PFAS in Biosolids

A Southern Arizona Case Study

October, 2020

PIMA COUNTY
WASTEWATER RECLAMATION

PIMA COUNTY
WASTEWATER RECLAMATION

Jacobs

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THE UNIVERSITY OF ARIZONA

This report was made possible through the collaborative efforts of Pima County Regional Wastewater Reclamation Department, Jacobs Engineering, the University of Arizona and the National Science Foundation. This project highlights our commitment to addressing emerging contaminants in our community and our environmental stewardship responsibilities. Together, these efforts are helping USEPA, researchers and our community partners identify and better understand PFAS contaminants, prevent future contamination and effectively communicate risks to the public.

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Executive Summary

Rationale for Study

PFAS are fluorinated compounds that comprise a family of anthropogenic chemicals used for decades to make products resistant to heat, oil stains, grease, and water. Of these, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been the most prominently used in the U.S. PFAS are now regarded by EPA to be "emerging contaminants".

PFAS are known as "forever chemicals" because most are resistant to microbial degradation, so that once introduced into the environment, they persist. They are ubiquitous and found in most soils, sediments, and water. All people in the U.S. are thought to have PFAS in their blood, with longer chain compounds like PFOA and PFOS remain in the body for many years.

Potential household exposure to PFAS include: textiles, carpets, cleaning agents, food wrappers, food products, drinking water, and household dust. Because of potential adverse health effects, PFOS and PFOA were voluntarily phased out of production in the U.S. beginning in the early 2000's and completed by 2015. The potential health effects have not been consistently demonstrated in humans, but laboratory studies indicate changes in liver and thyroid activity and reproductive problems. More recently PFAS have been suspected of being potential carcinogenic agents. Based on this the EPA has established lifetime health advisory limits for drinking water of 70 parts per trillion (ppt) for PFOA and PFOS.[1]

Biosolids are the solid endpoint of wastewater treatment and over 60% of biosolids produced nationally in the U.S. are land applied. In many parts of the country, land application has long been, and remains, the most efficient use for biosolids. In Pima County, 100% of locally produced biosolids have been land applied until recently. Biosolids are a proven effective organic fertilizer with multiple benefits for plant growth, crop production, and soil health. However, they also contain minute amounts of PFAS in the low parts per billion (ppb) range. Because of this the Pima County Board of Supervisors took a conservative approach of enacting a temporary moratorium on land application of biosolids until the risks from PFAS in biosolids could be fully evaluated. In particular, concern was expressed over the possibility of groundwater contamination. This moratorium was initiated January 1, 2020 resulting in a requirement for all biosolids generated in Pima County to be landfilled. This action has doubled management costs for biosolids and removed availability of beneficial product widely employed by local farmers for agricultural production. This action has also been the impetus for this current study, the goal of which was to fully evaluate the potential impact of land application on groundwater contamination by PFAS.

Approach

The study, one of the largest of its kind ever undertaken, was conducted at long term biosolids land application sites in Pima County. Through collaboration between Pima County Regional Wastewater Reclamation and local farmers, agricultural sites were identified where Class B Biosolids had been land applied since 1984, with known recorded application rates. Samples of soil, well water, and biosolids were collected and analyzed for a suite of PFAS compounds. The analyses were conducted by an international certified analytical laboratory, Eurofins TestAmerica, specializing in PFAS determination in soils. During sample collection, strict adherence to recommended precautions for eliminating sample contamination were followed. In all, 109 samples were collected including 72 soil samples at depths of 1, 3 or 6 feet from the surface, 9 groundwater samples from irrigation wells, 4 biosolids samples, and a surface soil sample. Soil and groundwater samples were collected from 5 field types: undisturbed desert soil (no agriculture); irrigated agricultural soil with no biosolids; and irrigated agricultural soils with biosolids at three different cumulative loading rates: ≤20 tons; 21-30 tons; and > 30 tons.

Results and Discussion

Analysis of soil samples from undisturbed sites with no history of land application of biosolids or irrigation were all non-detectable at all soil depths tested. In contrast, samples from irrigated agricultural sites with no history of biosolids application demonstrates low concentrations of PFAS, less than 3 ppb. Analysis of some irrigation waters were also positive for PFAS, suggesting that irrigation alone can be a source of PFAS in soils. PFAS in irrigation water did not appear to correlate to biosolids application. Agricultural soils that were irrigated and received biosolids contained PFAS, but again at very low concentrations. PFAS soil concentrations detected were low and minimally increased with increased biosolids loading, from less than 2 ppb at the lowest biosolids application rate to 4 ppb at the highest loading rate. These concentrations are well

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[1] Environmental Toxic Substance Assessment; Per- and Polyfluoroalkyl Substances (PFAS) in Pima County Water, December 2019.

below health-based screening levels developed for residential soil established by EPA.

Another significant result was the limited migration of PFAS within soils. Even in the irrigated agricultural soils, over 90% of the PFAS was attenuated within the top 6 feet of soil, with the vast majority being trapped in the surface foot of soil. Because depth to groundwater in Pima County regional agricultural areas is typically 150 – 200 feet beneath the surface, contamination of groundwater from biosolids application is extremely unlikely and is supported by the groundwater results.

CONCLUSION

This study took a broad look at PFAS contamination, retention, and migration in farm soils where biosolids were historically land applied. The data presented demonstrates very low concentrations of PFA compounds in soils receiving biosolids with migration attenuated in the first few feet of soil. The concentrations are lower than published health-based screening criteria published by the USEPA. The low concentrations of PFAS in biosolids coupled with depth to groundwater of 150’ – 400’ and Arizona’s low rainfall alleviates help minimize the impact on public health and groundwater.

1. Background

Biosolids provide a nutrient rich, organic soil amendment resulting from anaerobic digestion during wastewater treatment. The land application of biosolids began in 1984 in Pima County and has been proven to consistently enhance soil health. However, in 2020, Pima County Regional Wastewater Reclamation Department (PCRWRD) temporarily halted this practice in order to address concerns regarding PFAS substances and any role biosolids might potentially play in the spread of these contaminants.

While treated wastewater and biosolids are not sources of PFAS, they do reflect the activities of our community and receive PFAS through receipt of consumer product and industrial discharges therefore monitoring for PFAS is appropriate to understanding the transport and migration of these compounds within the environment. PCRWRD, in conjunction with the University of Arizona and Jacobs Engineering, initiated this study to assess the long-term implications for the leaching of PFAS from biosolids and its migration in soils.

PFAS have been manufactured and used by a variety of industries since 1940 and are very resistant to degradation due to the long-chain chemical structure consisting of strong carbon-fluorine bonds. The unique properties of these man-made compounds resulted in durable chemicals and materials with properties that include oil, water, temperature, chemical and fire resistance, as well as electrical insulating. Common applications of PFAS include water and stain repellant materials, coatings and paints, as well as firefighting products. Differences in chemical structure between the PFAS compounds can have important implications as to their mobility, fate and transport in the environment.

The strength of the carbon-fluorine bond also means that these compounds do not easily degrade and while the use of certain PFAS compounds have been discontinued, the unique and durable properties still make PFAS critical to the manufacture of electronic devices including cell phones, tablets and semi-conductors. Even commercial aircraft and electric vehicles rely on PFAS technology. It is estimated that there may be more than 4,000 PFAS in existence[2].

The prevalence of PFAS use has resulted in widespread PFAS contamination of drinking water across the United States. Most prevalent of the PFAS family of compounds in the environment are perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) which were commonly used in the manufacture of aqueous film forming foams (AFFF) for fighting aircraft fuel fires and other industrial and commercial products. Groundwater contamination of PFAS due to the use of AFFF and various manufacturing activities has been documented at numerous military sites, airports, and industrial facilities throughout the United States. Recognizing the public health and environmental harm resulting from these compounds, eight U.S. manufacturers announced a voluntary 95% reduction PFOS and PFOA by 2010 with complete phase-out by 2015, although foreign manufacturing using PFAS chemicals continues.

