading and percolation into a drinking water aquifer; groundwater recharge/reuse via subsurface injection into a drinking water aquifer; and urban landscape irrigation. The Panel's assignment was conducted in collaboration with the State Water Board staff and CDPH, with stakeholder input from a variety of public and private entities. On June 25, 2010, the Panel submitted to the State Water Board its final report, *Monitoring Strategies for Chemicals of Emerging Concern (CECs) in Recycled Water – Recommendations of a Scientific Advisory Panel* (Panel Report).

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[1] Letter from CDPH Division of Drinking Water and Environmental Management, dated September 13, 2010.
[2] Recycled Water Policy section 6.b.(3)(b), section 7.b.(4), and section 8.b.(2).
[3] Recycled Water Policy section 10.b.

CECs and Treatment Performance Surrogates

The Panel Report recommends monitoring of selected CECs in recycled water based on evaluation of CECs found in recycled water at concentrations with human health relevance with respect to the Panel's exposure screening approach. It also recommends monitoring of selected performance indicator CECs to evaluate the performance of treatment processes to remove CECs; and recommends monitoring of surrogate/operational parameters, such as turbidity, dissolved organic carbon, and conductivity, to verify that treatment units are working as designed.

The Panel selected health-based CECs to monitor using an exposure screening framework that compared measured environmental concentrations[4] (MECs) of CECs in recycled water to initial monitoring trigger levels[5] [6](MTL) established by the Panel for individual CECs. The Panel's process for selecting health-based CECs was based on evaluating the ratio of a compound's MEC to its respective initial MTL. Compounds in recycled water that were determined to have MEC/MTL ratio results greater than one were selected for monitoring as a health-based CEC. To be conservative in the selection process for health-based CECs, the Panel used data for secondary or tertiary recycled water and compared MEC 90th percentile values to the initial MTLs. The Panel selected initial MTLs using available toxicological information from various sources (i.e., CDPH derived benchmarks; U.S. Environmental Protection Agency (U.S. EPA), etc.) and prioritized the sources for selecting the benchmark to serve as an initial MTL. Based on the evaluation of MECs to initial MTLs, the health-based CECs selected for monitoring include caffeine, 17-beta-estradiol (17β-estradiol), n-nitrosodimethylamine (NDMA), and triclosan.

The Panel also selected a set of performance-based indicator CECs. Each selected performance-based indicator CEC represents a group of CECs. The removal of the performance –based indicator CEC through a treatment process provides an indication of the removal of the other CECs in the group. The six compounds selected to serve as performance-based indicator CECs are caffeine, gemfibrozil, n,n-diethyl-meta-toluamide (DEET), iopromide, NDMA, and sucralose. Caffeine and NDMA serve as both health and performance-based indicator CECs.

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[4] For the process of selecting health relevant CECs for monitoring, the Panel compiled available monitoring data for CECs in recycled water. The Panel set the MEC for screening at the 90th percentile. In other words, for the samples analyzed for a CEC, 90 percent of the concentrations of the CEC were below the MEC value. For the purpose of evaluating a recycled water project's monitoring data for monitoring response action, MEC is the concentration of a CEC detected in a sample.

[5] Initial monitoring trigger levels are levels for CECs that were selected by the Panel from drinking water benchmark concentrations established by various regulatory agencies (e.g., U.S. EPA, CDPH, and Australian Environmental Protection and Heritage Council), two papers published in scientific journals (Schwab *et al*. 2005, Schriks *et al*. 2009), and two peer-reviewed research reports focusing on the development of benchmarks for CECs (Snyder *et al*. 2008a, Cotruvo *et al*. 2010), to have health relevance that would warrant monitoring. The Panel cautioned that these are conservative values and the presence of a CEC above the monitoring trigger level would not verify a health risk.

