

## Reif, Maizie L - DNR

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**From:** Neal, Conor <Neal.Conor@epa.gov>  
**Sent:** Tuesday, September 4, 2018 2:21 PM  
**To:** Neste, David E - DNR  
**Cc:** Carey, Angela J - DNR  
**Subject:** Tyco PFAS groundwater data validation  
**Attachments:** Tyco\_DataValidation\_memo.docx; Low-Flow Sampling Forms\_4-30-18 and 5-1-18.pdf

Hi Dave,

EPA completed the data validation for the PFAS groundwater sampling event that occurred April 30-May 1 of this year. I am attaching the data validation memo and Tyco's field sampling logs for your information.

Let me know if you have any questions about this.

Thanks,  
Conor

**Conor Neal**  
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## MEMORANDUM

Subject: Data Validation for Perfluorinated Compound (PFC) Sampling at Tyco Site, Marinette, WI

Date: August 14, 2018

From: Zachary Sasnow  
QA/QC Coordinator, Remediation and Reuse Branch, LCD

To: Conor Neal  
Hydrogeologist, Remediation and Reuse Branch, LCD

This memorandum summarizes the results of data validation conducted on the data from the April 30<sup>th</sup> – May 2<sup>nd</sup>, 2018 sampling for perfluorinated compounds (PFCs) at the Tyco facility in Marinette Wisconsin. Monitoring well stabilization logs, created by Arcadis North America on behalf of Tyco, and analytical data generated by EPA's Chicago Regional Laboratory (CRL) were reviewed as part of the data validation. Data packages consulted in this validation can be provided upon request.

Additional data qualifiers are recommended for some samples, as discussed at the end of the memorandum. In addition, there are issues identified in the field monitoring logs, as discussed in the following section.

### Field Data Validation

Well stabilization logs were provided to EPA by Arcadis North America on behalf of Tyco. Logs were compared to the Arcadis SOP entitled "PFAS Sampling Procedures and Low-Flow Groundwater Purging for Monitoring Wells and Treatment System Influent" (March 2018). Non-conformances to the SOP were identified at the following wells:

MW-008M: Sampling was conducted 35 minutes into purging; at the time of sampling, turbidity, pH, dissolved oxygen, and temperature had not reached the criteria set in the SOP. Water level measurements indicated significant drawdown was observed; however, no explanation of the early sampling time was given. pH was recorded between 13.86 and 12.85 standard units during purging, which suggests instrument malfunction.

MW-108S: Sampling was conducted at 45 minutes into purging with turbidity not within criteria; the SOP states samples can be collected after one hour of purging if turbidity has not stabilized. pH was also recorded at 15.74 to 16.44 standard units during purging, which suggests instrument malfunction.

MW-041S: Sampling was conducted at 40 minutes into purging, with turbidity, pH, DO, and temperature not stabilized. pH ranged from 12.99 to 15.44 standard units during purging, which suggests instrument malfunction.

MW-032S: Sampling was conducted at 40 minutes, with temperature not within SOP criteria.

MW-054S: Sampling was conducted at 45 minutes, with temperature, turbidity, and dissolved oxygen not within SOP criteria.

Based on the pH readings and early purge times, further information is needed to determine if instrument malfunction was an issue or if samples were collected under representative groundwater conditions. The very high pH readings at some wells suggest the meter was not properly calibrated prior to use.

Sample volumes were also checked. While no specific range of volumes has been established as acceptable in the field or laboratory SOPs, the goal volume is set at 5 mL. The volumes collected in the field ranged from 4.9071 to 6.7073 mL as measured at CRL. All samples were analyzed with the full volume and concentrations were adjusted appropriately for the collected volume.

