City of Sedona
Class A+ Reclaimed Water Injection Well Test

TECHNICAL MEMORANDUM NO. 2
CONSTITUENTS OF EMERGING CONCERN WATER QUALITY EVALUATION PHASE II

FINAL
February 2014

Registered Professional Engineer (Civil)
CERTIFICATE NO.
44702
BRAD D.
JEPPSON
DATE SIGNED 2/4/14
ARIZONA, U.S.A.
EXPIRES 06-30-2015

4600 EAST WASHINGTON ST., SUITE 500 • PHOENIX, ARIZONA 85034 • P. 602.263.9500 • F. 602.265.1422

City of Sedona

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TECHNICAL MEMORANDUM
NO. 2

CONSTITUENTS OF EMERGING CONCERN
WATER QUALITY EVALUATION

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CONSTITUENTS OF EMERGING CONCERN WATER QUALITY EVALUATION

1.0 INTRODUCTION

The City of Sedona (City) is in the process of conducting an injection well test to verify the feasibility of aquifer injection (storage) as a water resource management strategy. This strategy involves storing reclaimed water in the aquifer at a depth of 600 feet to 1,200 feet below ground surface. An Underground Storage Facility (USF) permit will be utilized to account for stored water, which may allow the City to accumulate and recover groundwater credits in the future.

The stored water is Class A+ reclaimed water from the City's Wastewater Reclamation Plant (WWRP). Class A+ is the highest reclaimed water quality classification regulated by Arizona Department of Environmental Quality (ADEQ). The City is required to treat the wastewater stream to a high level of water quality in accordance with the WWRP's Aquifer Protection Permit (APP) issued by ADEQ, which requires that the groundwater at the edge of the WWRP property (or point of compliance, POC) to meet established Aquifer Water Quality Standards (AWQS) nearly equivalent to drinking water standards. Hence, the WWRP closely monitors the water quality of the Class A+ reclaimed water to ensure that all contaminant levels in the treated effluent are below the discharge limits set forth in the permit to protect groundwater quality. Regulated constituents include pathogens, nitrogen, metals, volatile organic compounds (VOCs), and other parameters.

1.1 Constituents of Emerging Concern

In addition to routine monitoring for regulated water quality parameters, the City has also performed sampling to assess the water quality for presently unregulated constituents of emerging concern (CECs). CECs is a general term for water quality constituents whose potential for health impacts is unknown, and are currently unregulated by the Federal Environmental Protection Agency (EPA) or the State of Arizona. CECs include compounds such as pharmaceuticals, personal care products (such as those found in lotions and shampoo, for example), food additives (caffeine, artificial sweeteners), and other consumer chemicals. The occurrence, fate and transport, and potential health effects of a wide array of these compounds have been the subject of intense scientific study over the last two decades, and industry consensus is that most CECs do not present a human health concern at the minimal concentrations found in high-quality reclaimed water. By way of reference, an average cup of coffee contains caffeine at a concentration of 1 gram per liter (g/L) or more. By the time wastewater has undergone basic and advanced treatment, similar to treatment performed at the Sedona WWRP, the concentration of caffeine measures in nanograms per liter (ng/L), which is approximately ***one billion*** times lower.

Recent work by Trussell et al (2013), which was validated through a national expert panel review, provides more specific guidelines on the concentrations of CECs that might be relevant for human health in a potable reuse context (treating reclaimed water for potable uses). As a conservative approach, the data produced by this injection study are reviewed in the context of these benchmarks (although the City is not planning this project for potable reuse applications). In addition, many CECs are typically further reduced in the aquifer by naturally-occurring biological processes, known as soil-aquifer treatment.

1.2 Sedona WWRP CEC Study

The CEC study was motivated by questions about how the storage of reclaimed water with trace levels of CECs may impact the existing groundwater quality. In this study, the City investigated the levels of CECs in the influent wastewater to the WWRP, the Class A+ reclaimed water (WWRP effluent), native (up gradient) groundwater in the area of the WWRP, and the groundwater at the current POC located down gradient from the injection test well. CECs selected for this evaluation include a wide array of compounds for which currently sensitive and reliable detection and quantification methods have been developed. The CECs investigated comprise pharmaceutical and personal care product (PPCP) compounds, natural and synthetic hormones, nitrosamines, fire retardants, and other chemicals contained in food, beverages, and consumer products. Samples were sent to one or both of two national laboratories (University of Arizona Snyder Laboratory and Eaton Analytical) that specialize in the analysis of CECs in environmental aqueous samples and that routinely conduct such analyses for municipalities in the U.S.

2.0 BACKGROUND

The infiltration and underground storage of reclaimed water into local aquifers has become a practice for a number of municipalities in the U.S. over the last decades as a critical strategy to realize local water management objectives including effluent management, groundwater replenishment, and establishing barriers against seawater intrusion into freshwater aquifers. Existing injection well systems are currently in operation in multiple areas of the country, including California, Arizona, and Florida. The main focus for managers and operators of these systems, regulators, and other public stakeholders when implementing and operating such systems is to preserve the quality of local groundwater resources. The key constituents of concern that are addressed in water quality monitoring studies are organics and disinfection byproducts, microbial pathogens, nutrients, salts, and organic trace pollutants, or CECs. The regulatory framework for groundwater replenishment systems, which include reclaimed water infiltration and injection into groundwater aquifers, varies by state.

While CECs are broadly recognized by many stakeholders to be an emerging concern, regulation of these compounds continues to remain a significant challenge for national and state regulators. In contrast to nutrients or pathogens, the environmental and human health effects of CECs, that comprise hundreds of trace organic compounds that can be detected in water and traced to anthropogenic influence, simply are not yet fully understood. For the large majority of compounds that we can detect in treated effluents and the aqueous environments it is still uncertain a) whether they have an effect on humans or aquatic life at environmental concentrations, and b) what the cause - effect relationship is.

With regards to CECs, the state of California has been a frontrunner in the U.S. in establishing regulations to manage the risk from CECs in groundwater replenishment operations. The California State Water Resources Control Board (CSWRCB) adopted in January 2013 an amendment to the California Recycled Water Policy (CSWRCB, 2013), which establishes monitoring requirements for CECs and surrogates in reclaimed water used for groundwater recharge.

3.0 PURPOSE OF THE SEDONA CEC WATER QUALITY EVALUATION

The Sedona CEC water quality evaluation was conducted to better understand the potential impact of storing reclaimed water underground on the overall quality of the local aquifer. Specifically, this project has the following objectives:

1. Characterize the reclaimed water proposed for aquifer storage in terms of CEC presence and concentration levels;
2. Characterize the local aquifer in terms of its current water quality related to CECs prior to operation of the reclaimed water injection test;
3. Compare the reclaimed water quality to the groundwater quality in a well that is partially influenced by current reclaimed water infiltration operations (point of compliance);
4. Identify any compounds that may be present in the reclaimed water at concentration levels that may pose a concern for human health, based on current research; and
5. Identify compounds in the reclaimed water and groundwater system that may serve as useful tracers in the future to indicate the presence and level of influence of groundwater that originated from reclaimed water in the local aquifer.

4.0 TEST PLAN

4.1 Selected Analytes

The sampling campaign comprised a total of 112 CEC compounds. The specific CECs selected for this evaluation are commonly present in municipal wastewater influents and treated effluents, and/or may pose a potential human health concern depending on their concentration levels. Table 2.1 lists the CEC compounds for which samples were analyzed, along with their typical uses and environmental sources. Compounds listed as “metabolites” are formed when other CECs break down. Depending on the compound, breakdown into metabolites can occur during human digestion, within the wastewater treatment process, or in the environment.

The analyte lists also included several common herbicides, for some of which regulatory limits or advisories in drinking water have been established. These herbicides were only analyzed by one of the two laboratories used in this study (Eaton Lab).

