

**Abstract:**

It is now widely appreciated that trace organic compounds can affect the finished quality of water that is served to the public for potable use. Chemical fate during infiltration and underground transport to points of recovery is therefore relevant to the quality of delivered water. As reclaimed water begins to play a more important role in our regional water resource portfolio, interventions including natural processes during infiltration and underground transport will assume additional importance.

Here we will attempt to (i) measure the levels of a specific trace contaminant, PFOS, in several locations along the Santa Cruz River that serve as drinking water sources for major metropolitan areas (including Tucson), and (ii) measure the degree to which infiltration and underground storage/transport processes contribute to overall attenuation of this compound.

**Keywords:** infiltration, trace contaminants, attenuation

**Introduction:**

This project was motivated by recent (2009) recognition that the trace organic contaminant perfluorooctane sulfonate (PFOS) is present in potable Arizona groundwater sources. PFOS was detected by the Tucson Water Department in their Microconstituent Sentinel Program in 2009 in all four groundwater production wells tested, at concentrations ranging from 3.9 to 65 ng/L. PFOS was also reported at a concentration of 0.21 ng/L in the “finished” water produced by the Clearwater Recharge and Recovery Facility (CRRF). The CRRF recharges Central Arizona Project (CAP) water, which is a mixture of water from the Colorado and Agua Fria Rivers, via infiltration basins at the Central Avra Valley Storage and Recovery Project (CAVSARP). Recharged water is subsequently extracted and served to the public. There is an Environmental Protection Agency (EPA) health-based advisory guideline of 200 ng/L for PFOS. PFOS was added to the Safe Drinking Water Act Contaminant Candidate List 3 (CCL3) in 2009. The CCL3 represents a chemical “watch list” consisting of chemicals that have been marked for potential regulation via promulgation of maximum contaminant limits.

Wastewater effluent is a major source of many such compounds in United States surface waters. Municipal water budgets are stressed in many parts of the country due to continuous growth in water demand and limited renewable water supply options. Increasingly, reclaimed water is considered for inclusion in regional water resource portfolios—particularly in the semiarid Southwest. Consequently, there is great interest in factors affecting the efficiency of trace organic destruction during municipal wastewater treatment and the fate of compounds that are released to the environment as effluent.

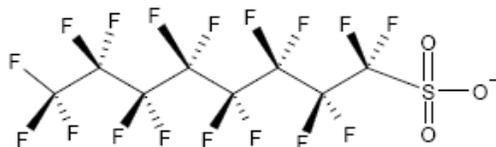
**Compound chosen for study:**

Perfluorooctane sulfonate (PFOS) and related chemicals known as PFAS (perfluorinated alkyl surfactants) are fully fluorinated surfactants in which all hydrogens have been replaced by fluorine atoms. The unique structure of these chemicals allows them to be both hydrophobic and oleophobic (oil-repellent) (Kissa, 2001). Due to these properties, PFOS and related compounds have been widely used in consumer products. PFAS compounds are of particular interest due to their tendency to bioaccumulate in higher organisms, persistence in the environment and toxicity. Use of these compounds has been restricted due to these concerns in recent years, but specific exceptions have been made. As a result of past and continuing usage, PFAS and its primary degradation product, PFOS, are ubiquitous in the environment. At this time, sources and pathways of PFOS in the environment are not well understood.

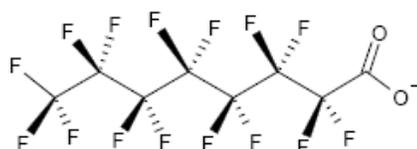
**Properties of PFOS:**

Perfluorinated alkyl surfactants (PFAS) are fully fluorinated compounds in which all hydrogen atoms have been replaced by fluorines. They have a molecular formula of  $\text{CF}_3(\text{CF}_2)_n\text{X}$ , where  $n$  varies from 3 to 11 and  $X$  is a substituent such as a hydroxyl or carboxylic acid group. (Kissa, 2001). These chemicals are unique in that they exhibit both hydrophobic and oleophobic properties, making them ideal for use in many consumer applications. In particular, the non-polar tail of the molecule reduces surface tension, improving wetting properties and stability beyond that of hydrocarbon chains (3M, 1999). The carbon-fluorine bond is unusually strong (485kJ/mol) in these compounds, and this coupled with the effective shielding of carbon by the fluorine atom and rigidity of the perfluorinated chain makes fluorinated surfactants inert to acids, bases, oxidizing and reducing agents, and microbial attack (Schultz et al, 2003).

