

# PFAS Groundwater Study Report

Michigan Department of Environment, Great Lakes, and  
Energy (EGLE)

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## Table of Contents

Executive Summary.....	i
<b>1. Introduction.....</b>	<b>1</b>
1.1 Objectives and Study Questions.....	1
1.2 Data Uncertainties and Limitations .....	1
1.3 Historical Site Information .....	3
1.3.1 Grayling Area PFAS Study Area .....	3
1.3.1.1 Residential Drinking Water Sampling .....	3
1.3.1.2 Remedial Investigation.....	3
1.3.2 North Kent.....	4
1.3.3 Richland .....	5
<b>2. PFAS Chemistry .....</b>	<b>7</b>
2.1 PFAS Manufacturing .....	7
2.2 Perfluorinated vs. Polyfluorinated Compounds.....	7
2.2.1 Chain Length.....	8
2.2.2 Isomers .....	8
2.2.3 Precursors and Indirect PFAS Emissions .....	9
2.3 PFAS Sources.....	10
2.3.1 AFFF - Grayling.....	10
2.3.2 Scotchgard™ – North Kent .....	10
2.3.3 Fume Suppressant – Richland.....	11
<b>3. Study Methodology.....</b>	<b>12</b>
3.1 Preparation Phase – Data Grouping.....	12
3.2 Preparation Phase – Table Creation.....	12
3.3 Evaluation Phase – Statistical Methods.....	13
<b>4. Results .....</b>	<b>14</b>
4.1 Grayling.....	14
4.1.1 Preparation Phase – Data Grouping.....	14
4.1.2 Preparation Phase – Table Creation .....	14
4.1.3 Evaluation Phase – Analytical Review.....	14
4.1.4 Statistical Results.....	15
4.2 North Kent.....	15
4.2.1 Preparation Phase – Data Grouping.....	15
4.2.2 Preparation Phase – Table Creation .....	15
4.2.3 Evaluation Phase – Analytical Review.....	15
4.2.4 Statistical Results.....	16
4.3 Richland .....	16
4.3.1 Preparation Phase – Data Grouping.....	16
4.3.2 Preparation Phase – Table Creation .....	16
4.3.3 Evaluation Phase – Analytical Review.....	16
4.3.4 Statistical Results.....	17
<b>5. Discussion .....</b>	<b>18</b>
5.1 Discussion of Primary Study Objectives .....	20
<b>6. Conclusion and Recommendations.....</b>	<b>22</b>
<b>7. References .....</b>	<b>23</b>

## Figures

- Figure 1. Primary Study Variables
- Figure 2. Grayling Area PFAS Study Area Residential, Monitoring Well and VAS Total PFAS Heat Map
- Figure 3. North Kent Study Area Residential, and Monitoring Well Total PFAS Heat Map
- Figure 4. Richland Study Area Residential, and Monitoring Well Total PFAS Heat Map
- Figure 5. Varying chemical structures in per and –poly carboxylic acids
- Figure 6. Example chemical structures of linear and branched PFOS
- Figure 7. PFAS exposure and transformation pathways (from Gebbink et al., 2015)
- Figure 8. Grayling Study Area Data Evaluation Groups
- Figure 9. FOD - All Data Average (MW, VAS and Residential) GAAF Groups 1-15
- Figure 10. North Kent Study Area Data Evaluation Groups
- Figure 11. Richland Study Area Data Evaluation Groups
- Figure 12. Select PFAS Mobility in Aqueous Systems Based on Log Kow and Chemical Solubility
- Figure 13. Comparison of PFOS from residential and monitoring wells from aggregated sites
- Figure 14. Comparison of PFOA from residential and monitoring wells from aggregated sites
- Figure 15. Comparison of PFHxS from residential and monitoring wells from aggregated sites

## Tables

- Table 1. Physio-Chemical properties of short-chain versus long-chain PFAS.
- Table 2. Reported PFOS concentrations in various commercial wetting agents.
- Table 3. Wilcoxon-Mann-Whitney Tests for Grayling Area Study Groups
- Table 4. Wilcoxon-Mann-Whitney Tests for North Kent Study Groups
- Table 5. Wilcoxon-Mann-Whitney Tests for Richland Study Groups

## Appendices

- Appendix A. Supporting Data Visualizations and Graphs

## Executive Summary

AECOM has prepared this PFAS Groundwater Study Report (report) to present an evaluation of investigative-derived environmental Per- and Polyfluoroalkyl Substances (PFAS) groundwater analytical data compared to residential drinking water PFAS analytical data. This report used data sets derived from three separate study areas: Grayling Area PFAS (Crawford County, MI), the North Kent Area PFAS (Kent County, MI), and North 34th Street, former Production Plated Plastics, PFAS site (Kalamazoo County, MI). This work was performed under funding allocated by the State of Michigan under direction and guidance of the Michigan PFAS Action Response Team (MPART).

The primary objectives of this study are to determine if data collected during environmental groundwater investigations accurately reflect PFAS footprint, plume behavior, aquifer conditions, and drinking water risks, and to determine if temporal PFAS concentrations behave differently than traditional target contaminants of concerns (COCs). Secondary objectives included maintaining geological or stratigraphic consistency (having wells screened in same lithostratigraphic unit) and minimizing distances both laterally and vertically (spatial distance between well screens and well locations).

Uncertainties and limitations were expected in developing the framework for this study, and several more were elucidated during evaluation of datasets. The primary data uncertainties found during evaluation included distance between sampling pairs (including horizontal and vertical distance), time (i.e. date) of sampling, and analytical method.

A process flow approach was used in evaluating each of the three site datasets. This approach included two phases, a preparation phase and an evaluation phase. The preparation phase included grouping and compiling data, both analytical and its associated spatial and geologic data. Spatial data for each individual study area is stored in a geodatabase using the Environmental Systems Research Institute (ESRI) software platform. All analytical data are stored in EarthSoft EQUiS™ database (EQUiS). Geologic data for environmental borings came from geologic logs produced during field investigation activities. Geologic data for residential wells was obtained from the EGLE Wellog online database, which compiles residential well installation, completion, and geologic information. The evaluation phase included filtering, sorting and data quality control (QC) of compiled data. The finalized dataset was then evaluated and processed using specific statistical analyses.

The following conclusions were ascertained:

- Significant difference in median PFBA concentration in residential wells versus monitoring wells was determined at the North Kent Study Area.
- Higher apparent median residential well concentrations of PFBS, PFHpA, PFOS and PFPeA were found in the North Kent Study Area; however, these compounds did not show significant difference using Wilcoxon-Mann-Whitney rank-sum tests.
- Higher apparent median residential well concentrations of PFBA, PFPeA, PFHxA, PFPxS, PFHpA and PFOS were found in the Grayling Study Area; however, these compounds did not show significant difference using Wilcoxon-Mann-Whitney rank-sum tests.
- Higher median residential well concentration of PFOS was found in the Richland study area; however, the number of samples did not allow for Wilcoxon-Mann-Whitney rank-sum testing.

# 1. Introduction

AECOM has prepared this PFAS Groundwater Study Report (report) to present an evaluation of investigative-derived environmental Per- and Polyfluoroalkyl Substances (PFAS) groundwater analytical data compared to residential drinking water PFAS analytical data. This report used data sets derived from three separate study areas: Grayling Area PFAS (Crawford County, MI), the North Kent Area PFAS (Kent County, MI), and North 34th Street, former Production Plated Plastics, PFAS site (Kalamazoo County, MI). This work was performed under funding allocated by the State of Michigan under direction and guidance of the Michigan PFAS Action Response Team (MPART).

## 1.1 Objectives and Study Questions

AECOM understands that the Michigan Department of Environment, Great Lakes, and Energy (EGLE), formerly the Michigan Department of Environmental Quality, is the regulatory authority in charge of protection of human health and the environment with regard to contamination present at each of the sites discussed in this report. Ongoing environmental investigations at each of these three sites have shown observed differences in analytical results between residential drinking water and environmental groundwater samples (i.e. groundwater samples collected from monitoring wells and vertical aquifer samples (VAS)). These observations by consultants and EGLE staff were largely anecdotal (unconfirmed) but suggested that on occasion various PFAS concentrations appeared to be higher in residential well samples than in the investigation-derived monitoring well or VAS samples. EGLE contracted AECOM to investigate and understand the potential differences between PFAS analytical results from residential drinking water and environmental groundwater samples.

The primary objectives of this study are:

1. Determine if data collected during environmental groundwater investigations accurately reflect PFAS footprint, plume behavior, aquifer conditions, and drinking water risks.
2. Determine if temporal PFAS concentrations behave differently than traditional target contaminants of concerns (COCs), including volatile organic contaminants (VOCs), metals, petroleum hydrocarbons or other COCs.

As the study evolved secondary objectives related to study design were added due to identified data uncertainties and project limitations. These objectives included maintaining geological or stratigraphic consistency (having wells screened in same lithostratigraphic unit) and minimizing distances both laterally and vertically (spatial distance between well screens and well locations).

## 1.2 Data Uncertainties and Limitations

The approach for comparing investigation data with residential data from each of the three sites required selecting study groups, which contained at least one residential well and one monitoring well or VAS device for comparative purposes (the approach is discussed in **Section 3**). Uncertainties and limitations were expected in developing the framework for this study, and several more were elucidated during evaluation of datasets. This section presents those uncertainties and limitations and the implications.

Data derived from the Grayling Area PFAS Study Area served as the initial “beta-test” where AECOM fine-tuned the approach for assessing and comparing residential and investigation-derived PFAS data. AECOM presented the results “Preliminary Data Comparisons Camp Grayling PFAS Groundwater Work Group” to members of EGLE on January 29, 2019. At that time, AECOM’s recommendations were to retain a similar work flow process, which entailed use of GIS mapping tied to database functionality, identifying target study groups and to determine the geological resolution (amount of detail) available in residential well logs. AECOM also recommended use of the Wilcoxon-Mann-Whitney rank-sum test (see **Section 3.3**) to evaluate whether the PFAS concentrations in residential and monitoring well/VAS samples were the same. The “beta-test” data included use of visualization tools such a radar plots and multivariate analyses, which were omitted from the North Kent and Richland study areas. This decision

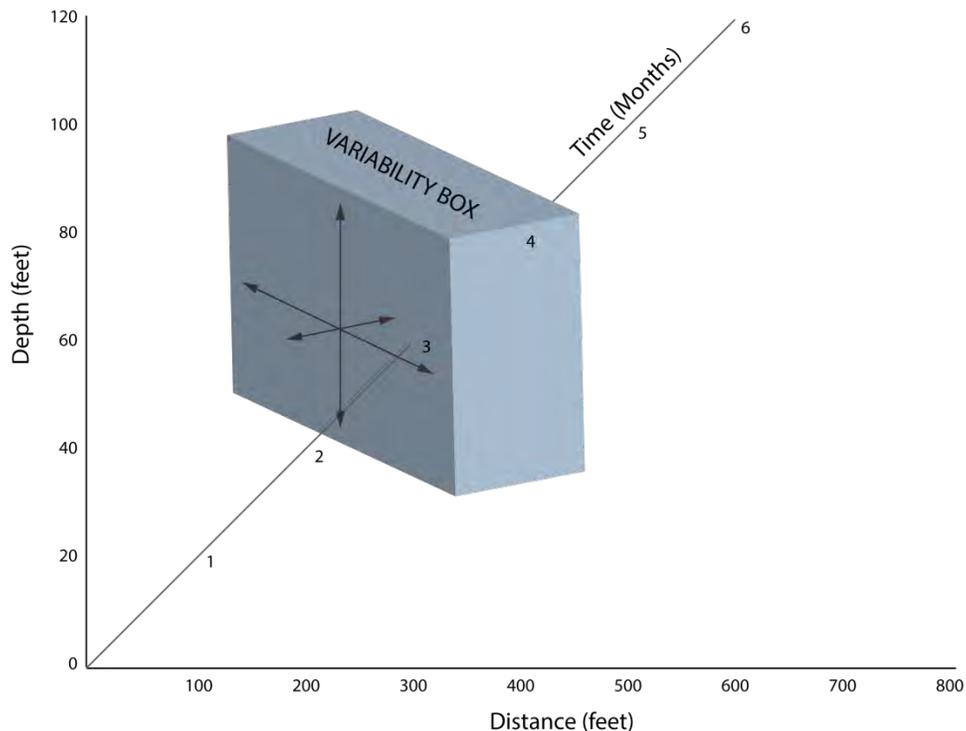
was made due to 1) the overwhelmingly large data set derived from the North Kent site, and 2) limited statistical use in looking at individual well clusters or groups (small sample sizes).

The primary data uncertainties included distance between sampling pairs (including horizontal and vertical distance), time (i.e. date) of sampling, and analytical method. **Figure 1** conceptually illustrates three of these uncertainties.

The locations of the residential and monitoring wells determined the horizontal distance between the data pairs selected. Similarly, the existing well screens determined the sample elevations between the data pairs. The geology may change between locations, especially with greater distance between the data pairs. In addition, the lithologic description provided on a residential drilling log is invariably less detailed in nature than one provided on a monitoring well log (and logged by a geoscientist).

In most cases the samples were not collected during the same time period. Varying water levels as a result of precipitation events could affect the concentrations observed in addition to movement of the plume(s).

Varying analytical laboratories and methods were used during the multi-phased sampling events at the sites. This could especially affect low level concentration results (i.e. results at or just above the detection limit).



**Figure 1. Primary Study Variables**

Conceptualized drawing showing primary study variables, including sampling depth (shown in feet), distance (feet) which represents the lateral space between sampling points, and time (presented in months). Time refers to an inexact temporal drift between sampling events. In this conceptualized drawing the “variability box” represents well screens approximately 40-100 feet in depth, lateral distances on range of 100-500 feet, and a sampling window within 2-4 months.

## 1.3 Historical Site Information

The following sub-sections detail the site backgrounds for each dataset used in evaluating the objective for this study.

