



PFOS levels in the general public have also been measured in Europe; samples of sera were taken from blood banks in Belgium, the Netherlands and Germany. Of these sample groups, the highest PFOS levels were observed in sera from the Netherlands (a mean value of 53 ppb) and the lowest in serum from Belgium (a mean value of 17 ppb) (OECD, 2002). In a study undertaken by the World Wildlife Fund, PFOS and six other perfluorinated chemicals were found in the blood samples of forty three people from various EU Member States (including the new EU countries) (WWF, 2004).

Recent reports provide evidence of PFOS production during wastewater treatment (Boulanger et al., 2005; Schultz et al., 2006; Sinclair and Kannan, 2006) and there is some speculation that PFOS may possibly be created during percolation in soil via the breakdown of precursor compounds (Murakami et al., 2008a; Murakami et al., 2009). PFOS contamination in ground water near the Tokyo metropolitan area has been attributed to infiltration of wastewater effluent and stormwater runoff, with effluent being the more important source (Murakami et al., 2009). That study also showed that PFOS concentrations in groundwater were similar to or higher than levels detected in municipal wastewater effluent. PFOS was detected in drinking water sources in the United Kingdom (McLaughlin et al., 2009), in Japan (Murakami et al., 2008b; Takagi et al., 2008), in China (Ling Mak et al., 2009), and in the Great Lakes region (Boulanger et al., 2004).

The European Union has regulation of PFOS. In June 2005, Sweden proposed a global ban on PFOS and related substances under the Stockholm Convention on Persistent Organic Pollutants. Previously, both Sweden and Britain filed for national bans on PFOS to the European Commission (EC), and urged the EC to pursue an EU-wide ban. In December 2005, the EC issued a proposal for a Directive to restrict the use of PFOS in carpets, textiles, clothing and other items.

PFOS is indefinitely persistent in the environment. Food, drinking water, outdoor air, indoor air, dust, and food packaging are all implicated as sources of PFOS to people (Renner, 2007) and contaminated food and drinking water are suspected to be the largest contributors (Trudel et al., 2008). When water is a source, blood levels have been found to be approximately 100 times higher than drinking water levels (Johnson, 2009; Post et al., 2009).

The origin of PFOS contamination in Tucson Basin ground water is unknown although it was strongly suspected that municipal wastewater effluent that recharges the local aquifer via the Santa Cruz River is a critical source. Our primary objective was to investigate the presence/fate of PFOS and to identify the source(s) of PFOS contamination to the Tucson Basin. The project yielded PFOS data at critical locations in the City of Tucson service area to establish the most probable source(s) of PFOS contamination (infiltration of municipal wastewater effluent, stormwater runoff, or infiltration of CAP water) among area ground waters. We established the fate of PFOS under highly controlled conditions--through recharge/recovery at the CAVSARP facility (CAP water) and at the Sweetwater Recharge Facilities (secondary effluent). This portion of the project provided preliminary data regarding the fate of PFOS during

infiltration/percolation. The City of Tucson provided in-kind support for this project, including access to facilities and assistance with water sample collection.

