AFFILIATIONS

Orange County Water District 18700 Ward Street Fountain Valley, CA 92708

Creating an Automated Annual MDL Verification Process

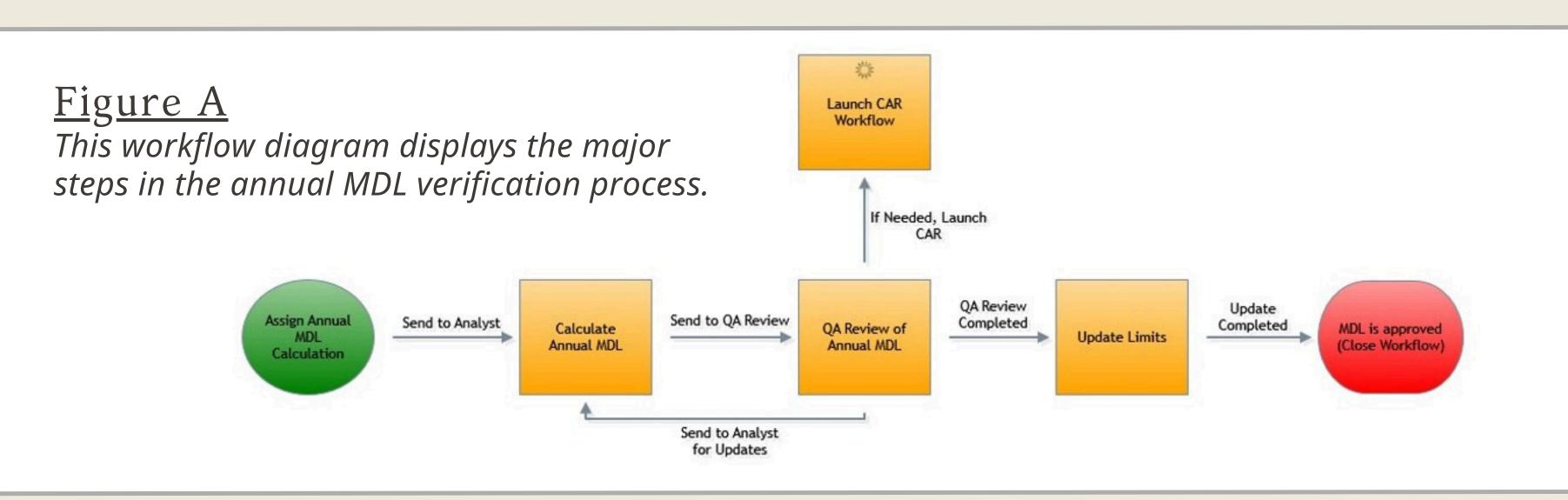


01. Introduction

USEPA published the Definition and Procedure for the Determination of the Method Detection *Limit, Revision 2* in 2016 to update the requirements necessary to establish initial MDLs and ongoing data collection and verification in the laboratory. To make this process simpler, the OCWD laboratory uses various software technologies to automate the process. The OCWD Laboratory and Information Services departments worked together to make an in-house LIMS-MDL web tool. After approximately 5 years of using the LIMS-MDL web tool, continuous improvements were made to better assign and track the annual verifications. The OCWD Lab uses a Quality Management System (QMS) software to assign MDL verifications to the primary Lab analyst. The workflow allows QA staff to check statuses, review reports, and track changes to updated values.

02. Key Objectives

- Establish a clear workflow process for lab staff (see *Figure A*)
- Easily calculate an MDL verification from an existing LIMS database
- Generate reports for traceability
- Improve communication between QA staff and Lab analysts
- Decrease the time it takes for Lab analysts and QA staff to review and report their MDL
- verifications for each analyte, analytical method, and analytical instrument
- Ensure compliance with federal and state regulatory limits



03. Methodology

- LIMS & MDL Calculation Tool
- QMS & MDL Workflow
- Comparison of Limits

Related literature

2016 TNI V1M4 1.5.2.4 EPA 821-R-16-006

The LIMS-MDL tool helps analysts easily review data related to the MDL calculation and generate reports from data collected in the past 24 months.