### 1.3.1 Grayling Area PFAS Study Area

The Grayling Area PFAS Study Area (Grayling SA) is located in and around the city of Grayling in Crawford County, MI. Detection of PFAS in groundwater and residential drinking water wells in the vicinity of the Grayling Army Air Field (GAAF) prompted EGLE to increase the sampling of residential and non-residential supply wells in the area. The airfield is owned by the United States Army and occupies 923 acres of land. Residential and commercial properties share property boundaries with GAAF. In 2017 EGLE contracted AECOM to perform remedial investigation (RI) activities and continue residential drinking water sampling in the vicinity of GAAF.

The Grayling SA is located within the Michigan Basin, an expansive undeformed intercratonic stratigraphic basin encompassing the Lower Peninsula, eastern half of the Upper Peninsula, Lake Michigan, Lake Huron, and parts of Wisconsin, Indiana, Ohio, and Ontario. Paleozoic sediments from an ancient sea were deposited within the basin, overlaying Precambrian and Cambrian basement rocks. The sedimentary beds dip towards the center of the basin at one degree or less (Gillespie et al., 2008).

The advance and retreat of glaciers during the Pleistocene shaped the topography of Lower Michigan creating landforms such as moraines, kettle lakes, and outwash plains. The most recent glaciation of Michigan occurred during the Wisconsin period, approximately 25,000-10,000 years ago. Glaciers up to one-mile thick carved away bedrock and transported this material until deposited as unconsolidated glacial drift overlaying Paleozoic strata. Grayling is located between two landforms, Grayling Fingers (several large, flat-topped glacial ridges the trend N-S) to the north and a moraine located south of the city. Schaetzl and Weisenborn (2003) interpret this area as having an outwash core of over 200 ft and associated with the deposition of several ice sheets. The Grayling Fingers were originally a high outwash plain that was later incised by ice retreat. The moraine south of Grayling is composed of like-age ice-contact outwash. The Au Sable River originates in this outwash plain, flows east and feeds into Lake Huron.

As such, glacial sediments encountered at the base are variable, containing poorly-sorted outwash sand, gravel and silt-clay sequences, and modern fluvial channel and over-bank deposits in proximity to the Au Sable River.

#### 1.3.1.1 Residential Drinking Water Sampling

As of the spring of 2019, AECOM has collected approximately 700 drinking water samples from residential wells adjacent to the GAAF. **Figure 2** shows ranges of total PFAS detected in drinking water samples and environmental investigation data collected through June 2019. Areas with higher concentrations of PFAS are in general down groundwater flow gradient of areas on the GAAF where high, on-airfield, concentrations of PFAS were detected in groundwater.

#### 1.3.1.2 Remedial Investigation

The RI focused on assessing the extent and concentration of PFAS in groundwater and to assist in understanding the potential risk to human health and the environment in the vicinity of the GAAF.

Phase I of the RI included collecting lithology and VAS from a total of 44 locations using direct-push technology (also shown on **Figure 2**). VAS was collected approximately every ten (10) feet from the top of the aquifer to termination of the boring. Over 200 VAS were collected during Phase I field activities.

Phase II of the RI included collecting additional lithology and installation of a groundwater monitoring well network that expanded on delineation of impacted groundwater from Phase I and provided long-term monitoring of potential future risk to human health and the environment.

A total of 74 nested monitoring wells were installed using Rotosonic drilling technology at approximately 20 locations, shown in **Figure 2**. All monitoring wells have been sampled a total of three times, an initial sampling after installation plus two quarterly rounds of sampling.

### 1.3.2 North Kent

North Kent data used for the study is an amalgamation of data derived from multiple investigations, including those initiated by EGLE and consultants working for Wolverine World Wide (WWW). In July 2017, residential well sampling near a former disposal area used by WWW detected the presence of PFAS in drinking water. WWW utilized the property located near House Street NE and Herrington Avenue NE for the disposal of industrial wastes generated from the production of water-resistant consumer products at the WWW Tannery. The property is located in rural Plainfield Township, Kent County, Michigan. Area residences surrounding the disposal area are served by private water wells. In the mid-1960s, the property was operated as a licensed landfill under Act 87 of the Public Acts of 1965 for the disposal of solid waste. WWW utilized the property primarily to dispose of lime-sludge wastes from the treatment of tanning wastes. The lime-sludge wastes were disposed of in trenches dug across the property. The property also contained seepage pits, which were used for disposing of lime liquor (a mixture of lime, water, dissolved protein, and fat), and other liquid wastes.

In April 2017, WWW under the oversight of EGLE, Kent County Health Department (KCHD) and the Michigan Department of Health and Human Services (MDHHS), sampled eight wells on Brent Drive, Brittney Drive, and Herrington Avenue. All the wells had PFAS below the U.S. Environmental Protection Agency (EPA) lifetime health advisory (LHA) level of 70 nanograms per liter (ng/L). In June 2017, while EGLE and WWW were in discussions regarding an investigation of the former disposal property, the Belmont Armory drinking water well was sampled and found to contain PFAS compounds above the U.S. EPA LHA. With this new information, in July 2017 EGLE and WWW began sampling residential wells south of the disposal area. The sampling was conducted in response to citizen concerns regarding the potential for the waste in the disposal area to have included PFAS.

The MDHHS, the KCHD, the Michigan Department of Natural Resources, EGLE and the Michigan Department of Agriculture and Rural Development (MDARD) are involved to support the effort. In consultation with EGLE, the KCHD and the MDHHS, WWW is voluntarily conducting response activities under Section 20114a of Part 201, Environmental Remediation, of the Natural Resources and Environmental Protection Act, 1994 PA 451, as amended. In 2018 EGLE established Residential Drinking Water Criteria (DWC) under Part 201 that is equivalent to the LHA presented by the U.S. EPA. Proactive measures are ongoing in testing area residential water well samples for PFAS. WWW is offering bottled water to all residents sampled, until analytical results are received, at which point further response actions will be determined. Some residential samples have detected Perfluorooctanoic Acid (PFOA) and Perfluorooctane sulfonic acid (PFOS) at combined levels above the Part 201 DWC. All residences exceeding the DWC are being offered either a National Sanitation Foundation International (NSF International) certified single source water filter or a whole house granulated activated carbon filter system, or both, depending upon the PFOS and PFOA concentrations. WWW along with state and local environmental experts and officials are sharing results and other information with residents of Plainfield Township and the surrounding community.

As a part of this ongoing work, EGLE has been investigating numerous locations where WWW allegedly disposed of wastes to determine whether these locations are potential sources for PFAS in groundwater. Technical memorandums and letters for the North Childsdale Study Area, Rezen Sampling Area, Childsdale Gravel Pit Study Area, and Blythefield Memorial Garden Ponds (adjacent to the Bittersweet Study Area) have been prepared, in which the previous investigations and conclusions are described in greater detail. Other sites were also investigated.

The North Kent Study area, not including the Ramsdell residential area and Douthett Dump area, comprises approximately 10,256 acres. Due to the size of the investigative area, the North Kent data set is the largest of the three study areas assessed in this report. The geological terrain is also the most variable, consisting broadly as glacial outwash sand and gravel and post-glacial modern alluvium; end-moraine of medium-textured till; and medium-textured undifferentiated glacial till (Stramel, Wisler & Laird, 1954; Farrand and Bell, 1982).

A heat map showing total PFAS concentrations derived from residential wells, VAS and monitoring wells is presented as **Figure 3**.

### 1.3.3 Richland

The Richland site (Site) is located approximately ½ mile east of the Village of Richland in northeastern Kalamazoo County. Agricultural, commercial, and residential properties are all present near the Site.

The former 46-acre Site was used as a plating facility from 1966 to 1989 and comprised a single 40,000-square-foot high-bay manufacturing building, minor appurtenant structures, above-ground storage tanks, settling and infiltration lagoons, and several sludge piles. During its operation, the facility manufactured painted and chrome-plated plastic parts used primarily in the automotive industry. Historic releases of process solutions and waste-treatment residuals into the subsurface at the facility resulted in the elevated concentrations of hexavalent chromium (Cr<sup>+6</sup>) and nickel (Ni) currently present in the Site soil and groundwater. Groundwater contamination was first discovered at the former Site in 1977. Other contaminant footprints are present at the Site, including chlorinated VOCs potentially derived from an unrelated nearby former dry cleaner facility (EGLE, 2019).

The Site is fenced, and a groundwater extraction and hydraulic control system is currently in operation. Groundwater is continuously extracted from four extraction wells and discharged to the City of Kalamazoo for treatment. For the past six years, the groundwater extraction system operation and maintenance (O&M) and groundwater quality monitoring activities were performed by URS (now AECOM) under its Level of Effort (LOE) Contract with the State. O&M has included monthly Site checks/computer data back-up, City of Kalamazoo POTW sampling/reporting, and periodic cleaning of the system transmission lines.

Numerous investigations have been completed at the Site including confirmation sampling to demonstrate the removal of wastes and impacted materials from the Site as part of the demolition and removal work conducted under the former PM Contract. A subsurface investigation conducted at the Site in 2002 confirmed the presence of a soil source area of heavily impacted soils beneath the former building structure extending from near ground surface to the water table which occurs at a depth of approximately 24 feet below ground surface (bgs). In addition to the source area under the former building, there are several “hot spot” soil areas previously identified to be impacted with high levels of chromium and nickel throughout the property.

Historic subsurface investigations identified groundwater contamination, including chromium and nickel, at the Richland site. Over the past three decades, groundwater has been extracted from two zones (shallow and deep) via a groundwater extraction system and discharged to the City of Kalamazoo POTW by way of the Gull Lake Sewer & Water Authority. Several upgrades and modifications of the extraction system have been executed on behalf of EGLE over the last ten years. These upgrades and modifications have been designed and installed based on the results of capture zone analyses for both the shallow and deep zones to improve the hydraulic containment beneath the project area to bring the point of compliance to the property boundary of the Site. Currently the groundwater extraction system consists of three shallow zone and one deep zone extraction wells at the property boundary of the Site.

Staff from the POTW sampled the outfall at Richland and sent samples to Pace Analytical, Inc. to be analyzed for PFAS. AECOM split samples with the POTW staff for analysis by Vista Analytical Laboratory (Vista) for PFAS. The resulting concentration from the POTW samples was around 8,000 ppt Perfluorooctane sulfonic acid (PFOS). The AECOM sample had a concentration of the PFOS of 9,640 ppt. In June 2018, the system was turned off in response to detection of PFOS in groundwater pumped from EW-1, EW-6, EW-7, and EW-9. An emergency treatment system was installed at the Site to treat extracted groundwater that was being discharged to the POTW. On July 31st, the emergency treatment was operational and was treating groundwater.

Environmental investigation of the PFAS footprint at the Richland Site is on-going and expanding. The investigation area currently comprises approximately 4,500 acres. The Site quaternary geology consists of glacial outwash and is highly variable, consisting primarily of sand and gravel and sand sequences in

the shallow aquifer, underlain by a low permeability clay unit. A varying thickness of a shallow-seated silt unit is also present in various locations within the study area (AECOM, 2019; EGLE, 2019).

A heat map showing total PFAS concentrations derived from residential wells, VAS and monitoring wells is presented as **Figure 4**.

## 2. PFAS Chemistry

PFAS are a complex family of more than 4,700 man-made fluorinated organic chemicals (OECD, 2018). PFAS are not found naturally in the environment. Due to their unique chemical properties, PFAS have been used in many industries and consumer products since the late 1950's such as carpeting, waterproof clothing, upholstery, food paper wrappings, fire-fighting foams, and metal plating. The Interstate Technology Regulatory Council (ITRC) has identified four primary sources of PFAS: fire training /fire response sites, industrial sites, landfills, and wastewater treatment plants/biosolids.

A high-level description of chemistry and manufacturing of PFAS is presented in **Section 3** to provide a better understanding of the current study and its complexity and limitations.

### 2.1 PFAS Manufacturing

There are two main PFAS manufacturing processes, electrochemical fluorination (ECF) and telomerization. ECF was first used to mass produce fluorosurfactants and fluorinated polymers by the company 3M beginning in the 1940s (Banks, Smart, and Tatlow 1994). Between 1949 and 2002 3M produced many PFAS families using ECF; 95% of the production was based on perfluorooctane sulfonyl fluoride (POSF) and POSF-related derivatives, and 5% based on perfluorooctanoyl fluoride (POCF) which was used to make PFOA and PFOA salts. During the production of POSF other PFAS by-products, such as PFBS were also produced (Paul et al., 2009). In 2002, 3M began using PFBS as a replacement for PFOS. Recently manufacturers followed suit by also removing PFOS and other long chain PFAS from their products in favor of shorter chained compounds like PFBS. However, China and other countries are still using ECF to produce PFAS, and in particular PFOS and PFOS-related compounds.

In 1942, DuPont developed telomerization as the second method for manufacturing PFAS. Telomerization is similar to polymerization, where single molecules are combined to form larger molecules. However, in telomerization, single molecules (called telogens) are combined with another single molecule (called a taxogen or chain transfer agent) to create a larger molecule (telomer). Fluorotelomer iodide (FTI) is an example of a PFAS produced using telomerization. In the United States ECF was used only by 3M, and all of the other PFAS were produced using telomerization to produce different PFAS families than those produce by ECF. Telomerization was used by many other manufactures outside the US for the production of many PFAS and is used in a large number of consumer products.

### 2.2 Perfluorinated vs. Polyfluorinated Compounds

Many PFAS that are also surfactants have a two-part body structure consisting of a tail and a head. The tail comprises two or more carbon (C) atoms attached to a functional group (head). Typically, the functionalized head consists of carboxylic or sulfonic acid. In perfluoroalkyl (also referred to as perfluorinated) substances, the tail is made up of carbon atoms which are fully fluorinated and have all the hydrogen atoms attached to carbon atoms being replaced by fluorine atoms. In polyfluoroalkyl (also referred to as polyfluorinated) substances, at least one of the tail carbon atoms is bonded with an atom other than fluorine, typically hydrogen (H) or oxygen (O). An example chemical structure of both a perfluorinated (Perfluoroalkyl carboxylic acid) and polyfluorinated (Polyfluoroalkyl carboxylic acid) compounds are depicted in **Figure 5**.

