



Perfluoroalkyl and polyfluoroalkyl substances (PFAS) in groundwater at a reclaimed water recharge facility



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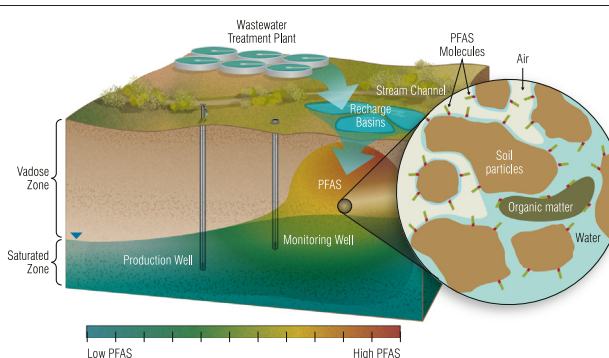
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HIGHLIGHTS

- PFAS originated from the retired wastewater treatment facility effluent.
- PFOS+PFOA concentrations linked to rising and falling groundwater levels.
- PFAS likely accumulated in the vadose zone.
- PFAS transported to groundwater during managed aquifer recharge events.

GRAPHICAL ABSTRACT



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ABSTRACT

Reclaimed water is becoming an increasingly important source of water in arid regions worldwide. In the City of Tucson, Arizona, reclaimed water comprises approximately 10% of the annual water supply. It is used to recharge the local aquifer, create surface flow in the Santa Cruz River, and irrigate parks, golf courses, and recreational fields. In December 2018, concentrations of perfluoroalkyl and polyfluoroalkyl substances (PFAS) an order of magnitude higher than the EPA lifetime health advisory of 70 ppt were discovered in the city's reclaimed water system. The PFAS were also detected in the Sweetwater Recharge Facility (SRF), adjacent to the Santa Cruz River, where reclaimed water is stored in the alluvial aquifer. PFAS have gained national attention as contaminants of emerging concern because of their widespread occurrence, toxicological impact to humans, and persistence in the environment. However, relatively little is known about their fate and transport in managed aquifer recharge systems. Results from this study show that PFAS in the SRF likely originated from the city's retired wastewater treatment facility, while lower PFAS concentrations are observed in the treated wastewater provided by the city's new treatment facility. Moreover, the combined PFOS and PFOA concentrations appear to be correlated to rising and falling groundwater levels, indicating that PFAS are likely trapped in the vadose zone and transported to the alluvial aquifer during managed aquifer recharge events.

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1. Introduction

Reclaimed water—water that has been recycled and put to a new use—is becoming a major water resource in water-stressed, arid regions

worldwide to increase water security (e.g., Garcia and Pargament, 2015). Arid regions, like Tucson, Arizona, that are highly dependent on groundwater and have limited local surface water supplies are more commonly exploring new uses of other available water resources like reclaimed water (Garcia and Pargament, 2015). Reclaimed water in Tucson is artificially recharged for aquifer storage, directly transported to irrigation systems across the city, and discharged into the Santa

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Cruz River to return surface flows and reestablish riparian habitat. Reclaimed water is not currently being used for potable purposes; however, as population increases it is likely to become a possibility.

In December 2018, the main public water utility in Tucson—Tucson Water—discovered perfluoroalkyl and polyfluoroalkyl substances (PFAS) in their potable and reclaimed groundwater systems at concentrations two orders of magnitude greater than the EPA lifetime health advisory of 70 ppt. PFAS have gained attention as emerging contaminants because of their potential toxicological impact to humans and their persistence in the environment (e.g., Ahrens, 2011; Rayne and Forest, 2009; Krafft and Riess, 2015; Wang et al., 2017; ITRC, 2018). PFAS' persistence in water have caused its introduction into the food web, which is also causing concern for human health (Domingo and Nadal, 2019). PFAS have been widely used since the 1940s due to their water, oil, grease, and heat repelling properties, making them excellent for cookware (Teflon), textile treatments, and as firefighting agents (aqueous film-forming foams (AFFFs)) (e.g., Cousins et al., 2016; Dery et al., 2019). Their widespread release into the environment is usually due to manufacture and use of PFAS, disposal of consumer products, or from degradation of other forms of PFAS (e.g., Buck et al., 2011). PFAS have been detected in rainwater, freshwater, seawater, groundwater, landfill leachates, soil, sediment, waste water treatment plant sludge and effluent, wildlife and even in the atmosphere in both urban and remote areas (e.g., Ahrens, 2011; Brusseau, 2020; Krafft and Riess, 2015; Rayne and Forest, 2009). Guelfo and Adamson (2018) found that wastewater treatment plants are significant contributors of PFAS in the environment. These outputs of PFAS tend to be minor compared to industrial sources, but because there are so many wastewater treatment plants their impact accumulates (Guelfo and Adamson, 2018). The use of PFAS-contaminated treated wastewater for aquifer recharge, irrigation, or other uses can potentially spread PFAS contamination and increase risk of exposures. Because of their recalcitrance, they tend to be very difficult and in turn expensive to remediate (ITRC, 2018; Wang et al., 2017).

PFAS' ubiquitous and evolving nature motivates cities and water managers worldwide to better understand the fate and transport of PFAS in groundwater. Tucson Water has already begun to mitigate the issues that PFAS are causing, terminating the use of 25 production wells in their potable system with combined PFOA and PFOS concentrations that exceeded the EPA lifetime health advisory (Dick Thompson, personal communication, 2020). PFAS concentrations were also discovered by Tucson Water in their reclaimed water system, particularly in the Sweetwater Recharge Facility (SRF). This facility serves as additional treatment—soil aquifer treatment—to effluent from an adjacent wastewater treatment plant, as well as storage for part of Tucson Water's reclaimed water. However, the SRF or soil aquifer treatment is not designed to treat PFAS. While it is unclear what the fate of potable and reclaimed water systems will be, media reports indicate some water supply systems and managed aquifer facilities are being abandoned due to PFAS.

While the presence of PFAS in wastewater effluent and groundwater has been identified, the transport behavior and fate of PFAS in the subsurface at the SRF remains unknown. This research aims to address this knowledge gap, and to identify and quantify relationships between different types of PFAS, and whether they have distinct sources, fate, and transport characteristics at the SRF. Specific objectives include: 1) Analyze PFAS based on their composition, concentration, co-occurrence, and spatial distribution to determine their source in the SRF. This could allow for insight as to how PFAS have travelled in the subsurface. And 2) determine if there are temporal trends or correlation between recharge into the basins, pumping at SRF, and PFAS concentrations to help evaluate their persistence and movement in the environment. Results of this study help delineate the behavior of PFAS in the subsurface and during enhanced aquifer recharge that will support Tucson Water management decisions and may be more widely applicable to other arid regions using or considering reclaimed water systems.

2. Background on relevant PFAS fate and transport processes

Past studies of PFAS associated with firefighting training sites found that the downward migration of PFAS is most likely due to direct infiltration from the surface, and that, generally, PFAS concentration decreased with depth (Dauchy et al., 2019). A recent meta-analysis of PFAS in soils and the vadose zone demonstrated similar observations for numerous sites (Brusseau et al., 2020). PFAS concentrations in soils and the vadose zone have been shown to be significantly higher than groundwater concentrations for many sites (Anderson et al., 2019; Brusseau et al., 2020). These studies and others (e.g., Guo et al., 2020) have indicated that soils and the vadose zone are likely to be major, long-term sources of PFAS for decades.

The migration of PFAS in soil and the vadose zone is influenced by several factors and processes, including the PFAS source type, infiltration rates, soil properties, and magnitudes of retention (e.g., Brusseau, 2018; Brusseau, 2020; Guo et al., 2020). PFAS retention in unsaturated soil systems is influenced primarily by two processes, sorption by the soil grains and adsorption at air-water interfaces (Brusseau, 2018). Sorption of PFAS by soils and sediments can be relatively complex, involving multiple mechanisms (e.g., Brusseau et al., 2019a; Guelfo et al., 2020; Wang et al., 2021). This is complicated further by the different head-group moieties comprising PFAS. Research using surface-tension measurements has illustrated the ability of PFAS to adsorb at air-water interfaces, as well as the influence of PFAS molecular structure and solution chemistry on adsorption (e.g., Brusseau, 2018; Brusseau, 2019; Silva et al., 2019; Brusseau and Van Glubt, 2019; Costanza et al., 2019). The impact of air-water interfacial adsorption on PFAS retention and migration in unsaturated soil has been confirmed by transport studies conducted with column systems (e.g., Lyu et al., 2018; Brusseau et al., 2019b).