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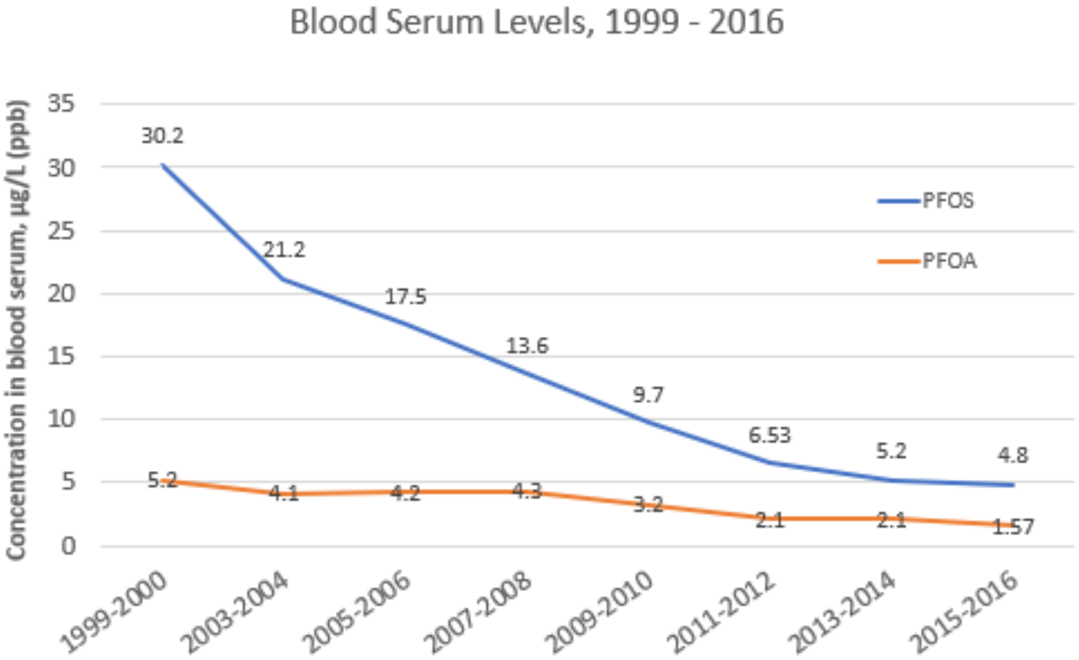
[2] Organization for Economic Cooperation and Development, 2018. Toward a New Comprehensive Global Database of Per- and Polyfluoroalkyl Substances (PFAS) Summary Report.

2. PFAS in Groundwater

Because PFAS chemicals were used extensively and do not degrade in the natural environment, it is estimated that every living person has detectible levels of PFOS and PFOA in their blood. Fortunately, these levels have declined steadily as a result of the manufacturing production phase out of these compounds beginning in 2002.



Data Source: Center for Disease Control and Prevention, Fourth Report on Human Exposure to Environmental Chemicals[3] and represent the median values for the 50th percentile, 95% confidence interval.

To further limit human exposure to these compounds, the USEPA established drinking water health advisory limits of 200 nanograms per liter (ng/L) for PFOS and 400 ng/L for PFOA[3] in 2009. In 2016, USEPA revised the Lifetime Health Advisory (LHA) limits to reflect a combined concentration of 70 ng/L (ppt)[4] in drinking water for both PFOS and PFOA prompting local water providers and PCRWRD to increase monitoring for these compounds with Tucson Water establishing a self-imposed limit of 18 ng/L (ppt).

Existing data and research indicate that detection of PFAS in groundwater is not widespread in Arizona and tends to be localized near firefighting facilities, airports and military sites[5]. Per ADEQ, there are no known large-scale industrial applications or manufacturing facilities within Arizona. Localized PFOS and PFOA contamination of groundwater in the vicinity of Davis-Monthan Air Force Base (DMAFB) and Tucson International Airport (TIA) is well documented and is consistent with the pattern of soil and or water contamination observed across the country. As a result, both Tucson Water and Marana Water have identified groundwater wells exceeding the LHA limit as well as several domestic wells located along the Santa Cruz River.

The historical timeline illustrated on the following page depicts PFAS development and uses, detection of PFAS in local groundwater, and USEPA establishment of public health advisory limits.

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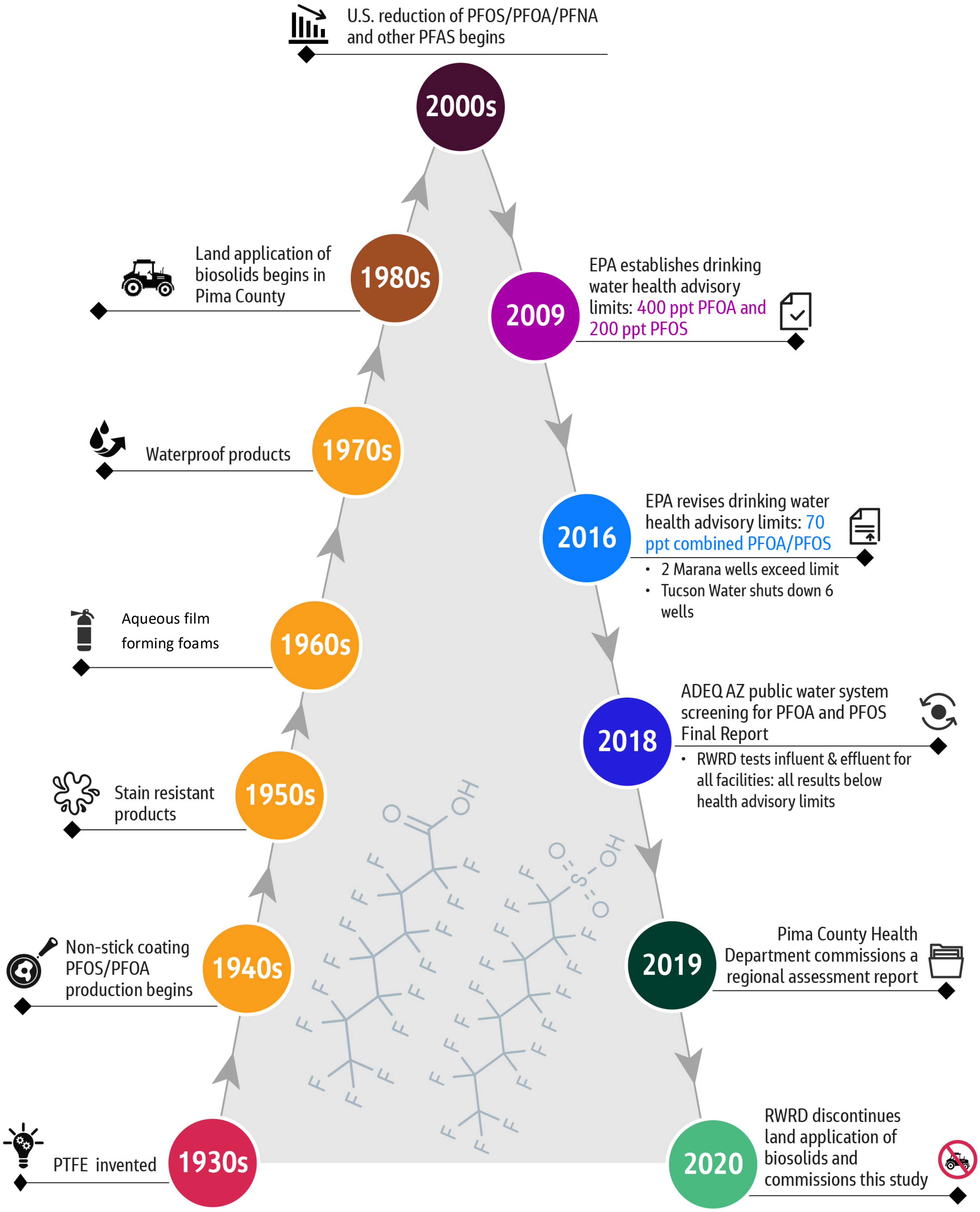
[3] https://www.cdc.gov/exposurereport/

[4] USEPA, May 2016, Drinking Water Health Advisory for PFOS and PFOA. EPA Documents 822-R-16-004 and 822-R-16-005, Office of Water, Health and Ecological Criteria Division.

[5] ADEQ, November 2018



1930s PTFE invented

1940s Non-stick coating PFOS/PFOA production begins

1950s Stain resistant products

1960s Aqueous film forming foams

1970s Waterproof products

1980s Land application of biosolids begins in Pima County

2000s U.S. reduction of PFOS/PFOA/PFNA and other PFAS begins

2009 EPA establishes drinking water health advisory limits: 400 ppt PFOA and 200 ppt PFOS

2016 EPA revises drinking water health advisory limits: 70 ppt combined PFOA/PFOS

- 2 Marana wells exceed limit
- Tucson Water shuts down 6 wells

2018 ADEQ AZ public water system screening for PFOA and PFOS Final Report

- RWRD tests influent & effluent for all facilities: all results below health advisory limits

2019 Pima County Health Department commissions a regional assessment report

2020 RWRD discontinues land application of biosolids and commissions this study

3. PFAS in Wastewater

Wastewater has been shown to contain PFAS due to non-point sources (consumer product use and bodily excretion) as well as point source discharges from industrial sources and AFFF containing source waters. Unfortunately only limited data is available for evaluating historical PFAS concentrations from these sources as increased monitoring coincides with the 2016 lowering of drinking water LHA limits.