A)



B)



**Figure 1:** Chemical structures of selected PFAS. A) Perfluorooctane sulfonate (PFOS), formula:  $C_8F_{17}SO_3^-$ , B) Perfluorooctanoic acid (PFOA), formula:  $C_7F_{15}COOH$

Property	Value
CAS #	275-39-3 <sup>1</sup>
Molecular Weight	538.22 g/mol <sup>1</sup>
Solubility	570 mg/L (pure water) <sup>1</sup>
Vapor Pressure	$3.31 \times 10^{-4}$ Pa at 20 °C <sup>1</sup>
Henry's Law constant	$3.19 \times 10^{-4}$ Pa m <sup>3</sup> /mol <sup>1</sup>
Log Kow	-1.08 (est.) <sup>2</sup>
pKa	-3.27 <sup>1</sup>
1-Kissa, 2001	
2-Hites, 2006	

### Synthesis:

PFOS and its analogues were used for more than 50 years in a myriad of consumer products. Examples of consumer goods containing PFOS include such trademarks as Scotchguard and Teflon. Perfluorinated compounds are synthesized by two methods; electrochemical fluoroination (ECF) and telomerization. Production of compounds by electrochemical fluoroination is largely inefficient, yielding a variety of linear and branched isomers (Lehmler, 2005). In ECF, current is passed through an organic precursor which is dissolved in anhydrous hydrogen fluoride (Lehmler, 2005). The process produces sulfonyl and carbonyl halides and changes all the C-H bonds to C-F bonds. The resultant chemicals are used as production intermediates for perfluorinated surfactants via hydrolysis. Telomerization, which is the preferred method of industrial production, is much more efficient, producing mixtures of linear and even-number carbon telomers which can be further purified by distillation (Lehmler, 2005). In this process, iodine pentafluoride and iodine are reacted with tetrafluoroethylene to produce a mixture of perfluoroalkyl iodides, which can then be further reacted to obtain perfluorinated surfactants.

### **Sources of PFOS:**

There are numerous sources of PFOS in the environment. In addition to its direct presence in Teflon, Scotchguard, Gore-Tex, fire fighting foams, paper applications, food containers, photographic and semiconductor applications, there are several precursor products which degrade to produce PFOS (EM, 1999). Volatile sulfonamide PFOS precursors include *N*-methyl perfluorooctane sulfonamidoethanol (*N*-MeFOSE), a carpet stain repellent, and *N*-ethyl perfluorooctane sulfonamidoethanol (*N*-EtFOSE), a paper treatment (Renner, 2004). Perfluorooctanesulfonamide is also a precursor (Lehmle, 2005). About 50 precursors were named in the 2004 proposed Canadian ban on PFOS (Pelley, 2004).

PFOS and related chemical contamination is ubiquitous in water and wastewater. In a 2008 study, levels of perfluorinated chemicals detected were 90-470 ng/L in recycled water, 2-47ng/L in surface waters, 19-192ng/L in groundwater, and 3-4300ng/L in wastewaters across the US (Plumlee et al., 2008).

### **Production and Regulation:**

In the United States, 3M is the single manufacturer of PFOS and related compounds. In response to regulatory pressure, 3M eliminated production of PFOS in 2003. Prior to the phasing out of PFOS from production lines, 6.5 million pounds of PFOS-containing products were produced in 2000 (EPA, 2000). Currently, uses of PFOS and related compounds are limited to specific applications where the chemical cannot be replaced by another compound (RPA-BRE, 2004). Needed chemicals are imported from sources in Asia or Europe. Applications exempt from the PFOS ban included aviation hydraulic fluid, photo-resistive solvent, anti-reflective films, surface tension coatings, and static discharge and adhesive films for photography (EPA, 2000).

### **Potential Human Health Effects:**

Concern about the bioaccumulative character and persistence in the environment of PFOS was first raised in 1976, when an organochlorine compound found in human blood serum was suggested to be PFOS. In 1997, 3M detected PFOS in blood from global blood banks (Environmental Working Group, 2009). PFOS was also recently linked to low birth weight in babies exposed pre-natally. The reduction was -69g for PFOS and -104g for PFOA (Betts, 2007). There is also a statistically significant association between PFOS exposure and bladder cancer and there appears to be an increased risk of episodes for neoplasms of the male reproductive system, the overall category of cancers and benign growths, and neoplasms of the gastrointestinal tract (OECD, 2002).