## METHODOLOGY

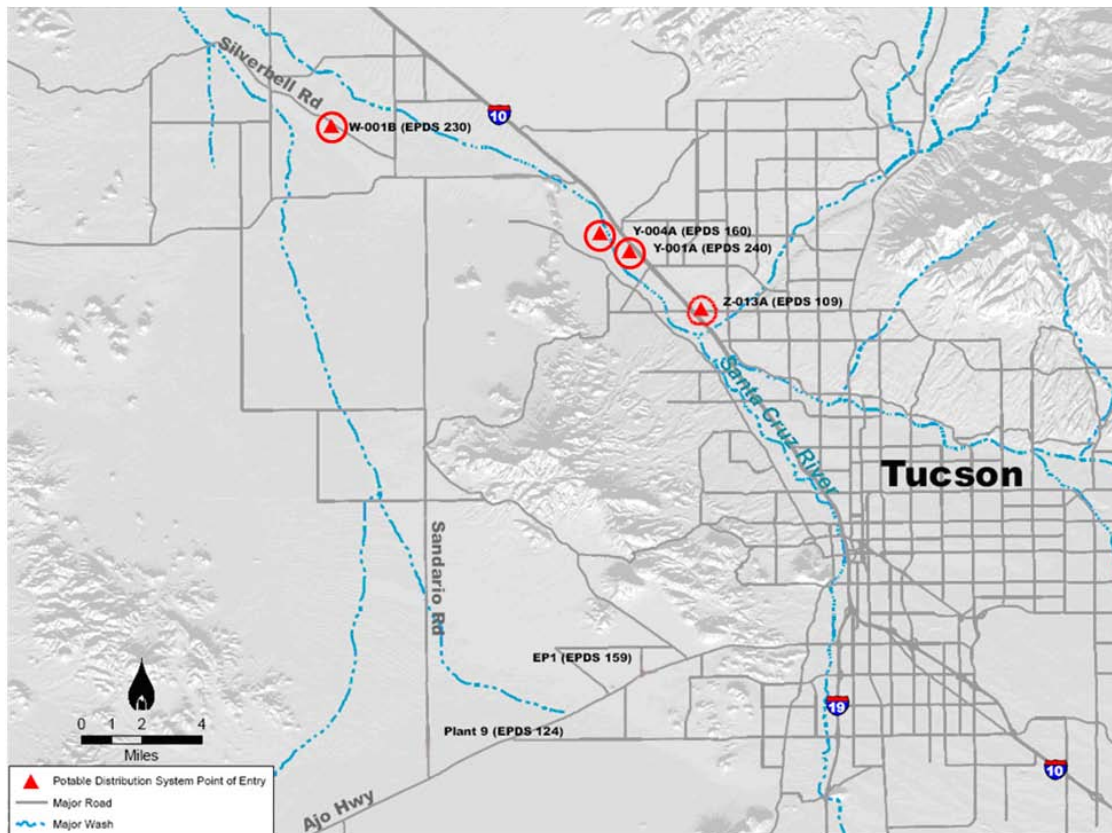
**Sampling Plan.** The sampling plan was structured to support hypothesis testing as follows.

*Hypothesis #1: Municipal wastewater effluent and stormwater runoff are sources 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.

To understand the importance of stormwater runoff as a contributor of PFOS to ground water, stormwater runoff was collected at nine locations (#5 - #13 in Table 1) within the City of Tucson during a summer 2010 monsoon storm event. Sampling was performed during and shortly after a storm that delivered 0.57 inches of rain (city of Tucson Airport, AZMET data) over a 1-hr period mid-day on September 22, 2010.

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 (#14 - #17 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 (#18 in Table 1) and monitoring wells at depths of 400 and 1000 feet below land surface (#19, #20 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 (#21 in Table 1) was also sampled.

Secondary effluent (#22 in Table 1) collected at Recharge Basin No. 1 and monitoring wells at depths of 15 and 130 ft below land surface (#23, #24 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 24 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	Storm runoff (CE bldg. roof)	St-CE roof	StW	1
6	Storm runoff (2 <sup>nd</sup> and Mountain, 12:00)	St.-2 <sup>nd</sup> 12:00	StW	1
7	Storm runoff (2 <sup>nd</sup> and Mountain, 12:20)	St.-2 <sup>nd</sup> 12:20	StW	1
8	Storm runoff (2 <sup>nd</sup> and Mountain, 12:40)	St.-2 <sup>nd</sup> 12:40	StW	1
9	Storm runoff (4 <sup>th</sup> and Park)	St.-4 <sup>th</sup> Park	StW	1
10	Storm runoff (parking lot, 6 <sup>th</sup> and Campbell)	St.-6 <sup>th</sup> Camp.	StW	1
11	Storm runoff (parking lot, 6 <sup>th</sup> and Highland)	St.-6 <sup>th</sup> High.	StW	1
12	Storm runoff (6 <sup>th</sup> and Stone)	St-6 <sup>th</sup> Stone	StW	1
13	Storm runoff (Santa Cruz R. at St. Mary’s bridge)	St.-SCR	StW	1
14	production well (Z013)	Well-Z013	GW	1
15	production well (Y001A, 2.6 mi below Ina WWTP)	Well-Y001A	GW	1
16	production well (Y004A, 3.3 mi below Ina WWTP)	Well-Y004A	GW	1
17	production well (W001B, 13.3 mi below Ina WWTP)	Well-W001B	GW	1
18	CAP water (before infiltration)	CAP-raw	SW	2
19	CAVSARP monitoring well (400’ bls)	CAP-400’	GW	2
20	CAVSARP monitoring well (1000’bls)	CAP-1000’	GW	2