- Web tool was created in-house and connected to the OCWD LIMS database • Analysts can search by date range, analytical method, instrument ID, and analyte
- Analysts can review selected data (analyte, analysis date, QC standard ID, analysis method, related LIMS worksheet ID, related qualifiers)
- Over time, OCWD developed the report to have the LIMS worksheet ID as a link that displays comments related to the batch (see *Figure B*) to allow easy review of gross errors
- The full summary report lists who calculated the value, when it was calculated, the analysis date range, analytical method, analyte, analytical instrument used, MDL spike levels, MDLs values, MDLb values, and a final comparison of the MDLs versus the MDLb
- A report comparing all related limits is generated to ensure compliance with LOQs, DLRs, and MCLs (see *Figure H*)

<u>Figure B</u>

Method:

	Jump to Blanks											
		QC	Code Test Group	<u>Lab#</u>	Test	Numeric Result U	nits	Instrument ID	<u>Analysis Date</u>	Detector Lab	Qualifiers	<u>WS#</u>
Select	Cascade Select	2	F 533	LFL10192300F	PFOS	1.9 n	g/L	QTRAP6500+A	10/19/2023	MS		<u>124662</u>
Select	Cascade Select		M 533	01MDL022124M	PFOS	1.91 n	g/L	QTRAP6500+A	02/21/2024	MS		<u>127664</u>
Select	Cascade Select	2	F 533	LFL11132300F	PFOS	1.91 n	g/L	QTRAP6500+A	11/13/2023	MS		126018
Select	Cascade Select		F 533	LFL09062300F	PFOS	1.92 n	g/L	QTRAP6500+A	09/13/2023	MS		<u>124020</u>
Select	Cascade Select	2	M 533	07MDL022324M	PFOS	1.93 n	g/L	QTRAP6500+A	02/23/2024	MS		<u>127705</u>
Select	Cascade Select		F 533	LFL08182300F	PFOS	1.93 n	g/L	QTRAP6500+A	08/21/2023	MS		<u>123620</u>
Select	Cascade Select	8	M 533	04MDL022324M	PFOS	1.94 n	g/L	QTRAP6500+A	02/23/2024	MS		<u>127705</u>
Select	Cascade Select		M 533	06MDL022324M	PFOS	1.94 n	g/L	QTRAP6500+A	02/23/2024	MS		<u>127705</u>
Select	Cascade Select		M 533	05MDL022324M	PFOS	1.95 n	g/L	QTRAP6500+A	02/23/2024	MS		<u>127705</u>
Select	Cascade Select		F 533	LFL0725230AF	PFOS	1.95 n	g/L	QTRAP6500+A	08/10/2023	MS		<u>123480</u>
Select	Cascade Select	9	F 533	LFL04272300F	PFOS	1.95 n	g/L	QTRAP6500+A	04/27/2023	MS		<u>120850</u>
Select	Cascade Select		F 533	LFL0417230AF	PFOS	1.95 n	g/L	QTRAP6500+A	04/18/2023	MS		<u>120602</u>
Select	Cascade Select	2	M 533	07MDL050224M	PFOS	1.96 n	g/L	QTRAP6500+A	05/07/2024	MS		<u>129071</u>
Select	Cascade Select		F 533	LFL1114230AF	PFOS	1.96 n	g/L	QTRAP6500+A	11/21/2023	MS		<u>126221</u>
Select	Cascade Select		F 533	LFL09262300F	PFOS	1.96 n	g/L	QTRAP6500+A	09/26/2023	MS		<u>124243</u>
Select	Cascade Select		F 533	LFL08152300F	PFOS	1.96 n	g/L	QTRAP6500+A	08/21/2023	MS		123623
Select	Cascade Select	2	F 533	LFL08242300F	PFOS	1.97 n	g/L	QTRAP6500+A	08/24/2023	MS	Q	<u>123903</u>
Select	Cascade Select	ž:	F 533	LFL08232300F	PFOS	1.98 ng	g/L	QTRAP6500+A	08/23/2023	MS		124019