Although there are state-issued soil and biosolids values developed for protection of shallow groundwater aquifers, these are not directly applicable to Arizona, or deep aquifer groundwater sources. There are currently no USEPA, Arizona, or local regulatory requirements or standards for PFAS in wastewater effluents or biosolids. To date, both influent and effluent concentrations at all PCRWRD facilities remain below the 70 ng/L (ppt) LHA limit established for drinking water as shown in the following table.

Water Reclamation Facility (WRF)	Location	Sample Date	PFOS ng/L	PFOA ng/L	Total ng/L
Agua Nueva WRF	Influent	12/8/16	7.5	4.6	12.1
	Effluent	12/8/16	6.6	8	14.6
	Effluent	12/29/16	9.9	11	20.9
	Effluent	6/21/17	5.4	7.7	13.1
	Influent	8/29/18	19	3.9	22.9
	Effluent	8/29/18	5.1	6.6	11.7
	Influent	8/26/20	ND	1.9	1.9
	Effluent	8/26/20	4.0	8.5	12.5
Avra Valley WRF	Effluent	12/29/16	1.6	9.2	10.8
	Influent	8/29/18	4.8	1.9	6.7
	Effluent	8/29/18	2.5	8.8	11.3
	Influent	8/26/20	ND	17	17
	Effluent	8/26/20	2.3	7.9	10.2
Corona de Tucson WRF	Effluent	12/29/16	ND	18	18
	Influent	8/29/18	ND	ND	ND
	Effluent	8/29/18	ND	14	14
	Influent	8/26/20	ND	1.5	1.5
	Effluent	8/27/20	1.5	17	18.5
Green Valley WRF	Effluent	12/29/16	2.8	26	28.8
	Influent	8/29/18	ND	4	4
	Effluent	8/29/18	4.5	28	32.5
	Influent	8/26/20	ND	4.3	4.3
	Effluent	8/26/20	3.4	31	34.4
Tres Rios WRF	Effluent	12/29/16	8.6	9	17.6
	Influent	8/29/18	5.5	5.1	10.6
	Effluent	8/29/18	4.2	6.1	10.3
	Influent	8/26/20	4.1	7.1	11.2
	Effluent	8/26/20	3.7	7.1	10.8

4. Project Sampling Plan

To assess the impact of PFAS concentrations within soils based on Pima County biosolids applied to local agricultural sites, PCRWRD developed a sampling strategy to determine PFAS levels found in various soil types based on the following criteria:

Undisturbed Soils
Sites indicative of ambient PFAS in the environment and reflective of air deposition and rainfall only. These sites are differentiated by;

- No agricultural activities
- No biosolids application
- No irrigation

Agricultural
Traditional agricultural sites indicative of PFAS contributions from routine farming practices consisting of applications of pesticides and contribution from irrigation water. These sites are differentiated by;

- No biosolids application
- Irrigated with groundwater

Group 1
Agricultural sites indicative of PFAS contributions resulting from low application rates of Pima County biosolids and of the shortest duration. These sites are differentiated by;

- Cumulative biosolids application is limited to ≤20 tons with a total application duration of 4-9 years.
- Irrigated with groundwater

Group 2
Agricultural sites indicative of PFAS contributions resulting from intermediate application rates of Pima County biosolids over a period an extended duration of time. These sites are differentiated by;

- Cumulative biosolids applications between 21 – 30 tons over a 12-20 year duration.
- Irrigated with groundwater

Group 3
Agricultural sites indicative of PFAS contributions resulting from heaviest application rate of Pima County biosolids over a short duration of time. These sites are differentiated by;

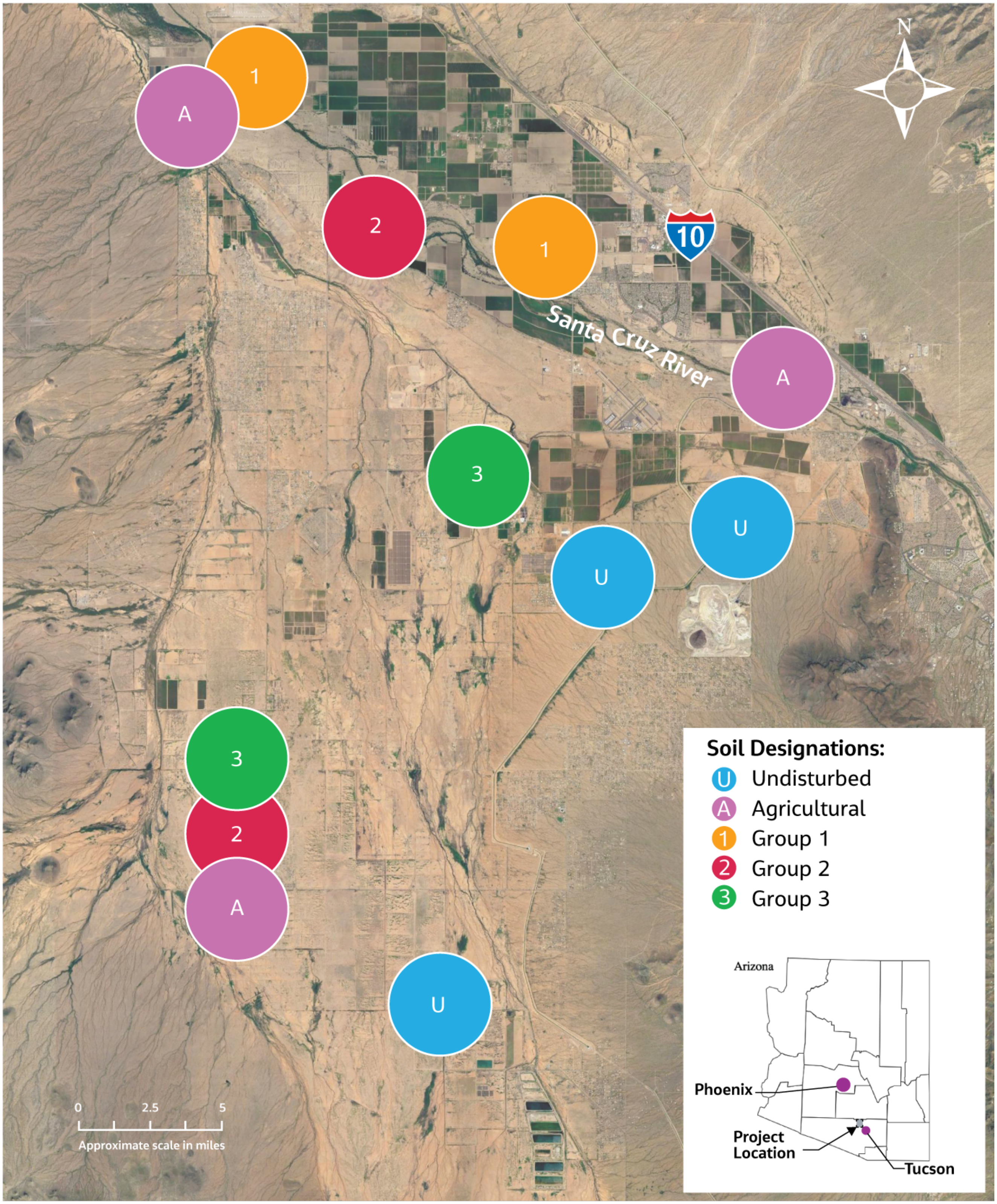
- Cumulative biosolids applications of >30 tons with a total application duration of 6-9 years.
- Irrigated with groundwater

The following table summarizes the project sample plan criteria.

	Soil Designation	Selection Criteria			
		Agricultural	**Irrigated**	**Biosolids Applied**	**Application Years**
🟦	**Undisturbed**	-	-	-	-
🟪	**Agricultural**	✓	✓	-	-
🟧	**Group 1**	✓	✓	≤ 20 tons/acre	4 - 9
🟥	**Group 2**	✓	✓	21-30 tons/acre	12 – 20
🟩	**Group 3**	✓	✓	> 30 tons/acre	6 - 9

5. Soil Sample Locations

The map below illustrates the general locations of soil samples taken for each soil group. Sample locations are situated northwest of Tucson within Pima County and two locations within Pinal County (not shown).



6. Study Methodology

This graphic illustrates the PFAS sampling zone in relation to groundwater depths for the agricultural sampling regions.

Soil samples were obtained from a distribution of locations with multiple sample locations representing each soil group category.

Soil sampling was conducted by use of hand-operated augers, from which samples were collected from a single 3.25” borehole at depths of 1-ft, 3-ft, and 6-ft below the surface.