In 2002, following the removal of PFOS from US production, the EPA issued a proposed Toxic Substances Control Act and Significant New User Rule prohibiting the use of 90 perfluorooctyl sulfonate compounds in commercial and industrial applications (EPA, 2000). In addition, in 2006, companies were asked to reduce emissions of PFOA by 95% by 2010 and completely eliminate usage by 2015.

### **PFOS in the Environment:**

PFOS has raised public concern due to its tendency to bioaccumulate in higher organisms, environmental persistence and toxicity (Schultz et al., 2003). Additionally, bioaccumulative potential of PFAS decreases with decreasing chain length (Conder et al., 2008). Therefore, the most common degradation product, PFOS, also has the longest chain (C8) and the most potential for bioaccumulation. Martin et al. reported a bioconcentration factor of 3100 in rainbow trout in 2003.

PFOS and related chemicals have been detected in human samples, wildlife biota, and environment matrices worldwide (Preveduoros et al., 2006). In a 2001 study of global distribution of PFOS found the chemical to be present in all biota samples, including fish, birds, amphibians and marine mammals from remote areas (Giesy et al., 2001). PFOS was found to be the dominant organohalogen contaminant in the liver of Canadian Arctic animals in 2004 (Martin et al., 2004). Presence of PFOS in remote areas is attributable to atmospheric and ocean transport of their volatile precursors (Preveduoros et al., 2006).

PFOS is not known to hydrolyze, photolyze, or biodegrade under environmental conditions, making it extremely persistent (Beach et al., 2006). Studies conducted by 3M demonstrated no hydrolytic or photolytic degradation at temperatures of 25 and 50°C, and pH range from 1.1 to 11 (Beach et al. 2006).

Due to its unique nature, PFOS binds to proteins rather than fatty tissues (Keml, 2006). Animal toxicity testing shows acute toxicity to aquatic vertebrates, invertebrates and mammals characterized by significant weight loss, hepatotoxicity, and reduction of serum cholesterol and thyroid hormones (IPEN, 2005). During mammalian oral and inhalation exposure, researchers have demonstrated that PFOS distributes to blood serum and can cross the blood-brain barrier (Plumlee et al., 2008). Furthermore, when present in a mixture, PFOS may enhance the toxicity of other compounds by increasing cell permeability (Plumlee et al., 2008). Adverse effects of related

compound exposure (PFOA) have been observed in rats at levels of 370µg/L, which differs from levels in humans by a safety factor of less than 100 (Plumlee et al., 2008).

