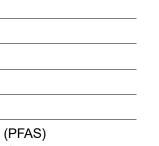


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Memo



То	Tauren Beggs		
From	David de Courcy-Bower and Carl Stay		
Date	12 April 2023		
Reference	0383990		
Subject	Additional Evaluation of Polyfluorinated Alkyl Substances (PFAS) Former Hamilton Industries Property, Two Rivers, Wisconsin BRRTS Activity #02-36-578316		

Dear Mr. Beggs,

This memorandum has been prepared to provide the Wisconsin Department of Natural Resources (WDNR) further evaluation of polyfluorinated alkyl substances (PFAS) at the Former Hamilton Industries Property located in Two Rivers, Wisconsin, BRRTS Activity #02-36-578316 (Site).

Background

WDNR issued a letter, Review of the Site Status Report and Remedial Action Options Evaluation, on July 16, 2021, which included a determination that additional work was necessary to complete the site investigation under Wis. Admin. Code ch. NR 716. This determination included the request for additional scoping, contaminant, and media evaluations. In response, ERM submitted the 2021 Work Plan Addendum - Additional Groundwater and Soil Investigation on September 10, 2021. A site investigation work plan notice to proceed was issued by DNR on September 23, 2021. The additional investigation work completed in 2021 addressed soil and groundwater sampling. The October and November 2021 Additional Groundwater and Soil Investigation memorandum dated February 11, 2022, was submitted to the WDNR for Technical Assistance (TA) review. A portion of the memorandum presented Site groundwater sampling data for PFAS. In the Technical Assistance response letter dated May 4, 2022, the WDNR made the following determination regarding PFAS at the Site:

PFAS: Additional sampling is needed before a determination can be made that PFAS is not associated with releases on-site. The highest PFAS concentrations are found where the highest chlorinated VOC concentrations are found. While there are PFAS concentrations upgradient as well, it is not conclusive that PFAS is not a contaminant of concern on-site at this time.

This Additional Evaluation of Polyfluorinated Alkyl Substances Memorandum has been prepared in response to the May 4, 2022, letter to provide WDNR the results of additional evaluation for PFAS for the Site.

Additional PFAS Evaluation

ERM completed the following tasks to further evaluate the presence of PFAS in groundwater at the Site:

- Evaluated the correlation between the concentration of PFAS compounds and Trichloroethylene (TCE) in groundwater at the Site to understand if the concentrations are related.
- Reviewed historical documentation to evaluate potential historical uses of PFAS on adjacent properties and identified the location of the former waste/paint storage building on the Site.
- Developed separate groundwater concentration contour plots for PFAS constituents that exceed either of the proposed ch. NR140 preventive action limit (PAL) or enforcement standard (ES).

Correlation between TCE and PFAS Compounds

An evaluation of the correlation between groundwater concentrations of TCE and PFAS compounds was completed by data evaluation with graphical and statistical methods. Scatterplots of the concentration of TCE plotted against the concentrations of PFAS constituents with a proposed ES exceedance were developed for PFAS compounds with an ES exceedance and are provided in Attachment A. If there is a positive correlation between TCE and PFAS concentration, then there will be clustering of data points from the bottom left (low TCE and low PFAS) to the top right (higher TCE and higher PFAS).

TCE vs PFHxS

The scatterplot for TCE vs PFHxS is provide as Figure A1. MW-15I has the highest concentration of TCE but one of the lowest concentrations of PFHxS. MW-04 located off-Site to the south has the highest concentration of PFHxS and one of the higher concentrations of TCE. However, there are multiple wells with concentrations of PFHxS between 2 to 10 ng/l that have low concentrations of TCE or are non-detect i.e., MW-24S, MW-08, MW-15S. Overall, the scatterplot does not show a clear linear relationship between TCE and PFHxS concentrations.

TCE vs PFOS

The scatterplot for TCE vs PFOS is provide as Figure A2. MW-15I has the highest concentration of TCE but one of the lowest concentrations of PFOS. MW-20S has the highest concentration of PFOS but has low concentrations of TCE. MW-04 located off-Site to the south has the higher concentrations of both PFOS and TCE. However, there are multiple wells with concentrations of PFOS between 2 to 10 ng/l that have low concentrations of TCE or are non-detect i.e., MW-19S, MW-26S, MW-15S, MW-17S. Overall, the scatterplot does not show a clear linear relationship between TCE and PFOS concentrations.

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TCE vs PFOA

The scatterplot for TCE vs PFOA is provide as Figure A3. MW-15I has the highest concentration of TCE but one of the lowest concentrations of PFOA. MW-15S has the highest concentration of PFOA but has low concentrations of TCE. Although MW-15S and MW-15I are located adjacent to each other, it is erroneous to conclude that the relatively high concentration of PFOA in groundwater at MW-15S is related to the relatively high concentration of TCE in MW-15I as they are screened across different intervals. MW-04 located off-Site to the south has the higher concentrations of both PFOA and TCE. However, there are multiple wells with concentrations of PFOA between 10 to 100 ng/l that have low concentrations of TCE or are non-detect i.e. MW-24S, MW-10S, MW-15S, MW-14S. Overall, the scatterplot does not show a clear linear relationship between TCE and PFOS concentrations.