### Analytical Data Validation

Data generated by EPA's Chicago Regional Laboratory (CRL) was validated during this effort. As of the writing of this memorandum, no established protocol for validating PFC analytical data has been promulgated by EPA. As such, CRL SOP OM021 (Standard Operating Procedure for the Analysis of Polyfluorinated Compounds of Interest to OSRTI in Water, Sludge, Influent, Effluent, and Wastewater by Multiple Reaction Monitoring Liquid Chromatography/Mass Spectrometry [LC/MS/MS], April 2018) and the National Functional Guidelines for Superfund Organic Methods Data Review (August 2014) were used as reference documents, in addition to the project-specific sampling memorandum, entitled Perfluorinated Compound Split Sampling at Tyco Fire Products, LP Facility, Marinette, Wisconsin (EPA, 2018).

It should be noted that all analytical results for 6:2 fluorotelomer sulfonate (6:2 FTS) were rejected due to poor overall quality control, and as such non-conformances of the 6:2 FTS data will not be referenced further in the following validation. The analytes considered during this effort are listed below with applicable abbreviations:

<b>Compound</b>	<b>Abbreviation</b>
4:2 FTS	4:2 fluorotelomer sulfonate
8:2 FTS	8:2 fluorotelomer sulfonate
NETFOSAA	N-ethylperfluorooctanesulfonamidoacetic acid
NMeFOSAA	N-methylperfluorooctanesulfonamidoacetic acid
PFDS	Perfluoro-1-decanesulfonate
PFHpS	Perfluoro-1-heptanesulfonate
PFNS	Perfluoro-1-nonanesulfonate
PFOSA	Perfluoro-1-octanesulfonamide
PFPeS	Perfluoro-1-pentanesulfonate
PFBA	Perfluorobutanoate
PFBS	Perfluoro-1-butanesulfonate
PFDA	Perfluorodecanoate
PFDoA	Perfluorododecanoate
PFHpA	Perfluoroheptanoate
PFHxA	Perfluorohexanoate
PFHxS	Perfluoro-1-hexanesulfonate
PFNA	Perfluorononanoate
PFOA	Perfluorooctanoate
PFOS	Perfluoro-1-octanesulfonate
PFPeA	Perfluoropentanoate
PFTreA	Perfluorotetradecanoate
PFTriA	Perfluorotridecanoate
PFuNA	Perfluoroundecanoate
4:2 FTS (Surr)	Isotopically-labeled 4:2 fluorotelomer sulfonate (surrogate)
8:2 FTS (Surr)	Isotopically-labeled 8:2 fluorotelomer sulfonate (surrogate)

NEtFOSAA (Surr)	Isotopically-labeled N-ethylperfluorooctanesulfonamidoacetic acid (surrogate)
NMeFOSAA (Surr)	Isotopically-labeled N-methylperfluorooctanesulfonamidoacetic acid (surrogate)
M3PFBS	Isotopically-labeled perfluoro-1-butanefulfonate (surrogate)
M3PFHxS	Isotopically-labeled perfluoro-1-hexanesulfonate (surrogate)
M8FOSA	Isotopically-labeled perfluoro-1-octanesulfonamide (surrogate)
M8PFOS	Isotopically-labeled perfluoro-1-octanesulfonate (surrogate)
MPFBA	Isotopically-labeled perfluorobutanoate (surrogate)
M6PFDA	Isotopically-labeled perfluorodecanoate (surrogate)
MPFDoA	Isotopically-labeled perfluorododecanoate (surrogate)
M4PFHpA	Isotopically-labeled perfluoroheptanoic acid (surrogate)
M5PFHxA	Isotopically-labeled perfluorohexanoic acid (surrogate)
M9PFNA	Isotopically-labeled perfluorononanoic acid (surrogate)
M8PFOA	Isotopically-labeled perfluorooctanoic acid (surrogate)
M5PFPeA	Isotopically-labeled perfluoropentanoic acid (surrogate)
M2PFTreA	Isotopically-labeled perfluorotetradecanoate (surrogate)
M7PFUnA	Isotopically-labeled perfluoroundecanoate (surrogate)

*Batch Criteria.* The following criteria were reviewed for the sample batch as a whole, and each of the three analytical batches ran on separate days. The initial analytical batch consisted of all samples, and the two subsequent batches consisted of sample dilutions.