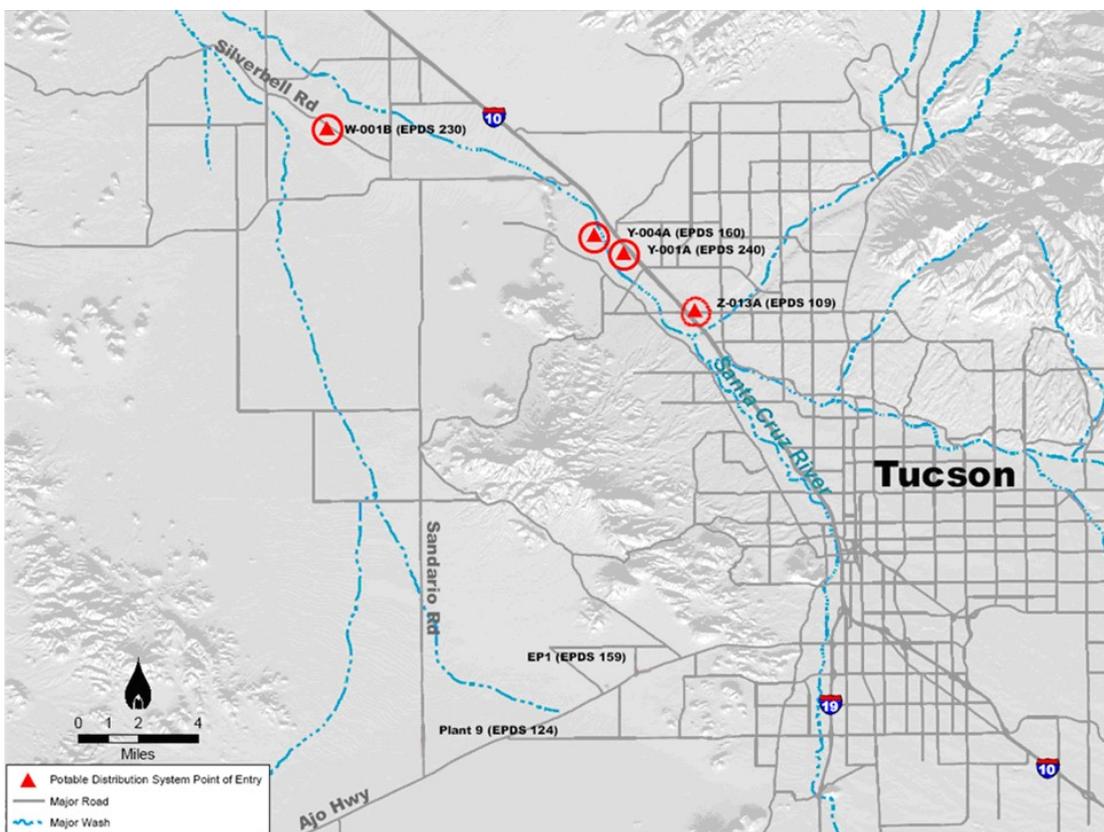
**Methods:**

*Sampling Plan.* The sampling plan was structured to support hypothesis testing as follows.

*Hypothesis #1: Municipal wastewater effluent is a significant source of PFOS in ground water in the Tucson Basin*

To understand the contribution of effluent to groundwater concentrations of PFOS, grab and 24-hr composite samples of secondary effluent from the Roger Road Wastewater Treatment Plant (#1, #2 in Table 1) and secondary effluent from the Ina Road Water Pollution Control Facility (#3, #4 in Table 1) were measured for PFOS.

Four groundwater production wells (City of Tucson service area) located near the Santa Cruz River at distances of 0, 2.6, 3.3, and 13.3 miles downriver (below) from the effluent outfall of the Ina Road Water Pollution Control Facility (Figure 2) were sampled (#5- #8 in Table 1).



**Figure 2.** Map showing groundwater well sampling locations (circled triangles) along the Santa Cruz River northwest of the City of Tucson, Arizona.

*Hypothesis #2: PFOS is not attenuated during percolation of municipal wastewater effluent/CAP water in unsaturated basin fill sediments.*

Raw CAP water (#9 in Table 1) and monitoring wells at depths of 400 and 1000 feet below land surface (#10, #11 in Table 1) were sampled at the CAVSARP facility to test Hypothesis #2 related to attenuation of PFOS during percolation of CAP water. Finished production drinking water produced by the Hayden-Udall Water Treatment Plant (#12 in Table 1) was also sampled.

Secondary effluent (#13 in Table 1) collected at Recharge Basin No. 1 and monitoring wells at depths of 15 and

130 ft below land surface (#14, #15 in Table 1) were sampled at the Sweetwater Recharge Facilities to assess if PFOS is attenuated during percolation of municipal wastewater effluent in unsaturated sediments. Duplicate 1-L samples were collected and the sampling was staggered over a two-week period according to known hydrology of the basin to follow the same “packet” of water during percolation.

In total, there were 15 sampling locations for PFOS determination (Table 1). Laboratory and field blanks were used, and samples were analyzed in triplicate. Extraction/analysis of samples was performed at the Arizona Laboratory for Emerging Contaminants (ALEC) using methods described below.

**Table 1.** Sampling locations for PFOS determinations.

Sample	Location description (details)	Abbrev.	Type	Hypoth.
1	Roger Road secondary effluent (grab)	RR-grab	WWTP	1
2	Roger Road secondary effluent (composite)	RR-comp.	WWTP	1
3	Ina Road secondary effluent (grab)	IR-grab	WWTP	1
4	Ina Road secondary effluent (composite)	IR-comp.	WWTP	1
5	production well (Z013)	Well-Z013	GW	1
6	production well (Y001A, 2.6 mi below Ina WWTP)	Well-Y001A	GW	1
7	production well (Y004A, 3.3 mi below Ina WWTP)	Well-Y004A	GW	1
8	production well (W001B, 13.3 mi below Ina WWTP)	Well-W001B	GW	1
9	CAP water (before infiltration)	CAP-raw	SW	2
10	CAVSARP monitoring well (400' bls)	CAP-400'	GW	2
11	CAVSARP monitoring well (1000'bls)	CAP-1000'	GW	2
12	Hayden Udall polished water (production water)	H-U DW	DW	2
13	Sweetwater Recharge Facility (SRF pond)	SRF pond	WWTP	2
14	Sweetwater Recharge Facility (SRF 15' bls)	SRF 15bls	GW	2
15	Sweetwater Recharge Facility (SRF 130' bls)	SRF 130bls	GW	2