Weber et al. (2017) report on a groundwater plume caused by artificially recharging treated wastewater produced in a military base that is somewhat analogous to the SRF site. This recharge site is down-gradient of the military base, which also served as a joint firefighting training facility wherein AFFF was employed. While the managed aquifer recharge ceased in 1995, high concentrations of PFAS persisted near the water table (Weber et al., 2017; Nickerson et al., 2020). These results likely mean that PFAS were retained in the sediments beneath the infiltration beds. This is similar to the general risks described by Page et al. (2019) for managed aquifer recharge of PFAS-containing effluent. Weber et al. (2017) suggest that PFAS is slowly desorbing as groundwater travels through this area. Furthermore, they state that precursors trapped in the vadose zone could be transforming into more mobile PFAS that can later make their way into the saturated zone (Weber et al., 2017). This study also estimated PFOS to travel 780 m in approximately 15 years based on 1-D advective transport. Weber et al. (2017) conclude that the unsaturated zone underneath the infiltration beds continues to be a source of PFAS after 18 years and 20 years of inactivity of the firefighting training area and the infiltration beds, respectively. Previous studies and this one demonstrate that fate and transport processes are complicated by the vadose zone and dynamic recharge operations at managed aquifer recharge sites.

3. Site description

The study area for this project is Tucson Water's Sweetwater Recharge Facility (SRF), an underground storage facility (USF). SRF has a permit to store approximately 1.6 M m³/year, making it the largest constructed USF to recharge effluent in Tucson (ADEQ, 2018). It is made up of 11 recharge basins and 10 extraction wells on both the west and east sides of the Santa Cruz River (Fig. 1). All together the basins sum up to approximately 162,000 m² of land that can be filled up to about 1 m high. Basin RB-004 was first in use receiving Class B secondary effluent from Roger Road Wastewater Treatment Plant (RRWTP) in 1989 followed by the construction of RB-001, RB-002, and RB-003,

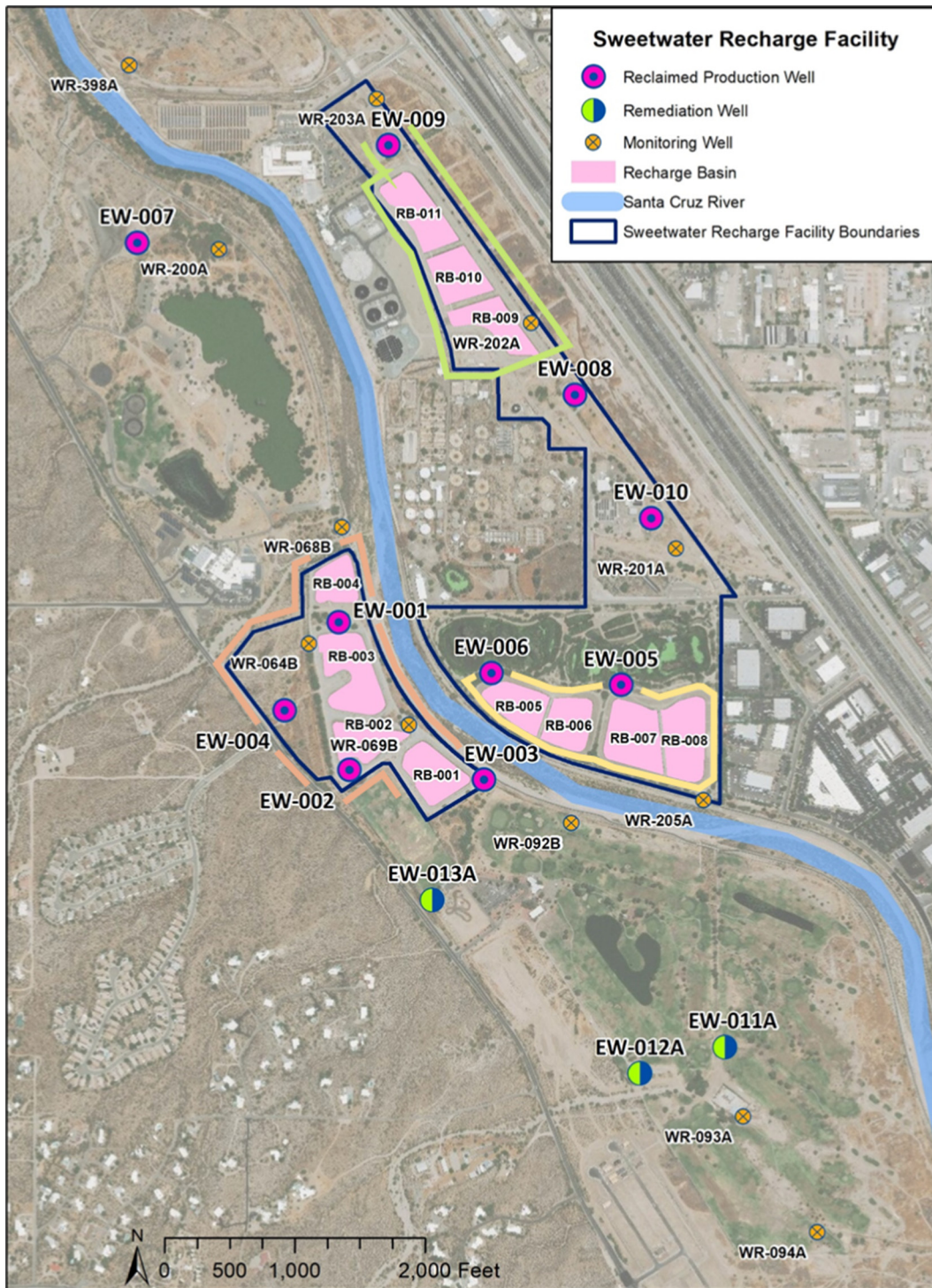


Fig. 1. Site map of the Sweetwater Recharge Facility adjacent to the Santa Cruz River in Tucson, AZ.

which were completed by 1991 (Kmiec and Thomure, 2004). Basins RB-005 to RB-008 were completed and in use by 1997.

To meet requirements mandated by the Arizona Department of Environmental Quality (ADEQ) and the Clean Water Act, the operation of RRWTP stopped and the supply of effluent was replaced by Agua Nueva Water Reclamation Facility (ANWRF) on March 12, 2014 (Nakolan et al., 2015). ANWRF includes new headworks, influent pumping, dissolved air flotation (DAF) clarification for primary treatment and sludge thickening, 5-Stage Bardenpho activated sludge secondary treatment with step-feed aeration, tertiary filtration, and chloramine-based disinfection. ANWRF delivers Class A tertiary effluent.

In July of 2014, SRF expanded once again to include the three final basins—RB-009 to RB-011, which have only received water from ANWRF. After water is treated at ANWRF, it is both chlorinated and released into the Lower Santa Cruz River or it is sent to the Tertiary Effluent Pumping Station (TEPS). Subsequently, the water is sent into the Reclaimed Water System after carbon-sand filtration and chlorination treatment or it is directed into the recharge basins for soil aquifer treatment and storage. ANWRF produces 95,000 m³/day but only has the capacity to supply 38,000 m³/day into the reclaimed water system. The remaining 57,000 m³/day and whatever extra water not needed during times of low demand is used to fill the recharge basins in SRF

before the excess water is chlorinated and sent down the River (Nakolan et al., 2015).

The basins consist of mostly gravel and sand, however, clay lenses are present below all of SRF but mostly deeper below the newest basins (RB-009 to RB-011) (Wilson et al., 1995; Quanrud et al., 2003). The basins are operated in wet-dry cycles to remove algae that build up due to the ponded water, which historically have been known to reduce infiltration rates if the basins are not maintained properly. The soil properties at the SRF are very similar to the soil properties in the Vinton soil used for the model in Guo et al., 2020 (Table A.9). The Vinton soil demonstrates strong retention capacity of PFOS and similar long-chain PFAS in the vadose zone.

4. Methods

Since PFAS were discovered in late 2018 Tucson Water regularly samples PFAS in their wells, creating a unique spatially and temporally distributed dataset. The suite of PFAS analyzed here are those that are detected at this site (Table 1). Sampling for total fluorinated compounds is recommended for future sampling at the SRF; the sampling and data used in this study were dependent on Tucson Water's need to meet local and state requirements. The relationship among the PFAS were analyzed with correlation matrices. Concentration data for each PFAS was statistically and spatially analyzed based on chain length to gain insight on preferential transport and the source of PFAS in the SRF. PFAS concentration changes with time were plotted to try to gain insight on their fate and transport. Lastly, changes in PFAS concentration are

analyzed and evaluated against change in water table elevations and the two direct factors affecting groundwater elevations at SRF—pumping and managed aquifer recharge events.