TCE vs Sum of EtPFOSA, NEtPFOSE, NMePFOSAA, FOSA, PFOS, and PFOA

The scatterplot for TCE vs Sum of EtPFOSA, NEtPFOSE, NMePFOSAA, FOSA, PFOS, and PFOA (Sum PFAS) is provide as Figure A4. MW-15I has the highest concentration of TCE but one of the lowest concentrations of Sum PFAS. MW-15S has the highest concentration of Sum PFAS but has low concentrations of TCE. Although MW-15S and MW-15I are located adjacent to each other, it is erroneous to conclude that the relatively high concentration of Sum PFAS in groundwater at MW-15S is related to the relatively high concentration of TCE in MW-15I as they are screened across different intervals. MW-04 located off-Site to the south has the higher concentrations of both Sum PFAS and TCE. However, there are multiple wells with concentrations of Sum PFAS between 10 to 100 ng/I that have low concentrations of TCE or are non-detect i.e., MW-24S, MW-10S, MW-15S, MW-14S. Overall, the scatterplot does not show a clear linear relationship between TCE and Sum PFAS concentrations.

Spearman's test

The correlation between trichloroethene (TCE) and all 33 PFAS compounds as well as the Sum PFAS compounds was analyzed with a non-parametric correlation test (Spearman's test). The results of the analysis are provided as Attachment A.

The null hypothesis in this test is that the Spearman correlation coefficient, ρ ("rho"), is 0. A ρ of 0 means that the ranks of one variable (TCE) do not covary with the ranks of the other variables (PFAS), meaning no significant correlation of a positive (increase) or negative (decrease) between them. The data does not hold evidence for rejecting the null hypothesis of no covariation for any pair of variables, as all p-values are greater than the critical value for rejection at a level of significance of 0.05. The Spearman's test supports that there is no correlation between the concentration of TCE and the concentration of any of the 33 PFAS compounds analyzed or the Sum PFAS compounds.

In conclusion, the WDNR statement that "The highest PFAS concentrations are found where the highest chlorinated VOC concentrations are found" is not supported by the data analysis performed. The data analysis supports the conclusion that the concentration of every PFAS compound detected in groundwater is unrelated to the concentration of TCE detected in groundwater at the Site.

Historical, Potential PFAS Compounds Use

In the June 18, 2021, memorandum, ERM evaluated whether any products containing emerging contaminants were used in historical operations, the duration of use, and any areas of the Site where emerging contaminants may have been used, stored, managed, or discarded. The operations at the Site were primarily manufacturing of wood furniture and steel appliances. No documentation reviewed indicated significant use of PFAS as part of Site manufacturing operations. Former operations at the property included hazardous waste incineration as an alternate boiler fuel source from 1974 until 1987, with most of the waste from off-Site locations. ERM concluded that due to these former waste operations, the use, presence, or absence of PFAS could not be ruled out. The location of the former waste/paint storage building is presented on Figures 1 through 4.

To evaluate potential uses off-Site, ERM reviewed the current and historical adjacent property uses. Historical document review included review of Sanborn maps that showed the following adjacent property uses that may have used PFAS:

- 1. Former printing operations located at the northwest corner of Jefferson St. and River Rd.
- 2. The Kahlenberg Laboratories/chemistry building located at 1316 E. River Rd.
- 3. Paint storage/manufacturing facility located at 1407 16th Street.

The location of these historical property uses is also presented on Figures 1 through 4.

PFAS Compound Distribution in Groundwater

In October 2021, ERM sampled 26 Site groundwater monitoring wells for Emerging Contaminants (PFAS compounds and 1,4-Dioxane). Of the 33 PFAS compounds analyzed in the Site groundwater samples six (6) have a proposed PAL or ES and include PFBS, PFBA, PFHxS, PFHxA, PFOS, and PFOA. Table 1 presents the proposed PAL and ES and provides an expanded description of the acronyms. Additionally, the Wisconsin Department of Health Services (DHS) has proposed a PAL and ES for the combined FOSA, NEtFOSE, NEtFOSA, NEtFOSAA, PFOS, and PFOA.

As shown on Table 1, PFHxS, PFOS, PFOA, and the combined substances mentioned above were detected at concentrations that exceeded a proposed PAL or ES in groundwater. Groundwater isoconcentration contour plots for each of the compounds were developed and are provided as Figures 1 through 5.