Table 2.1 CEC Compounds and their Typical Uses
Constituents of Emerging Concern Water Quality Evaluation
City of Sedona

CEC Compound	Typical Use
1,7-Dimethylxanthine	Caffeine metabolite
2,4-D	Herbicide
4-nonylphenol	Member of alkylphenol family, detergent metabolite
4-tert-Octylphenol	Member of alkylphenol family, detergent metabolite
Acesulfame-K	Artificial sweetener
Acetaminophen	Nonsteroidal anti-inflammatory drug (NSAID)
Albuterol	Bronchial dilater (active ingredient in inhalers)
Amoxicillin	Antibiotic
Andorostenedione	Natural hormone
Atenolol	Beta blocker (used to treat hypertension)
Atrazine	Herbicide
Azithromycin	Antibiotic
Bendroflumethiazide	Diuretic (used to treat hypertension)
Benzophenone	UV blocker (active ingredient in sunscreen)
Benzotriazole (BTA)	Corrosion inhibitor, also used in drug manufacturing
Bezafibrate	Fibrate drug (used to treat high cholesterol)
Bisphenol A (BPA)	Breakdown product of polycarbonate, a plastic commonly used to store water and food
Bromacil	Herbicide
Butalbital	Barbiturate drug (pain medication)
Butylparaben	Member of paraben family, used in lotions and body creams
Caffeine	Stimulant found in many beverages
Carbadox	Antibacterial drug used in animal husbandry
Carbamazepine	Anti-seizure drug
Carisoprodol	Muscle relaxant drug
Chloramphenicol	Antibiotic
Chloridazon	Herbicide
Chlorotoluron	Herbicide
Cimetidine	Heartburn / Reflux drug

Table 2.1	**CEC Compounds and their Typical Uses Constituents of Emerging Concern Water Quality Evaluation City of Sedona**
CEC Compound	**Typical Use**
Clofibric Acid	Herbicide
Cotinine	Nicotine metabolite
Cyanazine	Herbicide
DACT	Atrazine degradation product (see above)
DEA	Atrazine degradation product (see above)
DEET	Insect repellant
Dehydronifedipine	Metabolite of Nifedipine (see below)
Dexamethasone	Corticosteroid drug (anti-inflammatory used to treat many conditions, including rheumatoid arthritis)
DIA	Atrazine degradation product (see above)
Diazepam	Sedative, anti-epileptic, and muscle relaxant drug
(brand name Valium)	+
Diclofenac	Nonsteroidal anti-inflammatory drug (NSAID)
Dilantin	Anti-epileptic drug
Diphenylhydramine	Antihistamine (brand name Benadryl)
Ditiazem	Calcium channel blocker (drug used to treat hypertension, angina, and some types of arrhythmia)
Diuron	Herbicide
Erythromycin	Antibiotic
Estradiol (E2)	Natural steroid hormone
Estrone (E1)	Natural steroid hormone
Ethinyl Estradiol - 17α	Synthetic steroid hormone (used in birth control pills)
Ethylparaben	Member of paraben family, used in lotions and body creams
Flumequine	Antibiotic
Fluoxetine	Antidepressant drug (brand name Prozac)
Gemfibrozil	Fibrate drug (used to lower blood lipid levels)
Ibuprofen	Nonsteroidal anti-inflammatory drug (NSAID)
Iohexal	X-ray contrast medium
(helps make x-rays more visible)	+
Iopromide	X-ray contrast medium (helps make x-rays more visible)
Isobutylparaben	Member of paraben family, used in lotions and body creams
Isoproturon	Herbicide
Ketoprofen	Nonsteroidal anti-inflammatory drug (NSAID)
Ketorolac	Nonsteroidal anti-inflammatory drug (NSAID)

Table 2.1 CEC Compounds and their Typical Uses
Constituents of Emerging Concern Water Quality Evaluation
City of Sedona

CEC Compound	Typical Use
Lidocaine	Local anesthetic and anti-arrhythmic drug
Lincomycin	Antibiotic
Linuron	Herbicide
Lopressor (metoprolol)	Anti-hypertension drug
Meclofenamic Acid	Nonsteroidal anti-inflammatory drug (NSAID)
Meprobamate	Anxiolytic drug (tranquilizer)
Metazachlor	Herbicide
Methylparaben	Member of paraben family, used in lotions and body creams
Naproxen	Nonsteroidal anti-inflammatory drug (NSAID)
Nifedipine	Drug used to treat high blood pressure and angina
N-Nitrosodibutylamine (NDBA)	Member of the nitrosamine family, formed as disinfection byproducts primarily in chloramination.
N-Nitrosodiethylamine (NDEA)	Member of the nitrosamine family, formed as disinfection byproducts primarily in chloramination.
N-Nitrosodimethyl-amine (NDMA)	Member of the nitrosamine family, formed as disinfection byproducts primarily in chloramination.
N-Nitrosodi-n-propyl-amine (NDPA)	Member of the nitrosamine family, formed as disinfection byproducts primarily in chloramination.
N-Nitrosomethyl-ethyl-amine (NMEA)	Member of the nitrosamine family, formed as disinfection byproducts primarily in chloramination.
N-Nitrosomorpholine (NMOR)	Member of the nitrosamine family, formed as disinfection byproducts primarily in chloramination.
N-Nitrosopiperidine (NPIP)	Member of the nitrosamine family, formed as disinfection byproducts primarily in chloramination.
N-Nitrosopyrollidine (NPYR)	Member of the nitrosamine family, formed as disinfection byproducts primarily in chloramination.
Norethisterone	Synthetic hormone (used in birth control pills)
Norgestrel	Synthetic hormone (used in birth control pills)
Oxolinic acid	Antibiotic
Pentoxifylline	Drug that improves blood flow
Perfluorobutane sulfonic acid (PFBS)	Perfluorinated chemical (PFC), breakdown product of non-stick surface coatings (Teflon®, Scotch Guard®)
Perfluorodecanoic acid (PFDA)	Perfluorinated chemical (PFC), breakdown product of non-stick surface coatings (Teflon®, Scotch Guard®)
Perfluorohexanoic acid (PFHxDA)	Perfluorinated chemical (PFC), breakdown product of non-stick surface coatings (Teflon®, Scotch Guard®)

Table 2.1 CEC Compounds and their Typical Uses
Constituents of Emerging Concern Water Quality Evaluation
City of Sedona

CEC Compound	Typical Use
Perfluorooctanoic acid (PFOA)	Perfluorinated chemical (PFC), breakdown product of non-stick surface coatings (Teflon®, Scotch Guard®)
Perfluorootane sulfonic acid (PFOS)	Perfluorinated chemical (PFC), breakdown product of non-stick surface coatings (Teflon®, Scotch Guard®)
Phenazone	Analgesic and antipyretic drug (used to treat pain and reduce fever)
Prednisone	Synthetic corticosteroid drug (used to treat many diseases, including asthma, rheumatic, and allergic disorders)
Primidone	Anticonvulsant drug
Progesterone	Natural steroid hormone
Propazine	Herbicide
Propylparaben	Member of paraben family, used in lotions and body creams
Quinoline	Used for many purposes, also an herbicide metabolite
Simazine	Herbicide
Sucralose	Artificial sweetener
Sulfachloropyridazine	Antibiotic
Sulfadiazine	Antibiotic
Sulfadimethoxine	Antibiotic
Sulfamerazine	Antibiotic
Sulfamethazine	Antibiotic
Sulfamethizole	Antibiotic
Sulfamethoxazole	Antibiotic
Sulfathiazole	Antibiotic
Tris(2-chloroethyl) phosphate (TCEP)	Flame retardant chemical
Tris(2-chloropropyl) phosphate TCPP	Flame retardant chemical
Tris(1,3-dichloro-2-propyl) phosphate (TDCPP)	Flame retardant chemical
Testosterone	Natural steroid hormone
Theobromine	Chemical component of chocolate
Theophylline	Methylxanthine drug (used to treat respiratory diseases)
Triclocarban	Antimicrobial agent (used in hand soaps)
Triclosan	Antimicrobial agent (used in hand soaps)
Trimethoprim	Antibiotic
Warfarin	Anticoagulant (prevents blood clots), aka Coumadin