Using technology to improve the required process for verifying method detection limits on an annual basis

Authors: Erin J. Marshall, Daniel Salas, Christina Awad

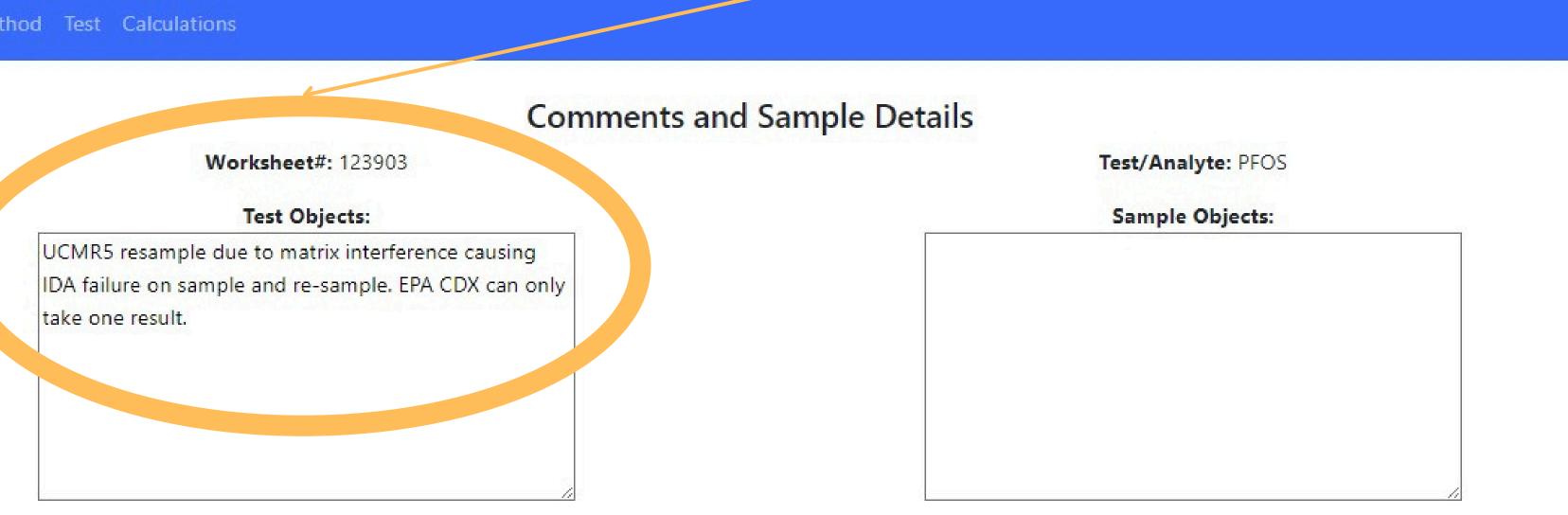
04. LIMS & MDL Calculation Tool

• A full summary report is generated for each method, analyte, and instrument, and saved in a PDF format (see *Figure C*)

The MDL tool displays QC sample data that will be part of the calculation and contains a hyperlink for analysts to immediately view additional comments and sample details if a qualifier was applied that requires further review.