[6] Because the Panel's resource and time constraints, it selected initial MTLs by using established drinking water benchmarks (see footnote 5). The Panel, however, recommended that future potable water use MTLs be derived incorporating allowable daily intakes (ADIs), relative source contribution (RSC), default bodyweight, and daily water consumption, as follows: MTL = [Screening Level ADI x 60 kg x RSC]/ [2 L/day].

Additionally, based on consultation with the CDPH, additional CECs were selected for monitoring for surface spreading groundwater recharge/reuse projects using recycled water including bisphenyl A, boron, carbamazepine, chlorate, hexavalent chromium (CrVI), diazinon, 1,4-dioxane, naphthalene, n-nitrosodiethyamine (NDEA), n-nitrosodi-n-propylamine (NDPA), n-nitrosodiphenylamine, n-nitrosopyrrolidine (NPYR), 1,2,3-trichloropropane (1,2,3-TCP), tris(2-carboxyethyl)phosphate (TCEP), and vanadium. Table 1 presents a list of the CECs recommended for monitoring and analytical method reporting limits, as recommended by the Panel and CDPH.

Monitoring of additional health-based CECs may be required by a Regional Water Board on a project specific basis. However, the process for selecting additional health-based CECs for monitoring would have to be consistent with the Panel's exposure screening approach (i.e., evaluation of MEC/MTL). The Panel's exposure screening approach is the recommended method for determining health-based CECs. The health-based CECs and performance-based indicator CECs should be included in recycled water monitoring programs for groundwater recharge/reuse[7] projects. Table 1 presents the health- and performance-based CECs selected for monitoring, along with recommended analytical method report limits, monitoring trigger levels, and expected removal percentage.

Analytical methods for analysis of CECs in recycled water samples should be selected to achieve the recommended method reporting limits listed in Table 1. Where a recommended method reporting limit may not be identified or achievable using currently available methodologies, an analytical method with a method reporting limit that is closest to the recommended method reporting limit with proven reliability should be selected. These analytical methods should be CDPH-approved.

Surrogates or operational parameters are parameters used to measure the performance of individual unit processes or treatment operations in removing trace organic compounds and/or assuring disinfection. Surrogates for use in evaluating treatment system performance may include ammonia, nitrate, dissolved organic carbon (DOC), conductivity, UVA absorption, turbidity, chloride residual, and total coliform. The selection of the appropriate surrogates will vary based on project specifics including the types of treatment processes, use of the recycled water, and the measurable occurrence of the parameter in the treatment train. Table 2 presents a list of recommended surrogate parameters and constituents and their expected removal percentage for groundwater recharge/reuse and landscape irrigation. Where applicable, surrogate parameters may be monitored using inline or hand-held devices provided appropriate calibration measures are implemented and documented.

The selection of appropriate performance-based indicator CECs and surrogate parameters is dependant on the type of treatment processes used and the recycled water use. For monitoring groundwater recharge/reuse projects using surface spreading basins, the selection is a function of the type of additional treatment prior to recycled water recharge to groundwater (i.e., percolation through soil/aquifer material versus reverse osmosis and advanced oxidation processes, respectively).

[7] For the purpose of this Staff Report, groundwater recharge/reuse is the practice of recharging groundwater using municipal recycled water.

Monitoring for health-based CECs and performance-based indicator CECs is not recommended for landscape irrigation projects, because of the low water ingestion rate with landscape irrigation use. The ingestion rate with groundwater recharge/reuse is much higher, since the intent of the use is to provide drinking water supplies.