To analyze PFAS in the SRF, the wells and basins were split into three sections depending on both their location and time of being in use (Fig. 1). Section 1 consists of the oldest infrastructure in the southwestern corner of SRF: Recharge Basins 1–4 and Extraction Wells 1–4. Section 2 is the only set of basins and wells west of the Santa Cruz River. Section 2 is mostly made up of the second set of basins and wells to come online in the southeastern corner of the SRF: Recharge Basins 5–8 and Extraction Wells 5–6, 8, 10. Lastly, section 3 consists of the newest basins and wells in the northeast corner of the facility: Recharge Basins 9–11 and Extraction Well 9. Extraction Wells 8 and 10, although they are two of the newest wells in the facility, are grouped in section 2 because of their proximity to the southeastern corner of the SRF and PFAS concentrations. EW-007A was included in most of the analyses but mostly as a point of reference, recharge does not occur near this well; thus, it likely is not prone to similar factors as the other wells.

5. Results

There are a few possible sources of PFAS at the SRF: 1) the retired Silverbell Landfill located upgradient (southeast) of and adjacent to the SRF; 2) other PFAS hotspots upstream of the Santa Cruz River; and 3) effluent from the old water treatment plant that supplied a lesser quality of reclaimed water to the recharge basins at the SRF. To test this, PFAS at the SRF and surrounding area were characterized, focusing on whether the effluent is the original source of PFAS or if it is intensifying existing PFAS concentrations.

The combined PFOS and PFOA concentrations over time at the SRF are generally higher in older wells completed prior to 1989, and in wells located further to the south of the SRF (Fig. A.2). This is further supported by the PFOS annual average concentration maps from 2016 to 2019 (Fig. 2). These maps demonstrate that the southwestern corner of the facility is where the PFOS concentrations are the highest. PFOA is more widespread than PFOS (Fig. 3). These maps were made using the annual average concentrations of PFOS and PFOA for the extraction wells that were available for each year. Not every well was sampled every year, due to operational reasons like pumps not working.

The 8 types of PFAS detected in the SRF, along with their complete names, chemical formulas, and available retardation factors are listed in Table 1. PFOS makes up the majority of the total PFAS concentration in most wells, especially the older wells (Fig. 4). Sample point 510, which is where the effluent from ANWRF is sampled before being discharged into the recharge basins, had the lowest concentration of total PFAS (Fig. 4).

Correlation matrices were created for all three sections to compare how often the 8 PFAS present in the SRF are found together (Table A.2 – A.3). PFOS and PFOA had some of the strongest correlations in sections 2 and 3 ($r^2 = 0.73$ and 0.93 , respectively). PFNA had significant correlations to PFOA in section 1 and to PFOS in section 2 ($r^2 = 0.80$ and 0.93 , respectively). In sections 2 and 3 PFHpA had the high correlations with PFOS ($r^2 = 0.76$ and 0.72 , respectively) and to PFOA ($r^2 = 0.81$ and 0.90 , respectively). PFHpA also had a strong correlation with PFHxA in section 1 ($r^2 = 0.83$). This pair had the opposite trend in section 3 with a strong negative correlation ($r^2 = -0.88$). Another negative correlation was seen in section 3 between PFHxA and PFHxS ($r^2 = -0.72$). Section 2 demonstrated a high correlation between PFHxA and PFBS ($r^2 = 0.71$). PFHxS had two of the strongest correlations with PFOA in section 1 and 3 ($r^2 = 0.85$ and 0.97 , respectively). Section 3 showed a significant correlation between PFHxS and PFOA ($r^2 = 0.84$) and a negative correlation between PFHxS and PFBS ($r^2 = -0.82$). Section 3 also revealed a strong correlation between PFHxS and PFHpA ($r^2 = 0.91$). In section 1 PFDA had a high correlation with both PFHxA and PFNA ($r^2 = 0.81$ and 0.77 , respectively). Finally, section 2 showed a strong negative correlation between PFDA and PFHxS ($r^2 = -0.71$).

Table 1

List of PFAS analyzed by Tucson Water and PFAS found in the SRF.

Detected in the SRF	Name	Formula	Retardation Factor (R)
✓	PFBS Perfluorobutanesulfonic acid	$C_4HF_9O_3S$	3.34
✓	PFHxS Perfluorohexanesulfonic acid	$C_6HF_{13}O_3S$	4.25
✓	PFOS Perfluorooctanesulfonic acid	$C_8HF_{17}O_3S$	18.47
X	PFBA Perfluorodecanoate, Perfluorobutanoic acid	$C_4HF_7O_2$	2.67
X	PFPeA Perfluoropentanoate, Perfluoropentanoic acid	$C_5HF_9O_2$	1.67
✓	PFHxA Perfluorohexanoic acid	$C_6HF_{11}O_2$	1.52
✓	PFHpA Perfluoroheptanoic acid	$C_7HF_{13}O_2$	2.26
✓	PFOA Perfluorooctanoic acid	$C_8HF_{15}O_2$	3.18
✓	PFNA Perfluorononanoic acid	$C_9HF_{17}O_2$	7.54
✓	PFDA Perfluorodecanoic acid	$C_{10}HF_{19}O_2$	32.82
X	PFUnA, or PFUnDA Perfluoroundecanoate, Perfluoroundecanoic acid	$C_{11}HF_{21}O_2$	–
X	PFDoDA, or PFDoDA Perfluorododecanoate, Perfluorododecanoic acid	$C_{12}HF_{23}O_2$	–
X	PFTriA, or PFTriA Perfluorotridecanoic acid	$C_{13}HF_{25}O_2$	–
X	PFTeDA, or PFTeDA Perfluorotetradecanoic acid	$C_{14}HF_{27}O_2$	–
X	N-EtFOSAA N-Ethyl perfluorooctane sulfonamido acetic acid	$C_{12}H_8F_{17}NO_4S$	–
X	N-MeFOSSA N-Methylperfluorooctane sulfonamidoacetic acid	$C_{11}H_6F_{17}NO_4S$	–