Test: PFOS 🗸 🔸 Calculate

MDL Spiked Sample Data(for MDL_s Calculation): 191 samples, 191 selected



	Mathad Dataati	on I o	val Danart
	Method Detecti	on Le	
	Calculated By:	cm	arshall
	Report Date:		/2024
	Analysis Date Search Ra	-	
	Method(s)	525	
	Test:		DRIN
	Instrument ID(s):	MS	
	Detector(s):	MS	
	Spike Level(s):		= 0.1 and M $= 0.1$
	Units:	ug/I	L
	Spike Samples Analysis Date R	ange:	10/27/2022 to 4/25/2024
	Number of MDL Samples:	ange.	24
	Mean of MDL Results:		0.07816667
	Standard of Deviation of MDL		
	Single-tailed 99 th Percentile t-Va	-	2.5
	MDL _b Det	terminat	tion
BI	ank Samples Analysis Date Range	e:	10/27/2022 to 4/25/2024
Νι	umber of Blank Samples:		26
Ni	umber of Blank Samples with Num	eric Rest	ults: 26
(If there are no	Blank samples with numeric results	s, the MD	M_b does not apply in the MDL calculated by M_b
	Highest Blan	k Result:	: N/A
(Used for MDL _b when	there are both numeric and non-ni	umeric Bla	ank results and less than 100 results a
	99th Percentile B	lank Res	ults: N/A
(Used for MDL _b when			nk results and more than 100 results a
		14 ~-	
	Mean of Blank Resul		
	Standard Deviation of Single-tailed 99th per		
	Single-tailed 99th per		Value: [2.485] DL _b when all Blank results are numeric
(Mean, Stan	uuru Devrainm, unu i-v aiae are ass	cargor the	0

05. QMS & MDL Workflow

The OCWD lab uses Ideagen Quality Management software to create a workflow that allows staff to:

- Submit full MDL summary reports to QA staff for review
- Improve communication by tracking review comments and removal of gross errors in calculations (see *Figure D*)
- Create an auditable record by showing a history of each workflow step with a name and time stamp
- Track the history of updates for each MDL entry by comparing previous and current calculations
- Generate various reports from annual MDL verification summaries to pending workflow statuses

<u>Figure D</u>

In the Ideagen QMS workflow, lab staff can directly upload their summary reports and record removals of gross errors.

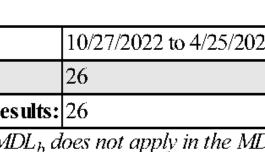
MDL Calculation Files Upload the full MDL calculation file(s) here. This is either generated by the MDL Tool or from the MDL Calculation Template (ID: 2279). Choose File No file chosen

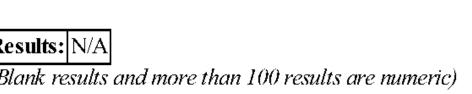
If you removed data from the annual MDL calculation, please note the removal and reason why. Only gross errors are allowed for removal. For additional guidance, refer to the <u>SOP MDL Procedure (ID: 1473)</u>

Documentation of Removal (e.g., screenshots) Removal Reason Choose File No file chosen

eport summary.

emarshall
5/6/2024
5/6/2022 to 5/6/202
525.2
ALDRIN
MS4
MS
F = 0.1 and $M = 0.7$
ug/L





06. Comparison of Limits

- QA staff uses a spreadsheet to compare and verify the annual MDL calculated by the tool against the lab's published MDL and reporting limit (see *Figure E*).
- The spreadsheet will flag results if verifications are out of limits (50 -200% of the lab's published MDL) or above the reporting limit. Any verifications out of limits are flagged in the QMS-MDL workflow and a corrective action report is automatically generated (see *Figure F*).
- MDL verification results uploaded into the LIMS database are tagged with their effective date and expiration date (if applicable). This allows the laboratory to keep track of historical changes (see Figure G). • All annual MDL verification results are uploaded into the LIMS database to generate a report that also shows other laboratory, state, or federal regulatory limits such as DLRs and MCLs. This report allows lab staff to see all limits in comparison to each other and is a helpful reference (see *Figure H*).

<u>Figure E</u>

A spreadsheet verifying the annual MDL has conditional formatting to easily see when the lab's published MDL needs to be updated.