Monitoring Locations/Points of Monitoring

The Panel's recommended approach for CEC monitoring includes monitoring for the presence of selected CECs and/or monitoring operational surrogate parameters and constituents to evaluate treatment unit and overall treatment process performance. Evaluation of treatment performance requires monitoring at specific locations during the treatment process, prior to groundwater recharge, and during retention in an aquifer. The monitoring locations or points of monitoring established for a recycled water facility and recharge area are dependent on the recycled water treatment and use. CDPH has developed draft regulations for groundwater recharge/reuse projects using recycled water. For applications of recycled water to percolation basins, the minimum level of treatment is typically disinfected tertiary[8]. For direct injection, recycled water is typically required to undergo additional treatment, following tertiary treatment, using reverse osmosis and advanced oxidation processes. Based on the Panel's recommendations, the appropriate points of monitoring for monitoring and evaluating recycled water quality for CECs for groundwater recharge/reuse projects are a follows:

Groundwater recharge/reuse – Surface Spreading Operations:

- Final effluent after tertiary treatment and prior to release to the spreading basin;
- At monitoring wells representing the uppermost groundwater and/or from shallow lysimeter wells underlying the spreading basin; and
- At down-gradient well(s) representing the potable source water prior to the potable water treatment plant.

Groundwater recharge/reuse – Direct Injection Operations:

- Between tertiary and membrane (reverse osmosis) treatment processes;
- Between membrane and advanced oxidation treatment; and
- Final effluent after advanced oxidation and prior to injection into an aquifer.

The recommended points of monitoring presented above are for the purposes of monitoring CECs, and are in addition to any other monitoring requirements required by the CDPH and the Regional Water Boards for a groundwater recharge/reuse or landscape irrigation project using recycled water.

[8] CDPH is providing recommendations for groundwater recharge/reuse facilities on a project-by-project basis and is in the process of developing regulations for them. The draft regulations posted at http://www.cdph.ca.gov/healthinfo/environhealth/water/Pages/Waterrecycling.aspx would require a minimum level of disinfected tertiary treatment as defined in California Code of Regulation, Title 22, Section 60301.230. Other requirements as specified in the draft regulations would be applicable.

Monitoring Frequency for Initial Assessment and Baseline Operations

Monitoring requirements for CECs at recycled water facilities should require an initial assessment of CECs in the facilities' recycled water. This initial assessment monitoring phase for existing facilities or new facilities starting up should be conducted over a one-year period. Following the initial assessment, the monitoring requirements should include three years of baseline operation CEC monitoring. Recommended monitoring frequencies during the initial assessment and baseline operation periods are presented below.

Initial Assessment:

- CECs - At a minimum, quarterly analysis for the first year.
- Surrogate parameters - Daily or Weekly[9]

Baseline Operations:

- CECs - Twice per year for a minimum of three years.
- Surrogate parameters - Daily or Weekly

Following the monitoring period for baseline operation, monitoring requirements should be re-evaluated and subsequent requirements should be determined on a project specific basis. Additionally, CEC monitoring on a semi-annual or an annual basis should be considered for a project that has demonstrated consistency in treatment and appropriate quality. However, the frequency of monitoring could be increased (i.e., more frequent monitoring) to further evaluate the effectiveness of the treatment process or the increased occurrence and/or concentrations of CECs.

Application of Performance-Based Indicator CECs and Surrogates

The effectiveness of a wastewater treatment process in removing CECs can be evaluated using performance-based indicator CECs and surrogate parameters and constituents. The rationale for using the performance indicator CECs and surrogates parameters and constituents is that their removal through a wastewater treatment process ensures removal of a wide range of CECs. The recommended approach of using indicator CECs and surrogates to evaluate wastewater treatment processes for removal of CECs is primarily for groundwater recharge/reuse projects. However, the use of performance-based indicator CECs and surrogates would be applicable to other types of recycled water use projects using the same practices and/or treatment methods.

Based on the results of the initial assessment phase, the appropriate performance indicator CECs and surrogate parameters and constituents should be selected for the baseline monitoring phase. Performance indicator CECs that were detected during the initial assessment phase should be selected for monitoring during the baseline monitoring phase.

[9] This is the Panel recommendation. Staff considers the frequency of monitoring to be a function of the parameter. Hence, some parameters may be monitored less frequently.

Surrogate parameters and constituents should be measured for each unit process during the initial assessment monitoring phase. Surrogate parameters and constituents that demonstrate measurable removal percentages for a given unit process should be selected for use in the monitoring programs for baseline[10] and standard operations.