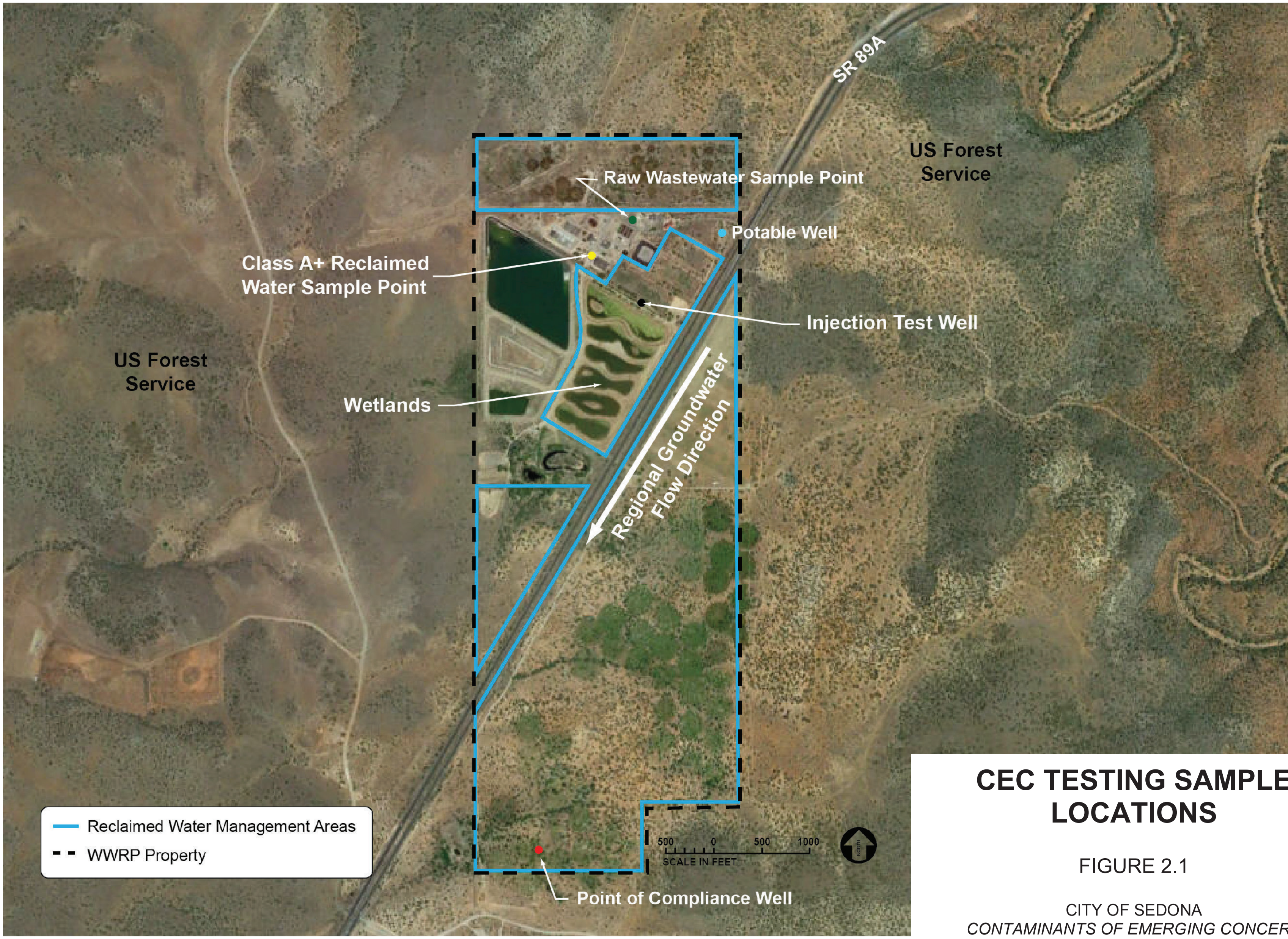
4.2 Sample Locations

Figure 2.1 illustrates the CEC sample locations relative to the WWRP. Note that reclaimed water management practices (i.e., spray irrigation and/or infiltration) have historically occurred within the blue areas. Sample locations were selected to assess CEC levels in the raw wastewater, treated reclaimed water, native groundwater, and “down-gradient” groundwater (prior and subsequent to the injection test). Table 2.2 summarizes the sample locations and the sampling plan.

Table 2.2 CEC Sample Locations and Sample Plan
Constituents of Emerging Concern Water Quality Evaluation
City of Sedona

Sample Location	Significance of Sample Location	Phase I[1]	Phase II		
			Pre-Test	Mid-Test[2]	End of Test[3]
Raw Wastewater	Measures CECs in untreated sewage	X			
Class A+ Reclaimed Water	Measures CECs in water used for aquifer storage	X	X	X	X
Native Groundwater (Potable Well)	Measures background CEC levels in aquifer up-gradient of reclaimed water management areas.	X			
Native Groundwater (Injection Well)	Measures background CEC levels in aquifer prior to the injection well test.		X		
Point of Compliance Well	Measures CECs in groundwater “down-gradient” of aquifer storage	X		X	X

Note:
(1) Phase I sampling occurred prior to the start of the injection well test.
(2) Samples taken after approximately 5 weeks of injection testing
(3) Samples taken after approximately 13 weeks of injection testing



CEC TESTING SAMPLE LOCATIONS

FIGURE 2.1

CITY OF SEDONA
CONTAMINANTS OF EMERGING CONCERN
WATER QUALITY EVALUATION

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4.3 Sampling Protocol

As standard analytical methods have not been formally adopted for unregulated CECs, duplicate sample sets of the grab samples from all four sampling locations in Phase I were sent to, and analyzed by, two independent contract laboratories as a quality assurance measure (Eurofins-Eaton Laboratory, located in Monrovia, California (Eaton Lab), and Arizona Laboratory for Emerging Contaminants run by Dr. Shane Snyder at the University of Arizona in Tucson (Snyder Lab)). Results proved to be generally consistent, and therefore, Phase II CEC samples were sent only to Eaton Labs.

The samples were collected as grab samples and immediately shipped on ice overnight to the analytical laboratories. Sampling protocols were provided by both laboratories, which were used by WWRP staff during the sampling activities. The protocols are included in Appendix A for reference. In addition, the labs also analyzed Quality Assurance/Quality Control (QA/QC) samples.

4.4 Laboratory Analysis

The full laboratory reports are included in Appendix B. Both laboratories employed the same method for CEC quantification, which is based on isotope dilution and solid phase extraction (SPE) followed by liquid chromatography and mass spectrometry in tandem (LC MS/MS). Eight of the 112 compounds (nitrosamine group) were analyzed using the EPA Method 521 for the Detection of Nitrosamines in Drinking Water based on GC MS/MS.

Results by both laboratories were reported as parts per trillion (ng/L) for all compounds analyzed. Both laboratories also reported the Method of Reporting Limit (MRL, the lowest concentration of an analyte in a sample that can be quantified with acceptable precision and accuracy) for each compound analyzed (see Appendix B), though the Eaton Lab denotes the MRL as a “detection limit” with compounds showing as “not detected” or ND if results are less than the MRL. The method detection limit (MDL) is the minimum concentration at which a compound can be detected in a sample, not necessarily reliably quantified. Due to the analytical challenges associated with analyzing for CECs, the ratio between MRL reported on laboratory reports and the MDL determined by the lab can range anywhere from less than 1 to 5.

A comparison to CEC monitoring recently mandated in California confirms that the labs’ MRLs are adequately protective of human health, based on the current understanding of health risks. California is the only state to promulgate specific requirements related to monitoring for CECs in reclaimed water. The California State Water Resources Control Board (CSWRCB) requires monitoring of recycled water slated for aquifer injection for a specific set of CECs indicator compounds, as shown in Table 2.3 (CSWRCB, 2013). This policy amendment was based on the advice of a national expert panel convened by the CSWRCB in 2009 (Drewes et al., 2010). With one exception (Estradiol), the MRLs provided by both laboratories for this project meet or exceed the MDL requirements put forth by the CSWRCB.