WWTP = wastewater treatment plant, DW = drinking water,  
GW = groundwater, SW = surface water

## **Analytical Methods**

### 1. Collection

Sweetwater Recharge Basin. Samples were collected from Sweetwater Recharge Facility Basin RB-1 from three different depths. Collection took place during two weeks in February 2011. Duplicate 1-L samples were collected discretely. Samples were collected from piezometers at increasing depths following recharge. During collection no additional water was added to the basin, and sampling events were staggered according to known hydrology of the basin in an attempt to follow the same “packet” of water. <sup>13</sup>C<sub>6</sub>-PFOS internal standard was added after SPE extraction and prior to UPLC-MSMS analysis.

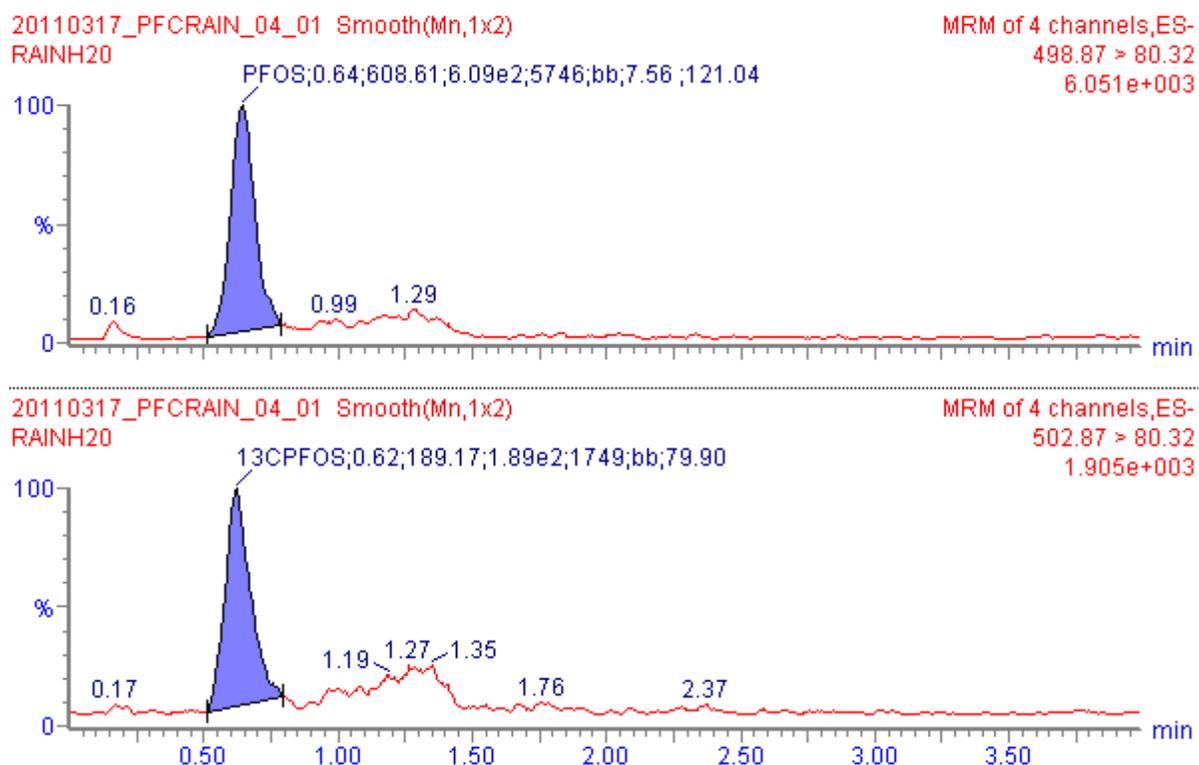
Groundwater Production Wells, CAP, and WWTP Samples. Water samples were collected in duplicate from CAVSARP and from wells in Tucson, AZ on Dec 6, 2010 and from the two major wastewater treatment plants (Ina Rd. and Roger Rd., managed by the Pima County Regional Wastewater Reclamation Department) on Jan 4 and 11, 2011, respectively. WWTP samples were collected as both 24 hour composite and discrete (grab). Samples were delivered on ice to the laboratory the same day. No internal standard was used for PFOS quantification in these samples.