The selection of the appropriate performance indicator CECs and surrogates will be dependent on project specifics including feed water quality and the type of unit treatment processes. During baseline and standard operations, the selected performance indicator CECs and surrogate parameters should be monitored, and removal differentials determined to evaluate treatment process performance.

The effectiveness of a treatment process to remove CECs should be evaluated by determining the change in performance indicator CEC concentrations and/or surrogate parameter values through the treatment process. This removal differential or removal percentage is the difference of measured concentrations of indicators and surrogate parameters and constituents in the influent compared to the effluent.

$$\text{Removal Differential} = \Delta X = [X_{inf} - X_{eff}]/X_{inf}$$

X_{inf} - Influent concentration
X_{eff} - Effluent concentration

For groundwater recharge/reuse projects using surface spreading, removal differential should be based on recycled water quality prior to discharge to the spreading area compared to recycled water quality in soil or groundwater beneath the surface spreading location. For groundwater recharge/reuse projects using direct injection, removal differential should be based on recycled water quality prior to and after treatment by reverse osmosis and advanced oxidation processes.

The expected removal percentages for performance indicator CECs and surrogate parameters and constituents are presented Tables 1 and 2. Measured removal percentages equal to or greater than the expected removal percentages provide an indication that the treatment processes are operating effectively.

Evaluation and Response to Monitoring Results

A measure of appropriate recycled water treatment plant performance would be the consistent production of recycled water with concentrations (i.e., MECs) of health-based CECs that are less than 5 times the ratio of MEC/MTL. MTL values for the health-based CECs are presented in Table 1.

For evaluation of health-based CEC monitoring results, the CEC Advisory Panel provided five tiers of thresholds and corresponding response actions. Groundwater recharge/reuse project agencies shall evaluate monitoring results for health-based CECs by comparing MEC/MTL ratio values to Panel recommended thresholds. Tiers of thresholds for evaluating monitoring results and recommended response actions excerpted from the Panel Report are as follows:

[10] Baseline operation is considered to represent the first three years of operation following initial assessment.

1) If no more than 25 percent of the sample results (i.e., MECs) for a health-based CEC exceed a MEC/MTL ratio of 0.1, then the CEC should be considered for removal from the monitoring program. In cases where a reduction of monitoring is considered, the MTL should be updated, if feasible, as part of the consideration for reducing monitoring requirements.

2) If the MEC/MLT ratio is greater than one and less than 10, check the data and continue to monitor.

3) If the MEC/MLT ratio is greater than ten and less than 100, check the data, resample immediately, analyze to confirm the MEC, and continue to monitor.

4) If the MEC/MLT ratio is greater than 100 and less than 1,000, do all of the above and implement a source identification program. Also, monitoring at a point in the distribution system closer to the point of exposure (i.e., groundwater recharge/reuse water entering drinking water supply) to confirm that attenuation of the CEC is occurring subsequent to the monitoring location and to confirm the magnitude of assumed safety factors associated with removal efficiency. The point of exposure should be selected with the approval of the CDPH and the Regional Water Board.

5) If the MEC/MTL ratio is greater than 1,000, do all of the above plus immediately confer with the CDPH and the Regional Water Board to determine the required response action. Confirm plant corrective actions through additional monitoring that indicates that CEC levels are below at least an MEC/MTL ratio of 100.

The recycled water/recharge agency should develop a response plan with specific actions to be implemented by the recycled water/recharge agency as part of interpreting appropriate responses to the monitoring results.

If CEC concentrations exceed the recommend tiered thresholds (presented above), the recycled water/recharge agencies should work with the CDPH and the Regional Water Boards to identify the need for increased monitoring to confirm the presence of problematic CEC(s), source identification studies, and toxicological studies. If appropriate, increased monitoring might involve engineering removal studies and/or modification of plant operation if found to be warranted. Consideration should be given to the basis of the MTL; the information available about the particular chemical; the chemical's potential health effects at the given concentration; the source of the chemical; as well as possible means of better control its presence, including treatment strategies if necessary, and other appropriate actions.