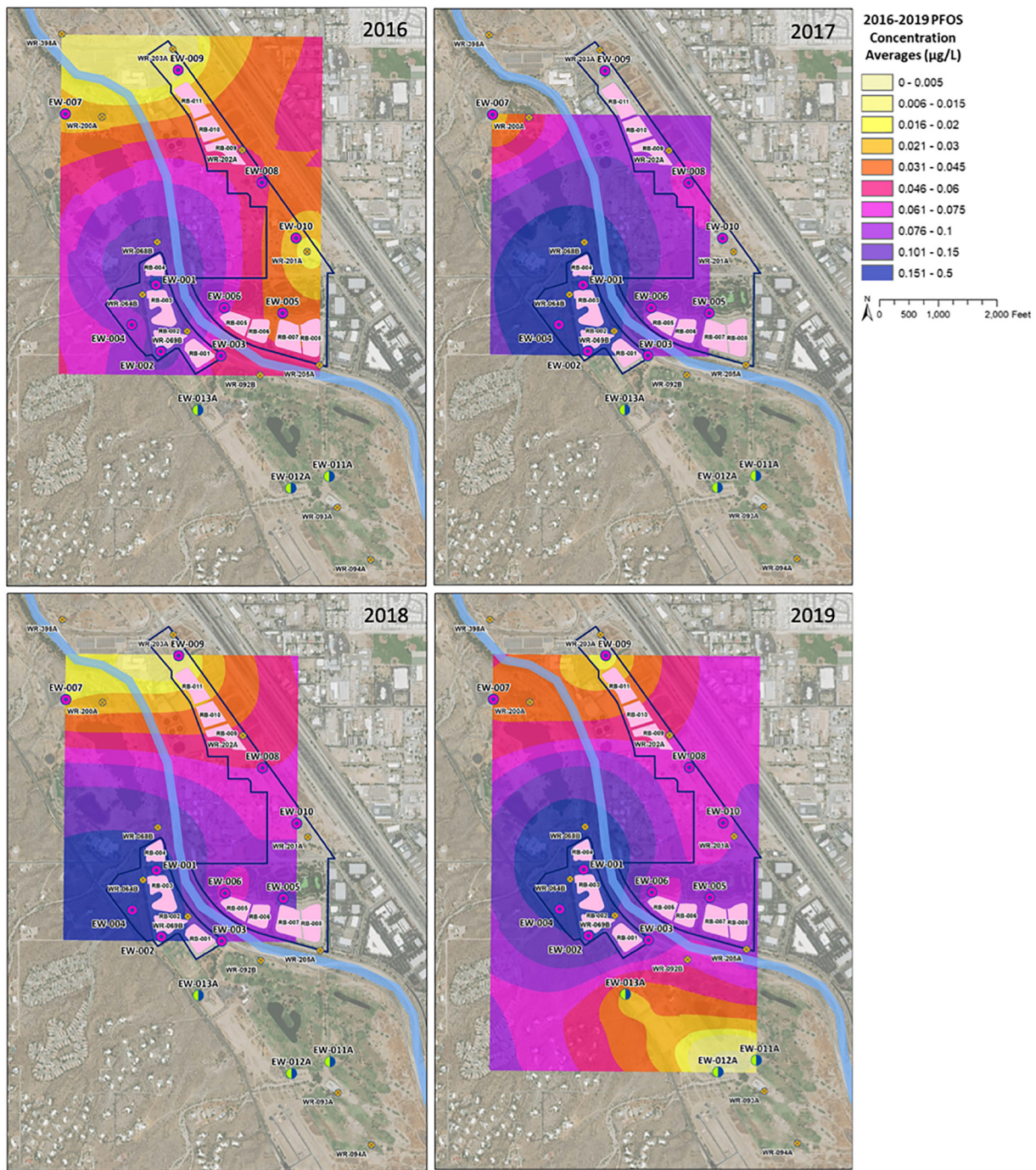


Fig. 2. Maps of 2016 to 2019 spatial distributions of PFOS concentrations (µg/L) at SRF, starting with 2016 on the top left corner, 2017 on the top right corner, 2018 on the bottom left corner and 2019 on the bottom right corner.

Although historical levels of PFAS could not be traced, a more detailed look at what is happening in the subsurface was achieved by plotting water table elevations of nearby monitoring wells and combined PFOS and PFOA concentrations in production wells over time (Fig. 5). Six of the 10 paired wells (EW-002A, 3A, 4A, 5A, 8A, and 10A) showed an approximate direct relationship between PFAS concentration and rising and falling groundwater levels. The correlations (r^2 values) between PFOS and PFOA concentrations and water table elevations at these six wells ranged from 0.23 (EW-008A) to 0.86 (EW-005A), which was the strongest positive correlation (Table A.4). This pattern was observed in most of the wells particularly those in the southern

half of the facility. PFAS concentration in those 6 wells generally increased when water table elevations rose. It should also be noted that not all the peaks and troughs of the PFOS and PFOA concentration correspond to those of the water table elevations. For example, in EW-002A in June and July of 2017 there was a peak in the PFAS concentrations and a trough in the water levels (Fig. 5A). The mismatched peak and trough are also present in the other wells in section 1 (EW-001A, 3A, and 4A) (Fig. A.2, A.3, and A.4). Out of all 10 extraction wells at the SRF, EW-001A had the weakest correlation ($r^2 = 0.07$) and EW-006A had the strongest negative correlation ($r^2 = -0.79$). The strongest positive correlation between PFDA (C10) and water table elevation

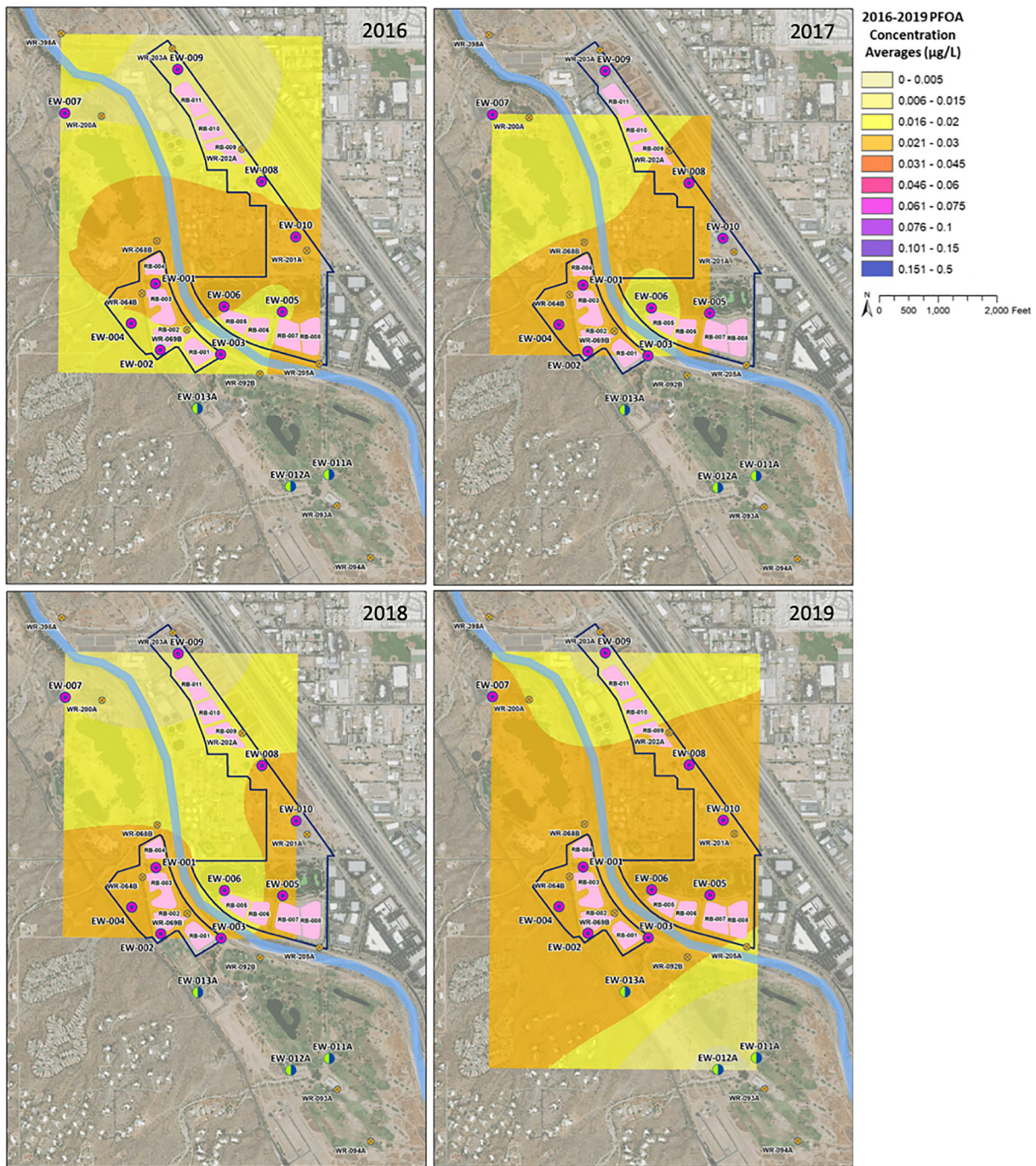


Fig. 3. Maps of 2016 to 2019 spatial distributions of PFOA concentrations ($\mu\text{g/L}$) at SRF, starting with 2016 on the top left corner, 2017 on the top right corner, 2018 on the bottom left corner and 2019 on the bottom right corner.

occurred in section 1 in well EW-002A and 4A ($r^2 = 0.85$ and 0.95 , respectively). EW-002A and 4A also had the strongest positive correlation to PFBS (C4) ($r^2 = 0.77$ and 0.99 , respectively).

The PFAS concentrations in section 1 seem to have a strong negative correlation for EW-003A and 4A with pumping events ($r^2 = -0.82$ and -0.89 , respectively), meaning that PFAS concentration and pumping events are inversely related (Table A.5). EW-003A had a fairly strong negative correlation to discharge ($r^2 = -0.59$) into the recharge basins too. This means that as pumping and discharge into the basins decreases, PFAS increases. EW-002A also had a negative correlation with pumping, however it was a weaker correlation ($r^2 = -0.31$) than that of EW-003A and 4A (Table A.5). EW-001A did not have a correlation to either pumping or discharge into the basins ($r^2 = 0.13$ and 0.10 ,

respectively). In section 2, EW-005A and 8A both had negative correlations to pumping ($r^2 = -0.59$ and -0.54 , respectively) and both wells had weak correlations to discharge into the basins ($r^2 = 0.24$ and -0.03 , respectively) (Table A.6). EW-006A had a stronger correlation to pumping ($r^2 = 0.47$), than it did to discharge into the basins ($r^2 = -0.33$). Pumping had the opposite effect on EW-006A than it did on EW-005A and 8A. EW-010A was the only well in section 2 that had a strong correlation to discharge into the basins ($r^2 = 0.71$). EW-009A is the only well in section 3 and it had a positive correlation to pumping ($r^2 = 0.52$) and a weak negative correlation ($r^2 = -0.30$) to discharge into the basins (Table A.7).