Strict protocol were followed to prevent PFAS contamination during sampling.

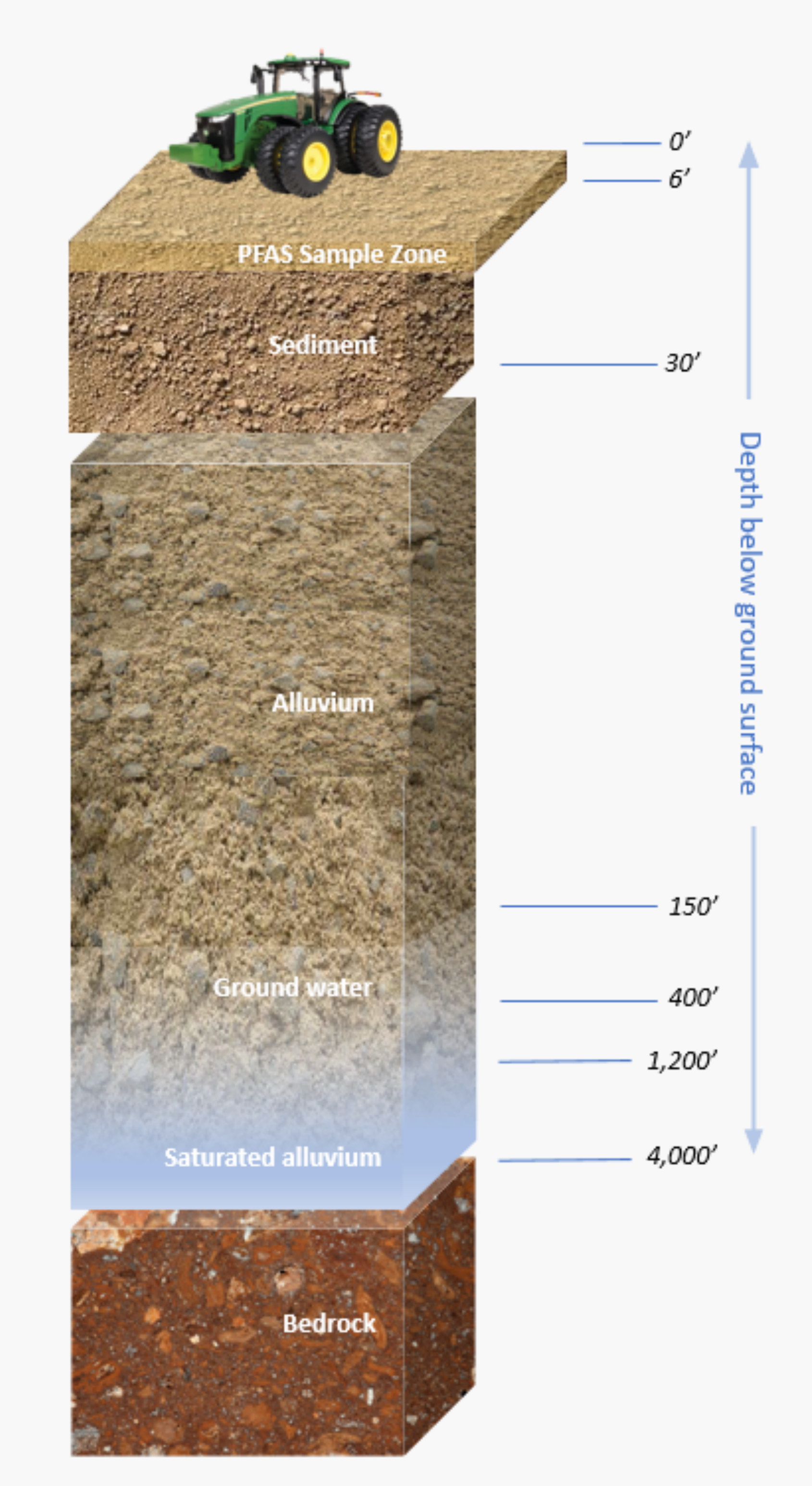
A surface sample representing undisturbed soil from a location in close proximity to long-term application sites was obtained for assessing possible airborne dust deposition of PFAS on adjacent properties resulting from routine agricultural activities.

Biosolids from the County’s Tres Rios Wastewater Reclamation Facility were sampled on four occasions.

Nine irrigation wells providing irrigation to the agricultural soil groups were sampled.

A total of 18 PFAS analytes were tested for soils, biosolids, and irrigation wells.

A complete list of PFAS analytes tested is provided in the appendix, with the best available analytical methods, reporting limits (RL), and the method detection limit (MDL) for each analyte.



7. PFAS Study Results

Biosolids

The Table below summarizes the PFAS test results for dewatered biosolids samples collected on 4 occasions at PCRWRD's Tres Rios WRF.

Location	TRES RIOS WRF			
Sample Date	7/16/2020	7/16/2020	7/27/2020	7/27/2020
Units	µg/kg (ppb)			
PFAS Contaminant				
DONA	ND	ND	ND	ND
F-53B (Major)	ND	ND	ND	ND
F-53B (Minor)	ND	ND	ND	ND
GenX	ND	ND	ND	ND
NEtFOSAA	ND	ND	ND	**11**
NMeFOSAA	21	22	23	**18**
PFBS	1.9	1.4	6.5	ND
PFDA	**12**	**13**	**12**	**12**
PFDoA	8	7.3	7.4	**6.5**
PFHpA	ND	ND	ND	0.15
PFHxS	3.7	3.5	15	ND
PFHxA	4.2	4.0	4.1	**2.0**
PFNA	ND	2.0	2.0	**1.1**
PFOS	**34.0**	**36**	**27**	**14**
PFOA	ND	ND	ND	**1.2**
PFTeA	3.2	3.3	ND	ND
PFTriA	ND	ND	ND	ND
PFUnA	2.3	2.1	2.4	1.8
Moisture	**81.7%**	**82.0%**	**81.0%**	**80.7%**

Notes:

µg/kg = micrograms of contaminant per kilogram of dry weight of biosolids, equivalent to parts per billion (ppb).

Black values indicate values above the method detection limit (MDL)

Blue values indicate values above the method reporting limit (MRL)

The results indicate extremely low levels of PFAS compounds and are consistent with previous concentrations from samples analyzed in 2017. These levels are consistent with domestic biosolids concentrations and not reflective of industrial contributions. Appendix Table A.3 provides reference PFAS data for comparison with other states.

Irrigation Source Wells

The table below summarizes the PFAS results for samples taken of irrigation source wells. Multiple irrigation sources are depicted for each soil group.

	AGRICULTURAL SITES			GROUP 1		GROUP 2		GROUP 3	
Contaminant	ng/L (ppt)			ng/L (ppt)		ng/L (ppt)		ng/L (ppt)	
DONA	ND	ND	ND	ND	ND	ND	ND	ND	ND
F-53B (Major)	ND	ND	ND	ND	ND	ND	ND	ND	ND
F-53B (Minor)	ND	ND	ND	ND	ND	ND	ND	ND	ND
GenX	ND	ND	ND	ND	ND	ND	ND	ND	ND
NEtFOSAA	ND	ND	ND	ND	ND	ND	ND	ND	ND
NMeFOSAA	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFBS	10	ND	3.8	ND	1.4	ND	0.68	0.68	3.6
PFDA	1.9	ND	ND	ND	ND	ND	ND	ND	0.57
PFDoA	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFHpA	5.3	ND	3.2	0.28	0.98	ND	0.26	ND	1.9
PFHxS	34	0.30	20	0.24	7.7	0.3	0.76	0.52	7.0
PFHxA	14	ND	8.6	ND	1.9	ND	ND	2.2	6.9
PFNA	3.4	ND	0.57	ND	0.28	ND	ND	ND	0.63
PFOS	80	ND	26	ND	11	0.53	ND	ND	15
PFOA	20	ND	9.1	ND	3.1	ND	0.81	ND	5.0
PFTeA	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFTriA	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFUnA	ND	ND	ND	ND	ND	ND	ND	ND	ND

Notes:
ND indicates not-detected.
ng/L = ppt
Black indicates values above the method detection limit (MDL)
Blue values indicate values above the method reporting limit (MRL)

OBSERVATIONS:

✓ PFAS was detected in all irrigation sources; some of the highest detected concentrations, including PFOS, are near biosolids-free locations

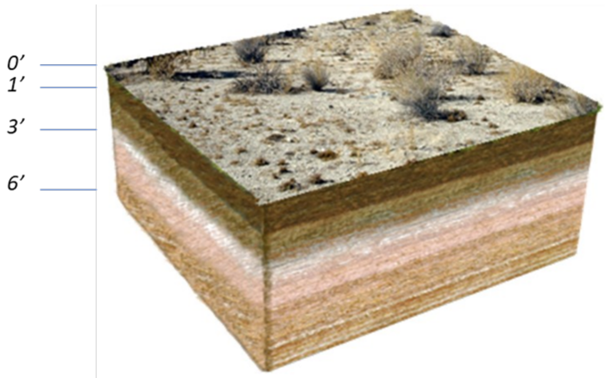
✓ PFAS concentrations are highest in irrigation wells that never received biosolids

Soil Samples

PFAS soil test results are summarized in the following pages for each of the 5 soil groups and irrigation wells associated with the agricultural sites.