2. Filtration. Water samples were collected in muffled (550°C) 1-L amber glass bottles and held at 4° C. All samples were filtered immediately upon return to the laboratory. Vacuum filtration was performed using 0.7um glass fiber filters (PALL, VWR, cat. # 28149-456). Filters were muffled at 200°C for 3 hrs prior to use and a minimal amount of filters per sample was used. Sample volumes were recorded.

3. Extraction. Filtered samples were extracted within 24 hours of collection by solid phase extraction (SPE). An automated solid phase extraction instrument (Caliper Life Sciences Autotrace) was used with a hydrophilic-

lipophilic balance sorbent (Oasis HLB, 6 mL, 150 mg Waters Corp, cat. # 186003365) to concentrate the target analyte and remove unwanted sample components (concentration factor = 1000x). Sorbent was conditioned with 5 mL of MeOH, 5 ml of MTBE and 5 ml of ultrapure water prior to use. EDTA (0.5g) was added to each 1-L water sample and allowed to dissolve completely prior to loading onto the SPE sorbent at a rate of 10 mL/min. Sorbent was then dried with N<sub>2</sub> for 40 min, followed by an elution sequence using 3 mL of MeOH, 3 mL of 0.5% NH<sub>4</sub>OH in MeOH, 3 mL of acetonitrile, and 3 mL of MTBE. Eluates were evaporated to 50 µL and resuspended to 1.0 ml in 0.5 mL 50% aqueous methanol for UPLC-MSMS injection. An isotopologue (<sup>13</sup>C<sub>6</sub>-PFOS) was added to the 1 mL extracts as an internal standard prior to UPLC-MSMS analysis.

**4. Liquid Chromatography - Tandem Mass Spectrometry.** Liquid chromatography was performed using 5-µL sample injections on a Waters Acquity UPLC system with an Acquity UPLC BEH C18 column (1.7 µm, 2.1 x 50 mm) and a gradient mobile phase of water and acetonitrile for 15 min (with ammonium acetate buffer) at 0.4 mL min<sup>-1</sup>. PFOS detection was accomplished by negative mode electrospray ionization tandem mass spectrometry. Electrospray ionization and mass spectrometer multiple reaction monitoring detection parameters were optimized as follows: SRF samples - cone voltage 68 V, capillary voltage 2.95 kV, drying gas 654 L/hr, collision energy 50 V, and collision gas pressure 0.00982 mbar; Well, CAP, and WWTP Samples - cone voltage 49 V, capillary voltage 2.90 kV, drying gas 650 L/hr, collision energy 42 V, and collision gas pressure 0.010 mbar. A multiple reaction monitoring method was used for detection of PFOS at the following transitions: 499.10 > 79.97 for Well, CAP, and WWTP samples, and 498.87 > 80.32 for SRF samples. <sup>13</sup>C<sub>6</sub>-PFOS detection was accomplished using a 502.87 > 80.32 transition. Examples of typical PFOS and <sup>13</sup>C<sub>6</sub>-PFOS chromatograms are provided in Figure 3.



**Figure 3 .** PFOS chromatograms obtained by UPLC-MSMS. Upper chromatogram shows the integrated PFOS peak in an example sample extract. Lower chromatogram shows the integrated peak for <sup>13</sup>C<sub>6</sub> labeled-PFOS (internal standard) added to each sample and used to correct PFOS quantification for matrix suppression in UPLC-MSMS.

**Quality Control.** A calibration curve consisting of at least 7 points was developed for PFOS. All water sample extracts were injected in triplicate. In the case of SRF samples, the PFOS analyte response was calculated with respect to the corresponding internal standard isotopologue. In the case of Well, CAP, and WWTP samples, duplicate sample collections were made and analyzed. For SRF samples the method limit of quantitation

(MLOQ) was 0.5 ng/L, and the MLOD was 0.1 ng/L. For Well, CAP, and WWTP samples the method limit of quantitation (MLOQ) and the MLOD were both 0.48 ng/L based on sufficient signal-to-noise (9:1 and 3:1, respectively) observed for the peak detected at the lowest concentration calibration standard used. Field blank samples collected during well sampling ranged in concentration from 6.6 to 13.8 ng/L (ppt) PFOS.