The water table elevation and average combined PFOS and PFOA concentrations for 2019 for the 10 reclaimed water productions wells

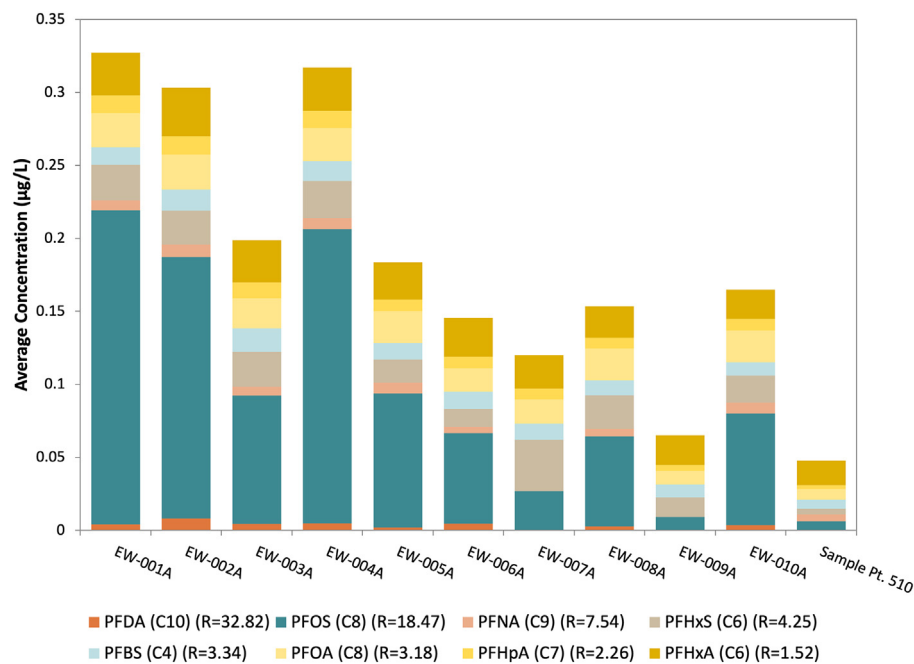


Fig. 4. Distribution of the different types of PFAS found in groundwater samples from reclaimed water production wells (EWs) in the SRF and in the effluent from ANWRF (Sample Point 510). Chain length for each PFAS is indicated by the C#, while R is the retardation factor.

at the SRF (EW-001A to EW-010A) and the 3 remediation wells installed in 2019 in the Silverbell Golf Course (EW-011A to EW-012A) were plotted along with their well construction diagrams (Fig. A.9). This figure can be used to visualize where each well draws its water from, since it also includes screen intervals and total depths for each well. The wells in the SRF have staggered screened intervals, section 1 having the deepest screened intervals and section 3 the lowest. Section 1 has the highest screen interval, about 10 m higher than EW-005A, 6A and 7A and 57 m higher than EW-008A, 9A, and 10A.

6. Discussion

6.1. PFAS composition, concentration, co-occurrence, and spatial distribution to determine their source

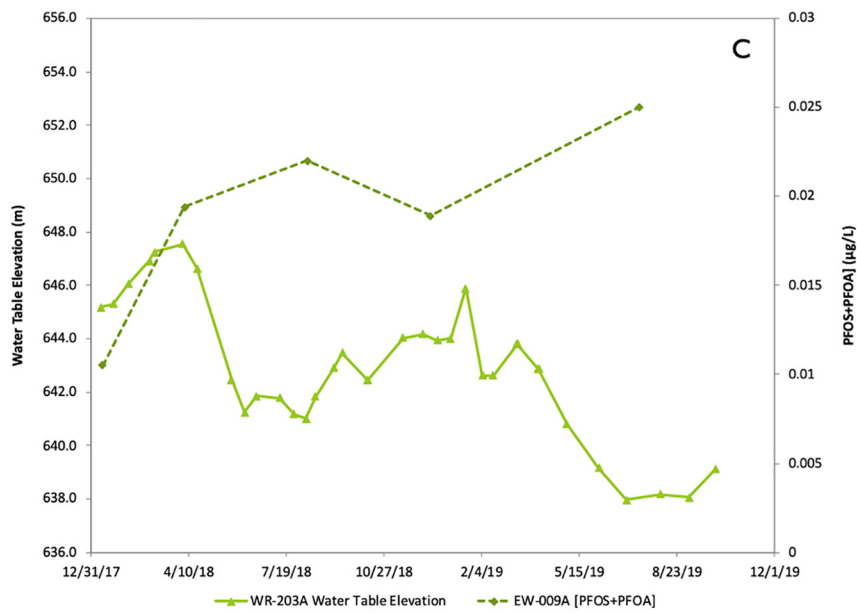
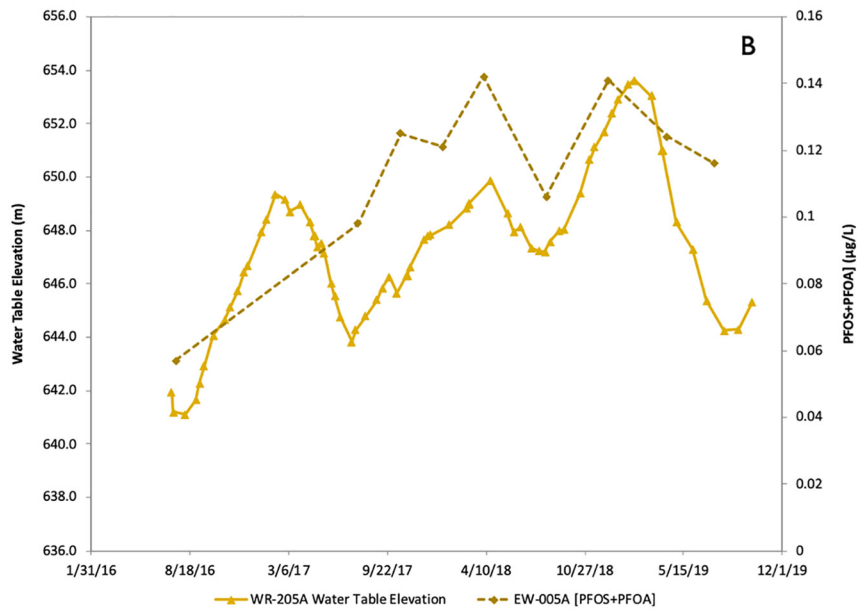
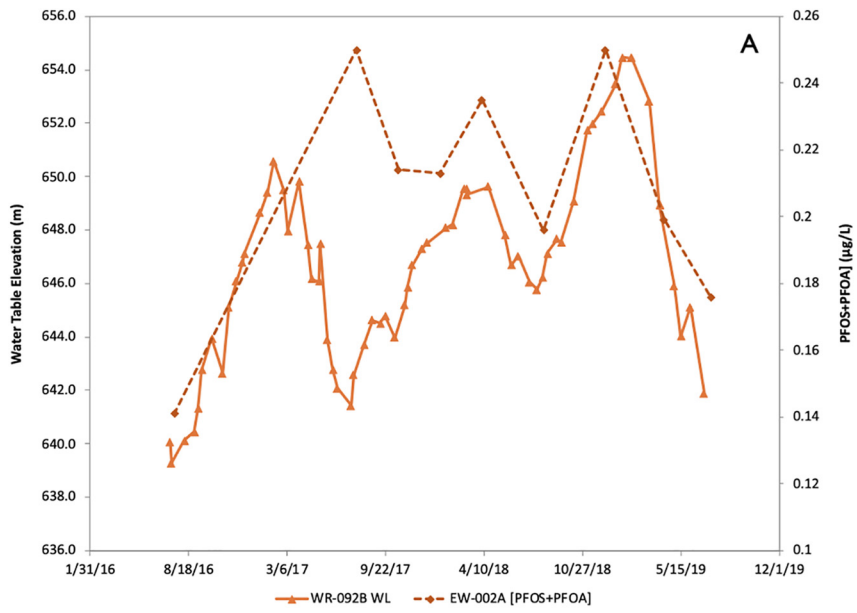
The first objective for this study was to determine the source of the high concentrations of PFAS in the SRF. PFAS concentrations in the treated wastewater exiting ANWRF and subsequently discharged into the basins (Sample Point 510) are lower than those present in groundwater extracted at the site (Fig. 4). Thus, the current ANWRF can be ruled out as being the only possible source. That leaves three probable additional sources of PFAS: the Silverbell Landfill, hotspots upstream of the Santa Cruz River, and effluent from the Roger Road Wastewater Treatment Plant.