**QA/QC field samples:** all field duplicates, matrix spike/matrix spike duplicate (MS/MSD), and field blanks were collected as specified in the work plan. One additional blank not specified in the work plan was collected by pouring deionized water over the water level meter (sample EB-32).

**Sample nomenclature:** samples were not named as specified in the work plan; each replicate set was labeled as normal and with an -A identifier (example: MW-102, MW-102A) as opposed to with -A and -B identifiers. This has no impact on the data usability.

**Sample dates/times:** all sample collection dates and times noted on the chain-of-custody matched those recorded by CRL.

**Sample matrix:** All samples were collected as groundwater or reagent water as specified in the work plan.

**Lab delivery date:** Samples were relinquished to CRL at 11:54 AM on 5/2/18.

**Sample temperature:** Samples were delivered to CRL at 2.3° C, within QC limits.

**Holding times:** All samples were delivered to CRL and analyzed within the 28-day holding time limit.

**Batch QC samples:** For 19 field samples, one reagent blank, two method blanks, one laboratory control sample/laboratory control sample duplicate (LCS/LCSD) set, and one reporting limit check sample are required. All requisite samples were analyzed for the batch.

**Initial calibration:** A nine-point quadratic calibration was conducted at the beginning of each analytical batch. All analytes had R<sup>2</sup> values for the quadratic fit within limits specified in the SOP.

**Second-source verification:** A second-source verification sample was analyzed after each initial calibration at the same level of the 7<sup>th</sup> calibration standard. All second-source analytes were recovered within QC limits.

**Continuing calibration verification:** Continuing calibration verification samples were analyzed at the appropriate frequency in each analytical batch.

**Method blank:** Two method blanks were analyzed; all detections were below the applicable limits.

**Reporting limit check:** Two reporting limit check samples were analyzed; all analytes were recovered within applicable QC limits.

**Laboratory control sample/laboratory control sample duplicate:** One LCS/LCSD sample set was analyzed; all recoveries and percent difference between duplicates were within QC criteria.

**Matrix spike/matrix spike duplicate:** Sample MW-102 was used for the matrix spike and matrix spike duplicate samples. All analytes were in requisite QC limits excepting the following:

Analyte	RPD		RPD Goal
	MS	MSD	
PFTriA	67.6%	69.5%	70-130%
PFHxA	234%	154%	70-130%
PFTreA	48.4%	49.3%	70-130%
M2PFTreA	50.3%	53.8%	70-130%

The suggested additional qualifiers as a result of these nonconformances are summarized at the end of this memorandum.

**Laboratory duplicate:** Sample MW-102 was used for the laboratory duplicate. All detected analytes were within applicable limits.

*Sample-specific criteria.* The following criteria were checked for every analyte on select samples, as listed below.

**Dilution calculations:** Samples MW-041A, MW-008, MW-054, and MW-044A were checked for the appropriate calculation of reported concentrations in diluted samples. All dilution calculations were performed correctly.

**Retention times:** Samples GWTS, MW-032, MW-102, and MW-054A were checked for analyte relative retention times to be within 0.06 min of the level 5 calibration standard of the corresponding batch, as specified in CRL SOP OM021. All analytes had relative retention times within those criteria.

**Ion ratios:** Samples MW-041, MW-032A, MW-102A, and MW-044 were evaluated for single reaction monitoring (SRM) confirmatory ion ratios. All ion ratios were within applicable QC limits or appropriately qualified by CRL.

**Calculated concentration:** Samples GWTS-A, MW-108, MW-108A, and MW-008A were checked for reported concentrations matching calculations from the applicable 9-point quadratic calibration curve. All reported concentrations were correctly calculated.

**Field blanks:** Quantization reports for samples EB-044, EB-032, and FB-008 were checked for detects present above the applicable method reporting limits. No detections were observed and as such no blank contamination qualifiers were necessary.