				1	MDL Ca	lculation Che	eck - Organic 1	Metho	ds	
Reviewe	d By:	CRA		Date Reviewed:	12/14/2023	8 & 12/19/2023				
Method	Ţ	Instrument T	Test ID 🔻	Test Name	Units 💌	Annual MD 🗸	Current MDI -	RL -	50% of Current MDL 💌	200% of Current MDL
533		6500+A	11CLPF	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	ng/L	0.27279846	0.151	2	0.075346905	0.30138762
533		6500+A	9CLPF3	9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	ng/L	0.30734958	0.117	2	0.05860453	0.23441812
533		6500+A	ADONA	4,8-dioxa-3H-perfluorononanoic acid	ng/L	0.29047534	0.130	2	0.06512345	0.2604938
533		6500+A	HFPODA	Hexafluoropropylene oxide dimer acid	ng/L	0.27910086	0.177	2	0.088318445	0.35327378
533		6500+A	NFDHA	Nonafluoro-3,6-dioxaheptanoic acid	ng/L	0.58968712	0.373	2	0.186462805	0.74585122
533		6500+A	PFBA	Perfluorobutanoic acid	ng/L	0.30576485	0.157	2	0.07835202	0.31340808
533		6500+A	PFBS	Perfluorobutanesulfonic acid	ng/L	0.27872354	0.149	2	0.074658395	0.29863358
533		6500+A	8:2FTS	1H,1H,2H,2H-Perfluorodecane sulfonic acid	ng/L	0.34863281	0.128	2	0.06399404	0.25597616
533		6500+A	PFDA	Perfluorodecanoic acid	ng/L	0.30516159	0.140	2	0.06988652	0.27954608
533		6500+A	PFDoA	Perfluorododecanoic acid	ng/L	0.26967783	0.168	2	0.08419856	0.33679424
533		6500+A	PFEESA	Perfluoro(2-ethoxyethane) sulfonic acid	ng/L	0.29392514	0.163	2	0.081576715	0.32630686

<u>Figure F</u>

QA staff fills out the Ideagen QMS workflow with review comments and the comparison spreadsheet to report the status of each annual MDL verification. If necessary, a nonconformance report is filled out to launch a corrective action report workflow.

QA Review - Supporting Documentation QA Review - Supporting Documentation (<u>Required)</u> QA only = Attach either screenshots of fixes to be made, the <u>MDL Calculation Check - Inorganic</u>, or the <u>MDL Calculation Check - Organic</u> when the review is complete. Choose File No file chosen

QA Review Decision of MDL Calculation QA only = A CAR would be launched by QA staff if the MDL is > RL.

Matrix To select multiple items, hold "Ctrl" while selecting

Drinking Water

Nonconformance Details

The subform below should be completed when the observed issue is determined to require corrective action.

Add Row				
Date of Occurrence	Section(s)/Depar	tment(s) Standard(s)	Description of Obs	erved Issue Immediat
Show Calendar	Inorganic Microbiology Organic Sample Receiving	<u>Show</u> <u>Standards</u>		

07. Conclusion

Implementing these tools and software reduced human error and significantly decreased the time and effort it takes for all laboratory staff to complete the annual MDL verification. The workflow process is regularly evaluated and improved to meet changing regulatory requirements.



<u>Figure G</u> This OCWD LIMS report summarizes the MDL data for each method, analyte, matrix, and instrument.