As previously stated, landfills have been sources of PFAS at other PFAS-impacted sites and thus was considered as a potential source of PFAS at the SRF. Furthermore, the Silverbell Landfill was in operation from 1966 to 1975 so PFAS may have migrated from the landfill to the downgradient location of the SRF which was not yet in operation. The Silverbell landfill can be eliminated as the sole source because the current hydraulic gradient is from the SRF to the landfill and the PFOA and PFOS concentrations in the landfill are relatively low compared to the SRF. Groundwater elevations are constantly fluctuating because of recharge and pumping events thus it is important to analyze hydraulic gradients from distinct periods of time. From 1994 to 1998, regional hydraulic gradients in the Tucson area trended toward the center of the city where the primary well field is located, which is southeast of both the SRF and the Silverbell Landfill (Tucson Water, 2018). Groundwater levels in the central well field began to rise in 2001 when the City of

Tucson secured long-term delivery of Colorado River water (Tucson Water, 2018). Since the SRF came online hydraulic gradients in the surrounding areas have retained a similar pattern. Depth to groundwater maps for January and March 2019 were constructed to determine the historical hydraulic gradients at the SRF (Fig. 6). In January large volumes of effluent from the ANWRF were discharged into the basins. During the month of March, the SRF was at capacity, meaning that Tucson Water could no longer store reclaimed water in the aquifer because their permit only allows a certain volume to be stored. Thus, March can be seen as a period of relaxation in groundwater elevations. For both months, however, hydraulic gradients are outward away from the facility. Consequently, it is unlikely that groundwater near the Silverbell landfill transported PFAS into the SRF traveling against the gradient, making it equally unlikely that the Silverbell landfill is the primary source of PFAS.

The second reason why the Silverbell landfill is unlikely to be a source is because of 2019 PFOA and PFOS concentration gradients near the SRF. The 2019 PFOS and PFOA maps, depicted in Figs. 2 and 3 respectively, were made using PFOS and PFOA concentrations from the three new extraction wells (EW-011A: EW-013A) in the Silverbell Golf course. Two of the new wells have concentrations lower than those found in the SRF and the groundwater extracted from the third well did not have any detectable PFAS. These maps also show PFOS and PFOA concentrations at the SRF for 2016, 2017 and 2018. Like the depth to water maps (Fig. 6), all the PFOS and PFOA maps show that the concentration gradient is declining from the SRF. According to the concentrations gradients it is unlikely that the PFAS were sourced from somewhere outside of the SRF. These maps not only further eliminate the Silverbell landfill as a source but also the second possible source of PFAS at the SRF—other hotspots along upstream portions of the Santa Cruz. There are two other major PFAS hotspots in Tucson that have affected Tucson Water's potable water system, Davis-Monthan Air Force Base and the Tucson Airport Remediation Project Site. These sites are more than 20 km southeast of the SRF. It is possible that PFASs from one of these two sites migrated to the SRF via the Santa Cruz River channel. However, as previously discussed, the PFAS plume at the SRF appears to be localized in and around the facility itself (Fig. 2).

This leads to the most likely hypothesis—the source of PFAS in SRF was the effluent received from the Roger Road Wastewater Treatment



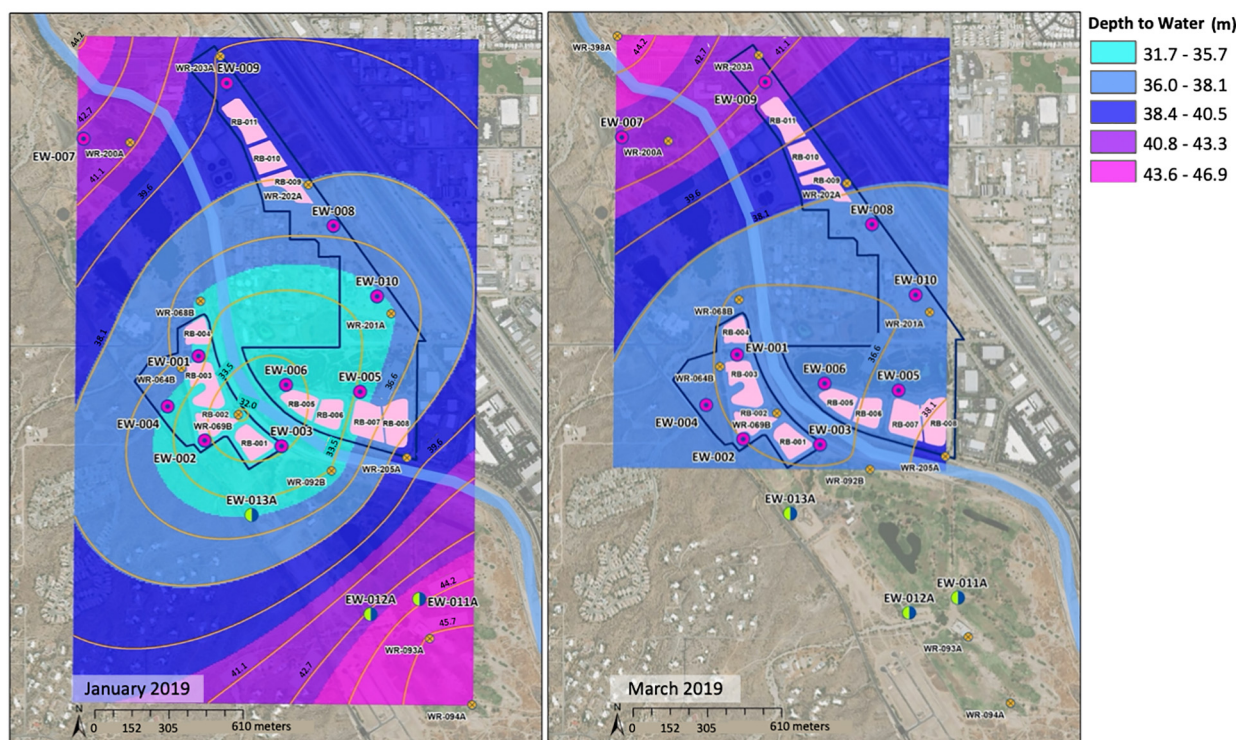


Fig. 6. Depth to water. Light blue is where depth to water is low and purple is where it is deep. The map on the left is of January 2019 when discharge into the basins was high and the one on the right is from March 2019 when recharge was low. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Plant (RRWTP) in prior years of operation. Combined PFOS and PFOA concentrations over time at each reclaimed water production well at the SRF and that of Sample Point 510 were plotted to analyze temporal trends in the SRF (Fig. A.1). As indicated in this plot, the wells in section 1 (EW-001A:EW-004A) have the highest concentrations of PFAS in the SRF, section 2 has the second highest (EW-005A, 6A, 8A, and 10A), and section 3 the lowest (EW-009A). This seems to be the case since 2016 when PFAS was first sampled at the SRF. It is important to note that section 1 is the oldest and has received the most water from RRWTP; on the other hand, section 3 did not receive any water from RRWTP, which further supports this hypothesis. A more definitive analysis would require extensive mathematical modeling, which is beyond the scope of the present study.

Another focus of this study was to analyze the distribution of PFAS at the SRF. The amount of each type of PFAS detected in the SRF was plotted to gain a better understanding of the type of PFAS located at the site (Fig. 4). Eight of the 16 types of PFAS that are part of Tucson Water's PFAS detection analyses were found at the SRF (Table 1). This figure highlights that PFAS concentrations in the oldest parts of the facility are the highest. It also facilitates the individual analyses of each of the 8 PFAS detected in the SRF. As expected, PFOS has the highest concentration in most of the reclaimed water production wells except for EW-009A and EW-007A. Those two wells are the northernmost wells of the SRF, and since PFOS is a long-chained PFAS it is less likely to travel to these wells. Nevertheless, groundwater extracted from these two wells do have PFOS, and given the assumption that RRWTP's effluent is the source, it can be suggested that the PFOS detected in these wells was transported from the older part of the facility. This is verified by the hydraulic gradient and PFOS and PFOA concentration gradients illustrated in Figs. 3 and 4, respectively.

