Madison Water Utility

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To: Water Utility Board members

From: Joe Grande, Water Quality Manager

Date: October 22, 2019

Subject: Report on PFAS Monitoring

Background

In February, the Water Utility Board directed staff to commence with PFAS [per- and polyfluoroalkyl substance] testing at all Madison wells using a modified EPA method capable of detecting a minimum of 24 PFAS with reporting limits in the low single-digit part per trillion range. This new requirement expanded PFAS monitoring beyond monthly testing at Well 15 – a well significantly impacted by PFAS contamination – and the more limited monitoring at wells presumably susceptible to contamination. The directive increased the number of PFAS evaluated from six to at least two dozen.

In preparing the monitoring plan, Madison wells were categorized by potential PFAS contamination risk based on well construction and proximity to known or suspected PFAS sources. Those classified among the most vulnerable included multi-aquifer wells with previous detections of organic contaminants such as PCE [tetrachloroethylene] or 1,4-dioxane.

Two private laboratories were already under contract to perform the analysis and so they continued to do this work. In addition, the Wisconsin State Laboratory of Hygiene was developing its capacity for PFAS analysis and working toward lab certification for EPA Method 537.1, the only EPA-approved standard method for PFAS analysis. Scientists from the state lab offered to collect and analyze samples, including field blanks, at no charge to the utility. Sample collection began in earnest during March and April, with all wells except the seasonal wells sampled during this period. Testing of the seasonal wells concluded in September.

This report summarizes the results of our 2019 PFAS monitoring and makes recommendations for future PFAS monitoring.

Monitoring Results Summary & Analysis

Of the twenty-three Madison wells tested, fourteen showed the presence of at least one PFAS while nine wells were free of all PFAS tested. Of the nine wells with no PFAS detections, six had been tested for 30 PFAS while the remaining three wells were tested for 24 PFAS.

The highest concentrations of total PFAS were found at Well 15 (56 ppt), Well 9 (52 ppt), and Well 23 (43 ppt) – see Figure 1. At other wells, most PFAS detections were too low to quantify accurately and, therefore, were reported by the laboratory as estimated values. At six wells, this estimated total PFAS level ranged from 2 to 10 ppt while at the remaining three wells the estimated PFAS level was between 10 and 20 ppt.

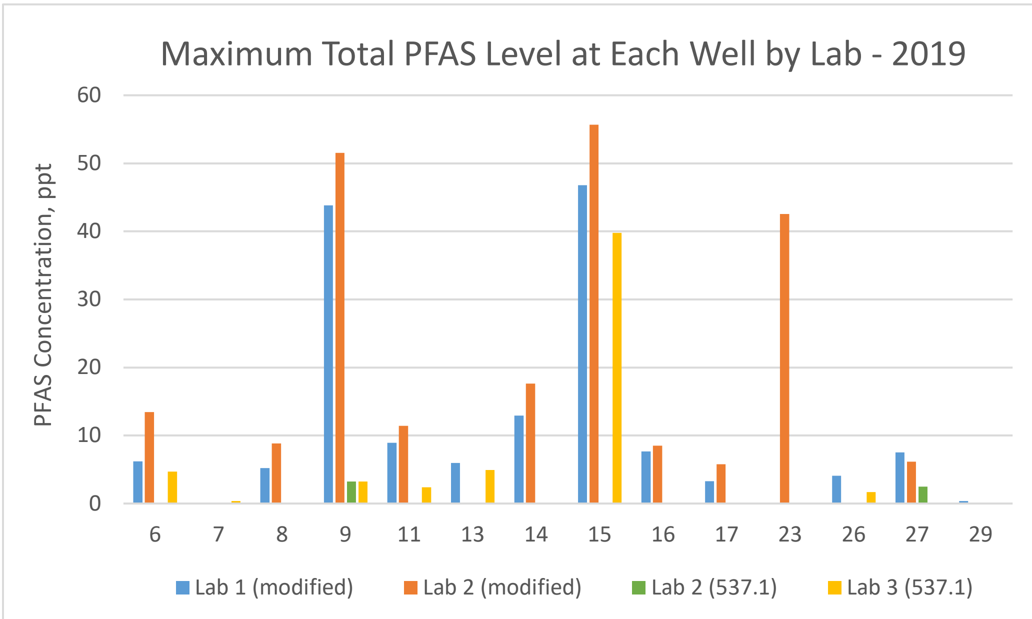


Figure 1. Composite results for fourteen wells where at least one PFAS was found in 2019.

Combined PFOA + PFOS levels at all wells were below 20 ppt, the groundwater enforcement standard recently proposed by the Wisconsin Department of Health Services. The highest PFOA + POS level is found at Well 15 where it measured 12 ppt. The next highest level was 6.6 ppt at Well 23, a seasonal well that has not delivered water to the system since 2017 due to other water quality concerns.

Individual PFAS rarely occur in isolation; more often, a mixture of six or more PFAS were found. The PFAS most commonly detected in Madison wells included PFHxS, PFOA, PFBA, PFOS, PFHxA, and PFHpA – see Table 1. A single PFAS chemical – PFHxS and *N*-EtFOSA – was found at Wells 7 and 29, respectively, at levels estimated at 0.4 parts per trillion (ppt).

Figures 3 through 14 show the range of results for each PFAS chemical detected at a well by at least one laboratory. For example, Figure 3 shows that water from Well 6 was tested by one lab in March and by three labs in April including the same lab that tested the March sample. PFHxS was detected in all four samples at levels ranging from 2.8 to 4.5 ppt. If an individual PFAS was not detected by that laboratory, an empty bar with dashed outlines depicts the detection limit for that PFAS. Figure 3 shows that PFHxA was detected by Labs 2 and 3 at levels ranging from 0.7 to 1.3 ppt; however, PFHxA was not detected by Lab 1 where the detection limit was 8.8 ppt. Table 2 presents a complete list of the method detection and reporting limits for all three laboratories.

A comparison of how individual PFAS test results vary across Madison wells is depicted in Figures 15 through 17. For example, Figure 16b shows that PFHxS was detected at thirteen wells and Well 15 has the highest level at around 20 ppt. However, most wells in which PFHxS was present tested at 1-5 ppt. It should be noted that Figures 15 through 17 report estimated values (measurements between the detection limit and the method reporting limit, and depicted by orange bars) in addition to the more reliable results that test above the method reporting limit (blue bars).

Table 1. Summary of all PFAS detected in Madison wells including the results for the well with the highest level of each PFAS.

PFAS	Number of Wells with Detections	Maximum Level Detected, ppt	Well with Highest Detection
PFBA	12	42	9
PFBS	9	3.4	15
PFPeA	8	5.9	15
PFPeS	4	3.2	15
PFHxA	10	6.2	15
PFHxS	13	21	15
PFHpA	10	2.5	15
PFHpS	1	0.3 (estimate)	15
PFOA	12	6.1	15
PFOS	11	5.9	15
FOSA	5	3.2	8
***N*-EtFOSA**	2	0.4 (estimate)	29
6:2 FTS	4	3.9 (estimate)	27

Figure 17d compares the results for FOSA and 6:2 FTS. It is noteworthy that for both PFAS each was detected only during one sampling event, detected only by a single laboratory, and the PFAS was also detected in the method blank. Further, the figure shows the detection limits from previous or subsequent samples in which the PFAS was not found. While we are reporting the results, some uncertainty remains as to whether they are reliable or reflect lab contamination. The ubiquitous nature of PFAS and inherent challenges with ultra-trace chemical analysis leads to a healthy skepticism regarding the validity of test results especially in the low or sub part per trillion range. Nevertheless, routine monitoring in the future is expected to diminish this uncertainty as patterns begin to emerge with more data points.

Finally, not surprisingly, PFAS affected more multi-aquifer wells than confined aquifer wells. Ten of the fourteen multi-aquifer wells were impacted by PFAS with seven having at least eight PFAS present. The three remaining wells had between four and six PFAS present. Only two of nine confined aquifer wells had more than a single PFAS present. Although well construction provides some level of protection, it alone does not eliminate the risk from PFAS contamination of drinking water.

<u>Comparison of Laboratories and Analytical Methods</u>

Over the last year, three laboratories provided PFAS analytical services to the Water Utility. Each used a different analytical approach. The State Lab of Hygiene tested a subset of Madison wells employing an EPA-approved, standard method for drinking water (EPA Method 537.1). This test method quantifies 18 PFAS including four next generation or alternative PFAS using a liquid chromatography tandem mass spectrometry (LC/MS/MS) technology. The detection limits are typically below 0.5 ppt for each PFAS – see Table 2.

Two private contract laboratories used a modified EPA Method 537 protocol to analyze 24 to 30 PFAS with similarly low detection limits. Detection and reporting limits for each PFAS are shown in Table 2. Test results from these two labs are not directly comparable, though, because each lab independently refined their own internal version of the test procedure. However, each lab used technology similar to that employed by the State Lab of Hygiene to quantify PFAS.

Testing to date shows that EPA Method 537.1, when compared to the modified methods, consistently results in lower total PFAS concentrations due primarily to the fact that the method tests for a smaller number of PFAS – see Figure 2. Furthermore, our limited analysis also suggests that EPA Method 537.1 may produce results lower than what is obtained by the modified methods when only the same 18 PFAS are considered. In other words, EPA Method 537.1 may underreport the "true" amount of PFAS present in a water sample.

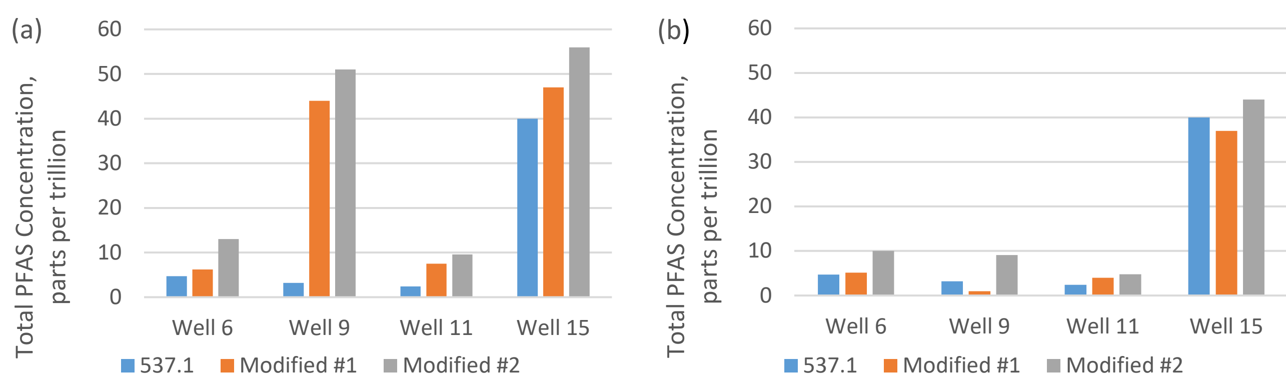


Figure 2. Comparison of PFAS results from three different analytical methods when considering (a) all PFAS measured by each method or (b) the 18 PFAS covered by EPA Method 537.1.