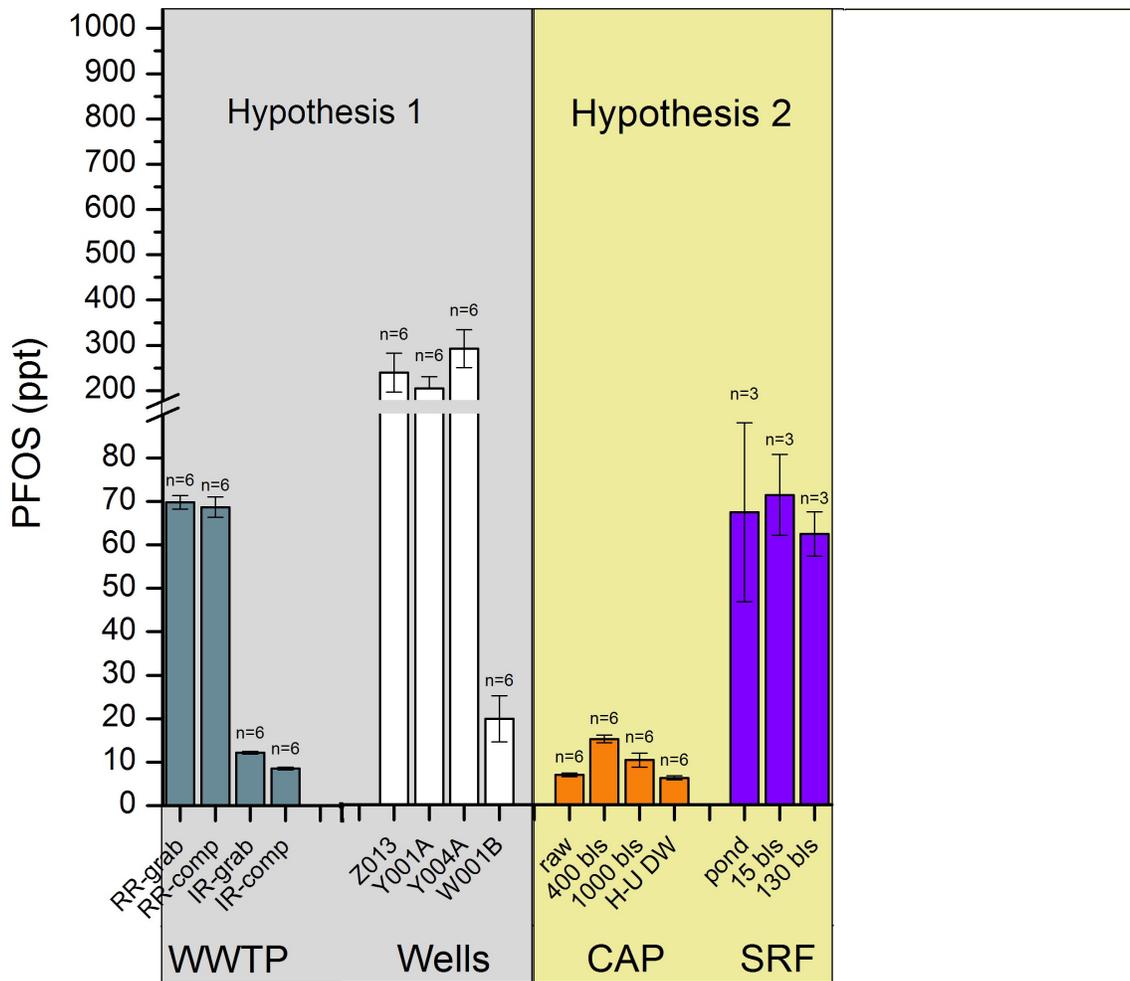
The project benefited from synergy with an ongoing Water Research Foundation grant (4269) to the University of Arizona led by Environmental Chemistry Prof. Jonathon Chorover, Co-director of the Arizona Laboratory for Emerging Contaminants (ALEC). Water Research Foundation project 4269, titled "Detection and quantification of EDC/PPCPs in source waters containing dissolved and colloidal organic matter" includes an assessment of EDC/PPCP levels and persistence in potable water sources and treated wastewaters in Tucson and three other U.S. metropolitan locations. Representative EDC/PPCPs, including PFOS, measured in the project are based on a number of criteria that included their widespread presence in waters impacted by the disposal of treated wastewater and reported detection limits (relative to expected levels in municipal wastewater).

The City of Tucson provided in kind support to the project, including assistance with sample collection at City-owned facilities. Gratitude is expressed to Danial Quintanar and John Kmiec (Tucson Water) for their valuable assistance to this project. In addition, the City of Tucson has an ongoing contract with a private analytical laboratory that provides for testing of perfluorinated compounds as part of their microconstituent testing program.