PFHxS

The extent of PFHxS in groundwater is shown on Figure 1. The only location where PFHxS exceeded the proposed ES of 40 ng/l was at MW-04 located off-Site to the southeast of the former Kahlenberg Laboratories property. PFHxS was detected in MW-17S at a concentrations 9.7 ng/l that exceeded the proposed PAL of 4 ng/l.

The extent of PFHxS in groundwater has been delineated and the highest concentration is located off-Site. The former Kahlenberg Laboratories property is the closest potential source of PFHxS for

the ES exceedance, and the former waste/paint storage building is the closest potential source of PFHxS for the on-Site PAL exceedance.

Based on the results, no further delineation of PFHxS is required and due to the very low concentrations on the Site no further additional sampling is recommended for PFHxS.

PFOS

The extent of PFOS in groundwater is shown on Figure 2. The only location where PFOS exceeded the proposed ES of 20 ng/l was at MW-20S located off-Site to the east of the former Paint Storage building. PFOS was detected in almost all groundwater wells at concentrations that exceeded the proposed PAL of 4 ng/l. In reviewing the laboratory analytical results, 7 samples with proposed PAL exceedances were flagged by the laboratory as having a detectable PFOS concentration in the laboratory blank sample. The location of these samples is shown on Figure 2 and presented on Table 1.

The extent of PFOS in groundwater appears to extent off-Site to the north and northwest of the Site and the highest concentration is located off-Site. The off-Site former Paint Storage property is the closest potential source of PFOS for the ES exceedance. There does not appear to be a specific source of PFOS that resulted in PAL exceedances on-Site.

Based on the results, there does not appear to be a specific source of PFOS at the Site. As there is no evidence of a specific source or release of PFOS on the Site no further additional sampling is recommended for PFOS.

PFOA

The extent of PFOA in groundwater is shown on Figure 3. PFOA concentrations were detected above the proposed ES in groundwater across the Site and also at upgradient and off-Site locations. Concentrations of PFOA above the proposed ES appear along the northern, eastern and southern portions of the Site and off-Site to the south, but do not correlate with the historic uses of PFAS either on Site or off-Site. There is no clear source of PFOA concentrations, and it appears that the concentrations of PFOA in groundwater likely represent accumulation of PFOA due to unrelated sources to the Site.

Based on the results, there does not appear to be a specific source of PFOA at the Site and no evidence of a release at the Site. As there is no evidence of a specific source or release of PFOA on the Site no further additional sampling is recommended for PFOA.

Combined FOSA, NEtFOSE, NEtFOSA, NEtFOSAA, PFOS, and PFOA

The extent of combined FOSA, NEtFOSE, NEtFOSA, NEtFOSAA, PFOS, and PFOA (Sum PFAS) in groundwater is shown on Figure 4. Sum PFAS concentrations were detected above the proposed ES in groundwater across the Site and at upgradient and off-Site locations. Concentrations of Sum PFAS above the proposed ES are similar to PFOA and appear along the northern, eastern, and southern portions of the Site and off-Site to the south, but do not correlate with the historic uses of PFAS either on Site or off-Site. There is no clear source of PFAS concentrations, and it appears that the concentrations of Sum PFAS in groundwater likely represent accumulation of PFAS due to unrelated sources to the Site.

Based on the results, there does not appear to be a specific source of PFAS at the Site and no evidence of a release at the Site. As there is no evidence of a specific source or release of PFAS on the Site no further additional sampling is recommended for PFAS.

Discussion

This memorandum was prepared understanding the context that PFAS are considered emerging contaminants that can pose a risk to human health and the environment. However, the regulation and technical understanding of PFAS compounds continues to evolve. The evaluation of PFAS at the Site was performed based on current guidance from the WDNR and DHS and used both the WAC NR 809 MCLs and proposed NR 140 PAL and ES as references for understanding the risks to human health and the environment at the Site.

The groundwater sampling completed identified exceedances of the proposed ES and proposed PAL both on-Site and off-Site on adjacent and upgradient properties. However, the nature and extent of PFAS detected in groundwater does not correlate to the nature and extent of TCE in groundwater. Except for PFHxS detected near the former waste/paint storage building, the data does not indicate that a Site-specific release of PFAS occurred at the Site. Concentrations of PFOA/PFOS are located both off-Site and hydraulically upgradient of the Site and are detected at relatively low levels without a clear hot spot or source on Site.

Although there is no clear source of PFAS at the Site, it is recognized that PFOA/PFOS were detected at concentrations that exceed the drinking water NR 809 MCL of 70 ng/l at two monitoring wells on Site MW-24S (74.8 ng/l) and MW-15S (110 ng/l) and one monitoring well off-Site MW-04 (79 ng/l), and that there are ubiquitous exceedances of the proposed PAL and ES for PFAS both on and off-Site.