Although EPA Method 537.1 is the only standard method for the analysis of PFAS in drinking water, it may not be the best analytical method for quantifying PFAS in water.

Recommendations for Future Testing

The Water Utility has gained important experience with PFAS analytical methods and, in particular, challenges associated with accurately measuring low levels of ultra-trace contaminants such as PFAS in drinking water. While EPA Method 537.1 is the standard method for measuring PFAS in drinking water, the method proved inadequate for quantifying the full range of PFAS present in Madison wells.

Recommendations for future PFAS testing include:

- Test all Madison wells at least once in 2020.
- Select a single laboratory for future testing to standardize the analytical methodology and allow for time-related comparisons.
- Consistently use the same modified EPA Method 537 for all PFAS analysis to facilitate detection of a wider range of PFAS than EPA Method 537.1.
- Use EPA Method 537.1 if directed by US EPA or Wisconsin DNR unless the modified method has been designated an "equivalent or better" method for PFAS analysis in drinking water.

Table 2. Method detection and reporting limits for laboratories using EPA Method 537.1 and modified Method 537 to quantify PFAS.

Per- and PolyfluoroAlkyl Substance (PFAS)	Acronym	Method Detection Limit, ng/L or ppt				Method Reporting Limit, ng/L or ppt			
		Lab 1 537 modified	Lab 2 537 modified	Lab 2 537.1	Lab 3 537.1	Lab 1 537 modified	Lab 2 537 modified	Lab 2 537.1	Lab 3 537.1
Perfluorobutanoic acid	**PFBA**	0.40	0.30 - 0.35			4.2 - 4.5	1.7 - 2.0		
Perfluorobutanesulfonic acid	**PFBS**	0.28	0.17 - 0.20	0.44 - 0.47	0.38 - 0.45	4.2 - 4.5	1.7 - 2.0	1.8 - 1.9	1.3 - 1.5
Perfluoropentanoic acid	**PFPeA**	1.7	0.41 - 0.49			4.2 - 4.5	1.7 - 2.0		
Perfluoropentane sulfonic acid	**PFPeS**	1.6	0.25 - 0.30			4.2 - 4.5	1.7 - 2.0		
Perfluorohexanoic acid	**PFHxA**	8.8	0.49 - 0.58	0.44 - 0.47	0.39 - 0.46	9.2	1.7 - 2.0	1.8 - 1.9	1.3 - 1.5
Perfluorohexanesulfonic acid	**PFHxS**	1.3	0.14 - 0.17	0.44 - 0.47	0.11 - 0.13	4.2 - 4.5	1.7 - 2.0	1.8 - 1.9	0.37 - 0.44
Perfluoroheptanoic acid	**PFHpA**	0.63	0.21 - 0.25	0.44 - 0.47	0.27 - 0.32	4.2 - 4.5	1.7 - 2.0	1.8 - 1.9	0.89 - 1.1
Perfluoroheptane sulfonic acid	**PFHpS**	0.44	0.16 - 0.19			4.2 - 4.5	1.7 - 2.0		
Perfluorooctanoic acid	**PFOA**	0.35	0.72 - 0.85	0.44 - 0.47	0.19 - 0.23	1.7 - 1.8	1.7 - 2.0	1.8 - 1.9	0.64 - 0.75
Perfluorooctanesulfonic acid	**PFOS**	0.44	0.46 - 0.54	0.44 - 0.47	0.11 - 0.14	4.2 - 4.5	1.7 - 2.0	1.8 - 1.9	0.38 - 0.45
Perfluorononanoic acid	**PFNA**	1.1	0.23 - 0.27	0.44 - 0.47	0.16 - 0.19	4.2 - 4.5	1.7 - 2.0	1.8 - 1.9	0.52 - 0.62
Perfluorononane sulfonic acid	**PFNS**	0.59	0.13 - 0.16			4.2 - 4.5	1.7 - 2.0		
Perfluorodecanoic acid	**PFDA**	1.2	0.26 - 0.31	0.44 - 0.47	0.23 - 0.27	4.2 - 4.5	1.7 - 2.0	1.8 - 1.9	0.76 - 0.90
Perfluorodecane sulfonic acid	**PFDS**	0.30	0.27 - 0.32			4.2 - 4.5	1.7 - 2.0		
Perfluoroundecanoic acid	**PFUnA**	1.5	0.93 - 1.1	0.44 - 0.47	0.41 - 0.48	4.2 - 4.5	1.7 - 2.0	1.8 - 1.9	1.4 - 1.6
Perfluorododecanoic acid	**PFDoA**	1.3	0.46 - 0.55	0.44 - 0.47	0.35 - 0.42	4.2 - 4.5	1.7 - 2.0	1.8 - 1.9	1.2 - 1.4
Perfluorotridecanoic acid	**PFTrDA**	1.3	1.1 - 1.3	0.44 - 0.47	0.22 - 0.27	4.2 - 4.5	1.7 - 2.0	1.8 - 1.9	0.75 - 0.88
Perfluorotetradecanoic acid	**PFTeDA**	2.0	0.24 - 0.28	0.44 - 0.47	0.24 - 0.28	4.2 - 4.5	1.7 - 2.0	1.8 - 1.9	0.79 - 0.93
Perfluorooctanesulfonamide	**FOSA**	0.52	0.30 - 0.35			4.2 - 4.5	1.7 - 2.0		
N-Methyl perfluorooctane sulfonamide	***N*-MeFOSA**	0.46				4.2 - 4.5			
N-Ethyl perfluorooctane sulfonamide	***N*-EtFOSA**	0.27				4.2 - 4.5			
N-Methyl perfluorooctane sulfonamidoacetic acid	***N*-MeFOSAA**	1.4	2.6 - 3.1	0.44 - 0.47	0.22 - 0.26	4.2 - 4.5	17 - 20	1.8 - 1.9	0.75 - 0.88
N-Ethyl perfluorooctane sulfonamidoacetic acid	***N*-EtFOSAA**	0.50	1.6 - 1.9	0.44 - 0.47	0.19 - 0.22	4.2 - 4.5	17 - 20	1.8 - 1.9	0.62 - 0.73
N-Methyl perfluorooctane sulfonamidoethanol	***N*-MeFOSE**	0.30				4.2 - 4.5			
N-Ethyl perfluorooctane sulfonamidoethanol	***N*-EtFOSE**	0.13				4.2 - 4.5			
4:2 Fluorotelomer sulfonic acid	**4:2 FTS**	0.81	4.4 - 5.2			4.2 - 4.5	17 - 20		
6:2 Fluorotelomer sulfonic acid	**6:2 FTS**	0.55	1.7 - 2.0			4.2 - 4.5	17 - 20		
8:2 Fluorotelomer sulfonic acid	**8:2 FTS**	0.15	1.7 - 2.0			4.2 - 4.5	17 - 20		
10:2 Fluorotelomer sulfonic acid	**10:2 FTS**	0.35				4.2 - 4.5			
HFPA-DA / HFPO-DA	**GenX**	0.29		0.44 - 0.47	0.38 - 0.45	4.2 - 4.5		1.8 - 1.9	1.3 - 1.5
ADONA	**ADONA**			0.44 - 0.47	0.29 - 0.34			1.8 - 1.9	0.96 - 1.1
F-53B Major	**F-53B Major**			0.44 - 0.47	0.13 - 0.15			1.8 - 1.9	0.42 - 0.52
F-53B Minor	**F-53B Minor**			0.44 - 0.47	0.25 - 0.29			1.8 - 1.9	0.83 - 0.98