Limits As Of	Test Group	Test ID	MDL Matrix	MDL Instrument ID	MDL	MDL Units	MDL Prep Type	MDL Calculated	MDL Effective
04/26/2024	X200.8	Be	DW+NPW	ICP/MS	0.16	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	AI	DW+NPW	ICP/MS	1.9	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	V	DW+NPW	ICP/MS	0.17	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	Cr	DW+NPW	ICP/MS	0.33	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	Mn	DW+NPW	ICP/MS	0.26	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	Co	DW+NPW	ICP/MS	0.25	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	Ni	DW+NPW	ICP/MS	0.21	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	Cu	DW+NPW	ICP/MS	0.31	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	Zn	DW+NPW	ICP/MS	1.71	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	As	DW+NPW	ICP/MS	0.23	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	Se	DW+NPW	ICP/MS	0.3	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	Sr	DW+NPW	ICP/MS	0.34	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	Мо	DW+NPW	ICP/MS	0.18	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	Ag	DW+NPW	ICP/MS	1.34	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	Cd	DW+NPW	ICP/MS	0.23	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	Sb	DW+NPW	ICP/MS	0.19	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	Ba	DW+NPW	ICP/MS	0.14	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	Gd	DW+NPW	ICP/MS	3.1	ng/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	Hg	DW+NPW	ICP/MS	0.4	ug/L	Digested	11/01/2023	12/01/2023
04/26/2024	X200.8	TI	DW+NPW	ICP/MS	0.42	ug/L	Digested	11/01/2023	12/01/2023

<u>Figure H</u>

A report can be generated by staff using the OCWD LIMS to view the lab's published MDL, reporting limit, warning flags (action level), and state MCL.

Limits As Of	Test Group	Test ID	MDL Matrix	MDL Instrument ID	MDL Prep Type	MDL	MDL Units	MDL Calculated	RL	Action Level	MCL
04/26/2024	533	PFBA	DW+NPW	QTRAP 6500+	Cartridge	0.4426	ng/L	12/01/2023	2		
04/26/2024	533	PFMPA	DW+NPW	QTRAP 6500+	Cartridge	0.24137 1	ng/L	12/01/2023	2		
04/26/2024	533	PFPeA	DW+NPW	QTRAP 6500+	Cartridge	0.234	ng/L	12/01/2023	2		5.0
04/26/2024	533	PFBS	DW+NPW	QTRAP 6500+	Cartridge	0.6115	ng/L	12/01/2023	2	375	15
04/26/2024	533	PFMBA	DW+NPW	QTRAP 6500+	Cartridge	0.379	ng/L	12/01/2023	2		
04/26/2024	533	PFEESA	DW+NPW	QTRAP 6500+	Cartridge	0.387	ng/L	12/01/2023	2	- 26	26
04/26/2024	533	NFDHA	DW+NPW	QTRAP 6500+	Cartridge	0.3359	ng/L	12/01/2023	2		
04/26/2024	533	4:2FTS	DW+NPW	QTRAP 6500+	Cartridge	0.4625	ng/L	12/01/2023	2		
04/26/2024	533	PFHxA	DW+NPW	QTRAP 6500+	Cartridge	0.5686	ng/L	12/01/2023	2		
04/26/2024	533	PFPeS	DW+NPW	QTRAP 6500+	Cartridge	0.39876 9	ng/L	12/01/2023	2	* =	12
04/26/2024	533	HFPODA	DW+NPW	QTRAP 6500+	Cartridge	0.4579	ng/L	12/01/2023	2	7.5	10
04/26/2024	533	PFHpA	DW+NPW	QTRAP 6500+	Cartridge	0.214	ng/L	12/01/2023	2	20	20
04/26/2024	533	PFHxS	DW+NPW	QTRAP 6500+	Cartridge	0.4327	ng/L	12/01/2023	2	2.2	10
04/26/2024	533	ADONA	DW+NPW	QTRAP 6500+	Cartridge	0.4758	ng/L	12/01/2023	2		
04/26/2024	533	6:2FTS	DW+NPW	QTRAP 6500+	Cartridge	0.4156	ng/L	12/01/2023	2		
04/26/2024	533	PFOA	DW+NPW	QTRAP 6500+	Cartridge	0.552	ng/L	12/01/2023	2	3	4

08. Future Considerations

As the OCWD laboratory is continually improving, the following are future considerations to better the annual MDL verification process:

- Migrate the MDL tool to the OCWD in-house built LIMS rather than being a web-based tool.
- Add LIMS capability to categorize outlier QC results into those used in ongoing QC calculations (like MDL) and gross errors that will not be included.
- Create the comparison spreadsheet as an automated report in the OCWD LIMS.