Recommendations

Based on the finding of this date review WDNR concurrence with the following is requested:

- 1) The nature and extent of PFAS at the Site has been sufficiently delineated for the purposes of Site Investigation.
- 2) The presence of PFAS in groundwater at the Site at concentrations that exceed the proposed PAL, proposed ES and the NR 809 MCL can be managed with a groundwater use restriction for the Site and no active remediation or further groundwater sampling for PFAS is required.

Please let us know if you would like to schedule a time to discuss the findings of this memorandum.

David de Courcy-Bower, P.E.

Molely B

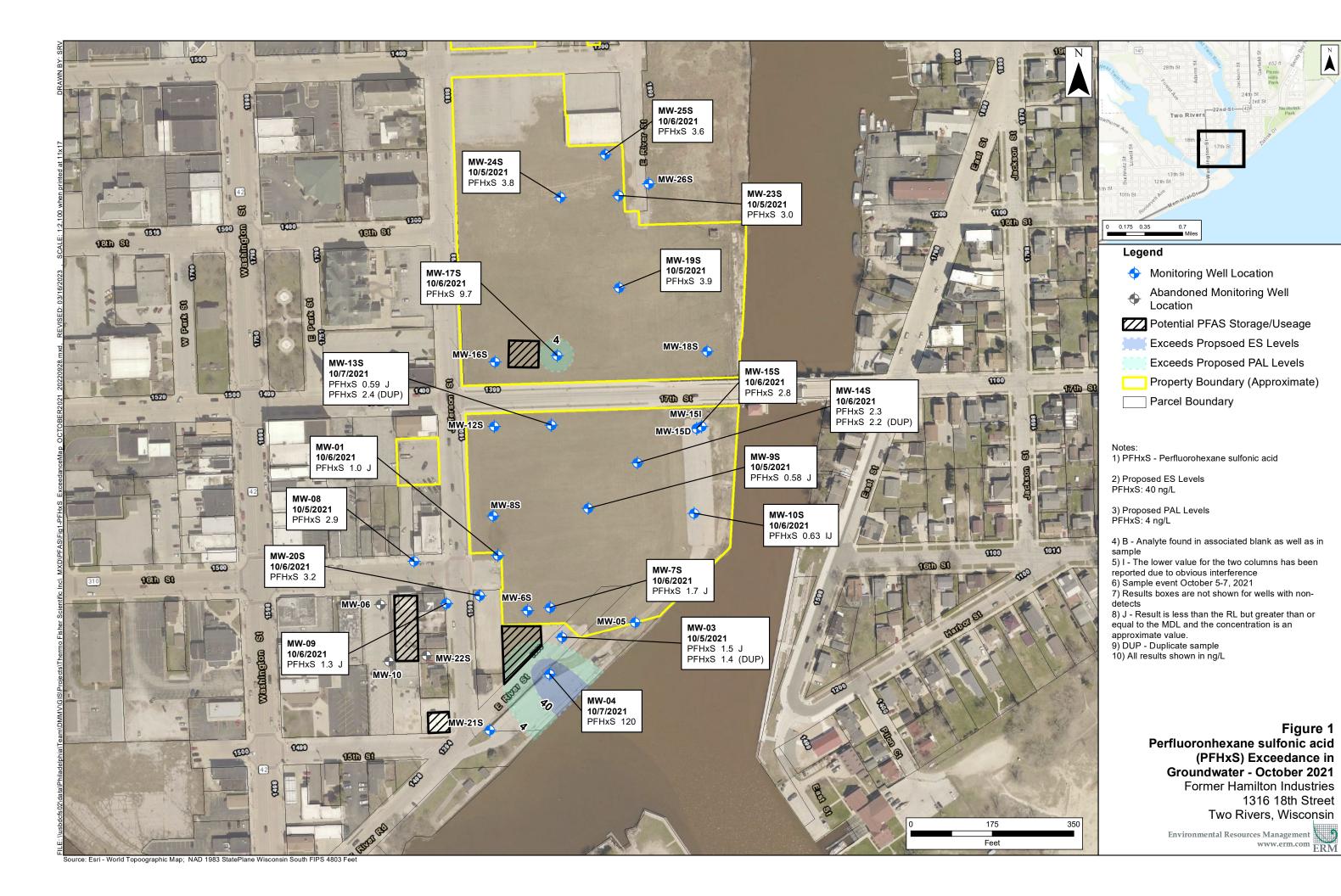