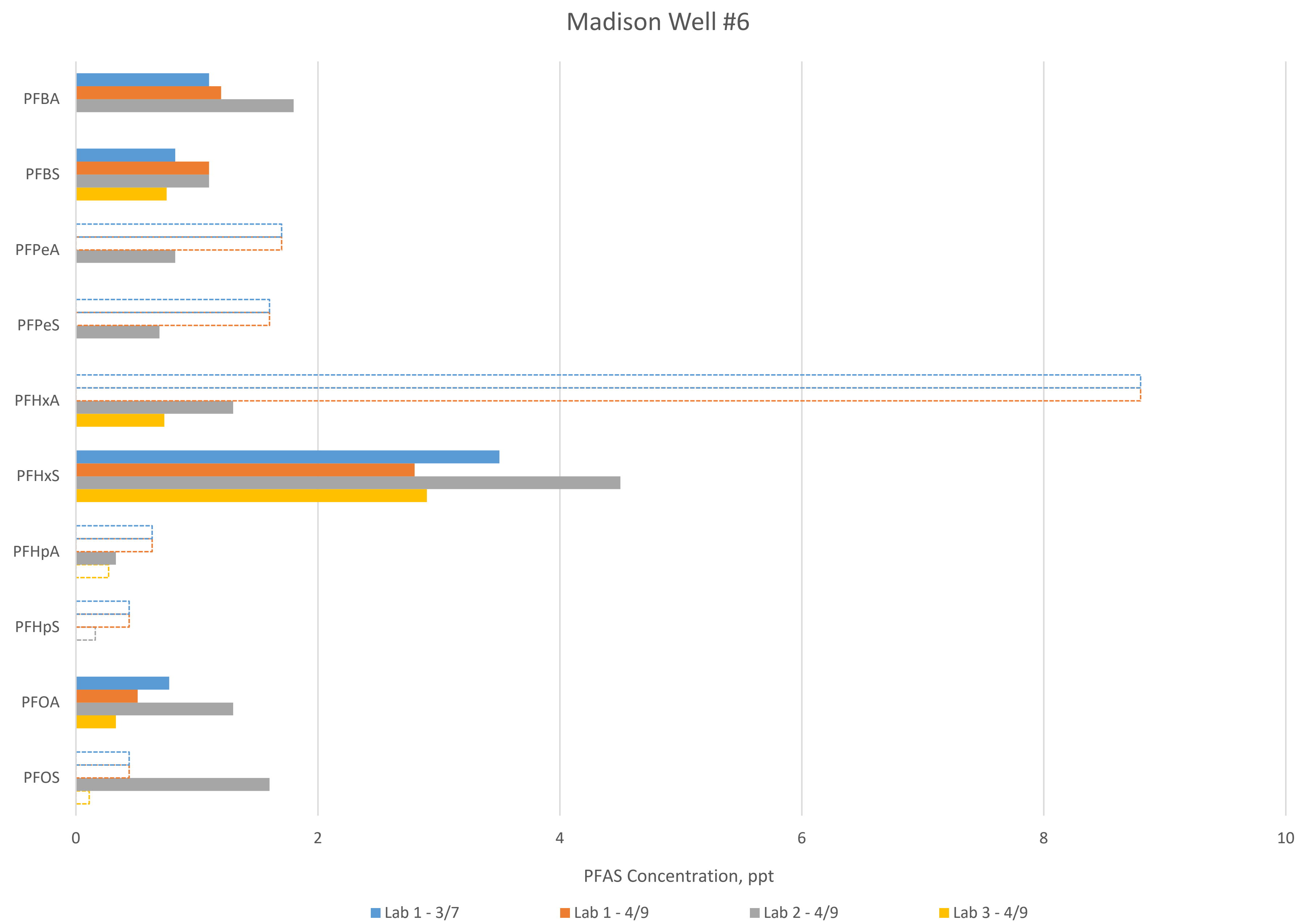


Figure 3. PFAS detections at Madison Well 6, a multi-aquifer well

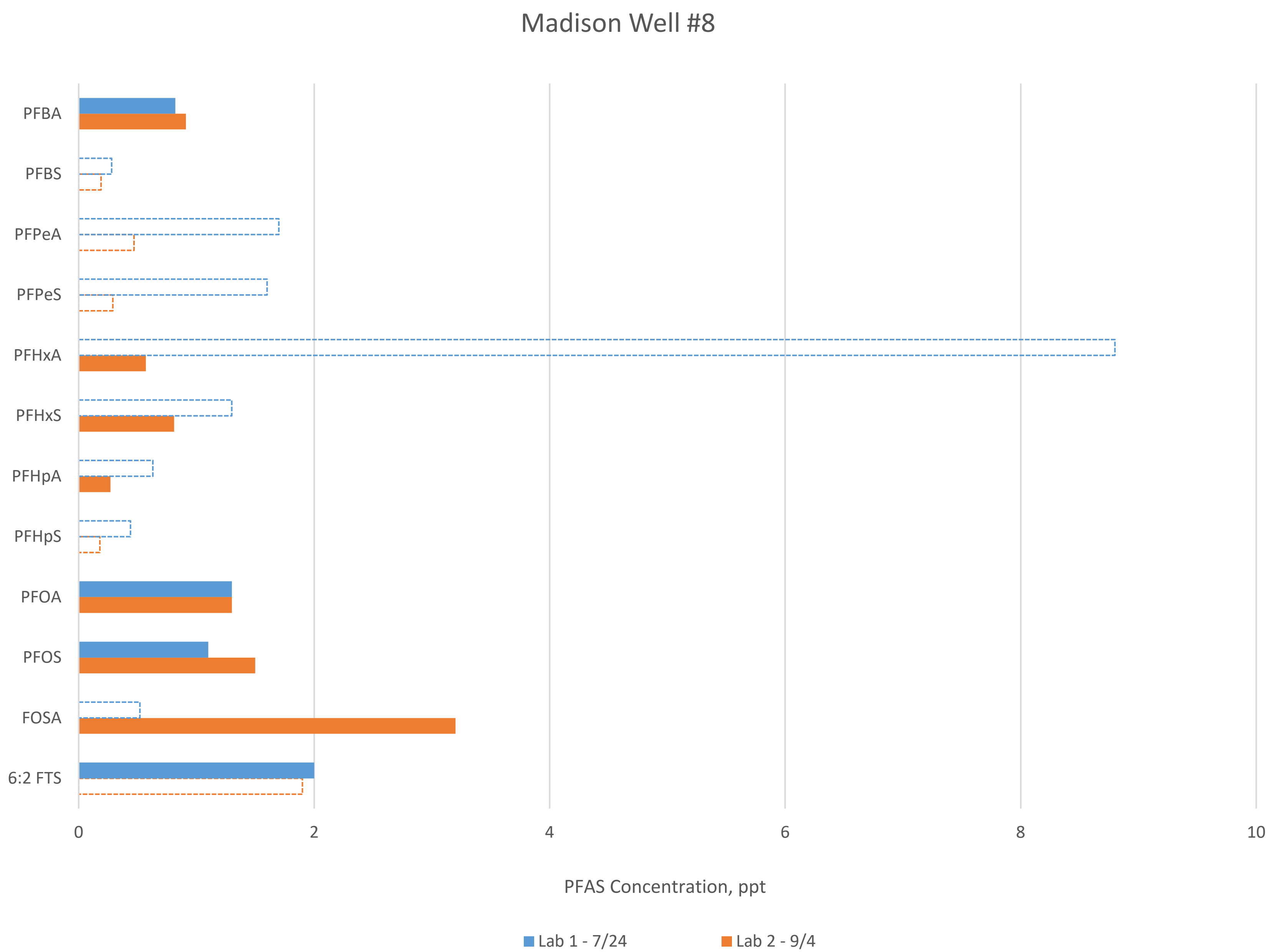


Figure 4. PFAS detections at Madison Well 8, a confined aquifer well

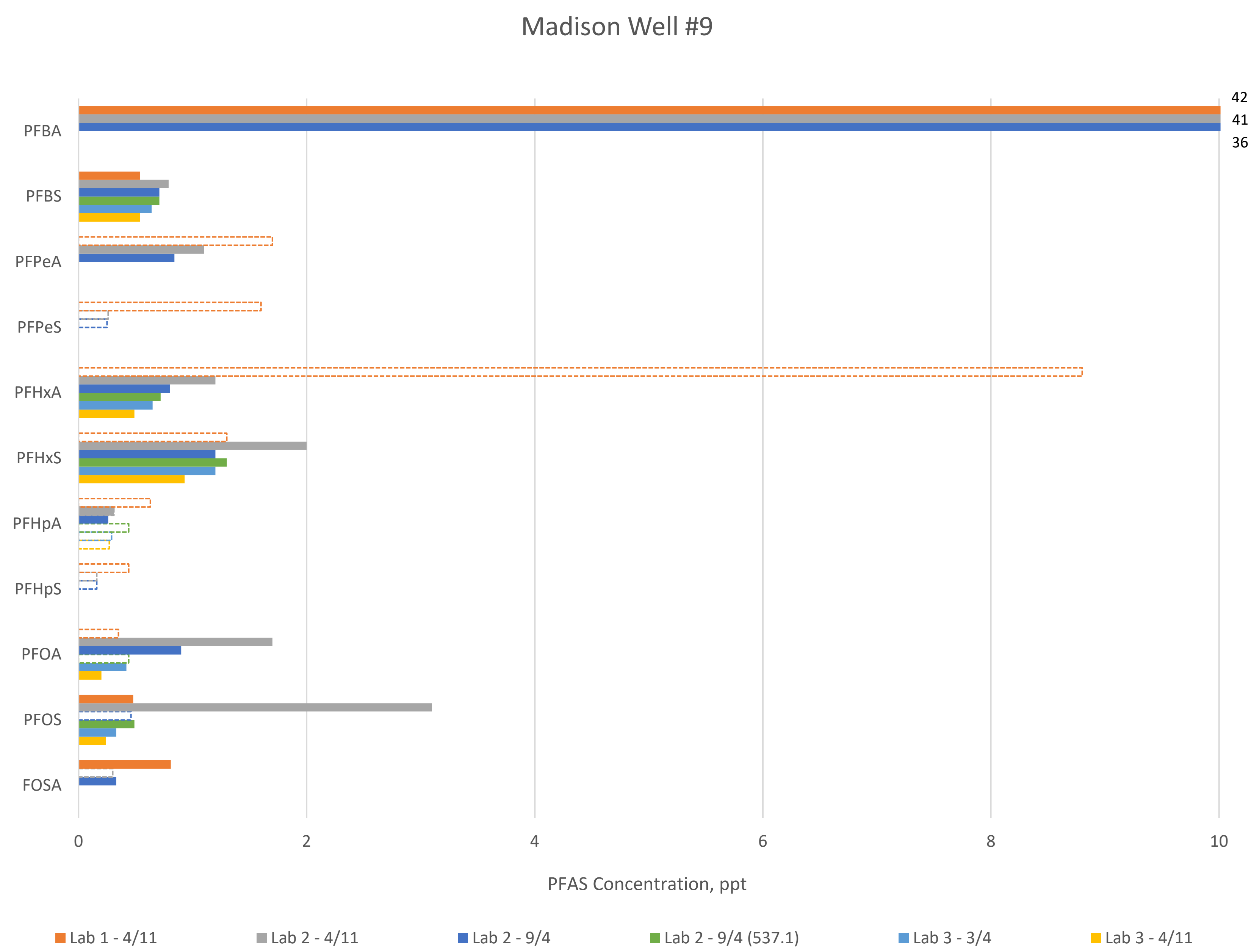


Figure 5. PFAS detections at Madison Well 9, a multi-aquifer well