It is important to note that these monitoring requirements apply only for scenarios intended for indirect potable reuse (i.e., aquifer storage and subsequent down-gradient recovery for drinking water supply purposes); no federal or state regulations exist at this time that require CEC monitoring for aquifer storage, as currently proposed by the City of Sedona. Therefore, while the comparison to the CSWRCB requirements is informative and the only comparison point currently available, it should be considered very conservative.

Table 2.3 List of CECs Required for Monitoring by California for Potable Reuse via Aquifer Injection (Subsurface Application)
Constituents of Emerging Concern Water Quality Evaluation
City of Sedona

CEC	Indicator Type(1)	California MRL Requirement(2)	Sample MRL Achieved in Reclaimed Water (Snyder/Eaton)
Estradiol	Health	1 ng/L	NA3 / 5 ng/L
Caffeine	Health / Performance	50 ng/L	4 ng/L / 5 ng/L
NDMA	Health / Performance	2 ng/L	1 ng/L / 2 ng/L
Triclosan	Health	50 ng/L	25 ng/L / 10 ng/L
DEET	Performance	50 ng/L	11 ng/L / 10 ng/L
Sucralose	Performance	100 ng/L	NA3 / 100 ng/L

Notes:
(1) The indicators listed by the CSWRCB (2013) are listed as health-based or performance-based indicators. Health-based indicators are included to ensure monitoring for compounds the CSWRCB has determined may have health risks. Performance-based indicators are included to assess the general performance of the treatment processes; these are not included because of health concerns.
(2) Required MRLs as listed by CSWRCB (2013).
(3) Parameter not measured by Snyder lab.

5.0 RESULTS

5.1 Phase I Results

During Phase I, samples were analyzed by two laboratories, the Snyder Laboratory at the University of Arizona (Snyder) and Eaton Analytical / Eurofins Laboratory (Eaton). For Phase I, the results of the CEC testing for all compounds for which a detection was reported in one or more of the four samples are presented in Table 2.4. Of all 112 compounds analyzed, 55 compounds were detected in at least one of the field samples collected (mostly in the WWRP influent). More than 50 percent (or 57 of all 112 compounds) were not detected or quantifiable in any of the four field samples, and only 39 compounds, or 35 percent of those analyzed, were detected in the Class A+ reclaimed water, none of which appear to present a significant health risk as will be discussed in more detail below.

Table 2.4 Phase I CEC Analysis Results
Constituents of Emerging Concern Water Quality Evaluation
City of Sedona

Analyte	Laboratory[1]	Results in ng/L[2]			
		GW[3]	POC[4]	Effluent[5]	Influent[6]
1,7-Dimethylxanthine	Eaton	ND	ND	**51**	**22,000**
4-tert-Octylphenol	Eaton	ND	ND	ND	**2,900**
Acesulfame-K	Eaton	ND	**170**	**140**	**56,000**
Acetaminophen	Eaton	ND	ND	ND	**170,000**
Amoxicillin	Eaton	ND	ND	**1,200**	**9,200**
Atenolol	Eaton/Snyder	ND	ND	**220/420**	**1,800/ 3,030**
Benzophenone	Snyder	**51**	**41**	**150**	**1,350**
Benzotriazole	Snyder	**5**	ND	**1,530**	**970**
Bisphenol A	Eaton/Snyder	ND	**320/478**	ND	**340/320**
Butalbital	Eaton	ND	ND	**63**	ND
Butylparaben	Eaton	ND	ND	ND	**24**
Caffeine	Eaton/Snyder	ND/**2**	ND/**1**	**81/31**	**170,000/ 11,700**
Carbamazepine	Eaton/Snyder	ND	ND	**500/360**	**160/120**
Carisoprodol	Eaton	ND	ND	**140**	**66**
Cotinine	Eaton	ND	ND	**30**	**2,700**
DEET	Eaton/Snyder	ND	ND	ND	**150/190**
Diazepam	Eaton	ND	ND	**6**	ND
Diclofenac	Eaton/Snyder	ND	ND	**21/71**	**26/260**
Dilantin	Eaton	ND	ND	**56**	**51**
Diphenylhydramine	Snyder	ND	ND	**120**	**1,800**
Ditiazem	Snyder	ND	ND	**28**	**150**
Erythromycin	Eaton	ND	ND	**26**	**660**
Estradiol	Eaton	ND	ND	ND	**13**

**Table 2.4 Phase I CEC Analysis Results
Constituents of Emerging Concern Water Quality Evaluation
City of Sedona**

		Results in ng/L(2)			
Analyte	**Laboratory(1)**	**GW(3)**	**POC(4)**	**Effluent(5)**	**Influent(6)**
Estrone	Eaton	ND	ND	ND	**53**
Fluoxetine	Eaton/Snyder	ND	ND	**42/35**	ND/**77**
Gemfibrozil	Eaton/Snyder	ND	ND	**30/31**	**4,400/ 4,280**
Ibuprofen	Eaton/Snyder	ND	ND	ND/**6**	**12,000/ 27,800**
Iohexal	Eaton	ND	ND	**53**	**75**
Ketoprofen	Eaton	ND	ND	ND	**150**
Ketorolac	Eaton	ND	ND	ND	**33**
Lidocaine	Eaton	ND	ND	**190**	**250**
Lincomycin	Eaton	ND	ND	ND	**11**
Lopressor	Eaton	ND	ND	**490**	**970**
Meprobamate	Eaton/Snyder	ND	ND	**130/140**	**470/290**
Naproxen	Eaton/Snyder	ND	ND	ND/**10**	**7,700/ 35,000**
Nifedipine	Eaton	ND	ND	ND	**210**
N-Nitroso-dimethylamine (NDMA)	Eaton/Snyder	ND	ND	ND	ND/**2.5**
N-Nitrosopiperidine (NPIP)	Eaton/Snyder	ND	ND	ND	**7.2**
Pentoxifylline	Eaton	ND	ND	ND	**40**
PFBS	Snyder	ND	ND	**9**	ND
PFOA	Snyder	ND	ND	**38**	ND
PFOS	Snyder	**1**	ND	**2**	**7**
Prednisone	Snyder	ND	ND	**16**	**76**
Primidone	Eaton/Snyder	ND	ND	**110/120**	**95/120**
Propylparaben	Eaton/Snyder	ND/**76**	ND/**34**	ND/**200**	**590/1,020**
Sucralose	Eaton/Snyder	ND	ND/**31**	**43,000/ 20,900**	**38,000/ 20,700**

Table 2.4 Phase I CEC Analysis Results
Constituents of Emerging Concern Water Quality Evaluation
City of Sedona

Analyte	Laboratory(1)	Results in ng/L(2)			
		GW(3)	POC(4)	Effluent(5)	Influent(6)
Sulfamethoxazole	Eaton/Snyder	ND	ND/**4**	**350/600**	**1,100/ 2,000**
TCEP	Eaton/Snyder	ND	ND	**270/620**	**740/260**
TCPP	Eaton/Snyder	ND/**12**	ND/**11**	**470/2,320**	**220/520**
TDCPP	Eaton	ND	ND	**460**	**200**
Theobromine	Eaton	ND	ND	**640**	**140,000**
Theophylline	Eaton	ND	ND	**160**	**14,000**
Triclocarban	Snyder	**7**	**4**	**22**	**310**
Triclosan	Eaton/Snyder	ND	ND	ND	**160/1,750**
Trimethoprim	Eaton/Snyder	ND	ND	**100/130**	**350/520**
Warfarin	Eaton	ND	ND	ND	**7.4**