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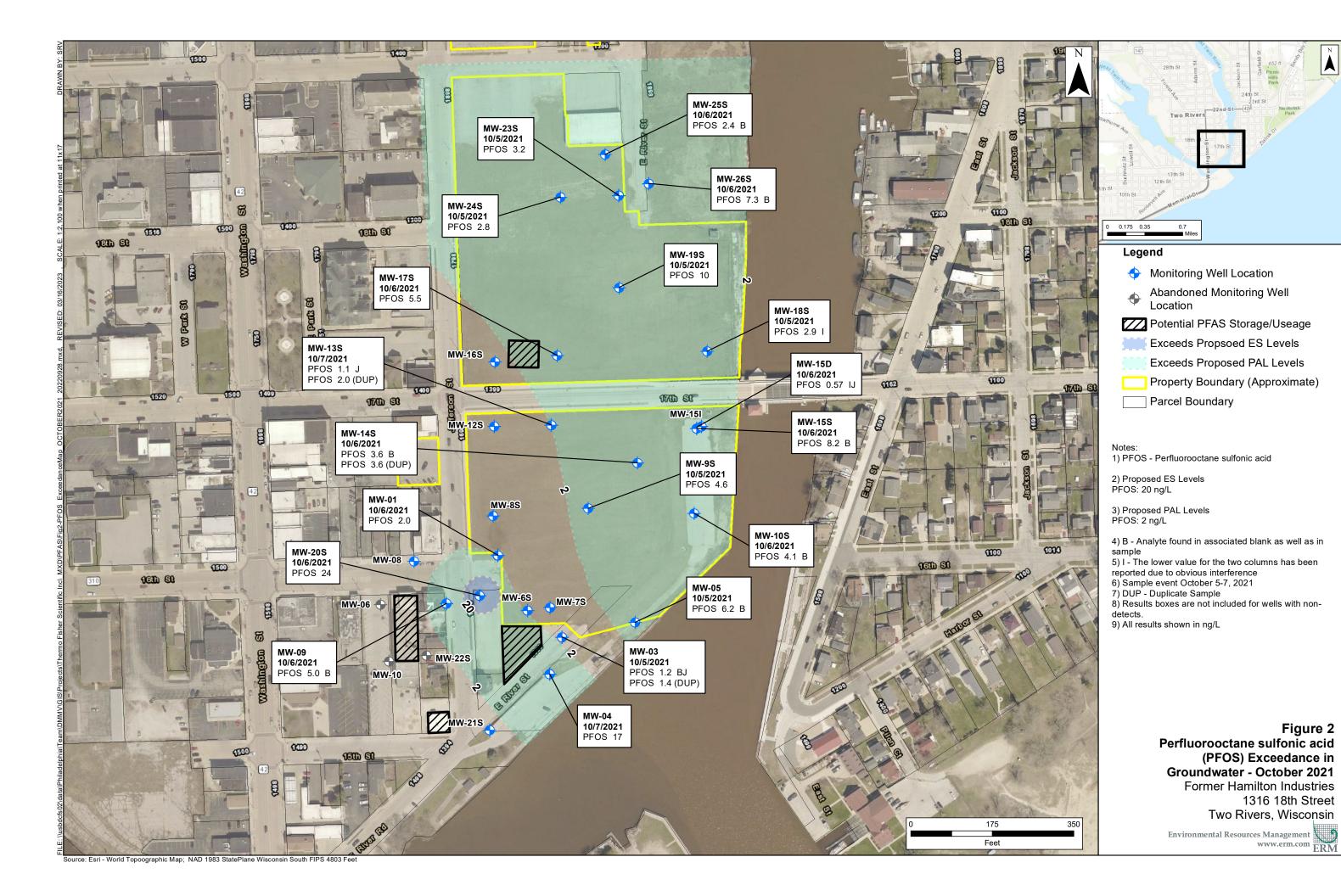
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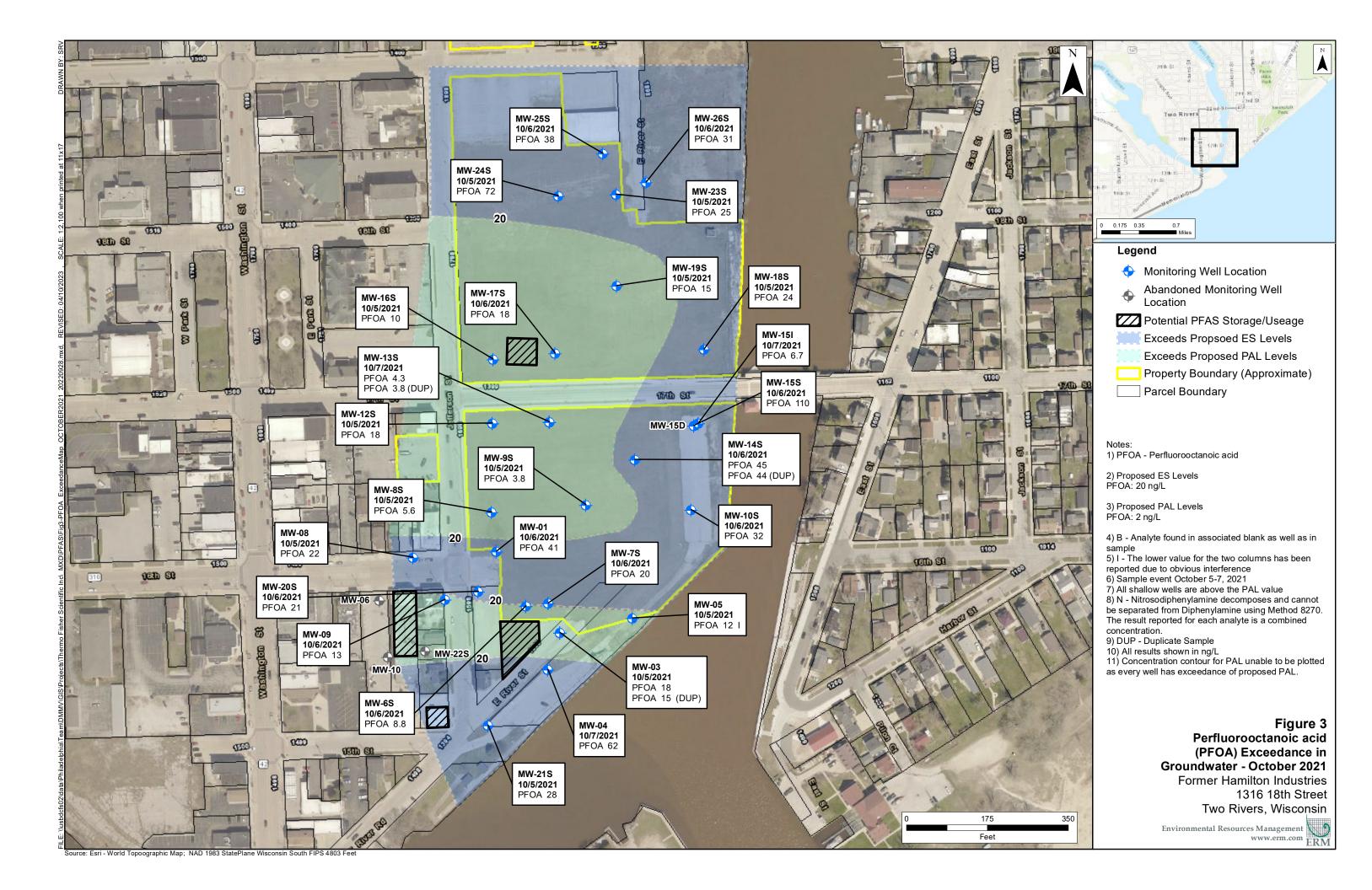
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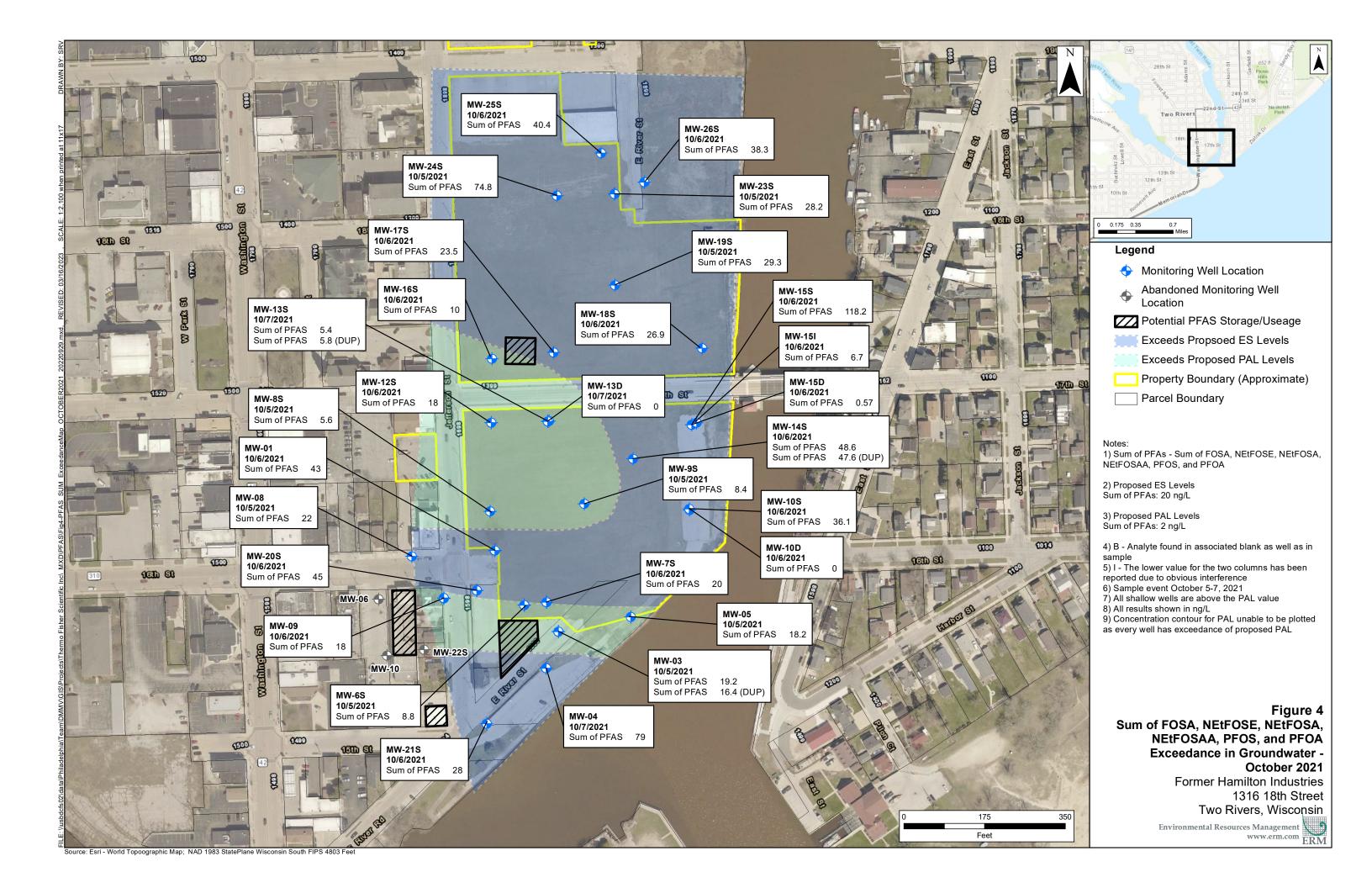
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attachments