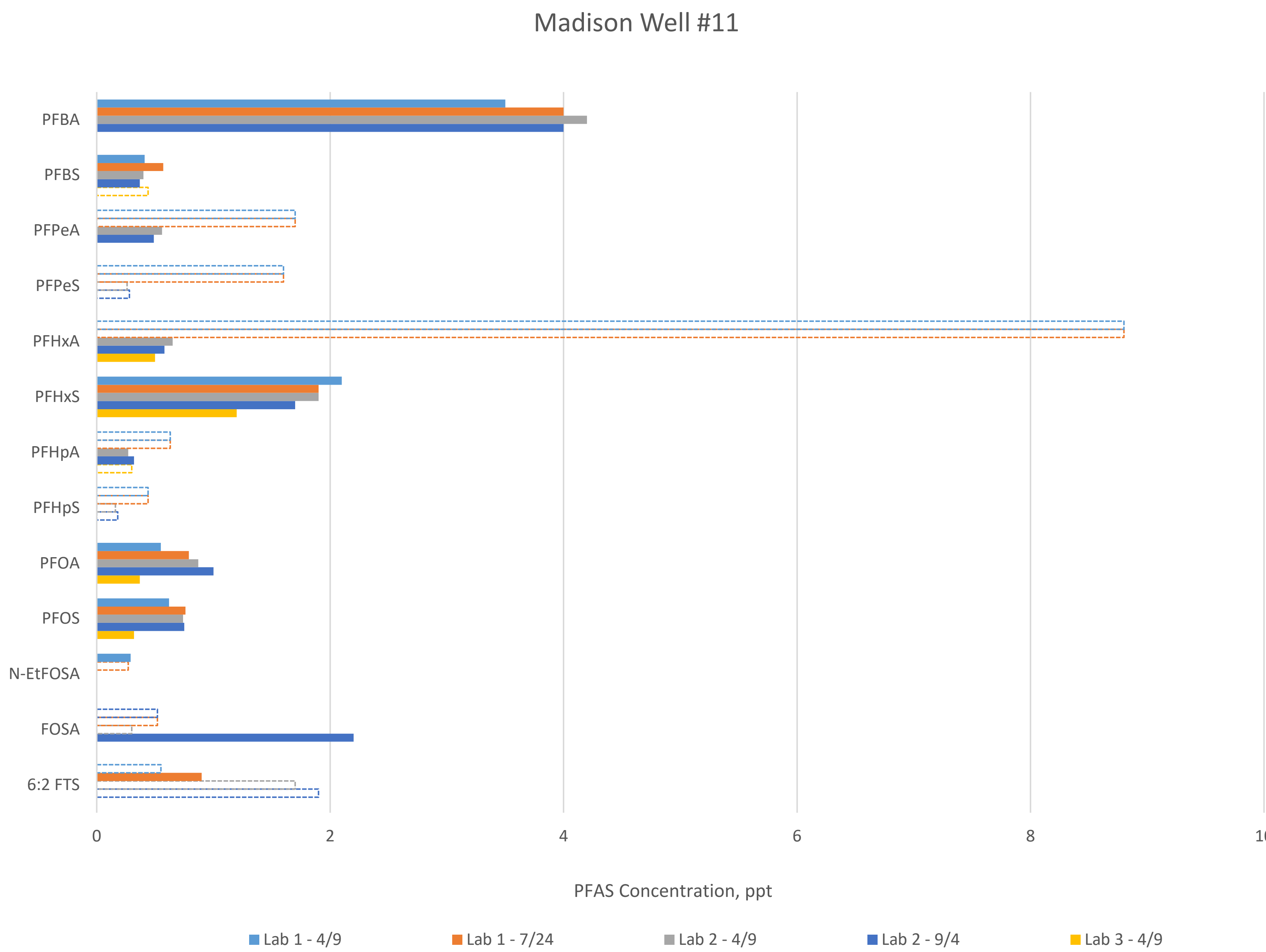


Figure 6. PFAS detections at Madison Well 11, a multi-aquifer well

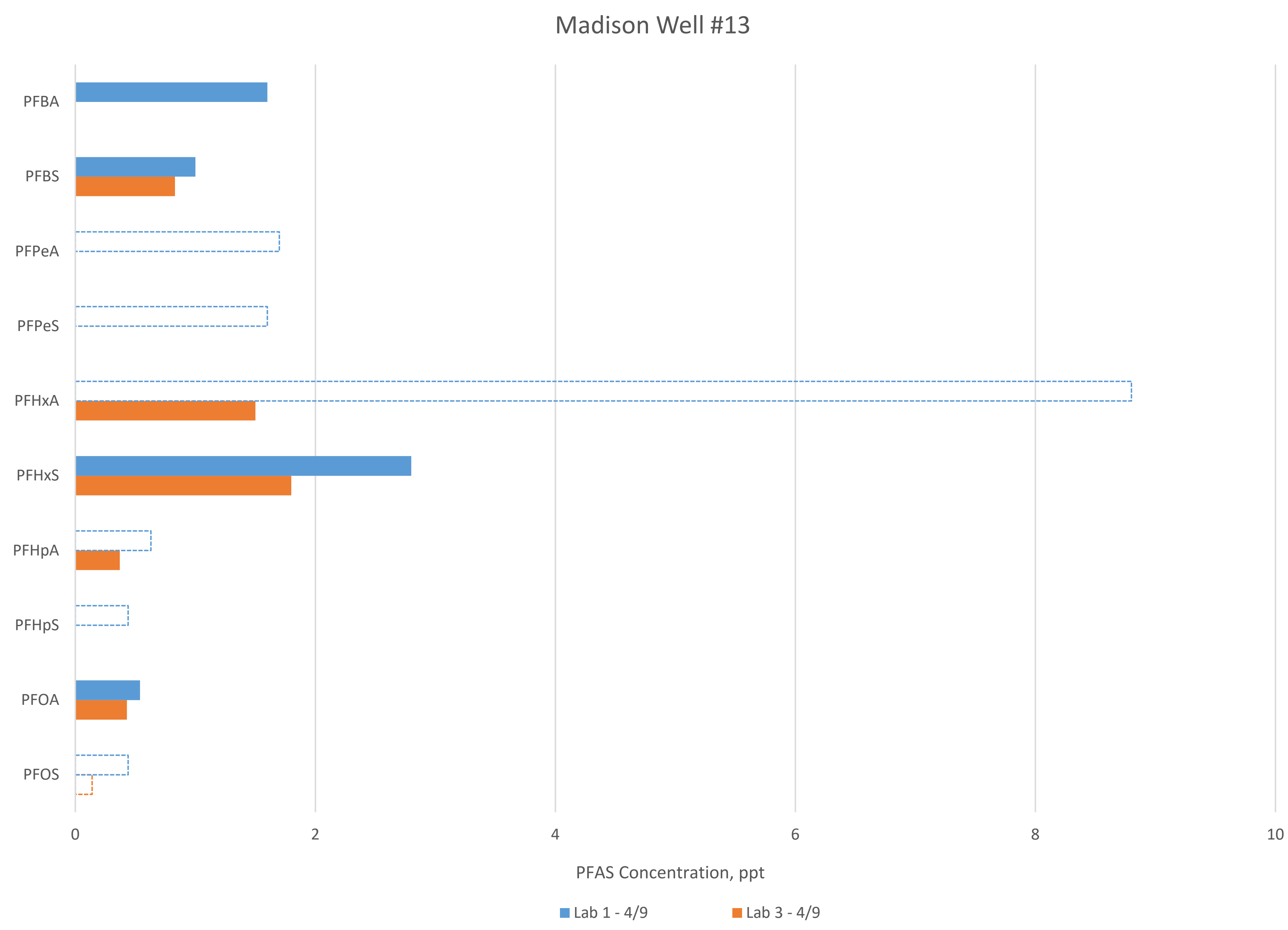


Figure 7. PFAS detections at Madison Well 13, a multi-aquifer well

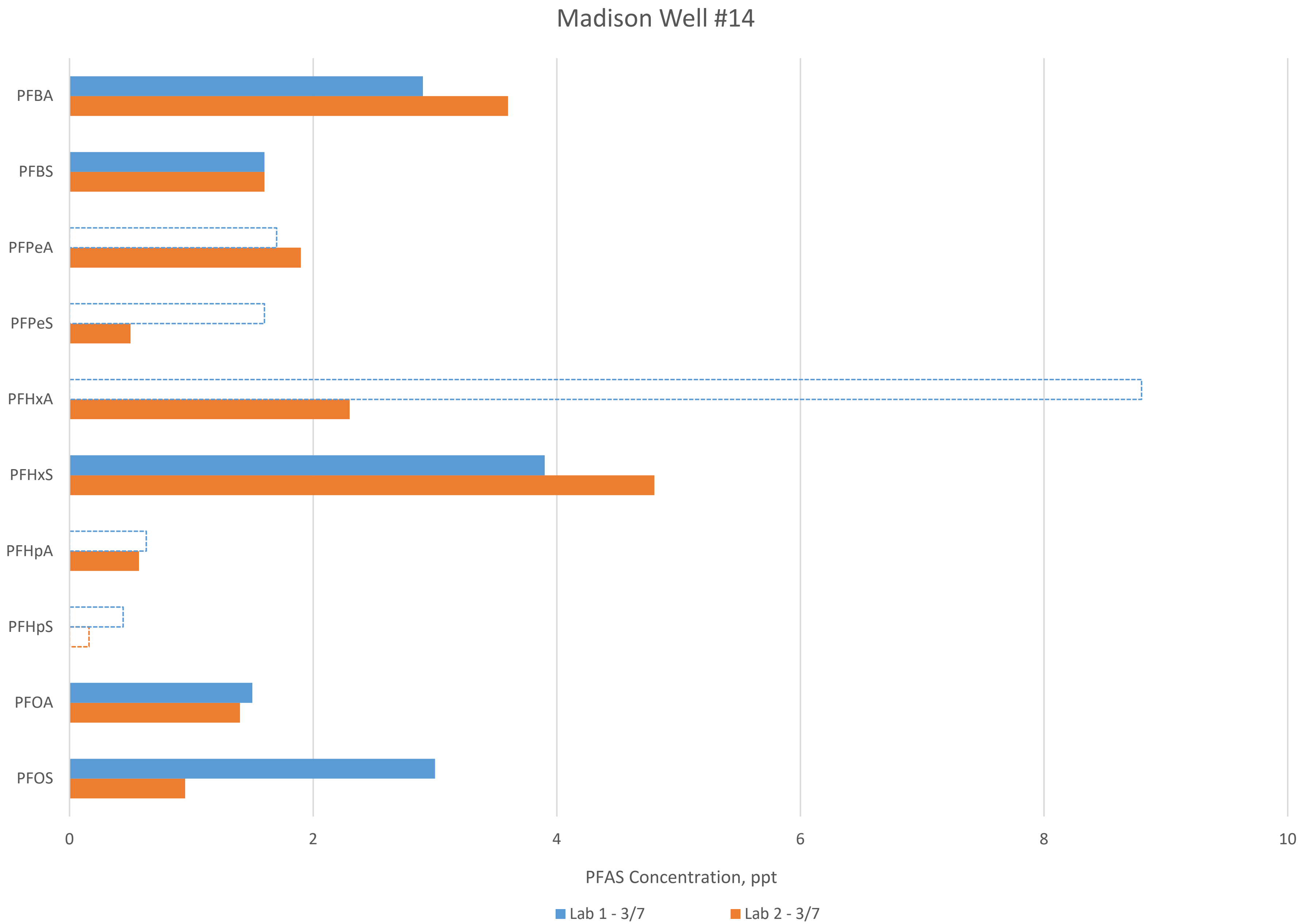


Figure 8. PFAS detections at Madison Well 14, a multi-aquifer well

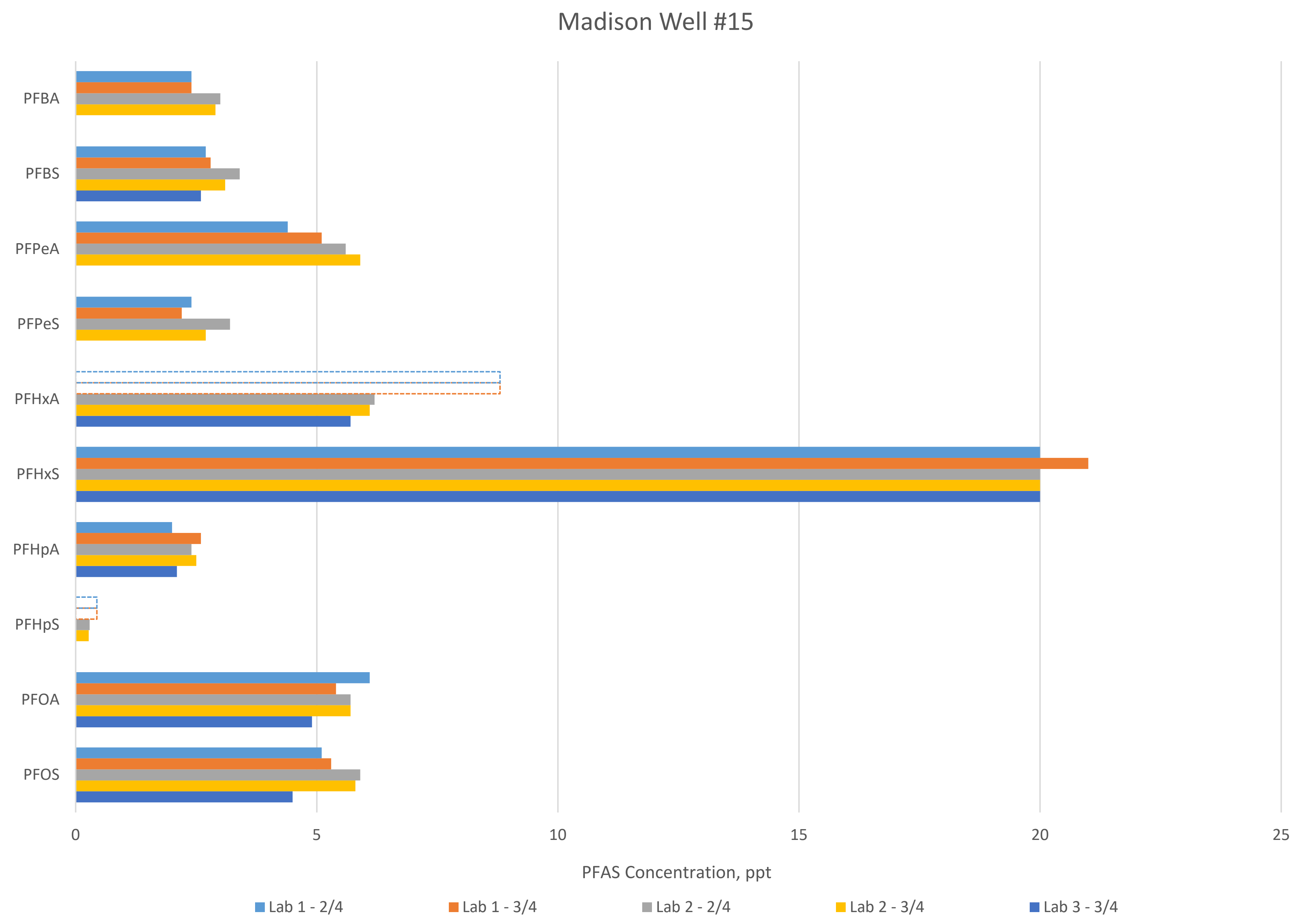