Furthermore, if a measured concentration of a CEC at the point of monitoring (i.e., groundwater beneath a surface spreading area or following reverse osmosis and advance oxidation process prior to groundwater injection) exceeds its respective MTL, the finding does not confirm a public health risk exists. The MTLs and their application were developed to be conservative and used only for the prioritizing CECs for monitoring. The MEC/MTL thresholds and MTLs should not be used to make predictions about risk.

CDPH Recommendations

CDPH has reviewed the Panel Report and has provided its recommendations to the State Water Board in a letter dated September 13, 2010. In this letter, CDPH recommended monitoring for certain additional CECs (shown in Table 1) besides those recommended in the Panel Report for groundwater recharge/reuse facilities that use surface spreading. Staff recommends monitoring for these additional CECs in recycled water for these facilities.

Recommended Research

The Panel Report provided recommendations for research that could be done to further establish monitoring protocols for CECs in recycled water. These are stated on Page 74 of the Panel Report. The recommendations for additional research are:

1) In order to populate a recycled water database of CECs with measured environmental concentrations and predicted environmental concentration data, conduct a comprehensive review of CECs likely to occur in recycled water based on peer-reviewed literature and occurrence studies outside California;
2) Develop robust and reproducible analytical methods to measure CECs in recycled water;
3) Perform laboratory performance and analytical method validation studies for CECs adopted by the State as monitoring priorities;
4) Develop a detailed procedure to estimate predicted environmental concentrations for CECs for which MECs are currently not available based on production, use and environmental fate;
5) The State Water Board should convene and charge a science advisory panel to scope out an investigative, short-term monitoring study (e.g. quarterly sampling over a one-year period) for CECs that exhibit relatively low MTLs (e.g. < 500 ng/L), but for which no or little MEC or predicted effluent concentration information is available for secondary/tertiary effluents used for the water reuse practices of interest; and
6) Encourage development of bioanalytical screening techniques that include CECs currently not identified but potentially present in recycled water ("unknown" chemicals). Develop appropriate trigger levels for these bioanalytical screening techniques that correspond to a response posing a concern from a human health standpoint.

The State Water Board has the option of seeking funding for and implementing all, some, or none of these recommendations.

Staff has reviewed the recommendations and has identified two paths the State Water Board could take. The first is to develop toxicity data and analytical methods for all the chemicals for which no water quality objectives have been established. This is the traditional method used for regulating toxic chemicals. Chemical-by-chemical evaluation, however, is a slow process and it would be difficult to individually evaluate all the chemicals, especially given the long list of these chemicals and the rate at which new ones are produced.

Our information is that there are currently more than 80,000 chemicals approved under federal law for use in the United States. Each day, a total of 42 billion pounds of chemical substances are produced or imported in the United States for commercial and industrial uses. An additional 1,000 new chemicals are introduced into commerce each year. Approximately one new chemical comes to market every 2.6 seconds, and global chemical production is projected to double every 25 years[11].

The alternative path would be to further develop the bioanalytical screening techniques described in research recommendation Number 6. If these screening techniques were fully developed, they could be used to evaluate whether recycled water has chemicals that produce biological responses such as estrogen receptor binding. If so, further tests would be performed to identify the responsible chemical or chemicals.

Staff recommends the second path as being the more productive route for expending research money. It sees the first path, the chemical-by-chemical approach, as being never ending, given the large number of chemicals in use. Hence, staff recommends seeking funding only for research recommendation Number 6 at this time. Further research may later be needed, however, to develop analytical methods and evaluate risk of those chemicals identified by the bioanalytical screening tests.