It is important to note that it is only a coincidence that ANWRWF treats wastewater to such an extent that it is filtering PFAS. ANWRWF was not

designed with this purpose; PFAS was yet to be discovered at the SRF when ANWRWF was built, and they are not currently regulated by the US EPA. The ANWRWF receives influent from Tucson, and an ADEQ study noted that there are no known industrial or commercial PFAS facilities within the area (Arizona Department of Environmental Quality (ADEQ), 2018). Thus, the PFAS present in the influent is likely due to the widespread use and disposal of consumer products that contain coatings and polymers of perfluoroalkyl moieties (Buck et al., 2011). Unknowingly the effluent produced by the RRWTP retained the PFAS from the influent and released them into the environment when the effluent was discharged into the recharge basins. PFAS compositions and concentrations can also be modified during the wastewater treatment process (e.g., Weber et al., 2017; Ahrens et al., 2009).

Although the SRF is a unique site, there are similarities to other sites reported in the literature, particularly when it comes to differential transport or chromatographic separation of PFAS with different chain lengths. PFAS with shorter chain lengths (C4-C6) have the tendency to be more mobile in soil and groundwater than PFAS with longer chains (C7+) like PFOS (e.g., Weber et al., 2017; Dauchy et al., 2019; Brusseau et al., 2020; Gagliano et al., 2020). Additionally, PFAS of chain lengths <C8 tend to be more dominant in groundwater (Yong et al., 2021). For groundwater, this behavior is due to the smaller distribution coefficients (K_d) as illustrated in Table 1 (e.g., Guelfo and Higgins, 2013; Higgins and Luthy, 2006). For soil and the vadose zone, the chain-length effect on transport is also due to the impact of air-water interfacial adsorption, wherein shorter-chain PFAS have smaller interfacial adsorption coefficients (Brusseau, 2019).

The distinct total PFAS percentages at different wells in the SRF was examined to gain understanding of the transport trends of different PFAS (Fig. 7). The proportion of shorter chain length PFASs like PFHxS and PFHxA increase downgradient of the Santa Cruz at wells EW-007A and EW-009A, demonstrating the effect of differential transport.

Fig. 5. Water level (lighter color line with triangle symbols) and PFOS and PFOA combined concentrations (darker line with diamond symbols) over time for A) EW-002A, B) EW-005A and C) EW-009A.

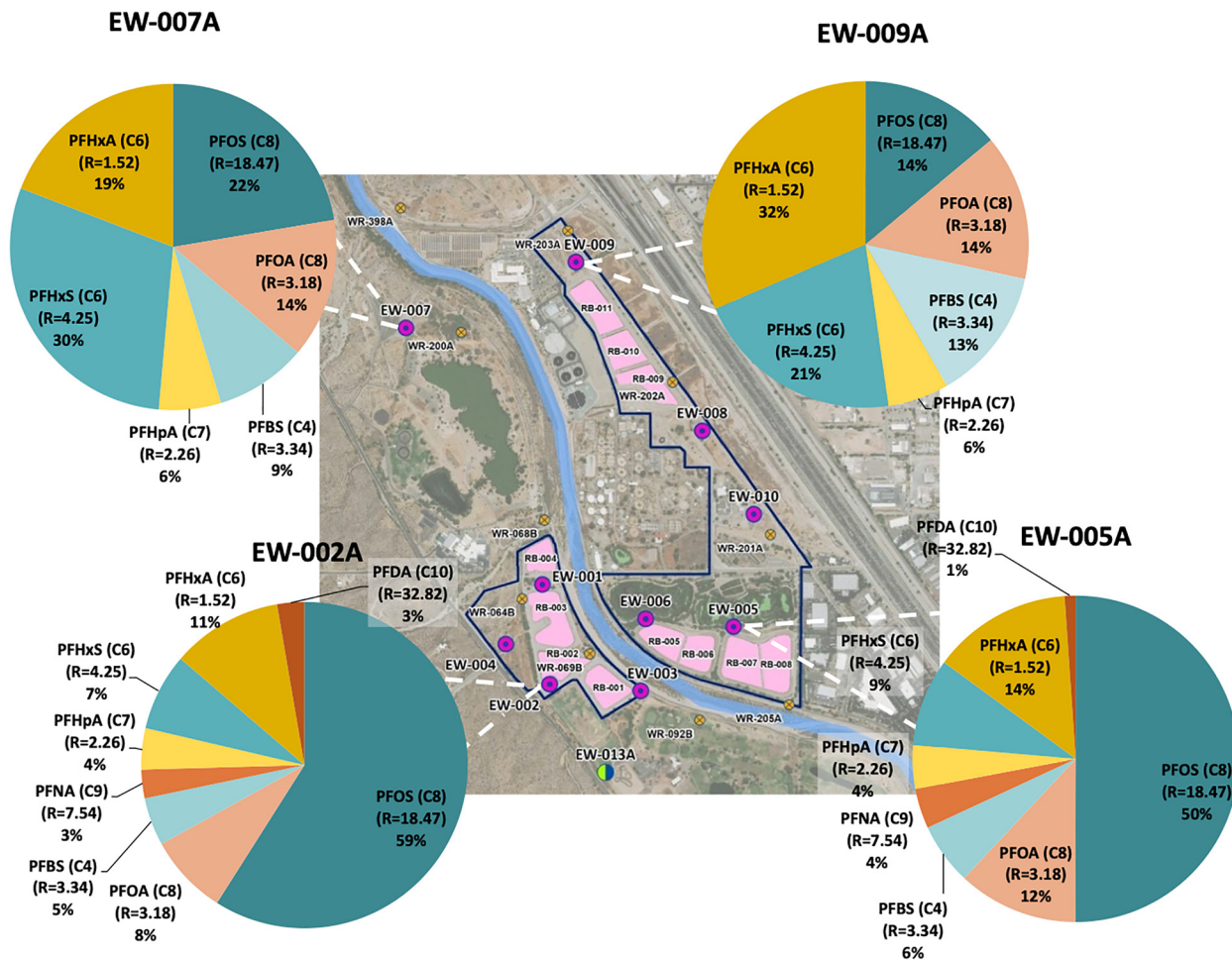


Fig. 7. Change in total PFAS with different reclaimed production well locations. Chain length for each PFAS is indicated by C#, while R indicates the retardation factors.

Conversely, PFAS like PFDA, which has the longest chain length among the PFAS detected at the SRF, is concentrated around the older areas of the facility where most of the RRWTP water was discharged. This observation further supports the hypothesis that RRWTP effluent is the primary source of PFAS. Because the southern and older part of the facility has a total PFAS composition comprised of PFAS with higher retardation factors it can be assumed that this area is the epicenter of PFAS contamination at the SRF.

The relationship among PFAS and their co-occurrence was another factor examined in this study. This was done to assess whether PFAS co-occur and also to study the precursor relationship among some of the PFAS. Among all the extraction wells in the SRF, PFHxS had two of the strongest correlations to PFOS and PFOA (Table A.1 and A.3). This makes sense because PFHxS, PFOS, and PFOA usually co-occur in sites impacted by polymer manufacturing and wastewater treatment plants (Guelfo and Adamson, 2018). Furthermore, PFHxS has been known to be a replacement of PFOS, thus, the presence of PFOS adds to the total concentration of PFHxS. PFOS and PFOA also had a strong positive correlation. Yet, this pair of PFAS are usually found together. PFHpA had high correlations to PFOS and PFOA. PFHpA is not known to be produced intentionally and it is likely due to precursor transformation (Guelfo and Adamson, 2018). PFHxA had a strong relationship with both PFBS and PFDA. PFHxA, PFBS, and PFDA are all used to make grease-resistant coatings; therefore, it makes sense that they would both be found together in wastewater. PFBS is more frequently associated with surface water impacted by PFAS (Guelfo and Adamson, 2018), and perhaps made its way into the groundwater when effluent from RRWTP was released into the Santa Cruz River beginning in 1951. The negative correlation

among PFAS are likely due to differential transport caused by chain-length impact on retardation in the subsurface. For example, in section 2, there is a strong negative correlation between PFDA (C10) and PFHxS (C6). PFDA has a longer chain and thus greater retardation. Therefore, PFHxS will migrate greater distances compared to PFDA, leading to an inverse relationship between the two. This behavior is seen again in section 3 with PFBS (C4) and PFHxS (C6).

6.2. Temporal trends and correlation between recharge into the basins, pumping at SRF, and PFAS concentrations

The second objective for this study was to investigate the relationship between recharge events, pumping events, and combined PFOS and PFOA concentrations at the SRF to evaluate their persistence and transport in the environment. A correlation matrix was made to explore the relationship between pumping from the reclaimed water production wells, volumes discharged into the recharge basins and PFOS+PFOA concentration separated by well and section (Tables A.4 – A.6). To supplement these correlation matrices, the correlation between water table elevations and PFAS for each of the reclaimed water production wells were also determined (Table A.7). The PFAS concentrations sampled from the wells in Section 1 generally have a negative correlation to pumping, suggesting that the wells in this section are more sensitive to pumping (Table A.4). EW-001A was the only well in section 1 that did not have a strong correlation to either pumping or discharge into the recharge basins.