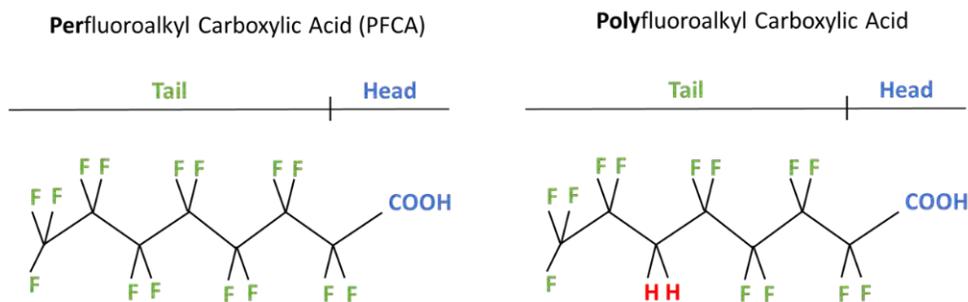


Figure 5. Varying chemical structures in per and –poly carboxylic acids

## 2.2.1 Chain Length

PFAS compounds belonging to a particular family have the same functional head with the only difference being the fluorinated carbon-fluorine chain length. PFAS with a shorter carbon chain length are referred to as short-chain, and the PFAS with a longer chain length are referred to as long-chain. For example, the carbon chain length of PFBS is formed with 4 carbon atoms (C4), and PFOS is composed of 8 carbon atoms (C8). PFBS is an example of a short-chain PFAS and PFOS is considered a long-chain PFAS. Both PFBS and PFOS are part of the PFAS family of perfluoroalkane sulfonic acids (PFASs). The carbon chain length of various PFAS families have been found to significantly affect the chemical and physical properties of PFAS. Long-chain and short-chain PFAS are assumed to have the overall properties described below when comparing the two chain lengths. Please note that the physical/chemical properties described below are global observations based on studies performed from several PFAS families and exceptions do exist (Buck et al. 2011).

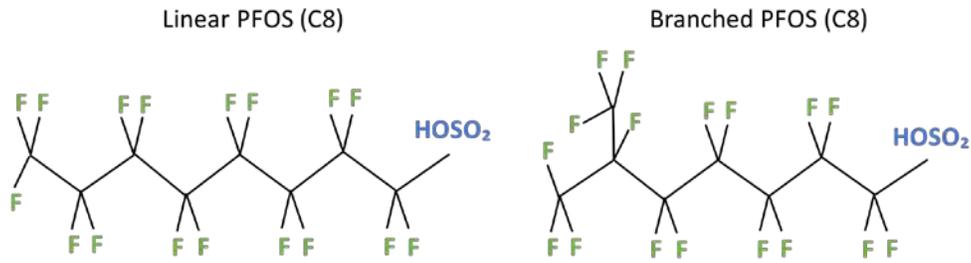
Physical/Chemical Properties	Short-Chain	Long-Chain
<b>Water Solubility</b>	Higher	Lower
<b>Bioaccumulation Potential in Biota</b>	Lower	Higher
<b>Accumulation Potential in Plants</b>	Higher	Lower
<b>Adsorption to Soil and Sediment</b>	Lower	Higher
<b>Overall Expected Toxicity</b>	Lower	Higher

Table 1. Physio-Chemical properties of short-chain versus long-chain PFAS

## 2.2.2 Isomers

The ECF process leads to carbon (C) chain rearrangement and breakage, resulting in a mixture of linear, branched, and cyclic isomers (Buck et al., 2011, OECD, 2018). The ratio of various isomers that are formed during the ECF process varies depending on how the process is controlled. Ratios of linear to branched isomers for PFOA and PFOS have been reported as being 70-80 percent linear and 20-30 percent branched (Buck et al., 2011). However, 3M has reported ratios of 60-66 percent of branched isomers to 34-40 percent linear isomers for the production of PFOS. There is not much information about cyclic isomers in the literature. The final branched and linear isomers could have either even- or odd-numbered carbon chain lengths (Concawe, 2016).

One example of branched and linear PFOS isomers is presented in **Figure 6**. Although technically there could be over 80 different branched PFOS isomers, less than six branched isomers have been typically identified in the environment.

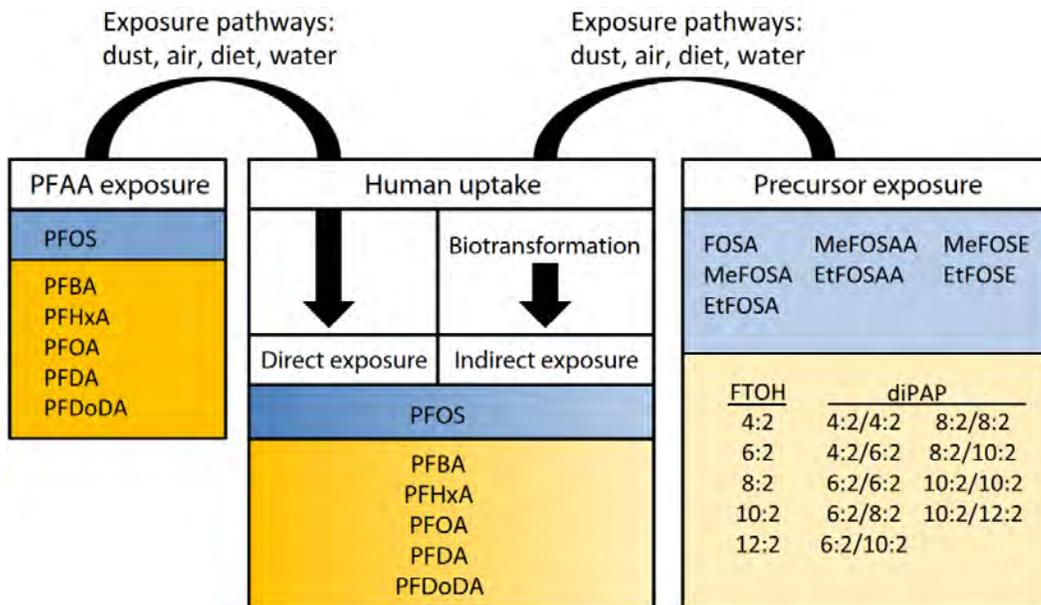


**Figure 6. Example chemical structures of linear and branched PFOS.**

If a branched or odd carbon number telogen is used, the telomerization process could result in a mixture of branched or odd-numbered carbon chain and such telogens have been described in patents. However, to date PFAS identified and produced using telomerization are found to have PFAS with only even-numbered and linear carbon tails (Buck et al., 2011; Lee, 2013).

### 2.2.3 Precursors and Indirect PFAS Emissions

The carbon and fluorine bond (C-F) is one of the strongest bonds in organic chemistry, and compared to hydrocarbons, PFAS have enhanced chemical properties such as higher surface activity, better dielectric properties, higher thermal stability, an increased chemical resistance, and a physiological inertness (Brendel et al., 2018). However, many PFAS are polyfluorinated or polyfluoroalkyl for which not all of the carbons are fluorinated and are susceptible to degradation. A large family of side-chain fluorinated polymers, for example, have PFAS attached to a non-fluorinated polymer backbone that is also susceptible to degradation. All of the PFAS that could degrade abiotically and biotically in the environment to dead end PFAS products are referred to as precursors. As a result, the prevalence of PFAS in the environment could be direct and indirect as well. The degradation of precursors is considered indirect emissions of PFAS in the environment. Examples of various precursors and PFAS families to which they will degrade is presented in **Figure 7** (Gebbinck et al., 2015). Many precursor PFAS families are known to degrade to perfluoroalkyl acids (PFAAs). Two of the most known PFAAs families are perfluoroalkyl carboxylic acids (PFCAs), which include PFOA, and perfluoroalkane sulfonic acids (PFSAs), which include PFOS. Many of the precursors used in side-chain fluorinated polymers have also been found to degrade to PFAAs.



**Figure 7. PFAS exposure and transformation pathways (from Gebbinck et al., 2015)**

## 2.3 PFAS Sources

The current study evaluates environmental data from the Grayling, North Kent, and Richland study areas. Each of these sites has different PFAS sources. The most probable PFAS source at Grayling is Aqueous Film Forming Foam (AFFF) that was used/stored on the airfield. However, the ongoing investigation has not ruled out the possibility of other PFAS sources. The PFAS source at the North Kent study area is Scotchgard™ which was used by Wolverine World Wide. At the Richland study area it is believed a mist suppressant used for chrome plating is the most likely source of PFAS. Like Grayling, there are potentially other PFAS sources that could be contributing to the impacted groundwater at North Kent and Richland.

The following sections describe in detail the production and use over time for each of the suspected PFAS sources described above.

### 2.3.1 AFFF - Grayling

The U.S. Navy Research Laboratory (NRL), in collaboration with 3M, were pioneers in the development of firefighting agents. A patent was filed in 1963 and approved in 1966 for a new method of extinguishing liquid hydrocarbon fires using PFOS and PFOA type fluorosurfactants (Tuve and Jablonski, 1966). The first military-specific (Mil-Spec) AFFF, MIL-F-23905A, was published in 1965. This AFFF was referred to as “Light Water” and was only able to be used with fresh water. However, these original AFFFs were not used extensively due to their limitations to fresh water only. Development of new AFFF using both hydrocarbon fluorosurfactants and fluorosurfactants made it possible to be used with both fresh and seawater. The Department of Defense (DoD) published a new Mil-Spec in 1969 known as MIL-F-24385. AFFF started to be used more extensively after 1970.

AFFFs were manufactured with PFAS produced using both ECF and telomerization processes. The predominant AFFF agents that were sold globally until May 2000 were PFOS-based (Prevedouros et al., 2006). Based on a survey conducted in 2004, it was found that 75% of the military AFFF inventory was ECF-based product (Darwin, 2004). This was expected, since 3M was the main supplier of AFFF to DoD from 1970's to 2000. Even though in 2002 3M voluntarily removed their AFFF products from manufacture, due to rising concern about PFOS/PFOA-based products, the 3M AFFF was able to be purchased for all DoD facilities until 2009 (Place and Field, 2012). Due to its long shelf-life, 3M AFFF is still stockpiled at some DoD installations.

One of the main differences between AFFF produced by 3M compared to other manufactures is that the 3M AFFF contained PFASs (PFOS family) and PFOS as an active ingredient. AFFF manufactured by 3M between 1989 and 2001, for example, had PFOS concentration between 6.7 g/L (6,700,000,000 ng/L) and 15 g/L (15,000,000,000 ng/L) (Back et al., 2013).

AFFFs are complex mixtures of various PFAS. To date a total of 57 PFAS classes and over 240 individual PFAS have been identified in AFFF formulations or groundwater from AFFF impacted sites. Many of the PFAS identified in AFFF are precursors that could undergo partial degradation in the environment to PFAS such as PFOA and PFOS. The PFAS families and concentrations present in AFFF formulations varied by brand and year.

### 2.3.2 Scotchgard™ – North Kent

Side-chain fluorinated polymers have been used extensively by the textile industry and by consumers for textiles such as carpet, apparel, and leather for the treatment of all-weather clothing, umbrellas, bags, sails, tents, parasols, sunshades, upholstery, leather, footwear, rugs, mats, and carpets to repel water, oil and dirt (stains).

The main PFOS derivatives were typically applied at 2–3% of the fiber weight for textiles and 15% for carpets. The PFOS derivatives used for textile and carpet surface treatment applications were the

acrylate, methacrylate, adipate and urethane polymers of N-ethyl perfluorooctane sulfonamidoethanol (EtFOSE). Before 2002 the most well-known soil and dirt repellents were:

- 1) Scotchgard™ (produced by 3M).
- 2) Capstone (produced by DuPont).
- 3) Products produced by Daikin, Asahi Glass, Clariant, Rudolf Chemie and others.

Scotchgard™ products were originally based on PFOS-related compounds but were replaced by PFBS related compounds in 2003. The primary PFAS substances used in Scotchgard™ after 2003 are fluorochemical acrylate polymer, fluorochemical urethane, perfluorobutanesulfonamide, and polyoxyalkylene.

The PFAS compounds present in the groundwater evaluated at the North Kent site is believed to have been due to the disposal of Scotchgard™ produced prior to 2002.

### 2.3.3 Fume Suppressant – Richland

PFOS and PFOS-related compounds were used in numerous wet-chemical processes of surface finishing due to their properties of good chemical resistance and as a wetting agent. PFOS has been used in hard and bright chrome electrolytes, in chromic acid plastic etchants, in alkaline zinc and zinc alloy electrolytes, in precious metal plating (e.g., strongly acidic gold-palladium), rhodium baths, nickel plating, and aluminum anodizing. In electroplating, PFOS has been used due to its very high chemical stability to strong oxidizers, chromium (VI), and to sulfuric acid/chromo-sulfuric acid. It is also able to decrease the surface tension of treatment baths, facilitate good wetting properties resulting in quality and uniformity of coatings, and reduce the amount of process solution carried over into subsequent tanks by means of more rapid drainage. The use of PFOS in chrome electroplating is also able to reduce the formation of chromium (VI) aerosols which make it an important contributor for occupational safety. A list of various wetting agents that contain PFOS used in various plating processes is listed in **Table 2** along with the PFOS concentrations.

Wetting Agent	PFOS Concentration (ng/L)
<b>Fumetrol 140 by Atotech</b>	43,000,000,000
<b>Bayowet FT 248 by Lanxess</b>	580,000,000,000
<b>Proquel Z Fa.Kiesow</b>	50,000,000,000
<b>Silken Wet 302</b>	45,000,000,000
<b>Ankor SRK</b>	69,000,000,000
<b>NCR by Blasberg-Werra-Chemie</b>	50,000,000,000

**Table 2. Reported PFOS concentrations in various commercial wetting agents.**

Alternative wetting agents (used to suppress fumes) that do not have PFOS have only been made available recently for some plating operations. Various chrome plater sites have historically used PFOS fume suppressant, including the former Diamond Chrome Plating (DCP) site, Howell, Michigan (EGLE, 2019b). The facility at Richland is also thought to have used one of the wetting agents that contain PFOS during their operations.