Figure 9. PFAS detections at Madison Well 15, a multi-aquifer well

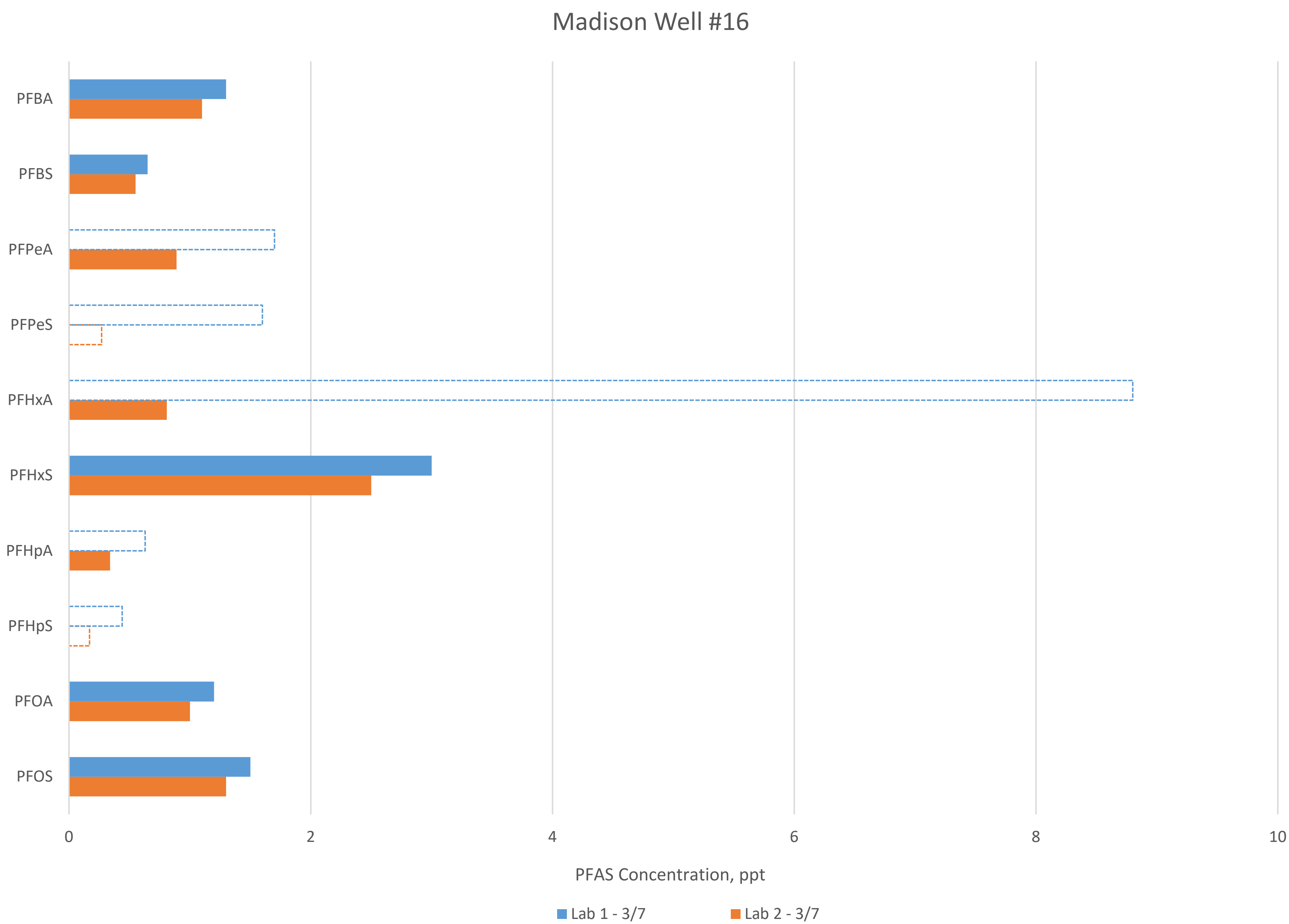


Figure 10. PFAS detections at Madison Well 16, a multi-aquifer well

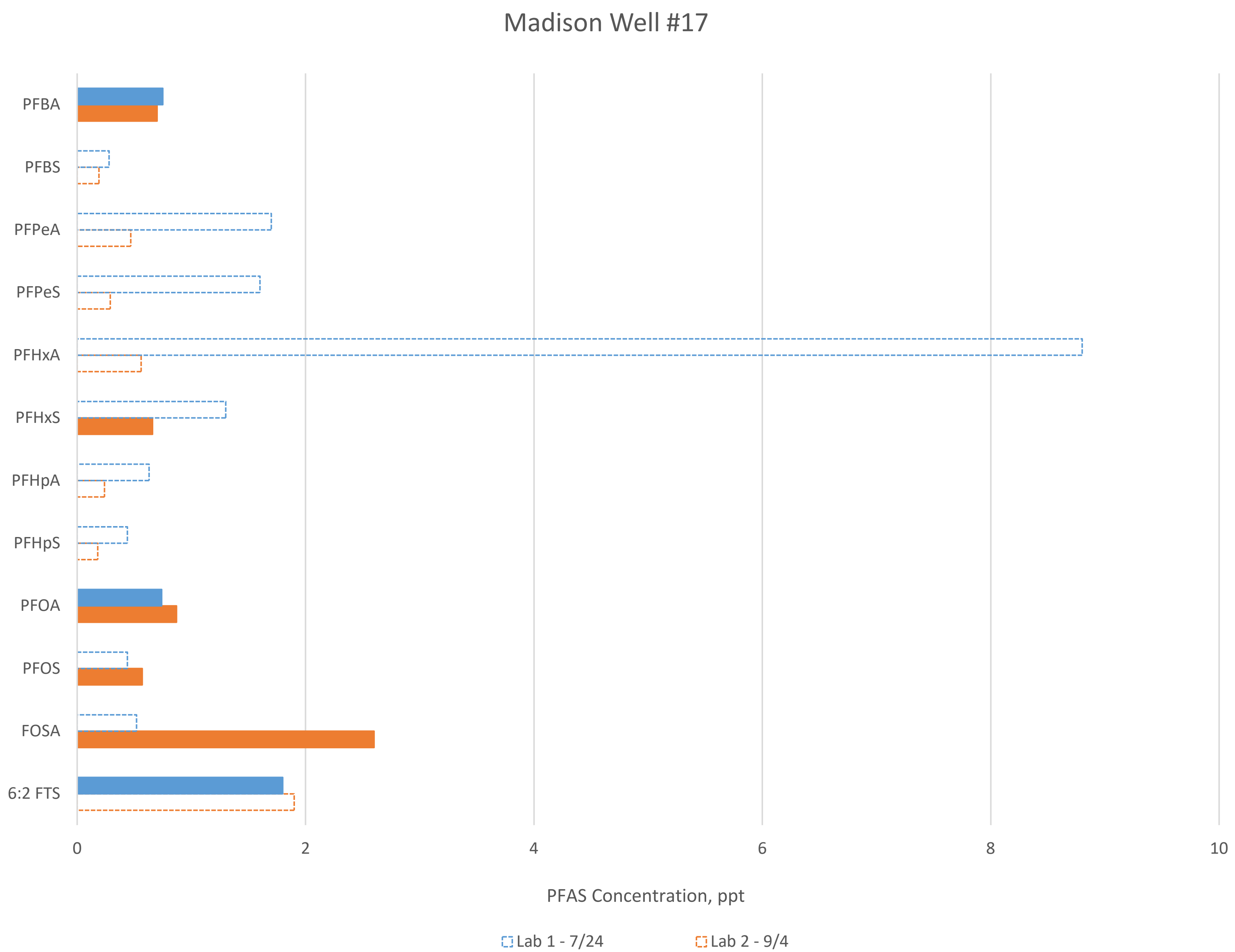


Figure 11. PFAS detections at Madison Well 17, a multi-aquifer well

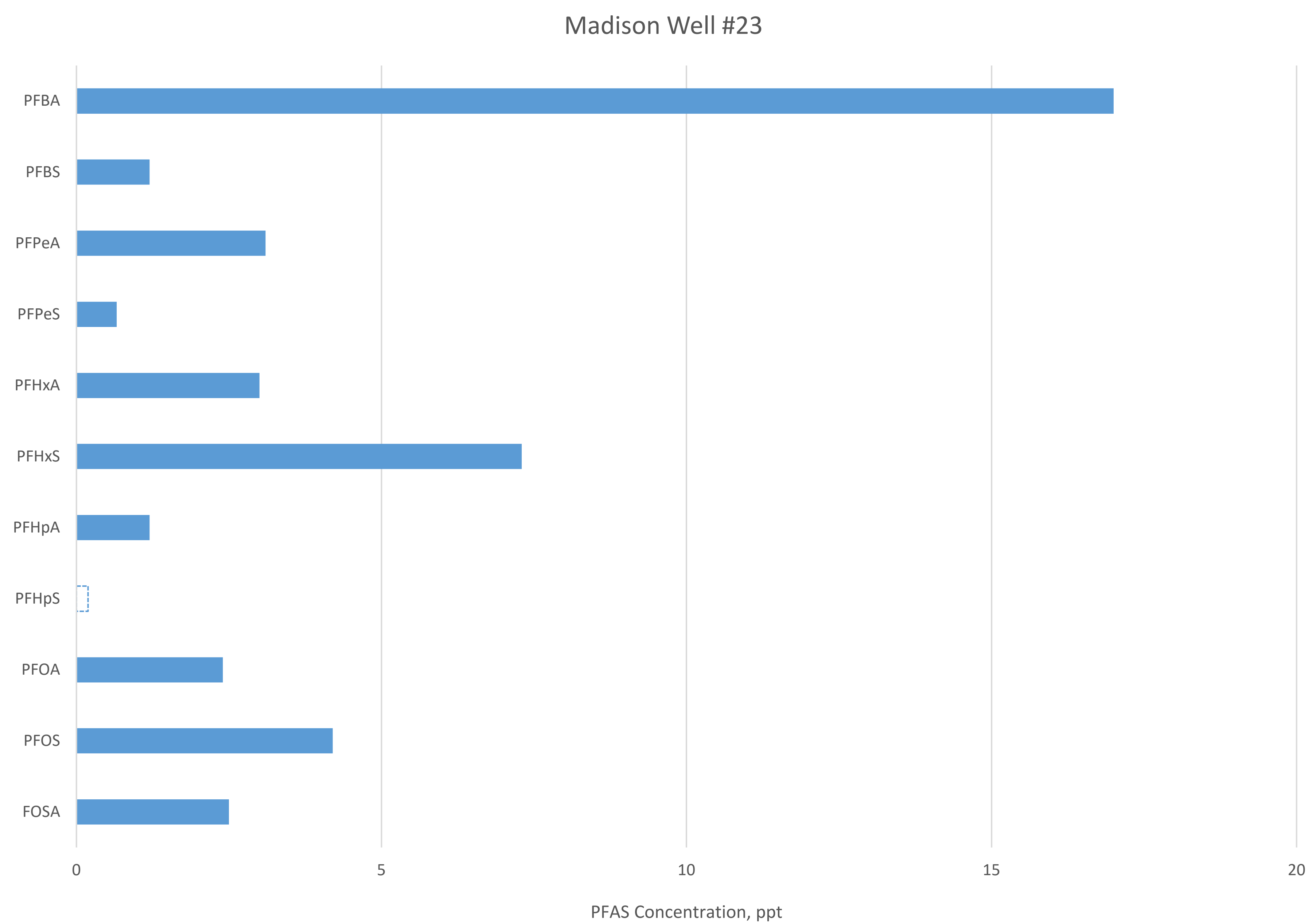