[11] California Department of Toxic Substances Control, 45-Day Public Notice and Comment Period for Proposed Rule Making, Safer Consumer Product Alternatives, Page 5, September 17, 2010

Table 1: CECs For Monitoring in Recycled Water For Groundwater Recharge/Reuse Projects

Constituent	CEC Recommen-dation Source	Indicator Type	Monitoring Trigger Level[1] (µg/L)[2]	Expected Removal (%)[3]	Recommended Method Reporting Limits (µg/L)[4]	Recycled Water Use Practice
Bisphenyl A	CDPH				--	SS[5] & DI[6]
Boron	CDPH				100	SS & DI
Carbamazepine	CDPH				--	SS & DI
Chlorate	CDPH				20	SS & DI
Chromium, hexavalent (CrVI)	CDPH				1.0	SS & DI
Diazinon	CDPH				--	SS & DI
1,4-Dioxane	CDPH				3.0	SS & DI
Naphthalene	CDPH				0.5	SS & DI
N-Nitrosodiethyamine (NDEA)	CDPH				--	SS & DI
N-Nitrosodi-n-propylamine (NDPA)	CDPH				--	SS & DI
N-Nitrosodiphenylamine	CDPH				--	SS & DI
N-Nitrosopyrrolidine (NPYR)	CDPH				--	SS & DI
1,2,3-Trichloropropane (1,2,3-TCP)	CDPH				0.005	SS & DI
Tris(2-carboxyethyl)phosphate (TCEP)	CDPH				--	SS & DI
Vanadium	CDPH				3.0	SS & DI
17β-estradiol	CEC Panel	Health	0.0009		0.001	SS & DI
Caffeine	CEC Panel	Health & Performance	0.35	>90	0.05	SS & DI
N-Nitrosodimethylamine (NDMA)	CEC Panel & CDPH	Health & Performance	0.01	25 - 50	0.002[7]	SS & DI[8]
Triclosan	CEC Panel	Health	0.35		0.05	SS & DI
Gemfibrozil	CEC Panel	Performance		>90	0.01	DI
Iopromide	CEC Panel	Performance		>90	0.05	SS
N,N-Diethyl-meta-toluamide (DEET)	CEC Panel	Performance		>90	0.01	SS & DI
Sucralose	CEC Panel	Performance		>25/>90[9]	0.1	SS & DI

[1] Monitoring trigger levels for groundwater recharge/reuse practice.
[2] µg/L – Micrograms per liter
[3] Expected removal from waste stream by reverse osmosis/advanced oxidation units for direct injection, or by the subsurface for surface spreading with a travel time of two weeks and no dilution, see details in Drewes et. al., 2008.
[4] CDPH's Drinking Water Analysis: Chemicals and Characteristics, September 30, 2009
[5] Groundwater recharge/reuse by surface spreading.
[6] Groundwater recharge/reuse by direct injection.
[7] CEC Advisory Panel Recommendation
[8] NDMA is a performance-based indicator CEC for direct injection practice.
[9] Surface Spreading/Direct Injection

Table 2: Surrogate Parameters and Constituents for Recycled Water Use Practices

Surrogate Parameters and Constituents	**Expected Removal[1] Differential (%)**	**Recycled Water Use Practice**
Ammonia	>90	GRR[2] – Surface Spreading
Conductivity	>90	GRR – Direct Injection
DOC[3]	>30/>90[4]	GRR – Surface Spreading and Direct Injection
Nitrate	>30	GRR – Surface Spreading
UVA[5] Absorption	>30	GRR – Direct Injections
Chlorine Residual	--	Landscape Irrigation
Total Coliform	--	Landscape Irrigation
Turbidity	--	Landscape Irrigation

[1] Expected removal from waste stream by reverse osmosis/advanced oxidation units for direct injection, or by the subsurface for surface spreading with a travel time of two weeks and no dilution, see details in Drewes et. al., 2008.
[2] Groundwater recharge/reuse
[3] Dissolved organic carbon
[4] Surface spreading/Direct injection.
[5] Ultraviolet light A