Notes:
(1) Samples were sent to two analytical laboratories, Eurofins-Eaton Laboratory (Eaton Lab) and the University of Arizona Snyder Laboratory (Snyder Lab).
(2) Results are shown as provided by the analytical laboratories. Detections are shown in bold font. ND indicates the analyte was not detected above the respective method reporting limit (MRL). MRLs for each analyte are shown in the full laboratory reports provided by each laboratory (see Appendix B).
(3) GW = groundwater sample from current potable water supply well, see Figure 2.1
(4) POC = sample from point-of-compliance well for reclaimed water, see Figure 2.1
(5) Effluent = sample of Class A+ reclaimed water effluent from the WWRP, see Figure 2.1
(6) Influent = sample of wastewater influent to WWRP, see Figure 2.1

The results from both laboratories vary for some of the compounds. A relative standard variation (defined as the ratio of standard deviation and average) of 20-30 percent for CEC results in inter-laboratory comparisons is to be anticipated and typically and can range up to 50 percent for certain compounds (Vanderford et al. 2012). Higher differences in reported concentrations may be a result of differences in standard preparations, analytical methods, or recovery efficiencies. In particular, in the lower concentration ranges close to the MRLs differences are noticeable between the data sets from both laboratories. The Eaton Lab uses slightly higher MRLs compared to the Snyder Lab. This resulted in the Snyder Lab reporting detections of a small number more compounds than the Eaton Lab in samples from both groundwater sources. In most cases, the difference is simply a difference in MRL, i.e., the Snyder Lab reports a concentration that is lower than the Eaton Lab's MRL. These differences do not indicate that the two data sets are inconsistent. Therefore, samples for

Phase II testing were sent only to the Eaton laboratory. This allowed for a more complete sampling plan (see Table 2.2) during Phase II.

5.2 Phase II Results

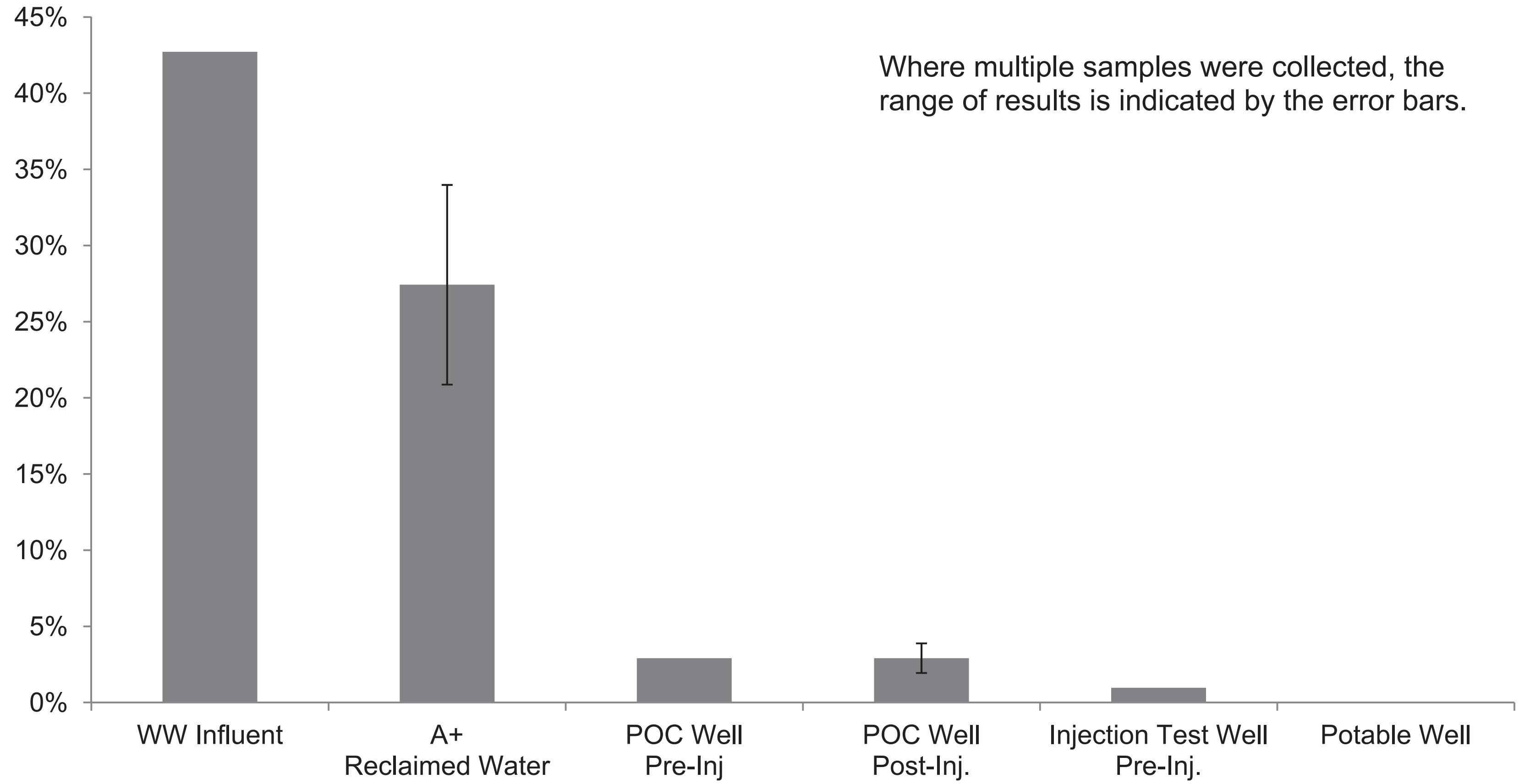
The full set of results reported by Eaton for Phases I and II are provided in Table C-1 (Appendix C). A summary of the results is also provided in Figures 2.2, 2.3, and 2.4. Figure 2.2 shows that an average of 43 percent of the compounds analyzed were detected in the wastewater influent, an average of 27 percent were detected in the A+ reclaimed water, approximately 3 percent were detected in the POC Well both before and after the injection test, and none were detected in background groundwater. A similar analysis of the concentrations illustrated in Figure 2.3 shows that the average concentration of detected compounds drops from 14,954 ng/L in the wastewater influent to 1,676 ng/L in the A+ reclaimed water, to 318 ng/L in the POC Well. This represents an 89% average reduction of CEC concentrations from raw wastewater to the A+ reclaimed water for those compounds that are detected in both. This measure underestimates the actual removal as the average concentration in the A+ reclaimed water does not include the compounds that were detected in the raw wastewater but not in the reclaimed water.

It is also interesting to evaluate the results without the artificial sweetener, sucralose, which is designed to not break down in biological systems, like the human body or, in this case, biological wastewater treatment. As a US Food and Drug Administration (FDA) approved food additive, sucralose is not considered to pose health concerns at levels encountered in this study. Figure 2.4 is identical to Figure 2.3, except that the averages shown do not include the concentrations of sucralose, which enters the WWRP at approximately 40,000 ng/L and is not degraded during treatment. With the omission of the sucralose data, the average raw wastewater concentration drops only slightly, to 14,418 ng/L, whereas the average concentration in the A+ reclaimed water drops to 182 ng/L, or a 99% removal of CECs, excluding sucralose, that are present in both samples.

5.3 Discussion

Of all 16 antibiotic drugs included in the sampling program, 11 compounds were not detected in any of the field samples. Five antibiotic drugs (Amoxicillin, Erythromycin, Lincomycin, Sulfamethoxazole, and Trimethoprim) were detected, but only in the wastewater influent and/or reclaimed water, not in any of the groundwater samples.

Of all five natural hormones included in the target compound list only Estradiol (E2) and Estrone (E1) were detected in the wastewater influent at concentrations of 13 ng/L and 53 ng/L, respectively. None was detected in the reclaimed water effluent or in the groundwater. Efficient removal of these hormones during wastewater treatment, particularly if this involves biological nitrogen removal, has been reported by others in the past (Andersen, 2003; Baronti, 2000, Joss, 2004).