Undisturbed Soils

- Non-Agricultural History
- Non-Irrigated
- Non-Biosolids Applied



The following data represents the mean of four soil boring locations at three depths for the PFAS analytes listed. All of the undisturbed soil sample locations have no history of agricultural activity but were located near agricultural sites.

An additional surface soil sample location was selected approximately 0.3 miles from agricultural parcels receiving the highest loading of biosolids to assess possible airborne dust deposition of PFAS generated during farming operations on nearby properties and residents.

Depth	**Surface**	**1’**	**3’**	**6’**
Contaminant	µg/kg (ppb)			
DONA	ND	ND	ND	ND
F-53B (Major)	ND	ND	ND	ND
F-53B (Minor)	ND	ND	ND	ND
GenX	ND	ND	ND	ND
NEtFOSAA	ND	ND	ND	ND
NMeFOSAA	ND	ND	ND	ND
PFBS	ND	ND	ND	ND
PFDA	ND	ND	ND	ND
PFDoA	ND	ND	ND	ND
PFHpA	ND	ND	ND	ND
PFHxS	ND	ND	ND	ND
PFHxA	ND	ND	ND	ND
PFNA	ND	ND	ND	ND
PFOS	ND	ND	ND	ND
PFOA	ND	ND	ND	ND
PFTeA	ND	ND	ND	ND
PFTriA	ND	ND	ND	ND
PFUnA	ND	ND	ND	ND
Moisture		5.1%	5.8%	5.5%

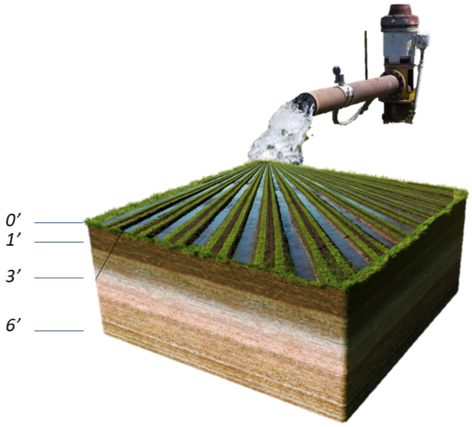
Notes:
ND indicates not-detected at the MDL

OBSERVATIONS:

- ✓ PFAS were not detected or were below the MDL for each analyte.
- ✓ PFAS was not detected in surface soil samples collected adjacent to sites receiving the highest loading of biosolids.
- ✓ The lack of PFAS detections in surface soil suggests PFAS is not transported significantly by airborne dust from local agricultural fields.

Agricultural Soils

- History of Agriculture
- Irrigated
- Non-Biosolids Applied



The following data represent the mean of four soil boring locations at each depth for agricultural soils. These land parcels represent historically farmed locations receiving groundwater irrigation but have not received biosolid applications. The table also indicates the presence of PFAS in the irrigation wells used for these land parcels.

Depth	1'	3'	6'	PFAS present in Irrigation Wells
Contaminant	µg/kg (ppb)			
DONA	ND	ND	ND	
F-53B (Major)	ND	ND	ND	
F-53B (Minor)	ND	ND	ND	
GenX	ND	ND	ND	
NEtFOSAA	ND	ND	ND	
NMeFOSAA	ND	ND	ND	
PFBS	0.03	ND	ND	✓
PFDA	0.05	ND	ND	✓
PFDoA	ND	ND	ND	
PFHpA	0.05	0.03	0.04	✓
PFHxS	0.07	0.06	0.09	✓
PFHxA	0.09	0.06	0.05	✓
PFNA	0.08	ND	ND	✓
PFOS	**1.85 ± 1.2**	**0.59 ± 0.37**	0.25 ± 0.17	✓
PFOA	**0.26 ± 0.14**	0.18 ± 0.12	**0.22 ± 0.09**	✓
PFTeA	ND	ND	ND	
PFTriA	ND	ND	ND	
PFUnA	ND	ND	ND	
Moisture	10.9%	12.1%	12.3%	
PFOS Attenuation	**N/A**	**63%**	**84%**	

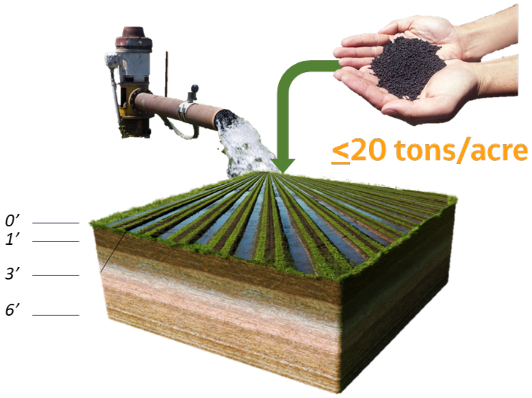
Notes:
N/A: Not applicable
ND indicates not-detected at the MDL.
Black values indicate above the MDL.
Blue values indicate values above the MRL.

OBSERVATIONS:

- ✓ PFOS and PFOA detected at very low concentrations.
- ✓ PFAS detected in soils are the same compounds detected in irrigation water.
- ✓ PFAS presence in irrigation source water likely contributes to PFAS detected in soil.
- ✓ PFOS concentration is observed to decrease (attenuate) with depth.
- ✓ 84% PFOS attenuation at 6'.

Group 1 – Agricultural soils amended with biosolids with a total of ≤ 20 tons/acre

- History of Agriculture
- Irrigated
- Biosolids Applied over 4-9 years



The following data represent the mean of four soil boring locations at the three depths. These land parcels have been farmed, received irrigation and received biosolid applications. The table also indicates which PFAS compounds were detected in the irrigation wells and biosolids used for these land parcels.

Depth	1’	3’	6’	PFAS present in	
Contaminant	µg/kg (ppb)			Biosolids	Irrigation Wells
DONA	ND	ND	ND		
F-53B (Major)	ND	ND	ND		
F-53B (Minor)	ND	ND	ND		
GenX	ND	ND	ND		
NEtFOSAA	ND	ND	ND		
NMeFOSAA	ND	ND	ND		
PFBS	ND	0.08	0.04	✓	✓
PFDA	0.10	ND	ND	✓	
PFDoA	ND	ND	ND	✓	
PFHpA	0.08	0.06	ND	✓	✓
PFHxS	0.10	0.17	0.04	✓	✓
PFHxA	0.14	0.11	ND	✓	✓
PFNA	0.06	ND	ND	✓	✓
PFOS	**1.58 ± 1.76**	0.29 ± 0.20	ND	✓	✓
PFOA	**0.32 ± 0.33**	**0.26 ± 0.26**	ND	✓	✓
PFTeA	ND	ND	ND	✓	
PFTriA	ND	ND	ND		
PFUnA	ND	ND	ND	✓	
Moisture	7.8%	9.5%	9.9%		
PFOS Attenuation	N/A	**82%**	**100%**		

Notes:
N/A: Not applicable
ND indicates not-detected at the MDL.
Black values indicate values above the MDL.
Blue values are above the MRL.

OBSERVATIONS:

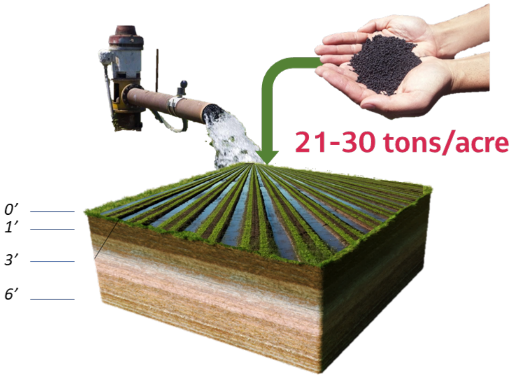
✓ PFOS and PFOA detected at very low concentrations and comparable to agricultural sites never receiving biosolids.

✓ PFOA and PFOS concentrations decrease (attenuate) with increased depth.

✓ Approximately 100% PFOS attenuation by 6’.