21	Hayden Udall polished water (production water)	H-U DW	DW	2
22	Sweetwater Recharge Facility (SRF pond)	SRF pond	WWTP	2
23	Sweetwater Recharge Facility (SRF 15' bls)	SRF 15bls	GW	2
24	Sweetwater Recharge Facility (SRF 130' bls)	SRF 130bls	GW	2

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

## ***Analytical Methods***

### **1. Collection**

**Stormwater Runoff.** Single stormwater samples were collected discretely shortly after a rain event on September 22, 2010. Runoff flowing along street edges was collected in 1-L amber glass bottles. <sup>13</sup>C<sub>6</sub>-PFOS isotopologue was added to the 1-mL extracts as an internal standard prior to UPLC-MSMS analysis.

**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.

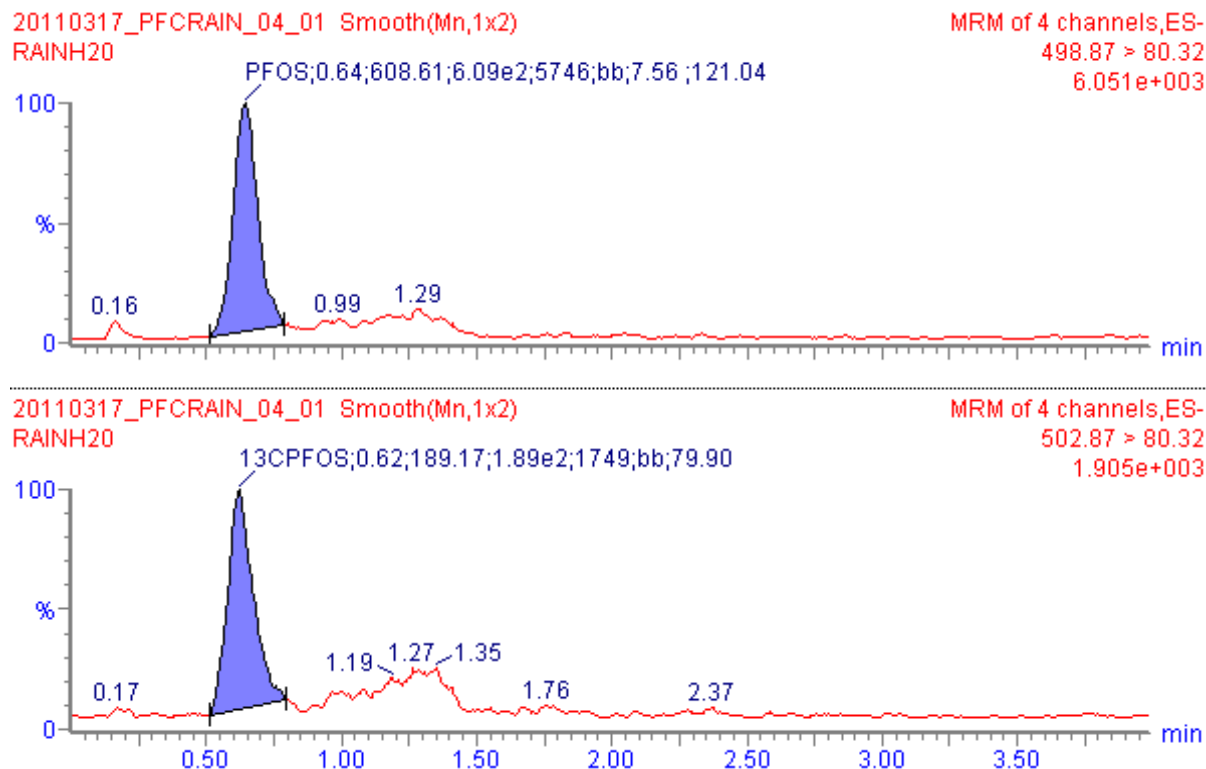
**3. Extraction.** Filtered samples were extracted within 24 hours of collection by solid phase extraction (SPE). An automated solid phase extraction instrument (Caliper Life Sciences Autotrace) (Figure 3) was used with a hydrophilic-lipophilic balance sorbent (Oasis HLB, 6 mL, 150 mg Waters Corp, cat. # 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  $\mu\text{L}$  and resuspended to 1.0 ml in 0.5 mL 50% aqueous methanol for UPLC-MSMS injection. An isotopologue ( $^{13}\text{C}_6\text{-PFOS}$ ) was added to the 1 mL extracts as an internal standard prior to UPLC-MSMS analysis.