**Recommendations**

Based on the conclusions from this data validation effort, it is recommended that the following samples have additional qualifiers applied:

Sample	Analyte	Recommended Qualifier	Reason
GWTS	PFTriA	J	MS/MSD outside control limits
	PFHxA		
GWTS-A	PFTriA		
	PFHxA		
MW-041A	PFHxA		
MW-032	PFTriA		
	PFTreA		
	PFHxA		
MW-032A	PFTriA		
	PFHxA		
MW-008	PFHxA		
MW-102	PFHxA		
MW-102A	PFTriA		
	PFHxA		
MW-054	PFTriA		
	PFHxA		
MW-054A	PFTriA		
	PFTreA		
	PFHxA		
MW-044	PFTriA		
	PFHxA		
MW-044A	PFTriA		
	PFHxA		

In addition, it is recommended that project staff review the groundwater monitoring logs and water quality meter calibration records for inconsistencies and make necessary judgments on the applicability of the data.







**ARCADIS**  
Low Flow Groundwater Sampling Form

Project/No. Stanton Street / WI001651.0001 Well: MW041S

Date: 5/1/18 Casing Material: PVC Casing Diameter: 2"

Static Water Level: 0.80 Measuring Point Description: N. edge TOC

Total Depth: 13.32 Purge Method: LOW FLOW Pump Intake Depth: NA

Time Pump On: 0941 Time Pump Off: 1040

Gallons Purged Prior to Sampling: ~0.5

Sampling Information

Analyte	Sample Volume	Bottle Type	# of Bottles	Preservative
PFAS	2 x 250 mL	Plastic	2	None

Sampled By: GVV Sample Time: 1025

QC Samples Collected: NONE

Time of Day (XX:XX)	Time Elapsed (min)	Purging Rate (mL/min)	Volume Purged (gal)	Turbidity (NTU)	pH (s.u.)	Spec. Cond. (µS/cm)	ORP (mV)	Diss. Oxygen (mg/L)	Temp. (°C)	Color	Appearance	Odor	
<del>0945</del>	<del>0</del>	<del>100</del>	<del></del>	<del></del>	<del></del>	<del></del>	<del></del>	<del></del>	<del></del>	<del>CLEAR</del>	<del>SOME PARTICULATES</del>	<del>NONE</del>	<u>DTW</u>
0950	0	100		73.8	12.99	8.241	-74.5	3.32	10.51	↓	↓	↓	0.90
0955	5	100		5.08	13.86	8.508	-95.0	3.14	11.54				0.80
1000	10	100		11.14	14.45	8.590	-103.2	2.85	11.60				0.80
1005	15	100		5.54	15.06	8.577	-108.5	2.08	10.78				0.80
1010	20	100		5.46	15.29	8.633	-111.5	1.39	10.69				0.80
1015	25	100		11.3 AU	15.35	8.600	-114.1	0.90	11.44				0.80
1020	30	100		67.6 AU	15.44	8.648	-115.8	0.80	11.50				0.80
1025	COLLECT MW041S FOR PFAS (2 x 500 mL POLY)												
				10%/<5	±0.1	3%	±10	10%/<0.5	3%				

Comments: \_\_\_\_\_

ARCADIS

Low Flow Groundwater Sampling Form

Project/No. Stanton Street / WI001651.0001 Well: NW044S

Date: 4/30/18

Casing Material: PVC Casing Diameter: 2"

Static Water Level: 0.25 Measuring Point Description: N. edge TOC

Total Depth: 12.71 Purge Method: Low-Flow Pump Intake Depth: —

Time Pump On: 1718 Time Pump Off: 1810

Sampling Information

Analyte	Sample Volume	Bottle Type	# of Bottles	Preservative
PFAS	2 x 250 mL	Plastic	2	None