Group 2 – Agricultural soils amended with biosolids with a total of 21-30 tons/acre

- History of Agriculture
- Irrigated
- Biosolids Applied over 12-20 years



The following data represent the mean of four soil boring locations at the three depths. These land parcels have been farmed, received irrigation, and received biosolid applications of 21-30 tons/acre. The table also indicates which PFAS compounds were detected in the irrigation wells and biosolids used for these land parcels.

Depth	1’	3’	6’	PFAS present in	
Contaminant	µg/kg (ppb)			Biosolids	Irrigation Wells
DONA	ND	ND	ND		
F-53B (Major)	ND	ND	ND		
F-53B (Minor)	ND	ND	ND		
GenX	ND	ND	ND		
NEtFOSAA	ND	ND	ND		
NMeFOSAA	ND	ND	ND		
PFBS	0.17	0.10	0.12	✓	✓
PFDA	0.56	0.06	0.05	✓	
PFDoA	0.04	ND	ND	✓	
PFHpA	0.09	0.09	0.06	✓	✓
PFHxS	0.03	0.04	0.05	✓	✓
PFHxA	0.13	0.09	0.09	✓	
PFNA	**0.43**	0.12	ND	✓	
PFOS	**3.11 ± 2.06**	**0.64 ± 0.31**	**0.22 ± 0.09**	✓	✓
PFOA	**0.47 ± 0.29**	**0.49 ± 0.18**	**1.65 ± 2.38**	✓	✓
PFTeA	ND	ND	ND	✓	
PFTriA	ND	ND	ND		
PFUnA	ND	ND	ND	✓	
Moisture	5.3%	10.5%	10.2 %		
PFOS Attenuation	N/A	**79%**	**93%**		

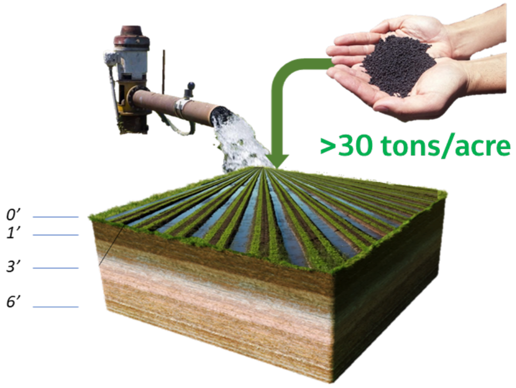
Notes:
N/A: Not applicable
ND indicates not-detected at the MDL.
Black values indicate values above the MDL.
Blue values indicate values above the MRL.

OBSERVATIONS:

- ✓ The main soil contaminants are PFOA and PFOS at low concentrations.
- ✓ PFOA and PFOS concentrations decrease with increased depth.
- ✓ 93% PFOS attenuation by 6’.

Group 3 – Agricultural soils amended with biosolids with a total of >30 tons/acre

- History of Agriculture
- Irrigated
- Biosolids Applied over 6-9 years



The following data represent the mean of four soil boring locations at the three depths. These land parcels have been farmed, received irrigation, and have received biosolid applications of greater than 30 tons/acre. The table also indicates which PFAS compounds were detected in the irrigation wells and biosolids used for these land parcels.

Depth	1′	3′	6′	PFAS present in	
Contaminant	µg/kg (ppb)			Biosolids	Irrigation Wells
DONA	ND	ND	ND		
F-53B (Major)	ND	ND	ND		
F-53B (Minor)	ND	ND	ND		
GenX	ND	ND	ND		
NEtFOSAA	ND	ND	ND		
NMeFOSAA	ND	ND	ND		
PFBS	**0.37**	**0.20**	0.14	✓	✓
PFDA	**0.98**	0.11	0.15	✓	✓
PFDoA	**0.24**	ND	0.08	✓	
PFHpA	**0.19**	0.16	**0.24**	✓	✓
PFHxS	0.12	0.15	0.16	✓	✓
PFHxA	**0.51**	**0.22**	0.13	✓	✓
PFNA	**0.43**	0.15	0.05	✓	✓
PFOS	**4.13 ± 1.86**	**1.22 ± 1.36**	**0.46 ± 0.46**	✓	✓
PFOA	**0.84 ± 0.48**	**1.32 ± 1.43**	**0.51 ± 0.61**	✓	✓
PFTeA	0.09	ND	ND	✓	
PFTriA	ND	ND	ND		
PFUnA	0.10	ND	ND	✓	
Moisture	9.5%	8.9%	10%		
PFOS Attenuation	**N/A**	**84%**	**90%**		

Notes:
N/A: Not applicable
ND indicates not-detected at the MDL.
Black values indicate values above the MDL.
Blue values indicate values above the MRL.

OBSERVATIONS:

- ✓ PFOS concentration remains very low.
- ✓ PFOS on soil with biosolids slightly higher than agricultural soils without biosolids
- ✓ PFOS levels decrease with increased depth.
- ✓ 90% PFOS attenuation by 6′.

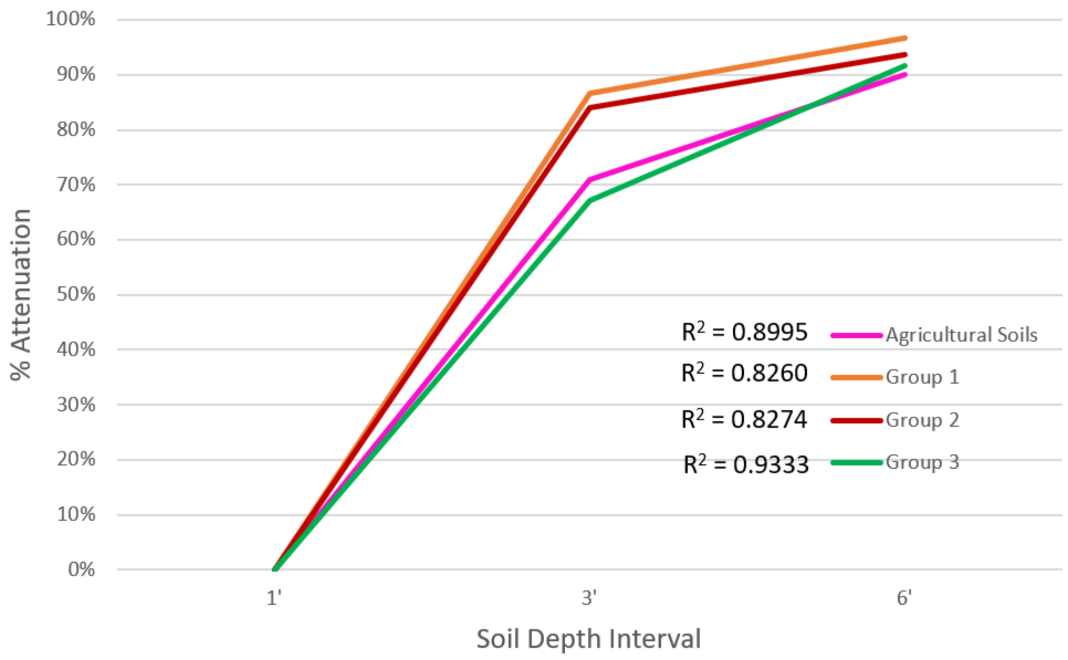
PFOS Attenuation with Soil Depth

% Attenuation	No Biosolids Agriculture Only			≤20 tons/acre Group 1 Soils				21-30 tons/acre Group 2 Soils			>30 tons/acre Group 3 Soils				
	3 locations			4 locations				3 locations			5 locations				
3’	67%	85%	75%	89%	84%	93%	91%	60%	81%	92%	55%	67%	84%	87%	93%
6’	85%	-	95%	95%	97%	-	-	85%	93%	-	86%	94%	92%	-	97%

PFOS concentrations are depicted at the 3’ and 6’ depths in comparison to the 1’ depth concentrations as percent attenuated, or percentage reduced, with depth. The data demonstrates diminishing PFOS concentrations within the first few feet of soil indicating minimal migration of PFOS in the soils. This is likely attributed to the low concentrations of PFOS in Pima County biosolids, lower than average biosolids loading rates, and low moisture conditions of the arid southwest conditions existing in Pima County.

PFAS compounds in biosolids are effectively adsorbed to both biosolids and colloidal soil particles and typically remain near the air-water interface region of the soil. Intermittent irrigation intervals and a lack of saturated soil conditions, and low soil moisture, effectively minimizes migration of PFAS compounds substantially. Despite intermittent irrigation cycles, PFOS appears to remain sorbed in the upper layer of soil.

The average attenuation for each soil group indicates a strong correlation of PFAS remaining sorbed in the first few feet of soil with minimal migration. Surprisingly, the agricultural only soils never receiving biosolids are nearly identical to the soils receiving the highest loading of biosolids with 90%-97% total attenuation at the 6’ depth for all soil groups.