Attachment A PFAS vs TCE Evaluation

Spearman's Test Results Former Hamilton Industries Site Two Rivers, Wisconsin

Method:

- -This spreadsheet contains the results of an analysis performed to identify potential correlations between TCE and PFAS species
- -Pairwise relationships between TCE and each PFAS species were evaluated (Spearman's rank correlation)
- -A series of tests were performed on each analyte pair to determine whether correlations were statistically significant (95% confidence level)
- -Spearman correlations were low (|rho| < 0.3) for all PFAS-TCE pairs
- -None of the correlations were statistically significant

Analyte	Spearman's Correlation with TCE	Statistically Significant	p-value
11CL.PF3OUDS	-0.103	FALSE	0.590
4.2.FTS	-0.134	FALSE	0.482
6.2.FTS	-0.012	FALSE	0.952
8.2FTS	-0.147	FALSE	0.437
9CL.PF3ONS	-0.198	FALSE	0.295
DONA	0.020	FALSE	0.915
EtPFOSA	-0.178	FALSE	0.347
FOSA	-0.223	FALSE	0.237
HxFPO.DA	-0.114	FALSE	0.548
NEtPFOSAA	-0.207	FALSE	0.272
NEtPFOSE	-0.119	FALSE	0.530
NMePFOSA	-0.222	FALSE	0.239
NMePFOSAA	-0.136	FALSE	0.473
NMePFOSE	-0.066	FALSE	0.731
PFBA	0.070	FALSE	0.712
PFBS	-0.096	FALSE	0.612
PFDA	-0.259	FALSE	0.167
PFDoDA	-0.041	FALSE	0.830
PFDoDS	-0.284	FALSE	0.128
PFDS	-0.238	FALSE	0.206
PFHpA	0.194	FALSE	0.305
PFHpS	0.125	FALSE	0.511
PFHxA	0.117	FALSE	0.539
PFHxS	0.214	FALSE	0.256
PFNA	-0.176	FALSE	0.353
PFNS	-0.173	FALSE	0.361
PFOA	0.104	FALSE	0.585
PFOS	0.223	FALSE	0.236
PFPeA	0.193	FALSE	0.308
PFPeS	0.138	FALSE	0.468
PFTeDA	-0.077	FALSE	0.684
PFTrDA	-0.147	FALSE	0.437
PFUnDA	-0.145	FALSE	0.444
EtPFOSA_NEtPFOSE_NMePFOSAA_FOSA_PFOS_PFOA	0.099	FALSE	0.602