PERCENTAGE OF COMPOUNDS FOUND ABOVE THE DETECTION LIMIT BY SAMPLE LOCATION

FIGURE 2.2

CITY OF SEDONA
CONTAMINANTS OF EMERGING CONCERN
WATER QUALITY EVALUATION

carollo

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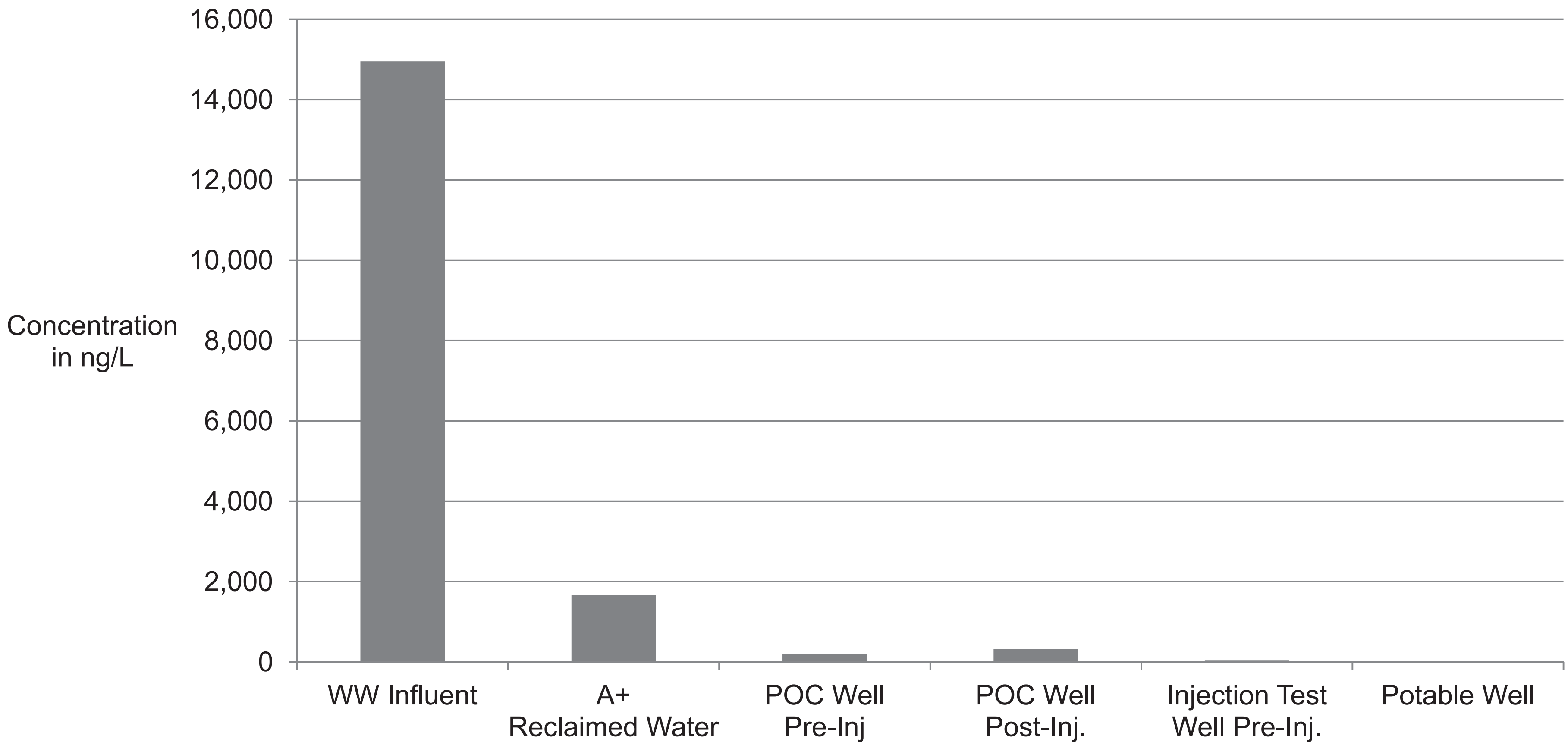
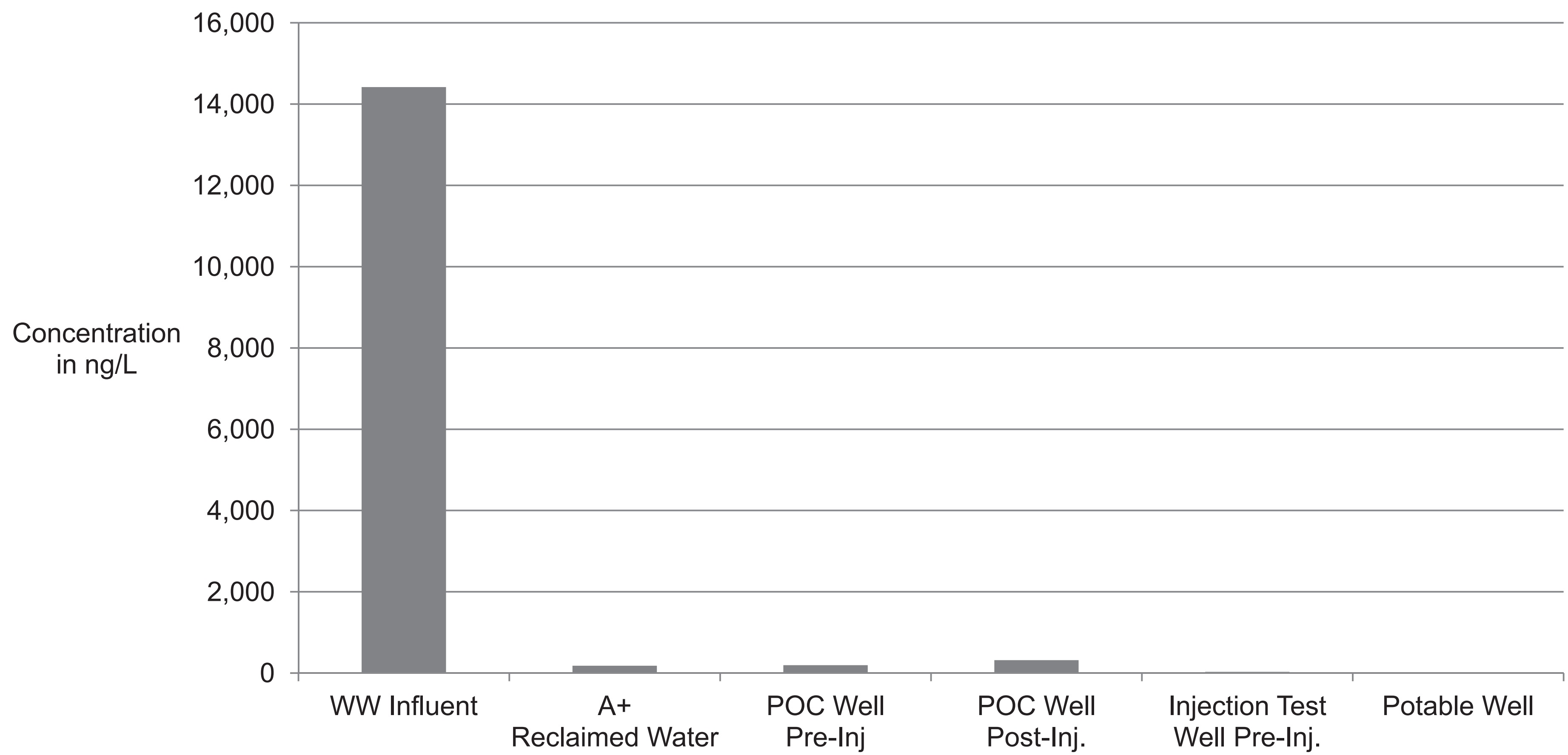


AVERAGE CONCENTRATION OF COMPOUNDS DETECTED BY SAMPLE LOCATION

FIGURE 2.3

CITY OF SEDONA
CONTAMINANTS OF EMERGING CONCERN
WATER QUALITY EVALUATION



AVERAGE CONCENTRATION OF COMPOUNDS DETECTED EXCLUDING SUCRALOSE

FIGURE 2.4

CITY OF SEDONA
CONTAMINANTS OF EMERGING CONCERN
WATER QUALITY EVALUATION

carollo

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The synthetic hormones Norethisterone and Norgestrel used in birth control pills were not detected in any of the samples.