8. Conclusion

Wastewater treatment provides a vital public health service and creates residual solids that every community must manage. Throughout the United States, high quality biosolids are recycled and put to productive use every day as beneficial soil amendments for enhancing soil health, increasing water holding capacity, recycling nutrients and reducing fertilizer and pesticide use, and restoring degraded lands. Farmers nationwide rely on biosolids applications because it works.

PFAS compounds are very resistant to degradation due to the long-chain chemical structure and strong carbon-fluorine bonds. While differences in chemical structure between the various PFAS compounds can have important implications affecting their mobility and transport in the environment, most of the PFAS compounds analyzed for this study remained tightly adsorbed within the upper soil layers with little migration into the soil depths. In particular, PFOS exhibited excellent attenuation with soil depth in all cases. PFOS soil concentrations detected were minimally increased with increased biosolids loading, from less than 2 ppb at the lowest biosolids application rate (Group 1) to approximately 4 ppb at the highest loading rate (Group 3).

The results of this study assessing regional long-term biosolids land application sites indicate that biosolids produced and land applied in Pima County pose minimal risks to ground water contamination, accumulation in soils, or impacts to adjacent properties and neighbors. The limited solubility of PFAS entering soil via land application, coupled with the low mobility and unsaturated soil conditions of the arid southwest, effectively sequesters these compounds within the upper soil surface layers.

While PFAS contamination in the environment continues to garner nationwide scrutiny, source control efforts have been demonstrated to by highly effective for reducing contamination. As a result of the manufacturing phase out of these compounds and source control management, concentrations of these compounds will continue to diminish in both wastewater influents, effluents and biosolids products.

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Appendix

A.1 Glossary of Terms

Accuracy: The degree to which a measured value agrees with the true value of the measured property. USEPA recommends that this term not be used, and that the terms precision and bias be used to convey the information associated with the term accuracy.

ADEQ: Arizona Department of Environmental Quality.

Aqueous Film Fighting Foam (AFFF): A fire suppressant used to extinguish flammable liquid fires such as fuel fires.

Anaerobic Digestion: A sequence of processes by which microorganisms break down biodegradable material in the absence of oxygen.

Analyte: The substance or chemical constituent being sought or measured in an analytical procedure.

Approved Method: An analytical test procedure or technique authorized by the Arizona Department of Health Services to test for the presence of a particular contaminant or characteristic and includes an alternate method approved by the Department under R9-14-610(C) and an approved method used with a method alteration approved by the Department under R9-14-610(C).

Biosolids: Biosolids are the nutrient-rich organic byproducts resulting from wastewater treatment. Biosolids have been treated and tested and meet strict federal and state or provincial standards for use as fertilizers and soil amendments.

Blank: A synthetic sample, free of the analyte(s) of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample. In general, blanks are used to assess possible contamination or inadvertent introduction of analyte during various stages of the sampling and analytical process.

Compound: A compound is a substance formed when two or more chemical elements are chemically bonded together. In mixtures, the substances present are not chemically bonded together.

Dry Weight: The weight of a sample based on percent solids. The weight after drying in an oven.

Duplicate: A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

Duplicate Samples/Field Duplicates (FD): Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

Equipment Blank: A sample of water which, prior to use, is known to be free of contaminants, and which is processed through the sampling equipment in the field in the same manner as the actual water sample to determine if field procedures introduce contaminants into the samples. This is critical in PFAS sampling, due to the pervasiveness of PFAS in various items.

Emerging Contaminant: synthetic or naturally occurring chemicals or any microorganisms that are not commonly monitored in the environment but have the potential to enter the environment and cause known or suspected adverse ecological and/or human health effects.

Field Blank: Usually an aqueous solution that is as free of analyte as possible and is transferred from one vessel to another at the sampling site and preserved with the appropriate reagents. This serves as a check on reagent and environmental contamination. One field blank should be analyzed with each analytical batch or every 20 samples, whichever is greater.

Method: A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed.

Method Detection Limit (MDL): The minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.

Method Reporting Limit (MRL): The minimum concentration of a contaminant reported after analyzing a sample, determined after corrections have been made for sample dilution and sample weight.

mg/L: milligrams per liter.

ND: Not detected. Below the Method Detection Limit.

ng/g: nanograms per gram.

ng/L: nanograms per liter.

Parameter: A specified characteristic of a population or sample. Also, an analyte or grouping of analytes. PFAS and PFOS are all “parameters.”

ppb: parts per billion

ppt: parts per trillion

Percent Moisture: An approximation of the amount of water in a soil/sediment sample made by measuring the weight before and after drying an aliquot of the sample at 105^{o}C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below 105^{o}C. Percent moisture may be determined from decanted samples and from samples that are not decanted.

Percent Relative Standard Deviation (%RSD): A statistic used to evaluate precision in environmental analysis.

Per- and polyfluoroalkyl substances (PFAS): A group of man-made chemicals that includes PFOA, PFOS, GenX, and many other chemicals.

pH: a figure expressing the acidity or alkalinity of a solution on a logarithmic scale on which 7 is neutral, lower values are more acid and higher values more alkaline.

Replicate samples: Two or more samples taken from the environment at the same time and place, using the same protocols. Replicates are used to estimate the random variability of the material sampled.

RWRD: Regional Wastewater Reclamation Department.

Sample Number (Lab Sample Number): A unique identification number designated by LIMS for each sample. The Lab sample number appears on the sample Chain-of-Custody, which documents information on that sample.

Standard Deviation (SD): In statistics, the standard deviation is a measure of the amount of variation or dispersion of a set of values. A low standard deviation indicates that the values tend to be close to the mean (also called the expected value) of the set, while a high standard deviation indicates that the values are spread out over a wider range.

USEPA: United States Environmental Protection Agency.

µg/L: micrograms per liter

A.2 PFAS Analytes and Methods

	ANALYTE	Carbon Chain Link	Method RL/MDL	
			537.1 Water (ng/L) (ppt)	**537 Mod Solids/Biosolids (µg/kg) (ppb)**
1	Perfluorohexanoic acid (PFHxA)	6	2.00/0.500	0.2/0.042
2	Perfluoroheptanoic acid (PFHpA)	7	2.00/0.500	0.2/0.029
3	Perfluorooctanoic acid (PFOA)	8	2.00/0.500	0.2/0.086
4	Perfluorononanoic acid (PFNA)	9	2.00/0.500	0.2/0.036
5	Perfluorodecanoic acid (PFDA)	10	2.00/0.500	0.2/0.022
6	Perfluoroundecanoic acid (PFUnA)	11	2.00/0.500	0.2/0.036
7	Perflurododecanoic acid (PFDoA)	12	2.00/0.500	0.2/0.067
8	Perfluorotridecanoic acid (PFTriA)	13	2.00/0.500	0.2/0.051
9	Perfluorotetradecanoic acid (PFTeA)	14	2.00/0.500	0.2/0.054
10	Perfluorobuanesulfonic acid (PFBS)	4	2.00/0.500	0.2/0.025
11	Perfluorohexanesulfonic acid (PFHxS)	6	2.00/0.500	0.2/0.031
12	Perfluorooctanesulfonic acid (PFOS)	8	2.00/0.500	0.5/0.200
13	N-ethylperfluorooctanesulfonamidoacetic acid (NEtFOSAA)	8	2.00/0.500	2/0.370
14	N-methylperfluorooctanesulfonamidoacetic acid (NMeFOSAA)	8	2.00/0.500	2/0.390
15	F-53B Major	10	2.00/0.500	0.2/0.027
16	HFOP-DA (Gen-X)	5	2.00/0.500	0.25/0.110
17	F-53B Minor	8	2.00/0.500	0.2/0.022
18	DONA	6	2.00/0.500	0.2/0.018

NOTES:
RL – Method Reporting Limit
MDL – Method Detection Limit
ng/L - nanograms per liter = parts per trillion, ppt
µg/kg – micrograms per kilogram = parts per billion , ppb

A.3 Comparison Data

A comparison of results obtained for this study to other similar studies recently conducted in the U.S., which reported PFAS levels in biosolids and soils receiving biosolids, is shown below.

Biosolids PFAS Comparisons

LOCATION	PFOA (µg/kg) ppb	PFOS (µg/kg) ppb
Pima County, 2017 - 2020	ND – 1.9 (average=1.6)	14 – 36 (average=28.4)
Maine, 2019	0.6 – 46 (average=8.5)	3.2 – 120 (average=25.4)
Massachusetts, 2019	ND – 15.1	4.7 - 120
New Hampshire, 2017	2.3	5.3
Georgia, 2007	80.3	58.7
Zareitalabad ET AL., 2013, research publication	37	69
Sepulvado ET AL., 2011, research publication	8 - 68	80 - 219
Venkatesan AND Halden, 2013, research publication	12 – 70 (average=34)	308 – 618 (average=403)

Notes: µg/kg = ppb

As shown, the relatively low levels of PFAS reported in PCRWRD biosolids may be due in part to a lack of industrial manufacturing facilities of PFAS in Pima County which may reach the sewer.