## 3. Study Methodology

A process flow approach was used in evaluating each of the three site datasets. This approach included two phases, a preparation phase and an evaluation phase. The preparation phase included grouping and compiling data, both analytical and its associated spatial and geologic data. Spatial data for each individual study area is stored in a geodatabase using the Environmental Systems Research Institute (ESRI) software platform. All analytical data are stored in EarthSoft EQuIS™ database (EQuIS). Geologic data for environmental borings came from geologic logs produced during field investigation activities. Geologic data for residential wells was obtained from the EGLE Wellog online database, which compiles residential well installation, completion, and geologic information.

The evaluation phase included filtering, sorting and data quality control (QC) of compiled data. The finalized dataset was then evaluated and processed using specific statistical analyses. The following sections detail specific components of the methodology used for this study.

### 3.1 Preparation Phase – Data Grouping

Analytical data from residential drinking water and environmental samples were grouped using horizontal proximity with ESRI's ArcGIS geospatial processing software suite. The initial data grouping parameter was to select samples that fall within 500 horizontal feet. This parameter was premised on negating the possible effect of geologic heterogeneity on PFAS concentration in groundwater. Consideration was also made regarding the topographic aspect or elevation change between residential wells and investigation wells.

Early in the grouping process a lack of data density within 500-feet was occasionally noticed for some study areas. To insure there would be enough data for comparisons, the grouping radius was expanded to allow larger sets of data to be compared. The maximum distance for any study area group was 1,000 feet. Local hydrogeological conditions (i.e. groundwater flow direction, geologic heterogeneity, proximity to topographically dissimilar areas) were evaluated prior to changing the grouping parameters to negate probable subsurface effects described above.

### 3.2 Preparation Phase – Table Creation

To create tables, data groups from GIS were combined with associated analytical data exported from the EQuIS database. Data from GIS were matched with data from EQuIS using sample IDs and/or location information, which was stored in both databases.

Columns were added to include the following data queries:

- Group, Group Radius (Feet)
- Sample Date, Sample Code, Location, Sample Type
- PFAS Concentration, including PFBS, PFHxS, PFOS, PFBA, PFPeA, PFHxA and PFOA (in some instances depending on PFAS analyte list, certain PFAS (e.g. PFBA in residential data) may have been absent from the dataset.
- Lithology
- Ground and screen elevations

Lithologic data was populated using geologic field logs (for environmental samples) or Wellog data for residential drinking water wells. Hydraulic conductivity was estimated using text book values published for clastic sediments (Freeze and Cherry, 1979).

Following table set up, data was subdivided into subgroups in which sample interval elevations (e.g. well screen interval) were within 10 to 20 feet. Like the horizontal grouping parameter, this vertical grouping parameter was used to further place data into groups which negated the potential subsurface factors

described above. Any data that could not be grouped using this vertical parameter were filtered (removed) from the table.

Quality Control (QC) was the final step in table creation. The spatial data and paired analytical data, assigned lithology, and hydraulic conductivity values were all checked prior to the evaluation phase.

### 3.3 Evaluation Phase – Statistical Methods

A statistical comparison between detected concentrations in monitoring wells and residential wells was conducted using USEPA's ProUCL software, version 5.1.002 (USEPA, 2016) for PFBA, PFBS, PFHpA, PFHxS, PFOA, PFOS, and PFPeA. The comparison involved a two-sample hypothesis test to compare the mean or median (further discussed below) detected concentration of monitoring and residential wells. The null hypothesis of this test was: Mean/Median Detected Concentration of Monitoring Wells = Mean/Median Detected Concentration of Residential Wells.

The test selected for each PFAS compound was determined by the distribution of detected concentrations in monitoring and residential wells. The normality of the distributions was determined using Goodness-of-Fit Statistics (Shapiro-Wilk test, significance level 0.05) in ProUCL 5.1.002. If both datasets are normally distributed, then a t-test was selected. If either data set was not normal, then a non-parametric Wilcoxon-Mann-Whitney test was selected. All data were found to be not normal (non-parametric) distribution; therefore, the Wilcoxon-Mann-Whitney Rank-Sum Test was used. The statistical approach is a non-parametric test of the null hypothesis that a randomly selected value from one sample will be less than or greater than a randomly selected value from a second sample. For normally distributed data, the mean (average) is a good indicator of the central tendency; however, the mean is not a good indicator for datasets that are skewed, such as the PFAS comparison data-sets. For all data in this study, median values were used in the statistical analysis.

For each test if the p-value is less than the significance level of 0.05 then the null hypothesis is rejected, and the medians were compared to determine which dataset have higher concentrations. If the p-value is greater than the significance level of 0.05 then the null is not rejected, and it was concluded that the datasets have similar medians.

## 4. Results

The study results for each of the three sites are provided in this section. The results include a summary of the data used for the comparisons (data grouping), review of PFAS chemicals detected (analytical review), and the statistical comparisons of the residential and investigation data sets (statistical comparisons).

### 4.1 Grayling

The Grayling SA was chosen as the initial dataset to evaluate the study methodology. The source of PFAS impacted groundwater was most likely the use of AFFF during on-base operations. Refer to **Section 2.3.1** regarding AFFF PFAS chemistry.

The Grayling SA was selected as the first dataset to analyze for the following reasons:

- The dataset included approximately 700 drinking water samples, 210 VAS, and 74 sampled monitoring wells.
- The site has favorable proximity of residential drinking water sample locations to environmental groundwater samples (VAS, monitoring wells).
- All samples (residential and environmental) were generally collected within 18 months of any two samples.

#### 4.1.1 Preparation Phase – Data Grouping

A total of 15 data groups were selected from the Grayling SA dataset (**Figure 8**). The selection radius for each group varied between 70 feet and 400 feet. A total of 32 residential drinking water samples were grouped with 52 monitoring well, and 46 VAS samples.

Many of the residential drinking water wells within the Grayling SA were installed prior to current residential drinking water reporting requirements, which limited the number of residential samples that were included in groupings.

#### 4.1.2 Preparation Phase – Table Creation

Post-table compilation of the data groups was further condensed by correlating sample depths. Samples that were not within a vertical “screen distance” of 20-feet between samples were removed from the table and not used in the evaluation phase. Using this parameter, both Groups 1 and 2 were removed in entirety. Groups 1 and 2 also corresponded to municipal well locations, or samples collected in deep litho-stratigraphic units not associated with the primary study area.

#### 4.1.3 Evaluation Phase – Analytical Review

As discussed in **Section 1.2** the analytical methods used for PFAS in groundwater and/or drinking water have changed several times since the beginning of investigation activities. This in turn varied which PFAS was reported for each analytical method. The first step in the Analytical Review was to determine which PFAS compounds were common to all samples in the table and determine the Frequency of Detection (FOD) of each compound.

**Figure 9** shows the PFAS common between residential and environmental samples and the FOD for each compound. The three most frequently detected PFAS in aqueous samples from GAAF were Perfluorohexane sulfonic acid (PFHxS) at 86.9%, Perfluorobutyrate (PFBA) at 73.8%, and Perfluoro-n-pentanoic acid (PFPeA) at 67.7%.

The average detected concentration of a given PFAS in residential drinking water samples verses environmental groundwater samples was plotted on a one-to-one line to visualize correlation trends (**Appendix A**). In general, if the average detected concentration of a given PFAS in environmental

samples were higher than the corresponding residential drinking water samples (above the 1-1 line) it might suggest that environmental data is conservative in detecting PFAS in groundwater compared to residential. If the average concentrations plot below the one-to-one line it would suggest the opposite, residential samples are conservative to environmental data (i.e. environmental data under-predicts PFAS concentrations in groundwater).

Plotted results shown in **Appendix A** indicate general agreement between detections in environmental and residential samples. However, individual group data ranges included in both figures show data from both sample types are highly variable.

#### 4.1.4 Statistical Results

The statistical results for the Grayling SA data comparisons are shown as **Table 3**. Three sample groups were compared: (1) Residential versus Monitoring Well Data, (2) Residential versus VAS data, and (3) Monitoring well versus VAS data. Using median values (the value separating the higher half from the lower half of a sample data, or middle value) for PFAS concentrations, and alpha (significance level) value of 0.05, no significant differences were found in median PFAS concentrations in residential well versus monitoring well data and residential versus VAS data.

However, the compound PFHxS was found to have a higher median concentration in VAS samples than in residential well samples. The statistical results are further discussed in **Section 5**.

## 4.2 North Kent

North Kent was used because it was one of the first projects that observed anecdotal differences between residential drinking water and proximal environmental sample locations.

- The dataset included approximately 1,700 drinking water sample locations and 550 monitoring wells.
- A large subset of the drinking water sample locations have been sampled multiple times, and in some cases on a weekly basis.
- The site has favorable proximity of residential drinking water sample locations to environmental groundwater samples (VAS, monitoring wells).
- All samples selected for this analysis (residential and environmental) were generally collected within three to four months of any two samples.

### 4.2.1 Preparation Phase – Data Grouping

A total of 19 data groups were originally selected from the North Kent dataset (**Figure 10**). The selection radius for each group varied between 500 feet and 1,000 feet. A total of 164 residential drinking water samples were grouped with 514 monitoring well samples.

Unlike the Grayling SA, many of the residential drinking water wells within North Kent were installed after current residential drinking water reporting requirements, which meant almost all residential samples had geologic and well completion data.

### 4.2.2 Preparation Phase – Table Creation

Post table compilation the data groups were condensed by correlating sample depths and sample date. Samples that were not within a vertical distance of 20-feet between samples were removed from the table and not used in the evaluation phase. If there were multiple sampling events for one location (i.e. residential or monitoring well) samples that were closest in time to each other were used. Using these criteria, Groups 11, 12, 14, 16, and 18 were eliminated from the evaluation.

### 4.2.3 Evaluation Phase – Analytical Review

As discussed in **Section 1.2** and the Grayling SA Analytical Review, analytical methods used for PFAS in groundwater and/or drinking water have changed several times since the beginning of investigation

activities. Furthermore, some of the data for North Kent was collected by several entities using different labs. This in turn varied which PFAS was reported for any one sample. Like the Grayling SA the first step in the Analytical Review was to determine which PFAS compounds were common to all samples in the table.

The predominant PFAS in aqueous samples from North Kent were PFBA, PFBS, PFHpA, PFHxS, PFOA, PFOS, and PFPeA.

The average detected concentration of a given PFAS in residential drinking water samples verses environmental groundwater samples were plotted on a one-to-one line to visualize correlation trends (**Appendix A**).

The one-to-one plots for North Kent indicate general agreement between detections in environmental and residential samples. However, individual group data ranges included in all figures show data from both sample types are highly variable.

## 4.2.4 Statistical Results

The statistical results for the North Kent study area data comparisons are shown in **Table 4**. One comparison was performed: Residential versus Monitoring Well Data. VAS data was not included in the comparisons primarily due being spatially isolated from the study groups. Using median values (the value separating the higher half from the lower half of a sample data, or middle value) for PFAS concentrations, and alpha (significance level) value of 0.05, no significant differences were found in median PFAS concentrations in residential well versus monitoring well data, except for perfluorobutryate/perfluorobutanoate (PFBA).

PFBA was found to be higher median concentration in residential well samples compared to monitoring well samples. The statistical results are further discussed in **Section 5**.

## 4.3 Richland

The Richland study area was used at the request of EGLE due to the nature of PFAS originating as a fume suppressant associated with a plater site (**Section 0**). Richland is the smallest study area with the smallest number of data points.

- The dataset included approximately 115 drinking water samples and 83 sampled monitoring wells.
- The site has favorable proximity of residential drinking water sample locations to environmental groundwater samples.
- All samples (residential and environmental) were generally collected within three to four months of any two samples.

### 4.3.1 Preparation Phase – Data Grouping

A total of 6 data groups were selected from the Richland dataset (**Figure 11**). The selection radius for each group varied between 90 feet and 500 feet. A total of 17 residential drinking water samples were grouped with 39 monitoring wells.

### 4.3.2 Preparation Phase – Table Creation

Post table compilation the data groups were condensed by correlating sample depths. Samples that were not within a vertical distance of 20-feet between samples were removed from the table and not used in the evaluation phase. Using vertical spacing as a screening parameter, Group 1 was eliminated from the evaluation.

### 4.3.3 Evaluation Phase – Analytical Review

Following the same first step as the Grayling SA and North Kent analytical review a FOD evaluation was used to determine which PFAS compounds were common to all samples in the table.

The predominant PFAS in aqueous samples from North Kent were PFBA, PFBS, PFHpA, PFHxS, PFOA, PFOS, and PFPeA.

One-to-one plots of average detected PFAS concentration indicate general agreement between detections in environmental and residential samples. Like the Grayling SA and North Kent individual group data ranges included in both figures show data from both sample types are highly variable.

#### 4.3.4 Statistical Results

The statistical results for the Richland study area data comparisons are shown as **Table 5**. One comparison was performed: Residential versus Monitoring Well Data. VAS data was not included in the comparisons primarily due being spatially isolated from the study groups. VAS data from the North Kent site was also congregated near PFAS source locations as part of GZA source investigations and not necessarily groundwater compliance monitoring points. Using median values (the value separating the higher half from the lower half of a sample data, or middle value) for PFAS concentrations, and alpha (significance level) value of 0.05, no significant differences were found in median PFBS, PFHxS and PFOA concentrations in residential well versus monitoring well data.

Richland data was a much smaller sampling pool due to limited number of residential wells and also the residential analyte list only considered 14 compounds. At least 8 detections are required in monitoring wells and residential wells to perform the Wilcoxon-Mann-Whitney rank-sum test, so no results are available for PFBA, PFHpA, PFOS and PFPeA.

The statistical results are further discussed in **Section 5**.