Section 2, like section 1, had a generally negative correlation to pumping (Table A.5). EW-006A, however, had a positive correlation to

pumping. The reason for this inconsistency is unknown but internal Tucson Water studies seem to show this is possibly due to a confining clay layer that impedes water from infiltrating into the aquifer and instead causes it to move laterally and leak through the riverbank (Dick Thompson, personal communication, 2020). This is further supported by EW-006A's strong negative correlation between groundwater elevation and combined PFOS+PFOA concentrations (Table A.7). It seems that for EW-006A, the greater the discharge, the less PFAS the well will draw; furthermore, the potential confining layer could be causing lateral transport into the Santa Cruz riverbank, in turn diluting the PFAS that can reach the groundwater. EW-003A is also close to the river and also has a negative correlation with discharge into the basins, however, groundwater elevations and PFOS+PFOA concentration demonstrated a significant positive correlation. EW-010A had a strong positive correlation to discharge into the recharge basins, suggesting that more recharge will lead to higher PFAS concentrations in this well.

Section 3, consisting of one well, EW-009A, experienced the opposite results to those of section 1 where PFAS concentration were positively correlated to pumping events (Table A.6). This means that PFAS concentrations increase as more pumping occurs, which implies that drawing water from this section is causing water from the older parts of the facility with higher concentrations to travel to section 3. This is further supported by the depth to water maps showing the hydraulic gradients are directed to section 3 and other areas on the outer bounds of the SRF and the negative correlation between water table elevations and PFOS and PFOA concentrations in EW-009A (Table A.7). The preliminary results obtained from these correlation matrices led to further examination of the relationship between water levels and PFAS concentrations in the subsurface.

The PFOS and PFOA combined concentrations for the extraction wells were plotted against the water levels of monitoring wells near the extraction wells to try to determine if there is a connection between PFAS and groundwater elevations (Fig. 5). In 6 of the 10 extraction wells there is a visible positive trend between the two—when water levels increase PFOS+PFOA concentrations increase and vice versa. Furthermore, PFOS+PFOA concentrations in EW-002A:EW-005A have a strong positive correlation to the change in groundwater elevations and this behavior could be indicative of PFOS+PFOA being trapped in the vadose zone (Table A.7). Previous studies that have sampled both groundwater and soil in the vadose zone found that PFOS+PFOA concentrations were orders of magnitude higher than those in the groundwater (Anderson et al., 2019; Guo et al., 2020; Weber et al., 2017; Brusseau et al., 2020). PFOS+PFOA in the vadose zone should be considered a critical and potentially long-term source of groundwater contamination at the SRF (Nakayama et al., 2019). At the SRF, it is hypothesized that as reclaimed water is discharged into the recharge basins, groundwater levels rise, causing PFOS+PFOA to desorb from the air-water interfaces as the vadose zone becomes saturated and air-water interfaces are destroyed. When water stops being discharged in a specific basin, the groundwater levels fall, and the area undergoes drainage and subsequently the PFOS+PFOA adsorbs onto the newly formed air-water interfaces. Infiltration rates were used to estimate the time it would take for the water discharged into the recharge basins to reach the water table (Table A.8). These calculations were done for RB-004 in section 1, RB-008 in section 2, and RB-009 in section 3, because they all have a directly adjacent groundwater elevation monitoring well. Infiltration rates vary greatly from month to month and among basins and are dependent on the frequency of maintenance done to the recharge basins. The variation of infiltration likely causes variation in the release of PFAS and its connection to groundwater levels. Slower infiltration rates could explain the slight delay between PFOS+PFOA and water table elevation peaks and troughs for EW-002A, 4A and 5A. Infiltration rates and water levels for each of these three recharge basins had positive correlations. RB-004 had the highest correlation ($r^2 = 0.72$) and RB-008 and RB-009 had slightly weaker positive correlations ($r^2 = 0.63$ and 0.57 , respectively) (Table A.8).

Besides groundwater table variations caused by recharge events at the surface, the second mechanism for PFAS release from the vadose zone into groundwater is a rising water table due to lateral recharge. It is likely that both mechanisms play a role at the SRF site. To analyze this, it is best to focus on EW-010A since there are no recharge basins around this well. In December of 2018 there is a spike in PFAS concentrations and water table elevations in EW-010A and this spike is also seen in EW-005A, which is adjacent to recharge basins. The similar behavior exhibited by these two wells could be indicative of the rising groundwater table elevation due to lateral recharge (Fig. A.8 and Fig. 7B, respectively). There is no recharge around EW-010A thus the rise in the water table and PFAS are more likely due to lateral recharge. Distinguishing between the two mechanisms is difficult for all the other wells because of the close proximity to other wells and recharge basins. Advanced mathematical models that represent the transient variably saturated flow and the comprehensive PFAS-specific transport processes in the vadose zone including adsorption at air-water and solid-phase interfaces would help to delineate the relative importance of the two mechanisms for PFAS transport (Guo et al., 2020).

Analyzing Fig. A.9 allows for greater insight on the location of PFAS with depth. EW-001A to 4A have the highest concentrations suggesting that the most intense part of the plume is at a higher elevation than the screen intervals of the rest of the wells. However, the elevated concentrations in EW-005A, 8A and 10A—all wells with lower screen intervals—implies that the PFAS is spreading, not only laterally, but vertically as well. EW-009A has similar screen intervals as those of EW-008A and 10A, but again, the low concentrations in that well are probably due to the well's spatial location. This also applies to EW-007A. EW-012A had non-detectable levels of PFAS and the other two remediation wells had PFAS concentrations similar to those observed in EW-009A and 7A, implying that the vadose zone around these wells is probably less contaminated. Furthermore, previous studies have shown that PFAS generally decreases with depth, which could explain why wells with deeper screen intervals have lower PFAS concentrations (Dauchy et al., 2019; Weber et al., 2017). This also suggests that PFAS are influenced more by lateral, rather than vertical groundwater flow.

7. Conclusions

The City of Tucson and other arid areas around the world can conserve water by using alternative sources like reclaimed water for less essential purposes such as turf irrigation. The elevated concentrations of PFAS found in the Sweetwater Recharge Facility has constrained Tucson Water's ability to use the reclaimed water currently in storage in the aquifer. Thus, it is crucial to gain a better understanding of how PFAS is affecting this site. That said, the fate and transport of PFAS at the SRF is very complex. Like other PFAS impacted sites, site-specific characteristics are essential to understanding the way PFAS move in the subsurface. This site and the information gained from it could be used to delineate the processes that affect the fate and transport of PFAS at other managed aquifer recharge sites. Based on the analysis of the PFAS data at the SRF, it is hypothesized that PFAS are trapped in the vadose zone and are flushed and released to groundwater during recharge events. It can also be inferred that PFAS is traveling with the groundwater as it moves outward from the SRF, which is supported by the increase in concentration of more mobile PFAS, such as PFHxA and PFHxS, away from section 1—the oldest part of the facility. This suggests that recharge and pumping events are causing fluctuations in PFAS concentrations in the groundwater. Future studies using advanced mathematical models (e.g., Guo et al., 2020) are needed to test these hypotheses.

Managed aquifer recharge events at the SRF have ceased for the time being until Tucson Water can delineate how PFAS is interacting with the recharged reclaimed water and the groundwater. The SRF has been active for many years and stopping recharge could allow Tucson Water to gain insight as to how to best treat this contaminated groundwater and has narrowed down the factors affecting the transport of PFAS in the

SRF. Continued research during this period will enable better determination of PFAS mobilization in the subsurface. This study points to the need for other wastewater treatment plants to monitor for PFAS, if they are not already. Especially if wastewater treatment plants are recharging the effluent into local aquifers, since PFAS could potentially be polluting local groundwater and accumulating in the vadose zone. Furthermore, facilities such as this one will likely have to monitor the progression of the PFAS trapped in the vadose zone. Sampling of PFAS concentrations in the subsurface will prove to be crucial.

CRedit authorship contribution statement

Tiffani T. Cádiz – Conceptualization, Data curation, Formal Analysis, Visualization, Writing.

Bo Guo – Methodology, Writing

Jennifer C. McIntosh – Conceptualization, Supervision, Visualization, Writing.

Mark L. Brusseau – Methodology, Writing

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.147906>.

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