Gallons Purged Prior to Sampling: NONE NO.5

Sampled By: GVV Sample Time: 1800

QC Samples Collected: NONE EB-02 @ 1815

Time of Day (XX:XX)	Time Elapsed (min)	Purging Rate (mL/min)	Volume Purged (gal)	Turbidity (NTU)	pH (s.u.)	Spec. Cond. ( $\mu$ S/cm)	ORP (mV)	Diss. Oxygen (mg/L)	Temp. ( $^{\circ}$ C)	Color	Appearance	Odor
1720	0	100		847m	10.92	6.8108	-134.1	4.53	6.38	CLEAR	GOOD	NONE
1725	5	100		12.3	10.69	7.057	-149.7	0.92	7.22	"	"	"
1730	10	100		8.88	10.40	6.187	-157.3	0.44	7.09	↓	↓	↓
1735	15	100		4.72	10.37	6.132	-157.3	0.42	7.01	↓	↓	↓
1740	20	100		4.89	10.37	6.094	-153.3	0.41	6.96	↓	↓	↓
1745	25	100		4.58	10.27	6.009	-147.7	0.41	6.82	↓	↓	↓
1750	30	100		4.81	10.28	5.999	-156.9	0.39	6.81	↓	↓	↓
1800	COLLECT		MW044S	FOR PFOS (2x 500mL)								
				10%/<5	$\pm$ 0.1	3%	$\pm$ 10	10%/<0.5	3%			

DTW  
0.25  
0.25  
0.25  
0.25  
0.25  
0.25  
0.25

*[Handwritten signature]*

Comments: \_\_\_\_\_

**ARCADIS**

Low Flow Groundwater Sampling Form

Project/No. Stanton Street / WI001651.0001

Well: MW0325

Date: 4/30/18

Casing Material: LEXAN

Casing Diameter: 2"

Static Water Level: 5.86

Measuring Point Description: N. edge TOC

Total Depth: 18.64

Purge Method: LOW FLOW

Pump Intake Depth: NA

Time Pump On: 1558

Time Pump Off: 1655

Sampling Information

Analyte	Sample Volume	Bottle Type	# of Bottles	Preservative
PFAS	2 x 250 mL	Plastic	2	None

Gallons Purged Prior to Sampling: ~ 0.5

EB-01 OVER WLEM

Sampled By: GW

Sample Time: 1640

QC Samples Collected: NONE

Time of Day (XX:XX)	Time Elapsed (min)	Purging Rate (mL/min)	Volume Purged (gal)	Turbidity (NTU)	pH (s.u.)	Spec. Cond. (µS/cm)	ORP (mV)	Diss. Oxygen (mg/L)	Temp. (°C)	Color	Appearance	Odor
1600	0	100		14.2	11.29	2.507	216.8	1.45	10.43	YELLOW	CLEAR	NONE
1605	5	1		51	11.65	2.613	-214.1	0.55	10.45			
1610	10	1		1074 AU	11.80	2.598	-215.6	0.47	10.80			
1615	15	1		41	11.94	2.637	-216.3	0.43	10.68			
1620	20	1		811 AU	12.04	2.631	-215.0	0.39	10.30			
1625	25	1		47	12.15	2.612	-217.0	0.36	10.38			
1630	30	1	48	<del>811 AU</del>	12.19	2.615	-216.3	0.34	10.78			
1635	35	1		47	12.20	2.628	-218.9	0.34	10.85			
1640	COLLECT MW0325 FOR PFAS (2 x 500 mL POLY)											
				10% < 5	±0.1	3%	±10	10% < 0.5	3%			

DTW  
6.23  
8.55  
8.22  
8.62  
9.01  
9.01  
9.01  
9.01

Comments: \_\_\_\_\_

**ARCADIS**

Low Flow Groundwater Sampling Form

Project/No. Stanton Street / WI001651.0001 Well: MW054S Date: 4/30/18 Casing Material: PVC Casing Diameter: 2"  
 Static Water Level: 3.95 Measuring Point Description: N. edge TOC Total Depth: 15.36 Purge Method: LOW FLOW Pump Intake Depth: NA