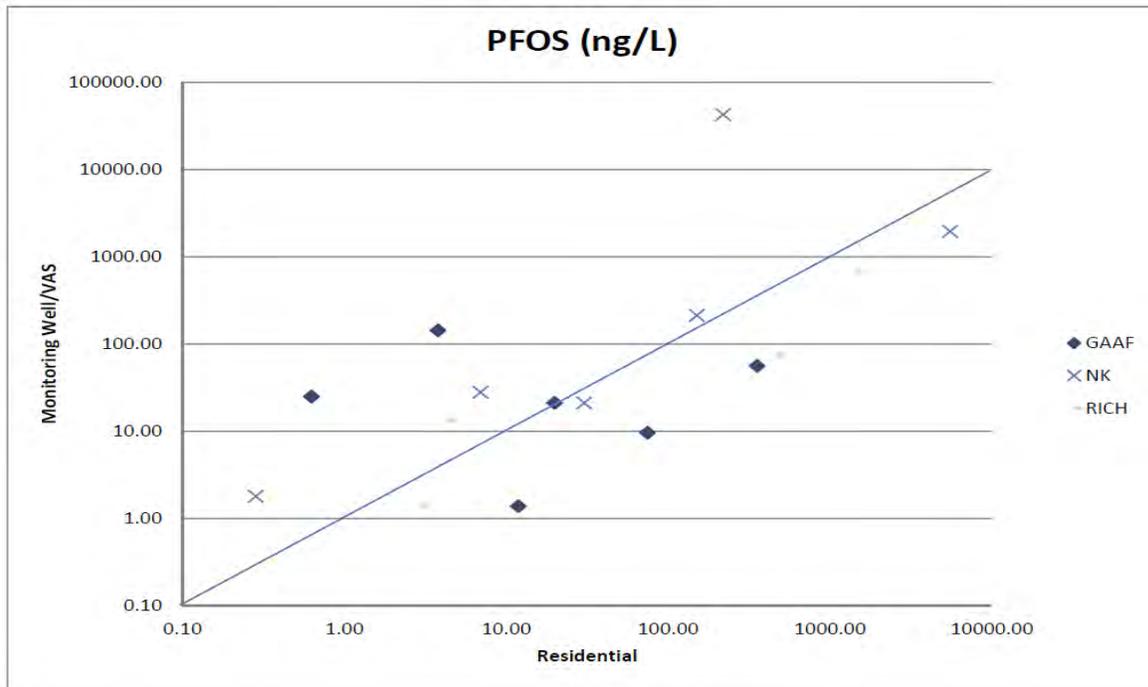


Figure 13. Comparison of PFOS from residential and monitoring wells from aggregated sites.

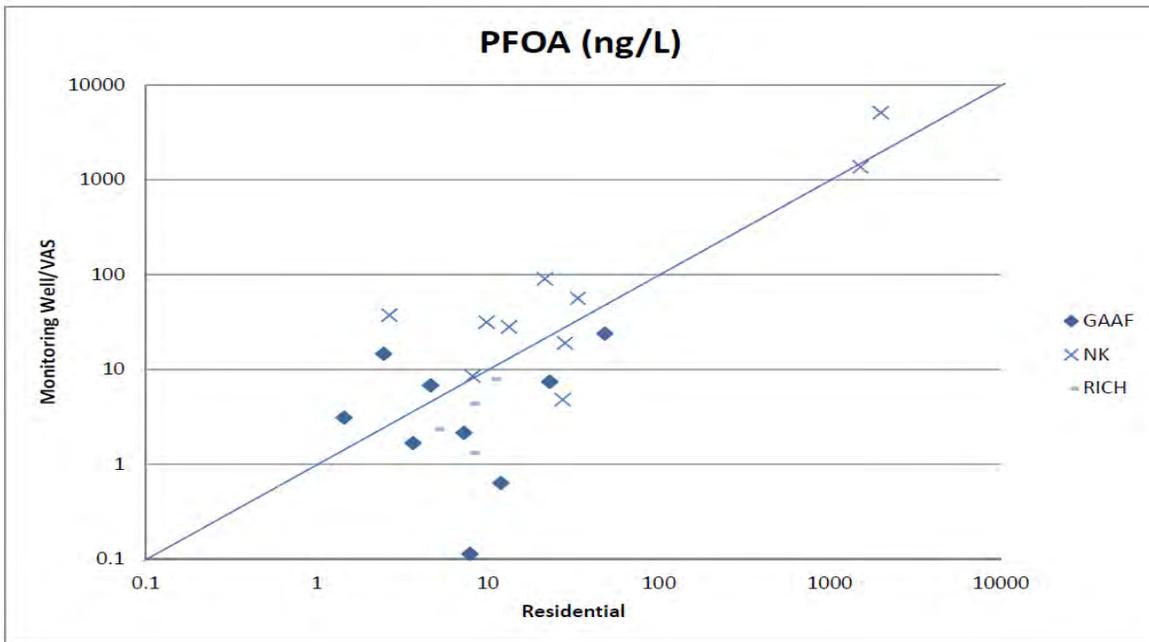


Figure 14. Comparison of PFOA from residential and monitoring wells from aggregated sites.

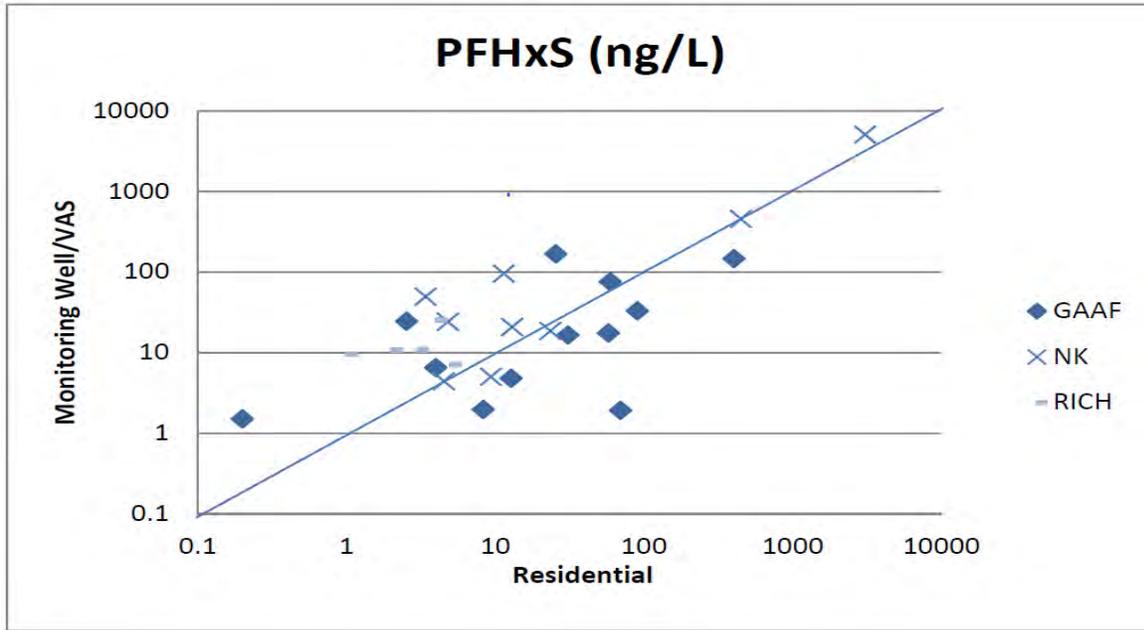


Figure 15. Comparison of PFHxS from residential and monitoring wells from aggregated sites.

## 5.1 Discussion of Primary Study Objectives

The primary objectives of this study were to (1) Determine if data collected during environmental groundwater investigations accurately reflect PFAS footprint, plume behavior, aquifer conditions, and drinking water risks, and (2) Determine if temporal PFAS concentrations behave differently than traditional target contaminants of concerns (COCs), including volatile organic contaminants (VOCs), metals, petroleum hydrocarbons or other COCs.

Based on the initial findings of this study, which evaluated three sites with varying geological conditions and PFAS footprints, AECOM believes that the data and data collection methodologies used for each of the sites accurately reflects aquifer conditions, including identification of PFAS compounds. Depiction of PFAS plume architecture and three-dimensional aspect is dictated by data resolution. Ideally, vertical aquifer profiling or use of multi-level sampling improves our interpretation of PFAS plume geometry. The use of high-resolution logging techniques (CPT, HPT, gamma logging and so forth) also improves an understanding of the relationship of PFAS footprint to sub-surface geological conditions. At the three study areas, the GAAF study area offered the highest resolution depiction of plume dimensionality primarily due to the use of vertical aquifer profiling across the site and not just limited to source area investigation. Future PFAS investigations should consider the use of vertical aquifer profiling techniques. The statistic results from the GAAF study area also suggest that at least one compound PFHxS was significantly higher in VAS compared to monitoring well data.

PFAS behavior, including the physio-chemical nature, and fate and transport mechanisms, vary not only between major taxonomic groups, such as perfluorinated sulfonic acids and carboxylic acids, but by each compound. By nature, PFAS are inherently stable and recalcitrant due to the presence of the carbon-fluorine bond. As such, the primary PFAS constituents of concern (e.g. Michigan's PFAS 24 List), including PFOS and PFOA, are less amenable to biotic and abiotic degradation or decay than VOCs, petroleum hydrocarbons and various metal species. This statement is not inclusive of PFAS precursor compounds and those amenable to biotransformation (e.g. MeFOSA or methylated PFAS compounds).

AECOM cautions the over-practiced application of using PFOS and PFOA as model chemicals (known in other unrelated disciplines as 'Krogh's Principle', such as using a pea or fruit fly for genetic studies) which can lead to fallacious generalization (Green, et al., 2018). PFAS fate and transport studies should be limited to individual compounds in context with their emplacement within varying environmental conditions.

## 6. Conclusion and Recommendations

The following conclusions are presented:

- Significant difference in median PFBA concentration in residential wells versus monitoring wells was determined at the North Kent Study Area.
- Higher apparent median residential well concentrations of PFBS, PFHpA, PFOS and PFPeA were found in the North Kent Study Area; however, these compounds did not show significant difference using Wilcoxon-Mann-Whitney rank-sum tests.
- Higher apparent median residential well concentrations of PFBA, PFPeA, PFHxA, PFPxS, PFHpA and PFOS were found in the Grayling Study Area; however, these compounds did not show significant difference using Wilcoxon-Mann-Whitney rank-sum tests.
- Higher apparent median residential well concentration of PFOS was found in the Richland study area; however, the number of samples did not allow for Wilcoxon-Mann-Whitney rank-sum testing.

The following recommendations are presented:

- Future work should minimize spatial and temporal variables (shown in **Figure 1**) through an approach using multi-level sampling arrays co-located near residential wells, including:
  - Horizontal distances of monitoring devices as close as practical to residential wells.
  - Use of multi-level continuous monitoring devices or nested monitoring wells.
  - Placement of vertical sampling devices (well screens) at same depth or within 5-feet of residential drinking water well screens within same lithostratigraphic unit.
  - Concurrent sampling of comparative groups.
- Use of real-time high-resolution lithology logging, using cone penetrometer testing or hydraulic profiling tool, to identify zones of high permeability or PFAS transport zones.
- Development of three-dimension conceptual site models (CSM) that depicts individual PFAS plumes in context with residential drinking water receptors (wells) and site stratigraphy.

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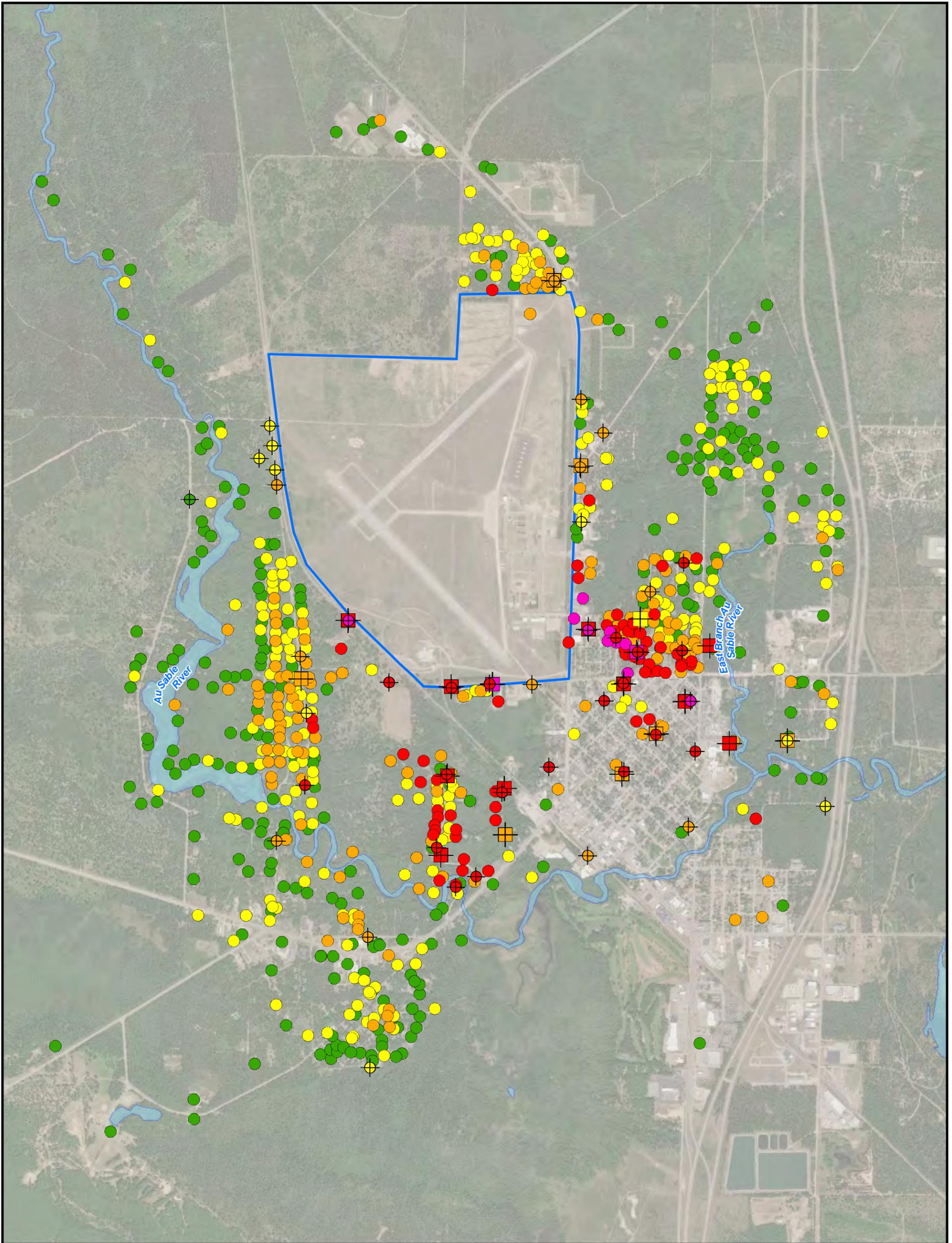
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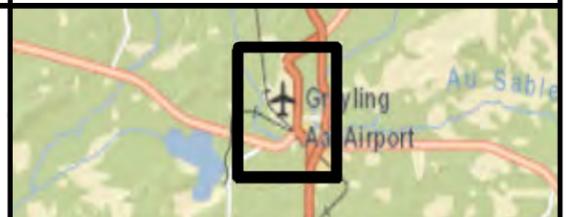
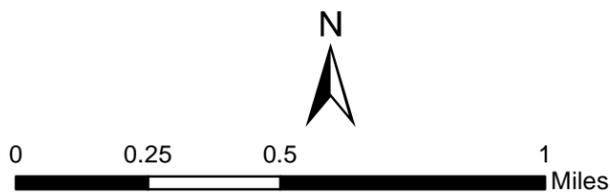
Figures