**Figure 3.** Autotrace solid phase extraction workstation (left) and liquid chromatography tandem mass spectrometer (right). Instruments are located at the UA's Arizona Laboratory for Emerging Contaminants.

**4. Liquid Chromatography - Tandem Mass Spectrometry.** Liquid chromatography was performed using 5- $\mu\text{L}$  sample injections on a Waters Acquity UPLC system (Figure 3) with an Acquity UPLC BEH C18 column (1.7  $\mu\text{m}$ , 2.1 x 50 mm ) and a gradient mobile phase of water and acetonitrile for 15 min (with ammonium acetate buffer) at 0.4  $\text{mL min}^{-1}$ . 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: StWR and 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 StWR and SRF samples.  $^{13}\text{C}_6\text{-PFOS}$  detection was accomplished using a 502.87 > 80.32 transition. Examples of typical PFOS and  $^{13}\text{C}_6\text{-PFOS}$  chromatograms are provided in Figure 4.



**Figure 4.** PFOS chromatograms obtained by UPLC-MSMS. Upper chromatogram shows the integrated PFOS peak in a stormwater sample extract. Lower chromatogram shows the integrated peak for  $^{13}\text{C}_6$  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 StWR and 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 StWR and 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

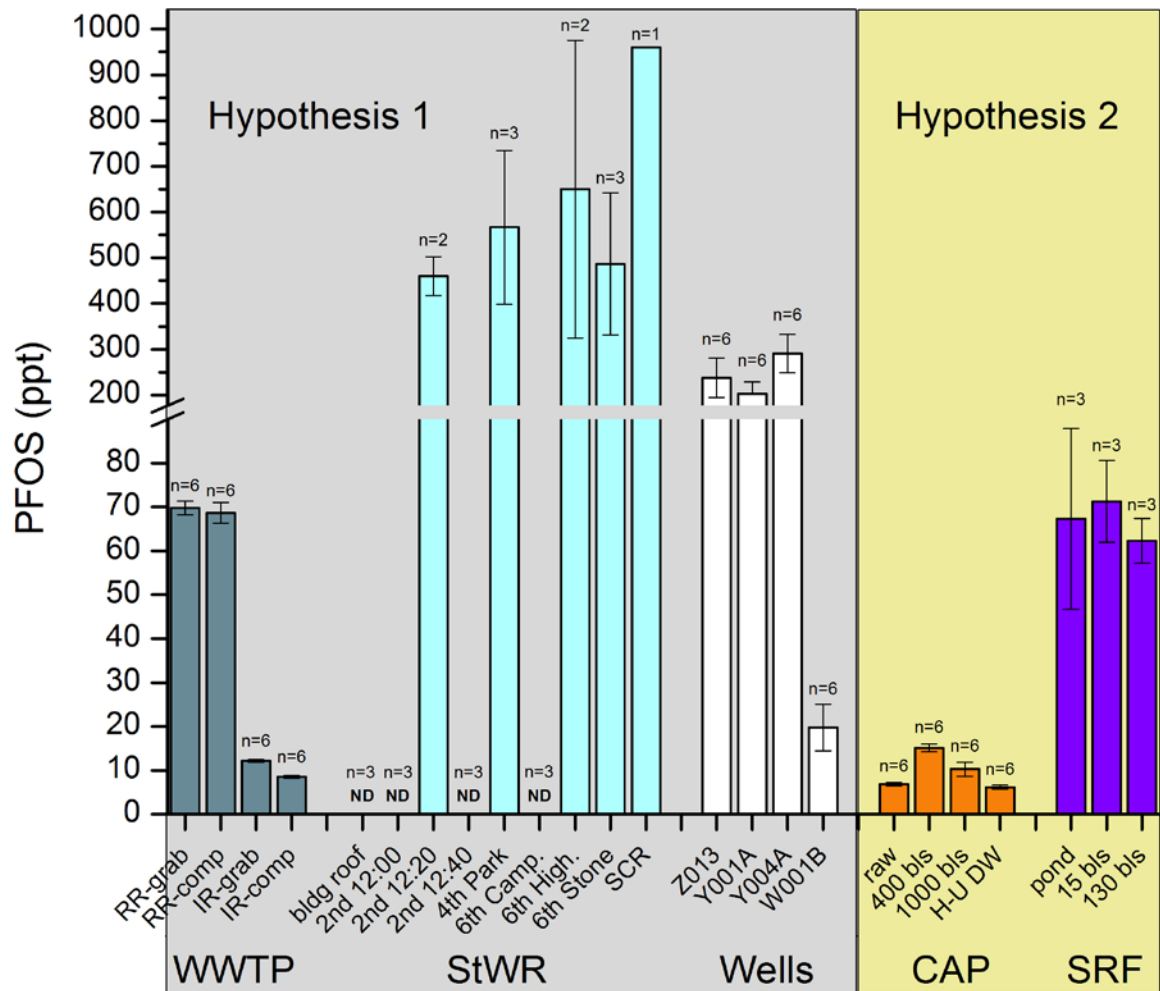
are based on a number of criteria that included their widespread presence in waters impacted by the disposal of treated wastewater and reported detection limits (relative to expected levels in municipal wastewater).