Figure 12. PFAS detections at Madison Well 23, a multi-aquifer well

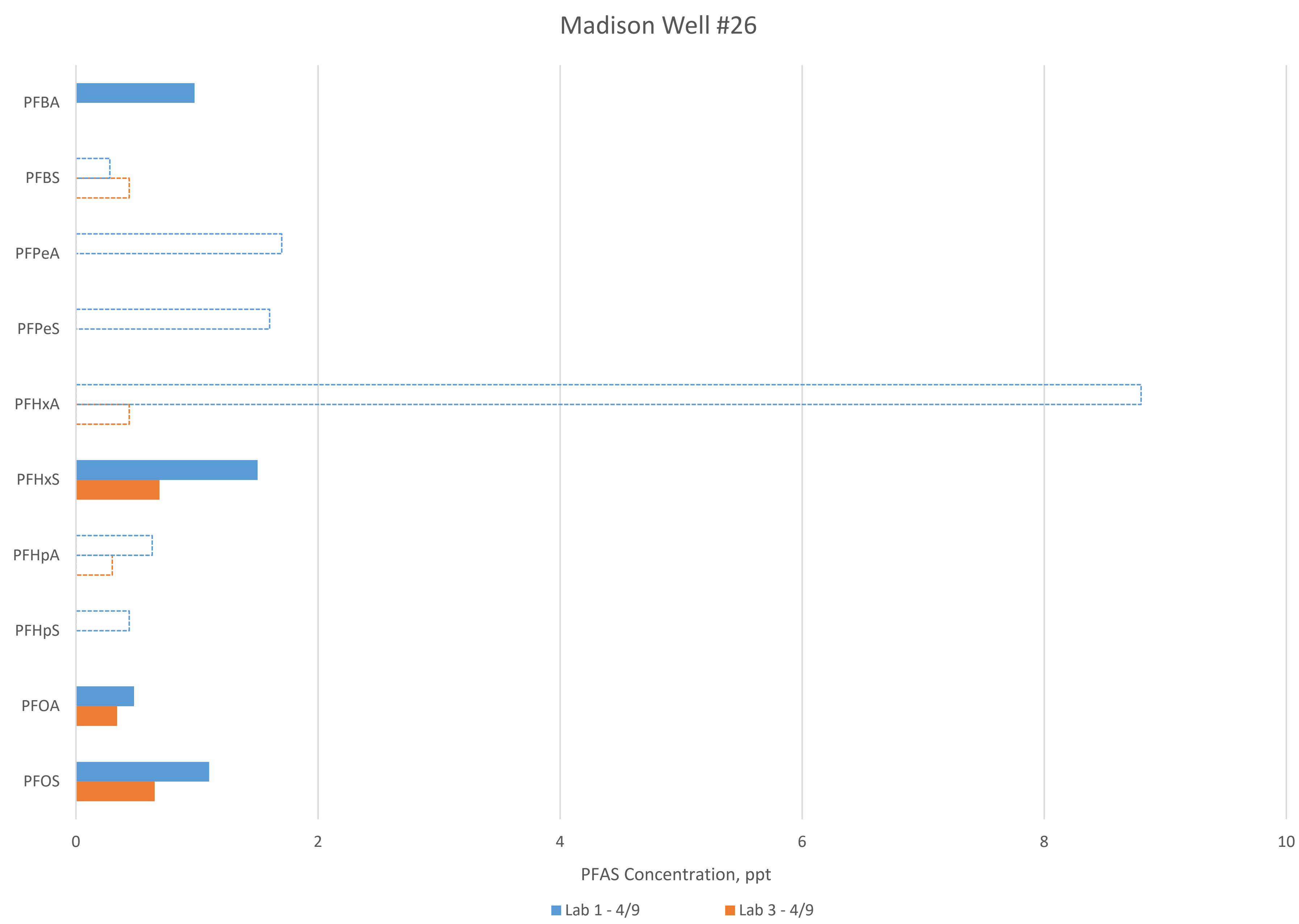


Figure 13. PFAS detections at Madison Well 26, a multi-aquifer well

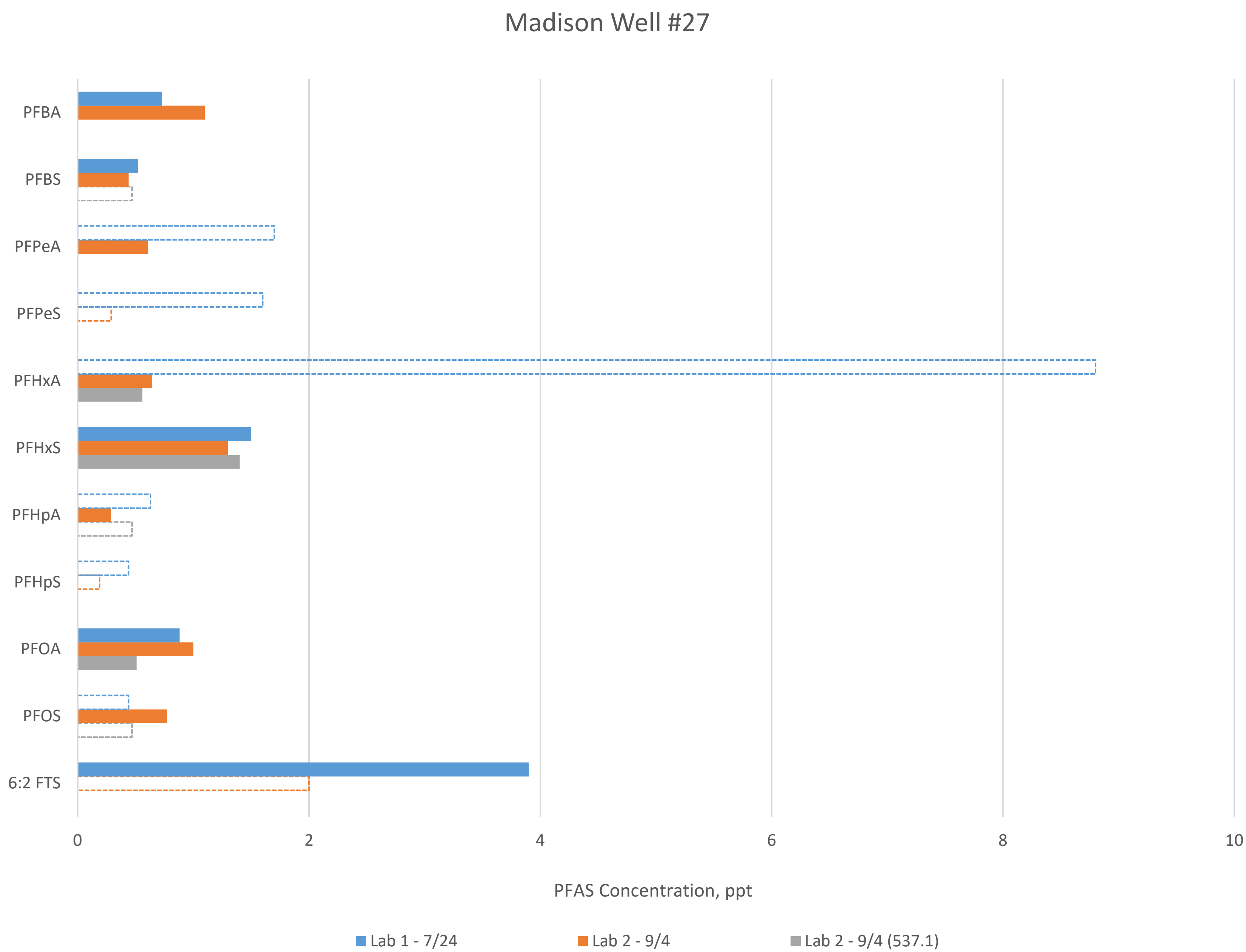


Figure 14. PFAS detections at Madison Well 27, a confined aquifer well

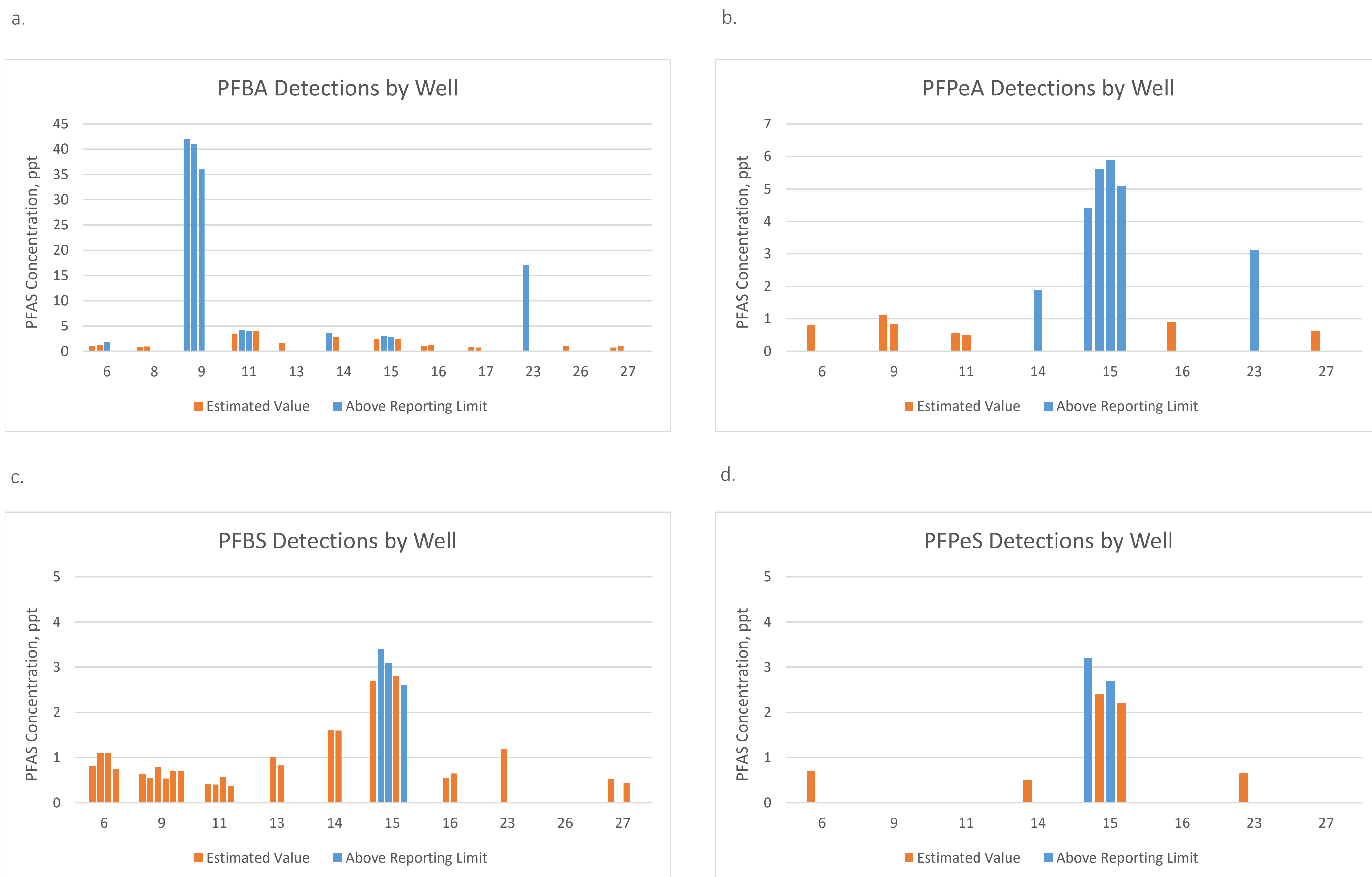
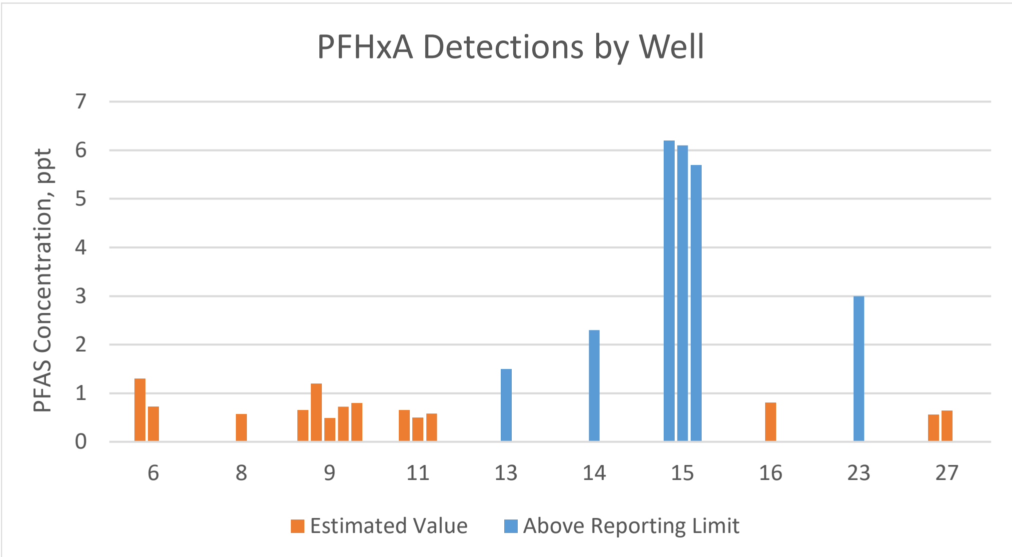