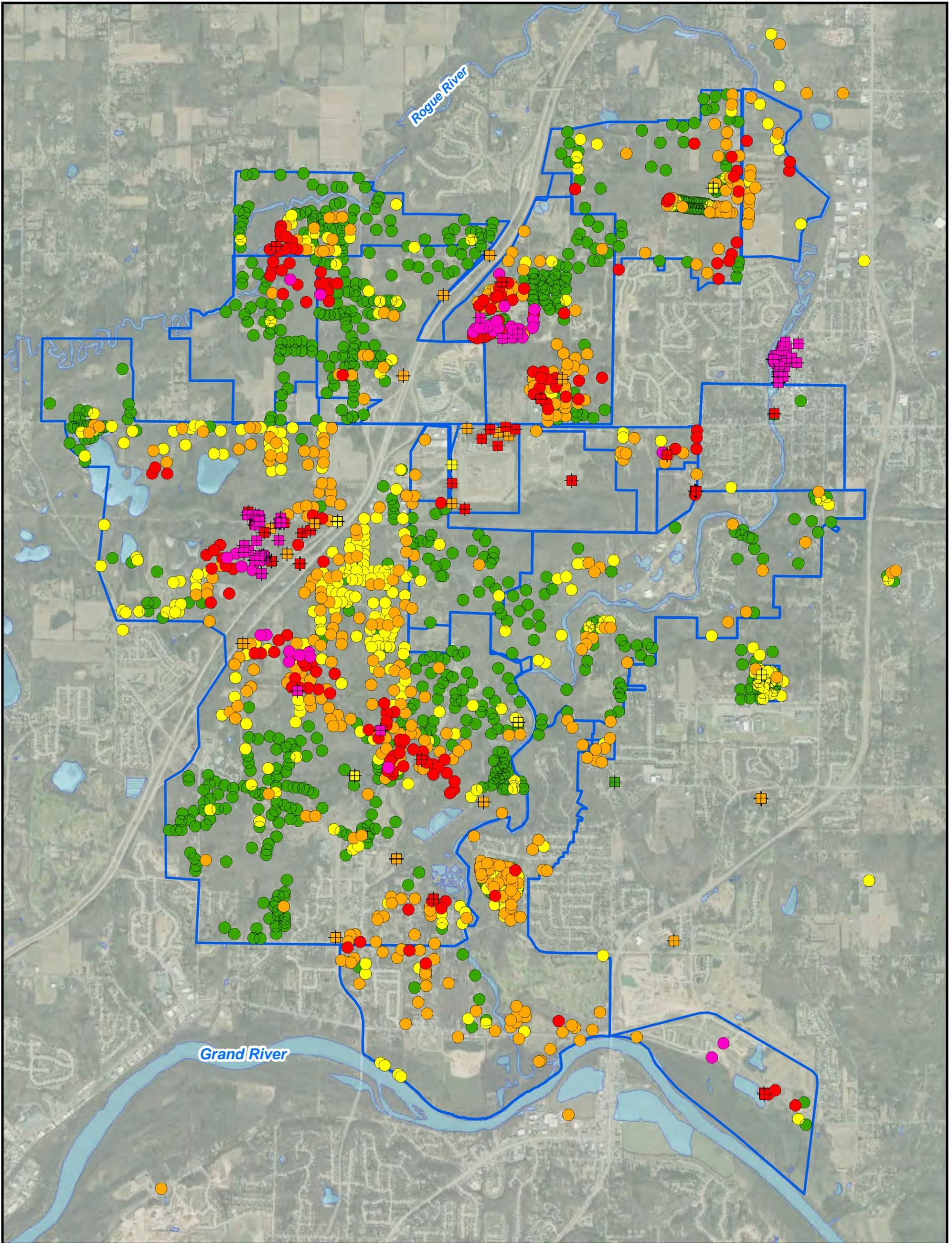
**Sampling Results - Total PFAS (ppt)**

Monitoring Wells	VAS	Residential Samples	Grayling Airfield Boundary
Green square: Non-Detect	Green circle: Non-Detect	Green circle: Non-Detect	Blue outline: Grayling Airfield Boundary
Yellow square: >0 to 10	Yellow circle: >0 to 10	Yellow circle: >0 to 10	
Orange square: >10 to 70	Orange circle: >10 to 70	Orange circle: >10 to 70	
Red square: >70 to 1,000	Red circle: >70 to 1,000	Red circle: >70 to 1,000	
Pink square: >1,000	Pink circle: >1,000	Pink circle: >1,000	

**FIGURE 2**  
**GRAYLING AREA PFAS STUDY**  
**AREA RESIDENTIAL, MONITORING**  
**WELL & VAS SAMPLING**  
**TOTAL PFAS HEAT MAP**  
**GRAYLING, MICHIGAN**



Prepared: 6/17/2019

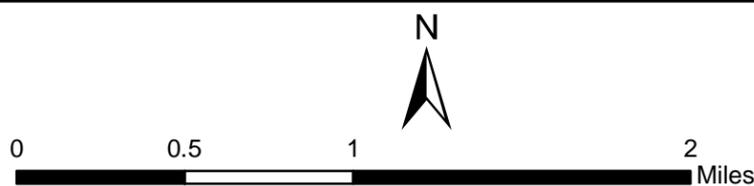


**Sampling Results - Total PFAS (ppt)**

Monitoring Wells	Residential Samples	North Kent Study Area
Non-Detect	Non-Detect	North Kent Study Area
>0 to 10	>0 to 10	
>10 to 70	>10 to 70	
>70 to 1,000	>70 to 1,000	
>1,000	>1,000	

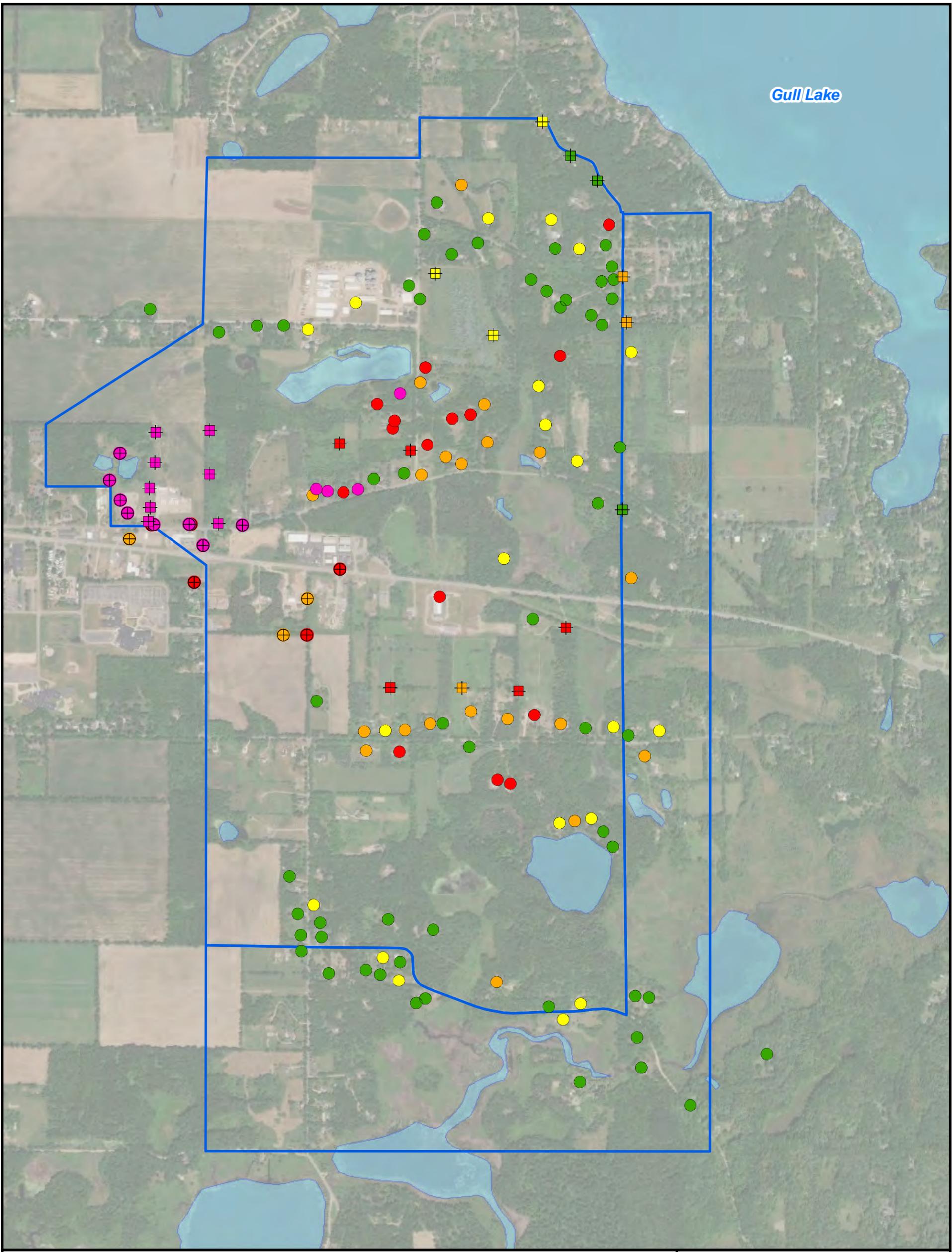
**FIGURE 3**  
**NORTH KENT STUDY AREA**  
**RESIDENTIAL & MONITORING WELL**  
**TOTAL PFAS HEAT MAP**

KENT COUNTY, MICHIGAN



Prepared: 6/17/2019





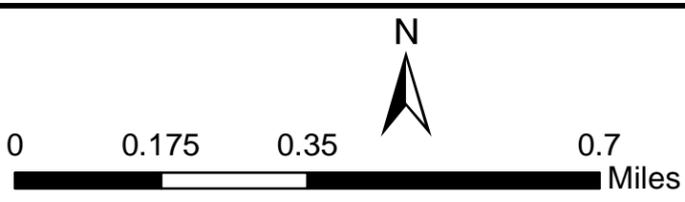
Gull Lake

**Sampling Results - Total PFAS (ppt)**

RI-18 Monitoring Wells	Existing Monitoring Wells	Residential Samples	Richland Study Area
Non-Detect	Non-Detect	Non-Detect	Richland Study Area
>0 to 10	>0 - 10	>0 to 10	
>10 to 70	>10 - 70	>10 to 70	
>70 to 1,000	>70 - 1,000	>70 to 1,000	
>1,000	>1,000	>1,000	

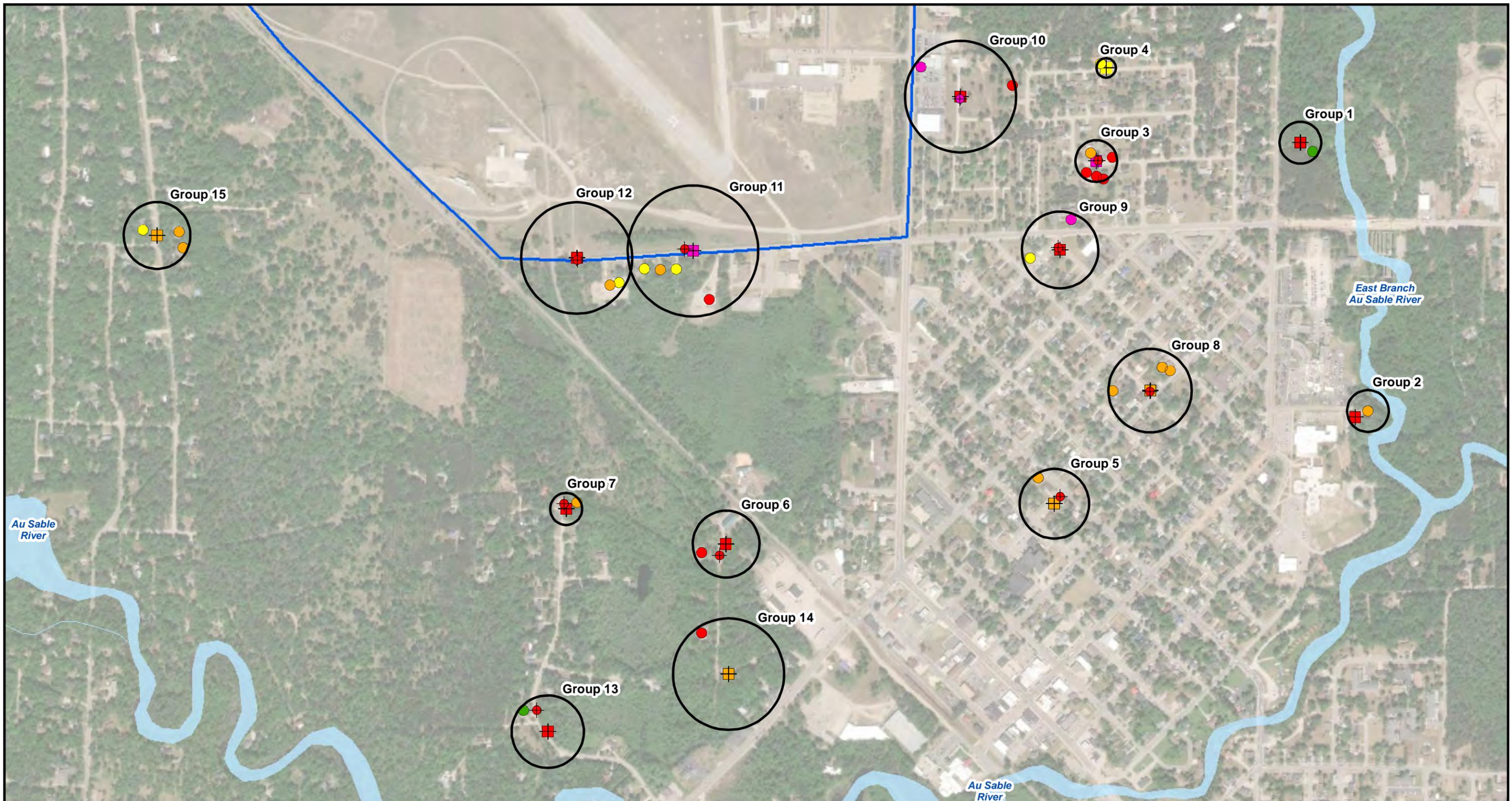
**FIGURE 4**  
**RICHLAND STUDY AREA**  
**RESIDENTIAL & MONITORING WELL**  
**TOTAL PFAS HEAT MAP**