Time Pump On: 1415 Time Pump Off: 1515

Gallons Purged Prior to Sampling: 0.5

Sampling Information

Analyte	Sample Volume	Bottle Type	# of Bottles	Preservative
PFAS	2 x 250 mL	Plastic	2	None

Sampled By: GVV Sample Time: 1505

QC Samples Collected: DUP-01; MS/MSD

Time of Day (XX:XX)	Time Elapsed (min)	Purging Rate (mL/min)	Volume Purged (gal)	Turbidity (NTU)	pH (s.u.)	Spec. Cond. (µS/cm)	ORP (mV)	Diss. Oxygen (mg/L)	Temp. (°C)	Color	Appearance	Odor
1420	0	100		69.8	8.22	0.756	-65.7	4.60	6.25	CLEAR		
1425	5			69.8	8.38	0.755	-75.5	1.93	6.74			
1430	10			52.2	8.45	0.757	-78.8	1.38	6.23			
1435	15			62.1 AU	8.50	0.755	-81.7	1.03	6.21			
1440	20			55.4	8.53	0.754	-83.4	0.91	6.65		GREEN PARTICLES	
1445	25			49.4	8.58	0.755	-84.6	0.87	6.66		GREEN TINT	
1450	30			23.5	8.61	0.757	-85.8	0.83	6.38		GREEN TINT	
1455	COLLECT		MW054S	TS	FOR	PFAS (6 x 500 mL POLY)						
1455				22.1	8.63	0.755	-86.4	0.84	6.07			
1500				17.3	8.64	0.752	-86.5	0.82	5.81			
1505	COLLECT		MW054S	TS	FOR	PFAS (6 x 500 mL POLY)						
				10% < 5	±0.1	3%	±10	10% < 0.5	3%			

DTW  
4.04  
4.04  
4.04  
4.04  
4.04  
4.04  
4.04  
4.04

Comments: \_\_\_\_\_

**ARCADIS**

Low Flow Groundwater Sampling Form

Project/No. Stanton Street / WI001651.0001 Well: 102S

Date: 4/30/18

Casing Material: PVC

Casing Diameter: 2"

Static Water Level: 4.10

Measuring Point Description: N. edge TOC

Total Depth: 17.4

Purge Method: LOW-FLOW

Pump Intake Depth: NA

Time Pump On: 1305

Time Pump Off: 1355

Gallons Purged Prior to Sampling: ~0.5

Sampling Information

Analyte	Sample Volume	Bottle Type	# of Bottles	Preservative
PFAS	2 x 250 mL	Plastic	2	None

Sampled By: G V V

Sample Time: 1345

QC Samples Collected: NONE

Time of Day (XX:XX)	Time Elapsed (min)	Purging Rate (mL/min)	Volume Purged (gal)	Turbidity (NTU)	pH (s.u.)	Spec. Cond. (µS/cm)	ORP (mV)	Diss. Oxygen (mg/L)	Temp. (°C)	Color	Appearance	Odor	DTU'
1310	0	100		2.33	7.89	0.736	-94.0	4.68	7.87	—	CLEAR	—	4.33
1315	5	100		2.34	8.29	0.776	-97.3	0.519	7.42	—	"	—	4.54
1320	10	100		2.20	8.32	0.774	-94.8	0.515	7.39	—	"	—	4.54
1325	15	100		3.07	8.31	0.774	-86.9	0.513	7.34	—	"	—	4.54
1330	20	100		4.58	8.32	0.771	-79.5	0.512	7.40	—	"	—	4.54
1335	25	100		3.89	8.27	0.771	-77.0	0.512	7.40	—	"	—	4.54
1340	30	100		3.34	8.31	0.772	-75.2	0.511	7.27	—	"	—	4.54
1345	COLLECT		MW-	02S	FOR	PFAS (2 x 250 mL)							
				10% < 5	±0.1	3%	±10	10% < 0.5	3%				

Comments: \_\_\_\_\_