The table below compares soil PFAS levels where biosolids were applied.

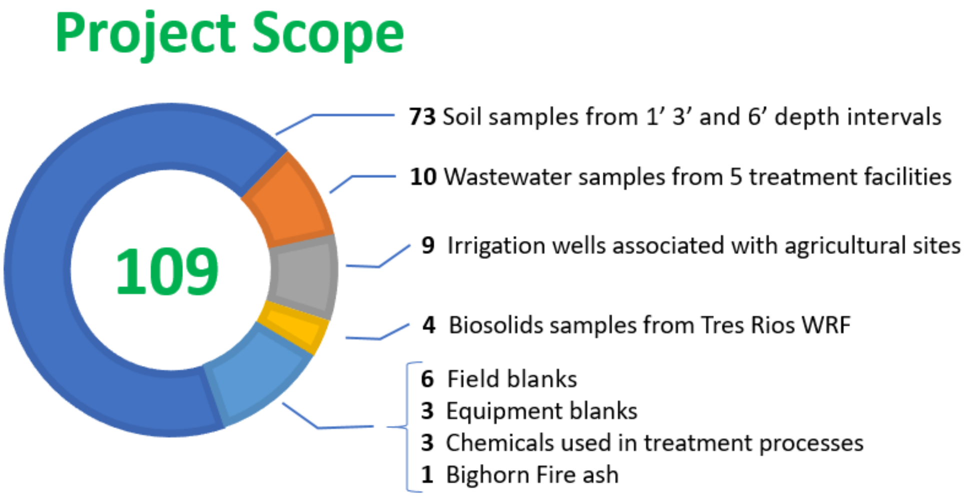
SOIL PFAS Comparisons

LOCATION	PFOA (µg/kg) ppb	PFOS (µg/kg) ppb
Pima County, 2020, background locations, 1’ depth	0.26	1.85
receiving biosolids <20 tons, 1’ depth	0.32	1.58
receiving biosolids 21 - 30 tons, 1’ depth	0.38	2.48
receiving biosolids >30 tons, 1’ depth	0.84	4.13
Vermont, 2019, 66 background soil locations	0.52 – 4.9	0.11 – 9.7
Vermont, 2019, 107 tests at 28 sites, biosolids amended soils	0.3 – 4.6	0.3 – 35.6
Maine, 2019, 29 sites receiving biosolids for 20+ years	12.9	2.1 – 20.9

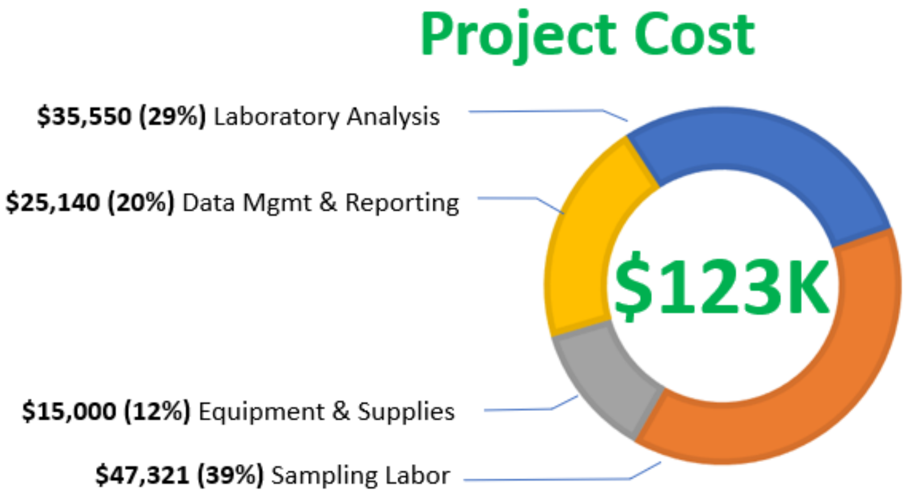
Notes: µg/kg = ppb

Although difficult to draw a direct comparison due to the highly variable nature of biosolids application practices and other local environmental variations, PFAS concentrations observed in PCRWRD soil receiving biosolids with a cumulative loading of >30 tons/acre over a 20-year period were substantially lower than soil concentrations observed in other states. It is important to note that soil concentrations at any site receiving biosolids were well below USEPA Soil screening levels regardless of location.

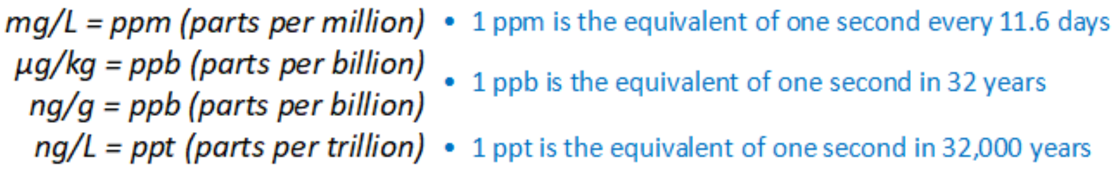
A.4 Study Metrics



A total of 109 samples were collected and submitted for laboratory analysis for both PFAS compounds and soil and groundwater characterization. In total, over 2,506 individual parameters were analyzed.

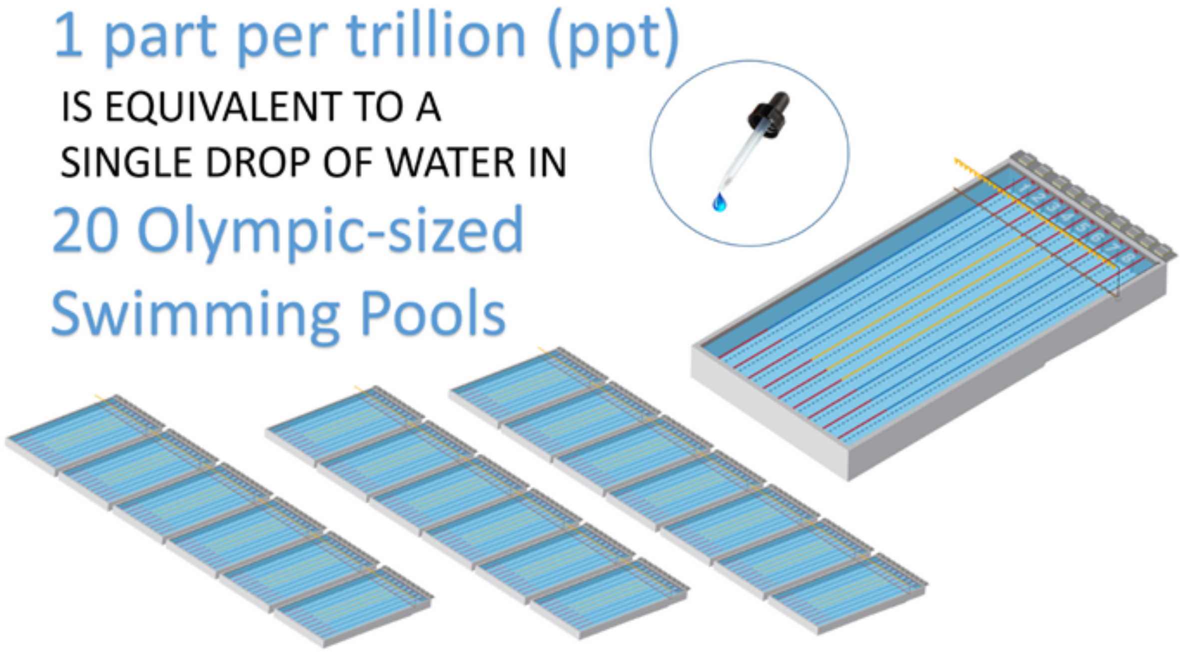


A.5 Things to Know



mg/L = ppm (parts per million)
µg/kg = ppb (parts per billion)
ng/g = ppb (parts per billion)
ng/L = ppt (parts per trillion)

- 1 ppm is the equivalent of one second every 11.6 days
- 1 ppb is the equivalent of one second in 32 years
- 1 ppt is the equivalent of one second in 32,000 years



1 part per trillion (ppt)
IS EQUIVALENT TO A
SINGLE DROP OF WATER IN
20 Olympic-sized
Swimming Pools

PIMA COUNTY