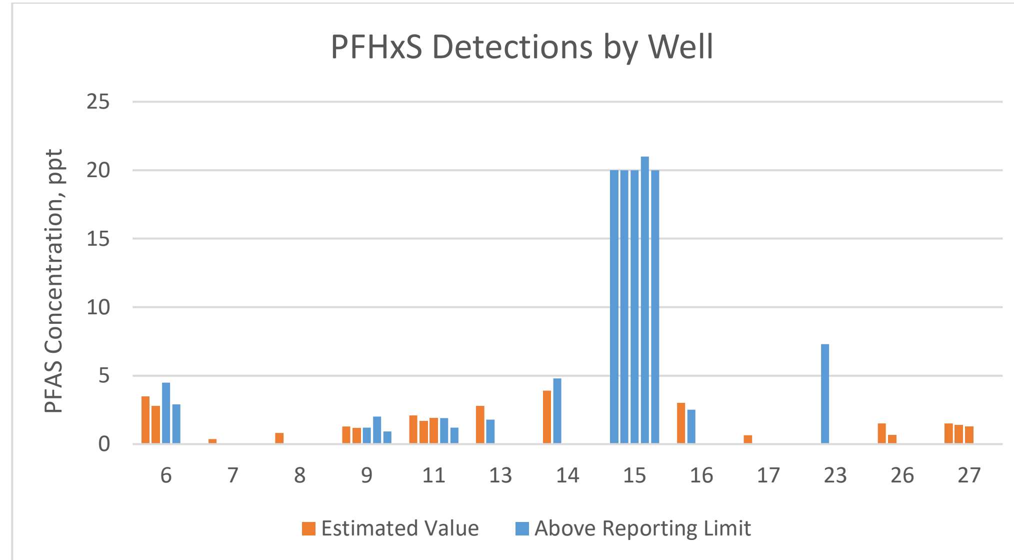


Figure 15. PFAS detections of (a) PFBA, (b) PFPeA, (c) PFBS, and (d) PFPeS at Madison wells

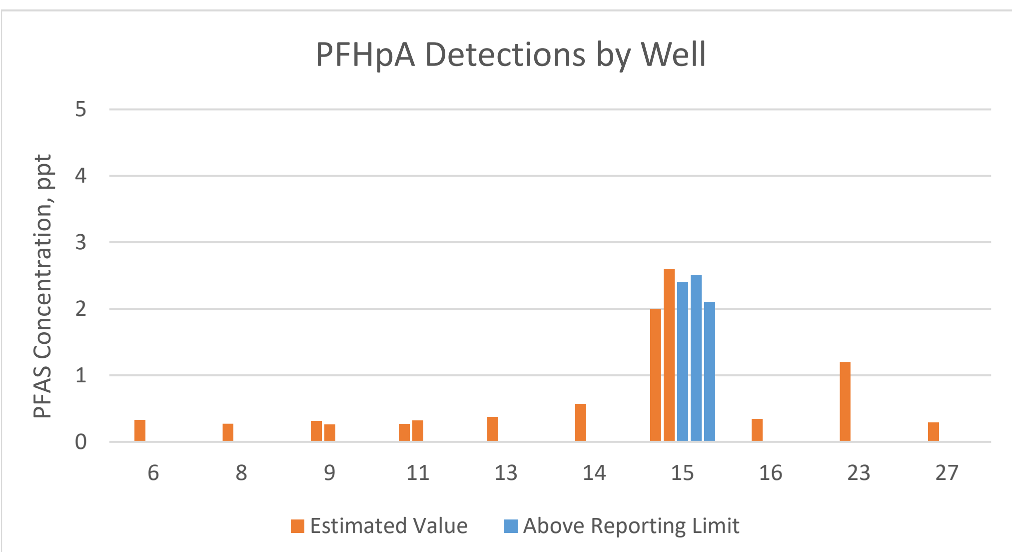
a.



b.



c.



d.

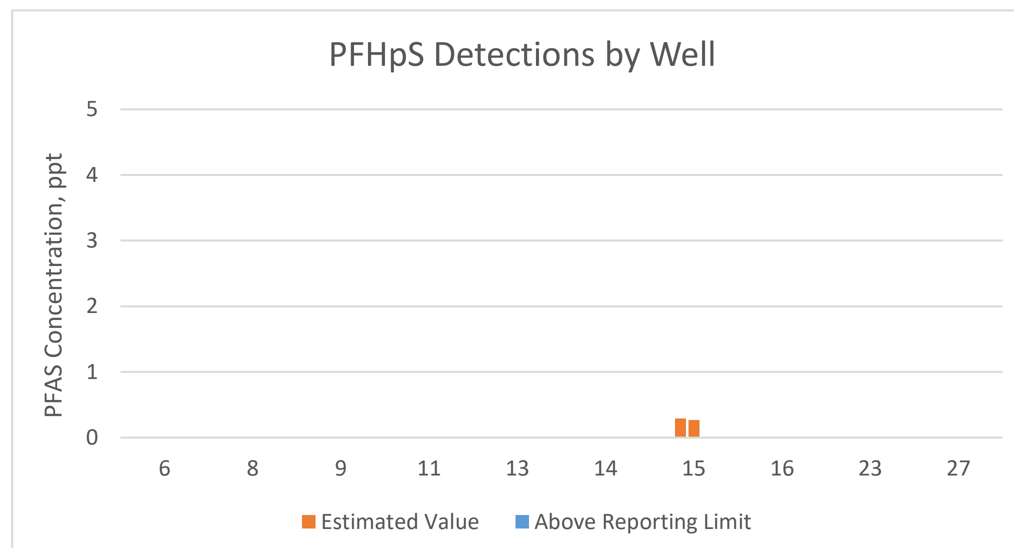


Figure 16. PFAS detections of (a) PFHxA, (b) PFHxS, (c) PFHpA, and (d) PFHpS at Madison wells