### **Findings/Discussion:**

#### *Assessment of Secondary effluent as a Contributor of PFOS in the Tucson Aquifer.*

PFOS was detected in all secondary effluent samples analyzed (Figure 4); concentrations in secondary effluent from the Roger Road WWTP (trickling filter process) were about 70 ng/L, approximately 7x greater than in effluent produced by the Ina Road WWTP (activated sludge process). At both WWTPs, there was little difference in results from grab versus 24-hr composite samples, suggesting that temporal composite sampling is not necessary to obtain representative PFOS measurements in secondary effluent. Assessment of the fate of PFOS during wastewater treatment was beyond the scope of this project but previous work has indicated PFOS is not attenuated during wastewater treatment and some have even suggested the possibility of PFOS production via breakdown of precursor perfluorinated compounds (Boulanger et al., 2005; Schultz et al., 2006; Sinclair and Kannan, 2006). Thus, we suspect that there is a much greater PFOS loading in the wastewater delivered to the Roger Road plant, perhaps due to an unknown point source.



**Figure 4 .** Mean PFOS concentrations, ng/L (ppt), in water samples obtained during this project. WWTP = wastewater treatment plant, Wells = Tucson production wells, CAP = Central Avra Valley Storage and Replenishment Project infiltration site, SRF = Sweetwater Recharge Facility infiltration site. The number of measurements is indicated above each bar. Error bars represent  $\pm$  one standard deviation. ND = nondetected.

All four of the City of Tucson production wells sampled during the project showed presence of PFOS. PFOS levels in three of the wells ( $\geq 200$ ng/L) were higher than observed in the secondary effluent samples. Given that these production wells extract a combination of native ground water along with a fraction of water originating from recharge along the Santa Cruz River, it was anticipated that PFOS concentrations in the wells would be lower than in effluent. In this study, PFOS concentrations in ground water (three wells downstream from the WWTPs, along the Santa Cruz River) were higher than in contemporaneous effluent. Similar findings were reported in Tokyo, Japan by Murakami et al. (2009). Possible explanations for this result could include: 1) PFOS concentrations in recharged effluent were higher in the past than at the present time 2) production of PFOS in the vadose zone/aquifer by biodegradation of perfluorinated precursor compounds, and/or 3) PFOS contamination of well water due to PFOS-containing materials in the well and/or pump that came in contact with the recovered water. PFOS was also detected in all three field blank samples collected during the well sampling, ranging in concentration from 6.6 to 13.8 ng/L. Possible sources of field blank contamination may have included lab instrument, water facility plumbing or some other source.

*Fate of PFOS during percolation of CAP Water and Secondary Effluent:*

PFOS was detected in all CAP and SRF samples collected during the project. Results from both infiltration sites indicate PFOS was not attenuated during percolation through unconsolidated sediment, supporting Hypothesis #2. Mean PFOS concentrations in ponded CAP water, 400 ft BLS, and 1000 ft BLS were 7, 14, and 10 ng/L, respectively (Figure 4). Similarly, PFOS concentrations were little changed during percolation of secondary

effluent through 130 feet of unconsolidated sediment at the Sweetwater Recharge Facilities. Mean PFOS concentrations in the pond, perched water (15 ft BLS), and in ground water (130 ft BLS) at the SRF were 67, 71, and 62 ng/L, respectively (Figure 4).

#### **Conclusion:**

This project investigated the presence of trace contaminants in secondary effluent that is discharged to the Santa Cruz River in the City of Tucson. The study also examined the fate of these compounds during soil percolation. Compounds were measured using ultra-performance liquid chromatography with tandem mass spectroscopy at the Arizona Laboratory for Emerging Contaminants located on the University of Arizona Campus. Secondary effluent contained high levels of trace contaminants, with concentrations ranging from 3.5 to almost 400 parts per trillion. Thus, both sources are contributors to the levels found in ground water in the region of the Tucson aquifer impacted by recharge along the Santa Cruz River. It should be noted that there remains the possibility of other sources of trace organic inputs to the Tucson aquifer. Landfills, feedlots and dairies, agricultural fields, septic systems, etc. that are located near the Santa Cruz River could be contributing sources. It was beyond the scope of this study to examine these other possible sources.

This study also found these compounds are not attenuated during percolation through soil; levels were essentially unchanged during percolation of secondary effluent through 130 ft of unconsolidated sediment. The project was designed as an initial step to identify major source(s) of trace organic inputs in ground water in the Tucson Basin and confirmed that secondary effluents play a role; future work is needed to determine the relative importance of these sources and of perhaps other as yet unknown contributors to the Tucson aquifer.

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