**RICHLAND, MICHIGAN**



Prepared: 6/17/2019



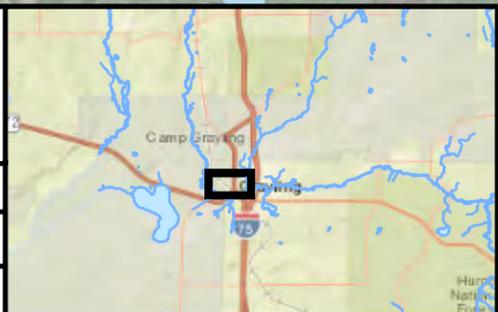


**AECOM**

Drawn: JS Date: 6/19/2019

Approved: Date: 6/19/2019

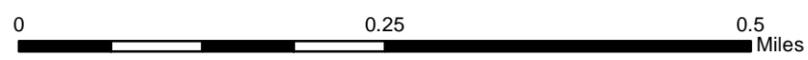
Project #: 60574998



**Sampling Results - Total PFAS (ppt)**

Monitoring Wells		VAS		Residential Samples	
	Non-Detect		Non-Detect		Non-Detect
	>0 to 10		>0 to 10		>0 to 10
	>10 to 70		>10 to 70		>10 to 70
	>70 to 1,000		>70 to 1,000		>70 to 1,000
	>1,000		>1,000		>1,000

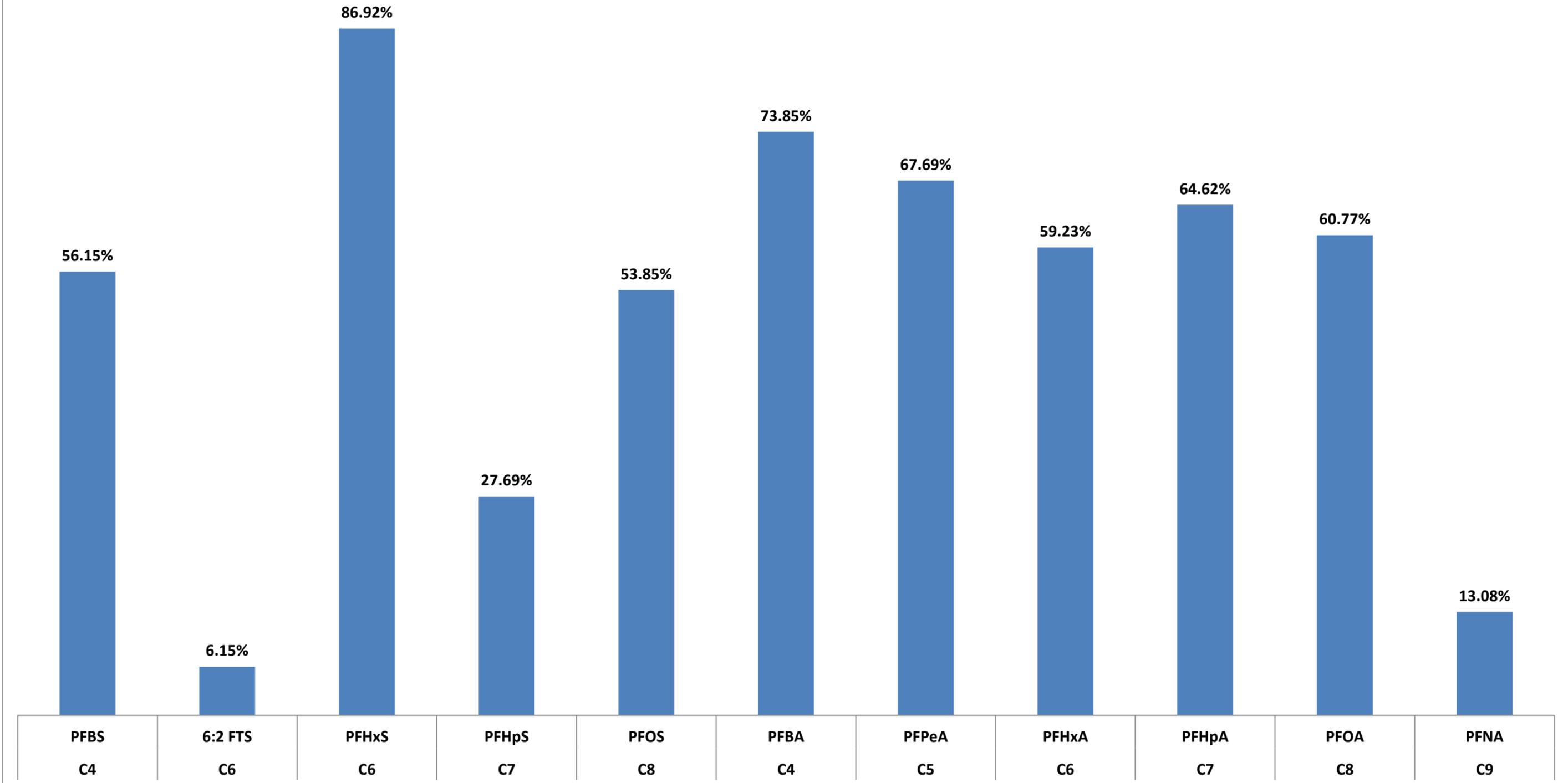
- Grayling Airfield
- Data Evaluation Groups

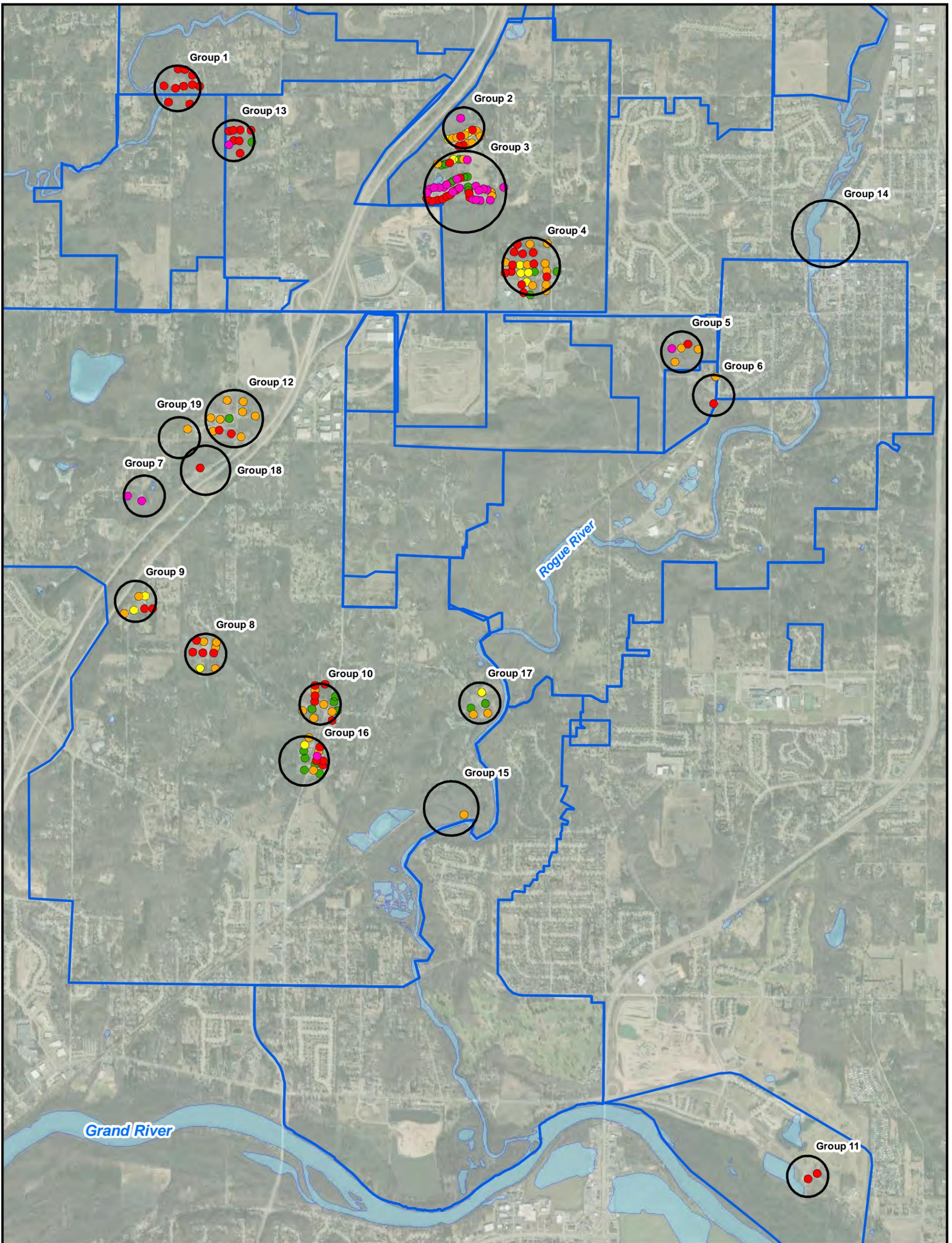


**FIGURE 8  
GRAYLING STUDY AREA  
DATA EVALUATION  
GROUPS**

**GRAYLING, MI**

**FIGURE 9**  
**FOD - All Data Average (MW, VAS and Residential) Grayling SA Groups 1-15**





**Sampling Results - Total PFAS (ppt)**

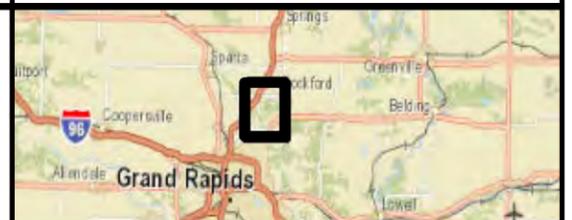
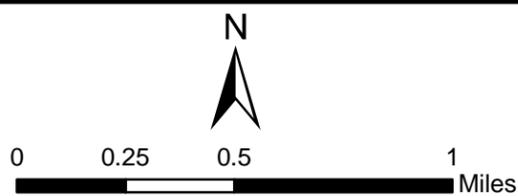
<b>Monitoring Wells</b>	<b>Residential Samples</b>	North Kent Study Area
Non-Detect	Non-Detect	Data Evaluation Groups
>0 to 10	>0 to 10	
>10 to 70	>10 to 70	
>70 to 1,000	>70 to 1,000	
> 1,000	> 1,000	

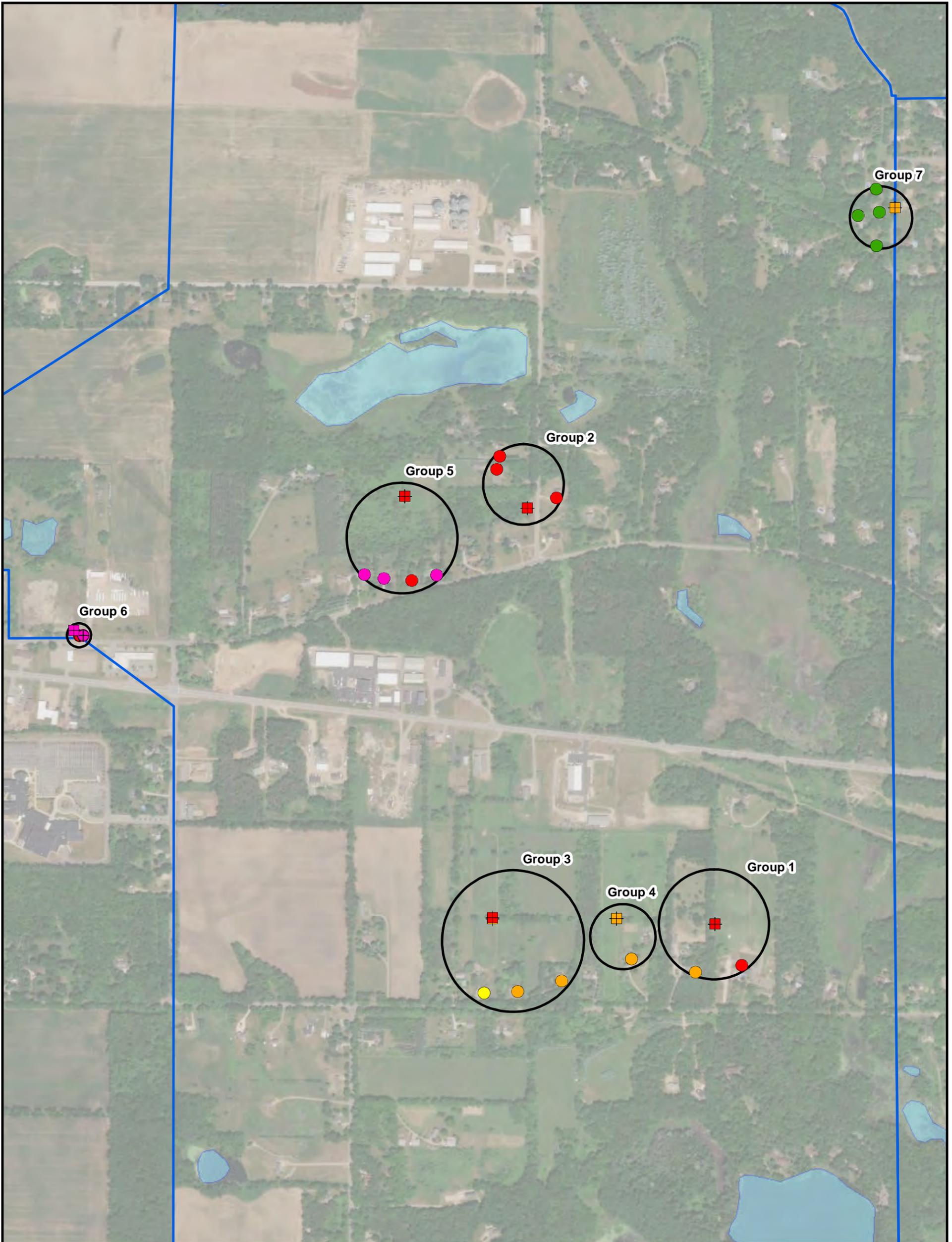
**FIGURE 10  
NORTH KENT STUDY AREA  
DATA EVALUATION GROUPS**