A more detailed discussion on the CEC results in the wastewater, reclaimed water, and groundwater samples is provided in the following sections.

5.3.1 CECs in Wastewater Influent

The wastewater influent was sampled during Phase I. As expected based on numerous previous studies of CECs in wastewater, the sample of City's wastewater influent contained a number of CECs at detectable concentrations.

The compounds with the highest concentrations in the wastewater influent sample (greater than 10,000 ng/L or 10 µg/L) are familiar to the general public. These include:

1. Caffeine (and its metabolite 1,7-Dimethylxanthine),
2. The artificial sweeteners Acesulfame-K and Sucralose,
3. The over-the-counter pain medications Ibuprofen (Advil®), Naproxen (Aleve®), and Acetaminophen (Tylenol®); and
4. Two components of chocolate (Theobromine and Theophylline).

Detections of caffeine, sucralose and the three painkillers in concentrations in the µg/L range in domestic wastewater influents are typical and have been reported in other studies (Stephenson and Oppenheimer, 2007; Salveson et al. 2012).

As shown in Table 2.4, the wastewater influent sample also contained additional compounds at lower concentrations, including prescription pharmaceuticals and antibiotics, synthetic and natural hormones, detergent metabolites, flame retardant chemicals, and components of sunscreen.

Each laboratory reported a low-level detection of one nitrosamine (NDMA and Npip by the Snyder and Eaton Labs respectively) in the wastewater influent sample.

5.3.2 CECs in Wastewater Effluent (Class A+ Reclaimed Water)

Both laboratories reported the presence of several CECs in the wastewater effluent sample, though generally at significantly lower concentrations than in the wastewater influent. Of the compounds with the highest influent concentrations, as listed above, significant reduction was achieved through the treatment process, as described below:

1. Caffeine and 1,7-Dimethylxanthine are each reduced by an average of 99 percent or more;
2. Acesulfame-K is reduced by over 99 percent;
3. Ibuprofen, naproxen, and acetaminophen are not detected in any reclaimed water samples, indicating a removal of at least 99.9 percent; and

4. Theobromine (detected in reclaimed water only once) and theofylline detected in reclaimed water twice) are reduced by over 99.5 percent and 98.5 percent, respectively.

The one significant exception to this trend is the artificial sweetener sucralose. Both phases of testing and samples analyzed by both laboratories indicate no significant change in concentrations between influent and effluent. Sucralose has been shown to be generally persistent during domestic wastewater treatment (Anderson et al. 2012) as this compound is, by design, an indigestible form of sugar and thus resistant to transformation both in the human body and during wastewater treatment. Acesulfame-K, which should be similarly recalcitrant to biodegradation, has been shown to be degradable by UV irradiation, whereas sucralose is not (Soh et al., 2011). The bulk of the Acesulfame-K transformation is therefore likely achieved through the recently expanded UV process step implemented at WWRP.

As shown in Table 2.4 and Table C-1, concentrations of the other CECs present at lower concentrations in the wastewater influent generally decreased as well, though the percent reductions were lower. The concentrations of the following compounds were highest (>500 ng/L) in the samples from the wastewater effluent:

1. Sucralose at an average of over 40,000 ng/L;
2. Total organophosphorus-based flame retardants (TCEP, TCPP, and TDCPP) at an average of 840 ng/L[1];
3. Benzotriazole at 1,530 ng/L[2];
4. Amoxicillin (a commonly prescribed antibiotic), measured at 1,200 ng/L during Phase I but at much lower concentrations (63 ng/L or less) during Phase II; and
5. Theobromine, measured at 640 ng/L during Phase I testing but not detected in Phase II testing.

Based on a comparison of influent concentrations to effluent concentrations, the treatment process at WWRP appears to be effective at reducing the concentrations of many of the compounds, especially those that are present in the influent at higher concentrations. Sucralose, benzotriazole, and amoxicillin are the only compounds detected in the wastewater effluent at more than one part per billion (1 μg/L) concentration.

Nitrosamines were detected in only one (January 2014) of the four reclaimed water sampling events, NDMA (6.1 ng/L) and NDPA (3.9 ng/L). The concentration of NDMA is below the threshold (10 ng/L) defined by NWRI.

[1] The total organophosporus-based flame retardant concentration omits the concentrations reported by the Snyder Lab, because the concentration of TCPP reported in the effluent is almost 5 times the reported influent concentration.

[2] Benzotriazole was analyzed only by the Snyder Lab. The reclaimed water concentration of reported by the Snyder Lab is over 50% higher than in the influent concentration.

A single detection of the herbicide diuron at 46 ng/L in the January 2014 sample of the A+ reclaimed water was well below its EPA Health Advisory level of 200 ng/L.

5.4 Native (Upgradient) Groundwater Sample Results

During Phase I, two samples were collected from the drinking water well upgradient of the current effluent management areas. No CECs were detected in the sample analyzed by the Eaton Lab. In the sample analyzed by the Snyder Lab detections were found (caffeine at 2 ng/L, PFOS at 1 ng/L, TCPP at 12 ng/L, triclocarban at 7 ng/L, in addition to benzophenone and propylparaben, which may have been sampling artifacts and are discussed further in Section 5.7). This difference between the labs is most likely attributable to the lower reporting limits provided by the Snyder Lab and does not necessarily represent a discrepancy in the data. While extremely low and not of concern for human health, these concentrations do imply the potential influence of wastewater of different origin in the upgradient groundwater. It is possible that the presence of these compounds in the native groundwater is at least partially attributable to upgradient septic systems.

5.5 Down-Gradient Groundwater Sample Results

During this study, samples were collected from two locations that may be potentially influenced by the existing reclaimed water management practices: The Point of Compliance (POC) Well, which is located at the southernmost (downgradient) boundary of the WWRP property, and the injection test well, which is located downgradient of the northern portions of the reclaimed water management areas.

5.5.1 POC Well

Both laboratories confirmed the presence of artificial sweeteners in the POC Well at very low concentrations that remained generally consistent throughout Phase I and Phase II testing (170/180 ng/L Acesulfame-K reported by the Eaton Lab, and 31 ng/L sucralose reported by the Snyder Lab). The sucralose concentration reported by the Snyder Lab is below the MRL reported by the Eaton Lab. No artificial sweeteners were detected in the upgradient potable water supply well.

Low-level concentrations of sulfamethoxazole (an antibiotic), caffeine, TCPP (a flame retardant chemical used in many types of fabrics), and triclocarban (an antimicrobial agent used in hand soap), were reported for the samples collected from the POC Well. Of those compounds, TCPP and triclocarban were also detected at similar concentrations in the sample collected from the potable water supply well, indicating that the detections of these compounds in the POC Well are not necessarily attributable to wastewater influence from the WWRP.

Bisphenol A, or BPA (a breakdown product of polycarbonate plastic containers) was detected in the samples from the POC Well sent to both laboratories at concentrations equivalent or higher than those detected in the wastewater influent. This detection was confirmed in two additional samples analyzed from the POC Well during Phase II testing. However, while present in the raw wastewater sample, BPA was not detected in the reclaimed water in any of the five samples analyzed. The interpretation of BPA detections in the samples from the POC Well is therefore not straightforward, though it is unlikely that the detections are the result of wastewater influence in the POC Well. It is possible that BPA detections were a result of polycarbonate components of sampling equipment installed in the well.

In summary, under the current level of wastewater influence, the detection of CECs in the POC Well is rare. Only four of 55 compounds detected in the wastewater influent were confirmed to be present in the POC Well by both laboratories. The concentrations of these compounds are generally in the lower ng/L range. This would seem to indicate that the current practice of reclaimed water spray irrigation in the effluent management area has not impaired the local groundwater quality relative to the CECs investigated in this study.