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.

## **PRINCIPAL FINDINGS AND SIGNIFICANCE**

*Assessment of Secondary effluent and Stormwater Runoff as Contributors of PFOS in the Tucson Aquifer.* PFOS was detected in all secondary effluent samples analyzed (Figure 5); 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 5.** Mean PFOS concentrations, ng/L (ppt), in water samples obtained during this project. WWTP = wastewater treatment plant, StWR = stormwater, 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.

PFOS was detected in the majority of stormwater runoff samples, albeit at widely ranging concentrations. A series of three runoff samples collected over a 40-minute period from the same location on 2<sup>nd</sup> Street at the UA campus showed PFOS levels ranging from nondetect (ND) to 460 ng/L. Runoff obtained along 6<sup>th</sup> street from campus going westward towards the Santa Cruz River ranged from ND to 960 ng/L PFOS in the Santa Cruz River at St. Mary's Road (highest value obtained during the project). It is not possible to assess temporal and spatial distribution of PFOS loading in stormwater runoff based on this preliminary work. Future efforts should be conducted with consideration of runoff hydrographs at specific sampling sites. The presence of PFOS in secondary effluent and in the majority of stormwater runoff samples, including from the Santa Cruz River, confirm Hypothesis #1 that both sources contribute PFOS to the region of the Tucson aquifer impacted by recharge from the Santa Cruz River.

All four of the City of Tucson production wells sampled during the project showed presence of PFOS. PFOS levels in three of the wells ( $\geq 200\text{ng/L}$ ) 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 5). 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 5).

*Summary of Findings:*

This project investigated the presence of PFOS in secondary effluent and in stormwater runoff that are discharged to the Santa Cruz River in the City of Tucson. The study also examined the fate of PFOS during soil percolation. PFOS was 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 and stormwater runoff both contained PFOS, with concentrations ranging from 10 to almost 1,000 parts per trillion. Thus, both sources are contributors to the PFOS 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 PFOS 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 PFOS sources.

This study also found that PFOS is not attenuated during percolation through soil; PFOS 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 PFOS in ground water in the Tucson Basin and confirmed that secondary effluent and

stormwater runoff play a role; future work is needed to determine the relative importance of these sources and of perhaps other as yet unknown contributors of PFOS to the Tucson aquifer.

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