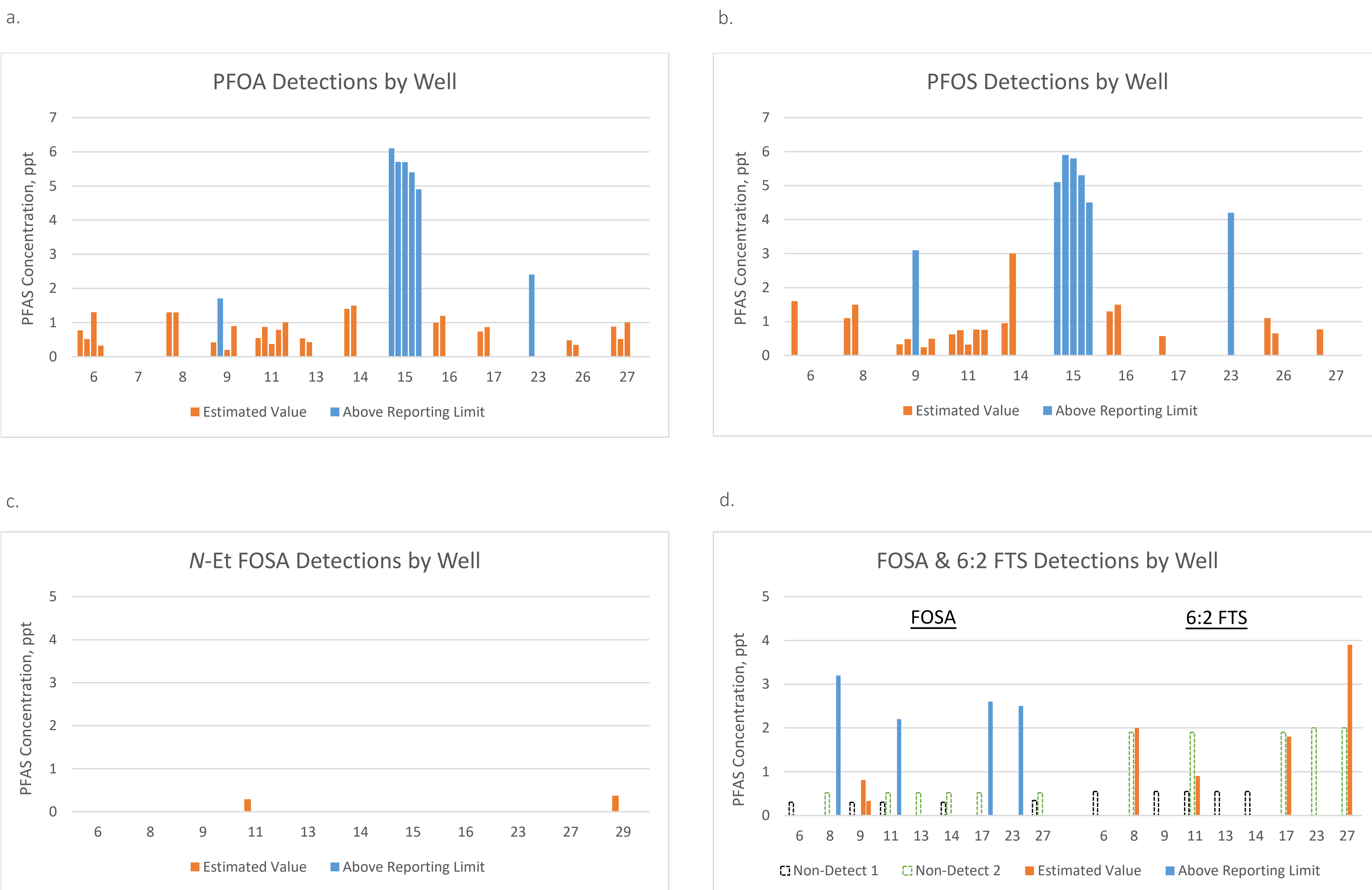


Figure 17. PFAS detections of (a) PFOA, (b) PFOS, (c) *N*-Et FOSA, and (d) FOSA & 6:2 FTS at Madison wells

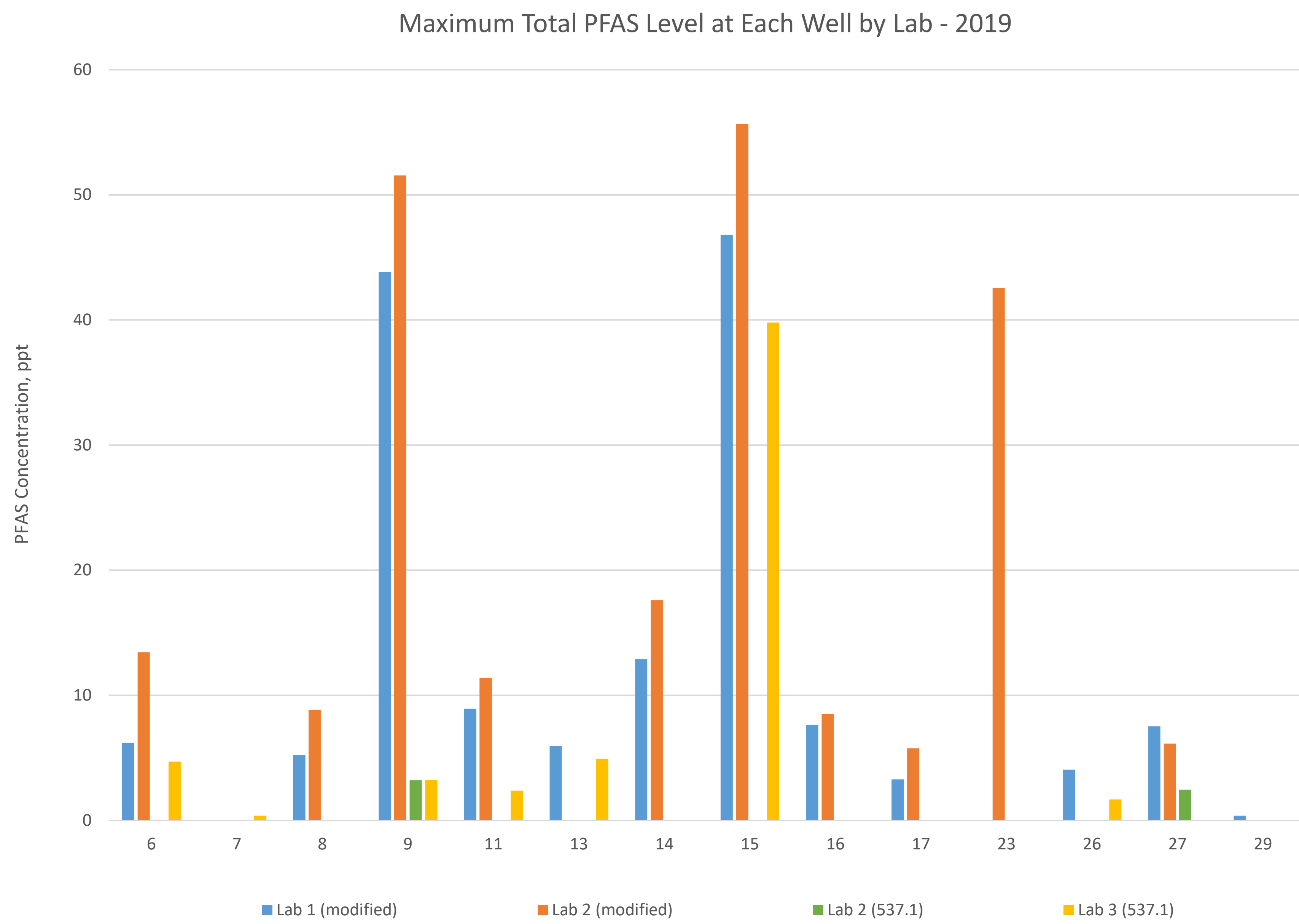


Figure 18. Composite results for Madison wells where at least one PFAS was found in 2019. These results include all reported values regardless of whether they were above or below the laboratory's method reporting limit.

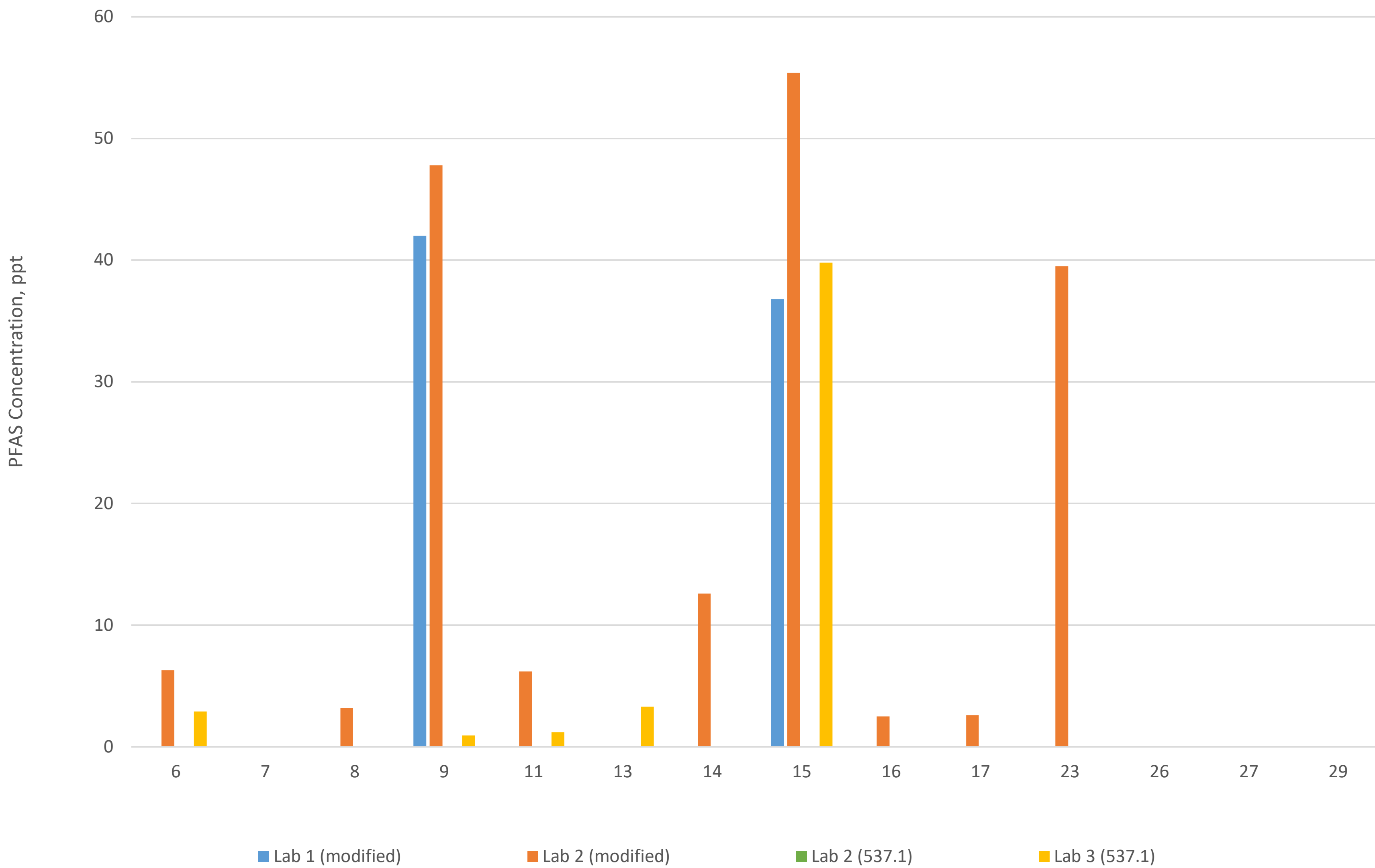


Figure 19. Total PFAS levels at Madison wells not including reported values that were below the laboratory's method reporting limit.