Figure A1 - TCE vs PFHxS Scattergram

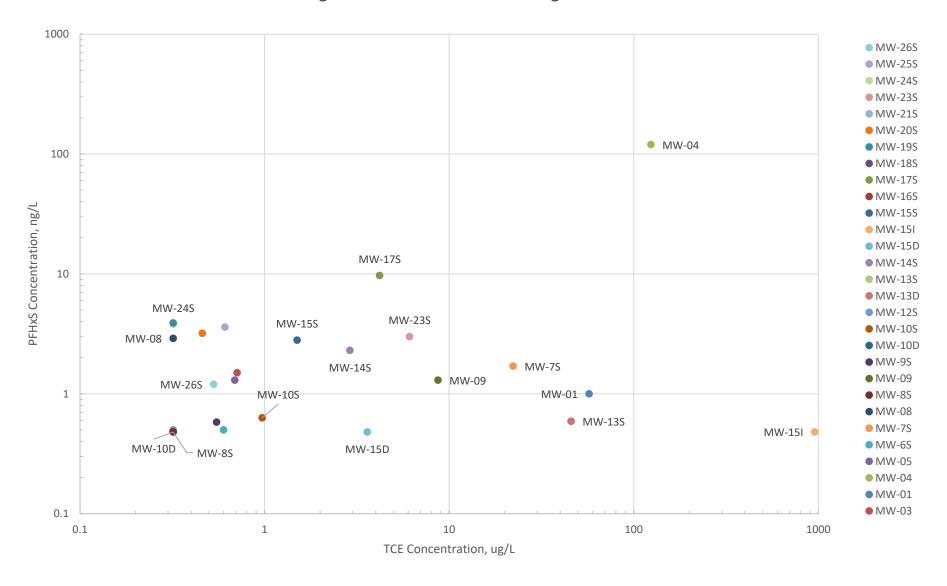


Figure A2 - TCE vs PFOS Scattergram

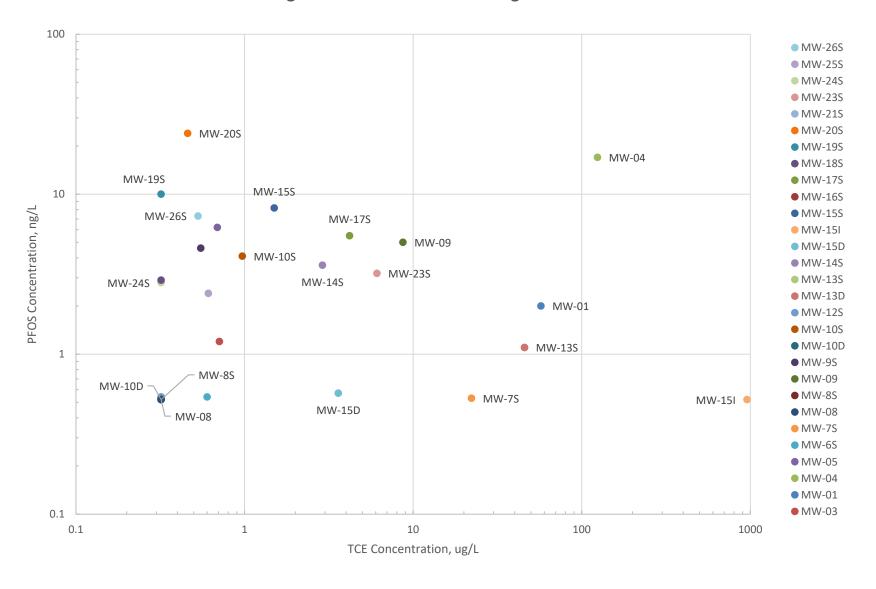


Figure A3 - TCE vs PFOA Scattergram

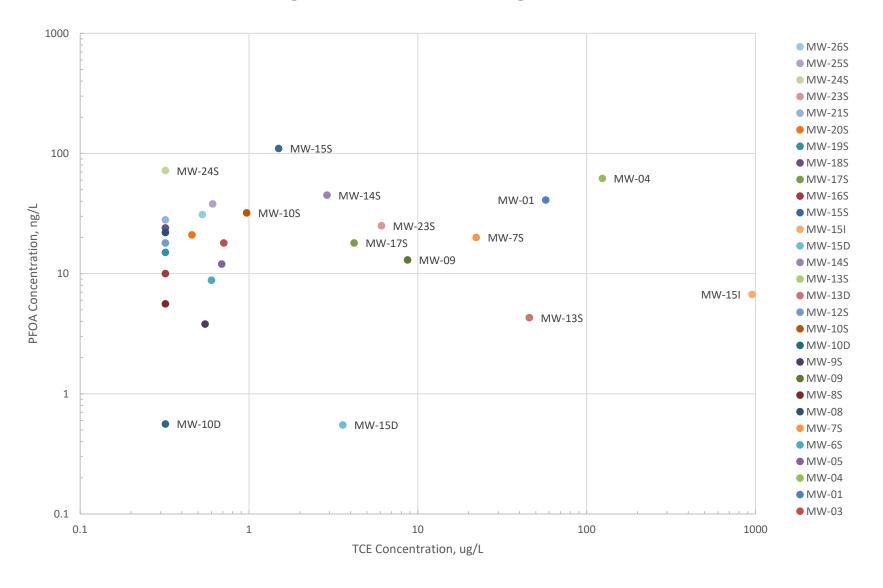


Figure A4 - TCE vs Sum of EtPFOSA, NEtPFOSE, NMePFOSAA, FOSA, PFOS, and PFOA Scattergram