5.5.2 Injection Well

During Phase II, a single sample was collected from the injection test well prior to the start of the injection test, which resulted in the detection of only one compound: Acesulfame-K reported at 31 ng/L. This may indicate some level of influence from the existing wastewater management areas. Given that the groundwater near this well was influenced by only a portion of those wastewater management areas, it is reasonable to expect even lower concentrations than those found in the POC Well.

5.6 Current Research and CEC Guidance Levels

As stated above, most of the compounds discussed in this evaluation are not regulated at the Federal or State level. That said, significant scientific research has been conducted with respect to the potential environmental and human health risks associated with many of the compounds analyzed. While no binding treatment requirements for CECs currently exist in the U.S. for wastewater treatment facilities, several states have established non-binding guidance values and/or monitoring requirements for reclaimed water used for potable reuse for several of the compounds included in this study. The majority of the research has focused on direct potable reuse applications (i.e., no additional treatment prior to human consumption).

A recent WateReuse Research Foundation study[3] concluded, based on a combination of existing guidance values and scientific research that save for a few specific exceptions, treatment processes that could reduce individual CECs concentrations to below 1 µg/L (1,000 ng/L) in reclaimed water would be sufficient for use in *direct potable reuse* applications (Trussell et al., 2013). The concentration thresholds developed by this study were confirmed by a panel of national experts in water reuse, toxicology, and human health

[3] WateReuse Research Foundation Project No. 11-02, *Equivalency of Advanced Treatment Trains for Direct Potable Reuse*.

risk assessment convened by the National Water Research Institute (NWRI) in the context of the project.

The three classes of compounds that were found by the panel to require lower concentrations to ensure the safety of public health for direct potable reuse of reclaimed water included nitrosamines, perfluorochemicals (PFCs), and steroid hormones. Analytes representing one or more compounds in each of these groups were included in the analyses conducted for this evaluation, and none of the concentrations of these compounds in the wastewater effluent sample exceeded the threshold values listed by the NWRI panel. For these compound groups, Table 2.5 lists the recommended threshold values confirmed by the NWRI panel and the results reported for the wastewater effluent. Of those compounds, only PFOS and NDMA were detected, once each, at concentrations above their respective reporting limits. PFOS was detected at a concentration 100 times less than the NWRI threshold value. NDMA was detected at 6.1 ng/L, which is also below its NWRI threshold, and only slightly above the method reporting limit of 2 ng/L (Eaton Lab). It was also only detected in one out of five total samples collected from the reclaimed water.

The NWRI panel also specifically listed sucralose, stating that it can be used as a conservative tracer for wastewater influence as it is resistant to removal by a variety of processes. The report also notes that sucralose is approved for use as a food additive and lists a recommended threshold of approximately 150 mg/L, or 150 *million* ng/L. Benzotriazole and amoxicillin are not specifically addressed by the panel, but concentration thresholds listed by the panel for pharmaceuticals generally range from 1 µg/L to 200 µg/L.

Table 2.5 CECs with NWRI Panel Thresholds of Less than 1 µg/L
Constituents of Emerging Concern Water Quality Evaluation
City of Sedona

CEC Compound	NWRI Threshold Value	WWRF A+ Reclaimed Water
NDMA (nitrosamine)	10 ng/L	6.1 ng/L
PFOA (PFC)	400 ng/L	<11 ng/L[1]
PFOS (PFC)	200 ng/L	2 ng/L
Ethinyl Estradiol (hormone)	None, but if established, it will approach detection limit (low ng/L)	<5 ng/L[2]
Estradiol (hormone)		<5 ng/L[3]

Notes:
(1) MDL of 11 ng/L as reported by Snyder Lab.
(2) MDL of 5 ng/L as reported by Eaton Lab.
(3) MDL of 5 ng/L as reported by Eaton Lab.

It bears repeating that the NWRI panel's recommendations are based on a *direct potable reuse* scenario, which means that they assume no further treatment of the reclaimed water occurs before it is considered safe to drink. That is not the case here, as the reclaimed water is proposed for aquifer storage, which would allow for additional attenuation of these compounds during subsurface travel. Therefore, the recommendations provided by the NWRI panel should be seen as a very conservative benchmark for the current evaluation.

5.7 Data Quality Assurance / Quality Control (QA/QC) Analysis

Field and laboratory blanks were collected to provide an effective QA/QC program for the sampling campaign. As a result of this additional analysis, one data quality issue was identified with the analytical data in Phase I. The Snyder Lab reported detections of benzophenone (a UV blocker) at and propylparaben (commonly used in lotions) at 34 ng/L and 76 ng/L in the POC and drinking water well samples, respectively. Reported MRLs for these compounds are 3 ng/L and 2 ng/L, respectively, which would indicate that those compounds were clearly present in the samples analyzed. However, the field blank analyzed by the Snyder Lab was reported as having similar concentrations of these compounds, which are both commonly used in sunscreen. The field blank results indicate likely sample contamination with these two compounds, and therefore the results reported for these two compounds should not be interpreted as reliable.

Propylparaben was not detected in the samples analyzed by the Eaton Lab (MRL of 5 ng/L) which corroborates the conclusions above and indicates that this compound is likely not present in either well; benzophenone is not on the list of compounds analyzed by the Eaton Lab.

No data quality issues were identified in the Eaton data set, though no field blank samples were provided or analyzed by this laboratory during Phase I testing. However, for analytes common to both laboratories, the Eaton Lab did not detect the presence of any samples that were not confirmed by the Snyder Lab.

Phase II testing, which was conducted exclusively by the Eaton Lab, included field blanks and no additional QA/QC issues were identified.

6.0 CONCLUSIONS

The City of Sedona is in the process of conducting an injection well test with Class A+ reclaimed water, the highest reclaimed water quality classification regulated by ADEQ. The City has conducted an investigation of levels of contaminants of emerging concern (CECs) in the influent wastewater, reclaimed water, and groundwater surrounding the WWRP to better characterize the reclaimed water proposed for aquifer injection and to identify any CECs that may present a potential health concern, based on current research.

The sample results indicate that many CECs are present in the raw wastewater flowing into the WWRP. This is consistent with findings at many other wastewater treatment plants and reflects the use of pharmaceuticals and personal care products by the population in the WWRP service area. The analytical results for the sample collected from the wastewater effluent (i.e., the Class A+ reclaimed water used in the injection test) indicates that significant attenuation of CECs occurs during the treatment processes used at the WWRP, especially for compounds present in high concentrations in the raw wastewater.

While no binding treatment requirements for CECs currently exist in the US for wastewater treatment facilities, recent studies (NWRI, 2013, Trussell, 2013) have provided treatment goals for deriving potable water directly from reclaimed water (direct potable reuse, or DPR). The results of the CEC water quality investigation were compared to these threshold concentrations, which should be seen as a very conservative benchmark for the current evaluation, since additional attenuation is likely to occur in the subsurface. Based on this comparison and the current state of knowledge, no significant health risks associated with the CECs concentrations measured in the A+ reclaimed water sample have been identified.

Detections of CECs in the samples collected from the potable water supply well reflect some potential low-level anthropogenic influence on the aquifer upgradient of influence from the WWRP. For the sample collected from the POC Well, the same compounds plus a few additional CECs at low ng/L (parts per trillion) levels and two artificial sweeteners at slightly higher levels were detected. This indicates a limited influence of reclaimed water irrigation practices in the POC Well. Concentrations in the POC Well did not significantly rise as a result of the injection well test. Due to the fractured nature of the bedrock aquifer, it is difficult to accurately estimate the time required for the injected water to travel to the POC well. This analysis was beyond the scope of this project.

Of all compounds included in this analytical study, the sweeteners Acesulfame-K and Sucralose are recommended as indicators for assessing the influence of reclaimed water in the groundwater aquifer in the future. Neither compound was detected in the native groundwater, both are present in the A+ reclaimed water, and they are unlikely to degrade significantly in the subsurface.

7.0 REFERENCES

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