**KENT COUNTY, MICHIGAN**



Prepared: 6/19/2019





**Sampling Results - Total PFAS (ppt)**

**RI-18 Monitoring Wells**

- Non-Detect
- >0 to 10
- >10 to 70
- >70 to 1,000
- > 1,000

**Existing Monitoring Wells**

- Non-Detect
- >0 - 10
- >10 - 70
- >70 - 1,000
- >1,000

**Residential Samples**

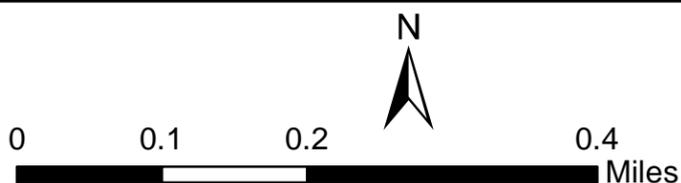
- Non-Detect
- >0 to 10
- >10 to 70
- >70 to 1,000
- > 1,000

Richland Study Area

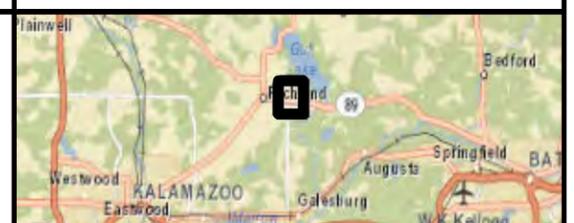
Data Evaluation Groups

**FIGURE 11**  
**RICHLAND STUDY AREA**  
**DATA EVALUATION GROUPS**

**RICHLAND, MICHIGAN**



Prepared: 6/19/2019



Tables

**Table 3**  
Wilcoxon-Mann-Whitney Tests  
for Grayling Area PFAS Study Groups

Residential Wells Compared to Monitoring Wells									
Analyte	Number of Detected Samples Groups 3-15		Median of Detected Concentrations Groups 3 - 15 (ng/L)		Distribution of Detected Concentrations		Two-Sample Hypothesis Test (a)		
	Residential	Monitoring Well	Residential	Monitoring Well	Residential	Monitoring Well	Test	p-value	Conclusion
PFBS	13	21	2.97	2.34	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.697	No Difference in Median Detected Concentration
PFBA	13	33	5.19	4.26	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.15	No Difference in Median Detected Concentration
PFPeA	16	27	20.55	8.54	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.128	No Difference in Median Detected Concentration
PFHxA	16	23	15.7	8.73	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.248	No Difference in Median Detected Concentration
PFHxS	23	40	25	3.57	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.0605	No Difference in Median Detected Concentration
PFOS	15	22	20	4.31	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.286	No Difference in Median Detected Concentration
PFOA	16	21	3.505	4.92	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.988	No Difference in Median Detected Concentration
PFHpA	15	26	6.1	3.5	Approximately Normal	Not Normal	Wilcoxon-Mann-Whitney	0.208	No Difference in Median Detected Concentration
Residential Wells Compared to Vertical Aquifer Samples									
Analyte	Number of Detected Samples Groups 3-15		Median of Detected Concentrations Groups 3 - 15 (ng/L)		Distribution of Detected Concentrations		Two-Sample Hypothesis Test (a)		
	Residential	Vertical Aquifer Sample	Residential	Vertical Aquifer Sample	Residential	Vertical Aquifer Sample	Test	p-value	Conclusion
PFBS	13	32	2.97	2.175	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.726	No Difference in Median Detected Concentration
PFBA	13	42	5.19	3.7	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.127	No Difference in Median Detected Concentration
PFPeA	16	37	20.55	8.19	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.226	No Difference in Median Detected Concentration
PFHxA	16	31	15.7	9.37	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.234	No Difference in Median Detected Concentration
PFHxS	23	42	25	12.8	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.978	No Difference in Median Detected Concentration
PFOS	15	28	20	14.7	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.619	No Difference in Median Detected Concentration
PFOA	16	35	3.505	4.68	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.761	No Difference in Median Detected Concentration
PFHpA	15	37	6.1	3.45	Approximately Normal	Not Normal	Wilcoxon-Mann-Whitney	0.275	No Difference in Median Detected Concentration
Monitoring Wells Compared to Vertical Aquifer Samples									
Analyte	Number of Detected Samples Groups 3-15		Median of Detected Concentrations Groups 3 - 15 (ng/L)		Distribution of Detected Concentrations		Two-Sample Hypothesis Test (a)		
	Monitoring Well	Vertical Aquifer Sample	Monitoring Well	Vertical Aquifer Sample	Monitoring Well	Vertical Aquifer Sample	Test	p-value	Conclusion
PFBS	21	32	2.34	2.175	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.971	No Difference in Median Detected Concentration
PFBA	33	42	4.26	3.7	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.979	No Difference in Median Detected Concentration
PFPeA	27	37	8.54	8.19	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.913	No Difference in Median Detected Concentration
PFHxA	23	31	8.73	9.37	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.937	No Difference in Median Detected Concentration
PFHxS	40	42	3.57	12.8	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.00391	Monitoring Well < Vertical Aquifer Sample
PFOS	22	28	4.31	14.7	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.452	No Difference in Median Detected Concentration
PFOA	21	35	4.92	4.68	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.624	No Difference in Median Detected Concentration
PFHpA	26	37	3.5	3.45	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.738	No Difference in Median Detected Concentration

(a) Tests have null hypothesis: "Median Detected Concentration of Wells of Sample Type 1 = Median Detected Concentration of Wells of Sample Type 2". If the p-value of the two-sample hypothesis test is less than alpha (0.05), then the null hypothesis is rejected.

**Table 4**  
Wilcoxon-Mann-Whitney Tests  
for North Kent Study Groups

Analyte	Number of Detected Samples Groups 1,2,3,4,5,6,7,8,9,10,13,15,17,19		Median of Detected Concentrations Groups 1,2,3,4,5,6,7,8,9,10,13,15,17,19 (ng/L)		Distribution of Detected Concentrations		Two-Sample Hypothesis Test (a)		
	Monitoring Well	Residential	Monitoring Well	Residential	Monitoring Well	Residential	Test	p-value	Conclusion
PFBA	23	18	6.3	18	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.043	<b>Monitoring Well &lt; Residential Drinking Water</b>
PFBS	37	54	11	12.5	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.602	No Difference in Median Detected Concentration
PFHpA	26	36	7.3	12	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.113	No Difference in Median Detected Concentration
PFHxS	35	44	18.4	15.5	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.824	No Difference in Median Detected Concentration
PFOA	43	59	26.3	20	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.941	No Difference in Median Detected Concentration
PFOS	31	35	43	100	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.345	No Difference in Median Detected Concentration
PFPeA	19	23	7.3	20	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.0727	No Difference in Median Detected Concentration

(a) Tests have null hypothesis: "Median Detected Concentration of Wells of Sample Type 1 = Median Detected Concentration of Wells of Sample Type 2". If the p-value of the two-sample hypothesis test is less than alpha (0.05), then the null hypothesis is rejected.

Table 5  
 Wilcoxon-Mann-Whitney  
 for Richland Study Groups

Analyte	Number of Detected Samples Groups 2,3,4,5,6,7		Median of Detected Concentrations Groups 2,3,4,5,6,7		Distribution of Detected Concentrations		Two-Sample Hypothesis Test (a)		
	Monitoring Well	Residential	Monitoring Well	Residential	Monitoring Well	Residential	Test	p-value	Conclusion
PFBA	10	0	3.68	-	-	-	-	-	-
PFBS	14	8	5.46	6	Not Normal	Normal	Wilcoxon-Mann-Whitney	0.759	No Difference in Median Detected Concentration
PFHpA	9	5	3.95	3	-	-	-	-	-
PFHxS	15	8	22.4	23	Not Normal	Not Normal	Wilcoxon-Mann-Whitney	0.518	No Difference in Median Detected Concentration
PFOA	14	8	9.14	9	Not Normal	Normal	Wilcoxon-Mann-Whitney	0.733	No Difference in Median Detected Concentration
PFOS	14	7	84.8	470	-	-	-	-	-
PFPeA	8	0	2.965	-	-	-	-	-	-

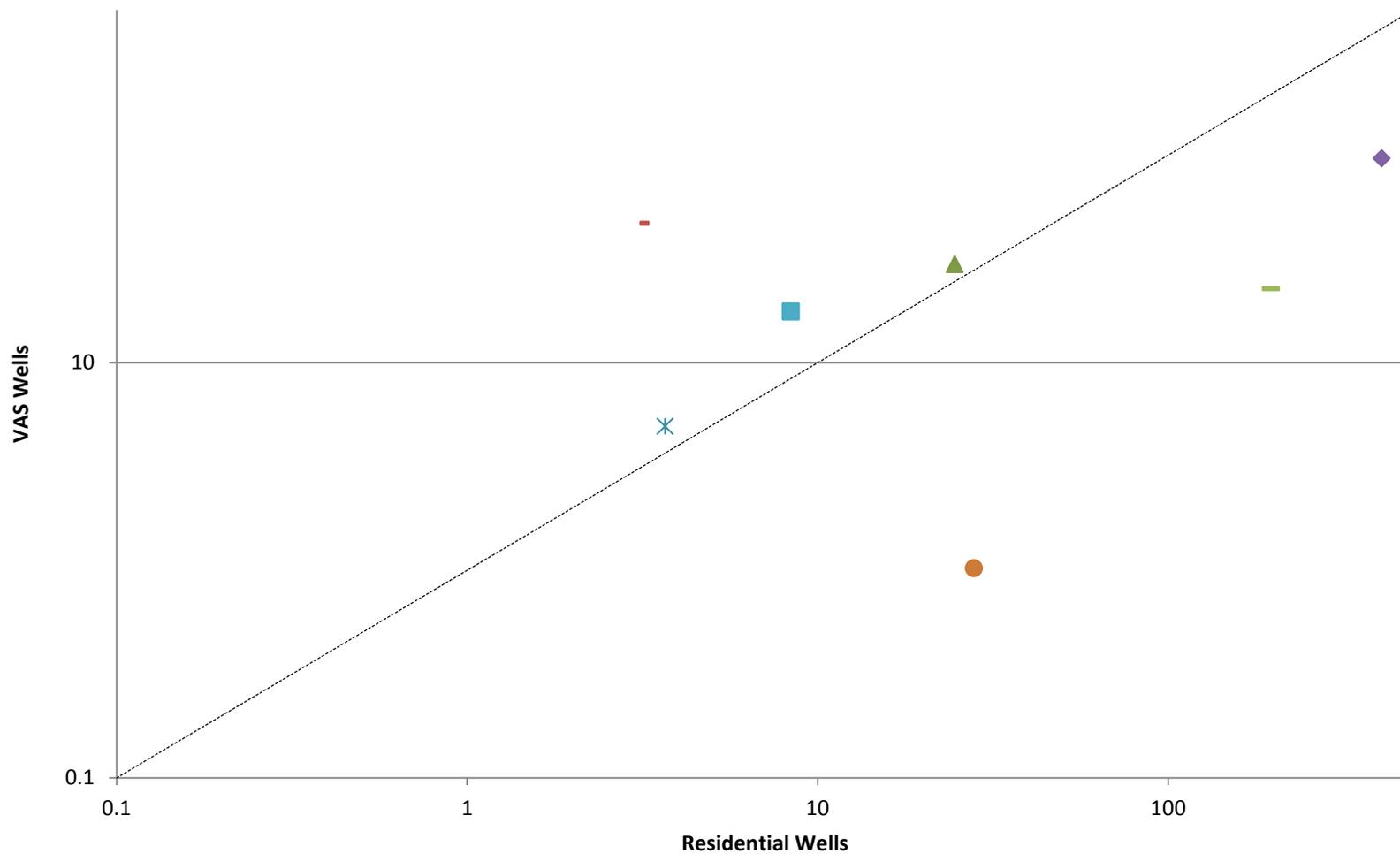
(a) Tests have null hypothesis: "Median Detected Concentration of Wells of Sample Type 1 = Median Detected Concentration of Wells of Sample Type 2". If the p-value of the two-sample hypothesis test is less than alpha (0.05), then the null hypothesis is rejected.

At least eight detections are required in monitoring wells and residential wells to run population comparison tests.

# Appendix A

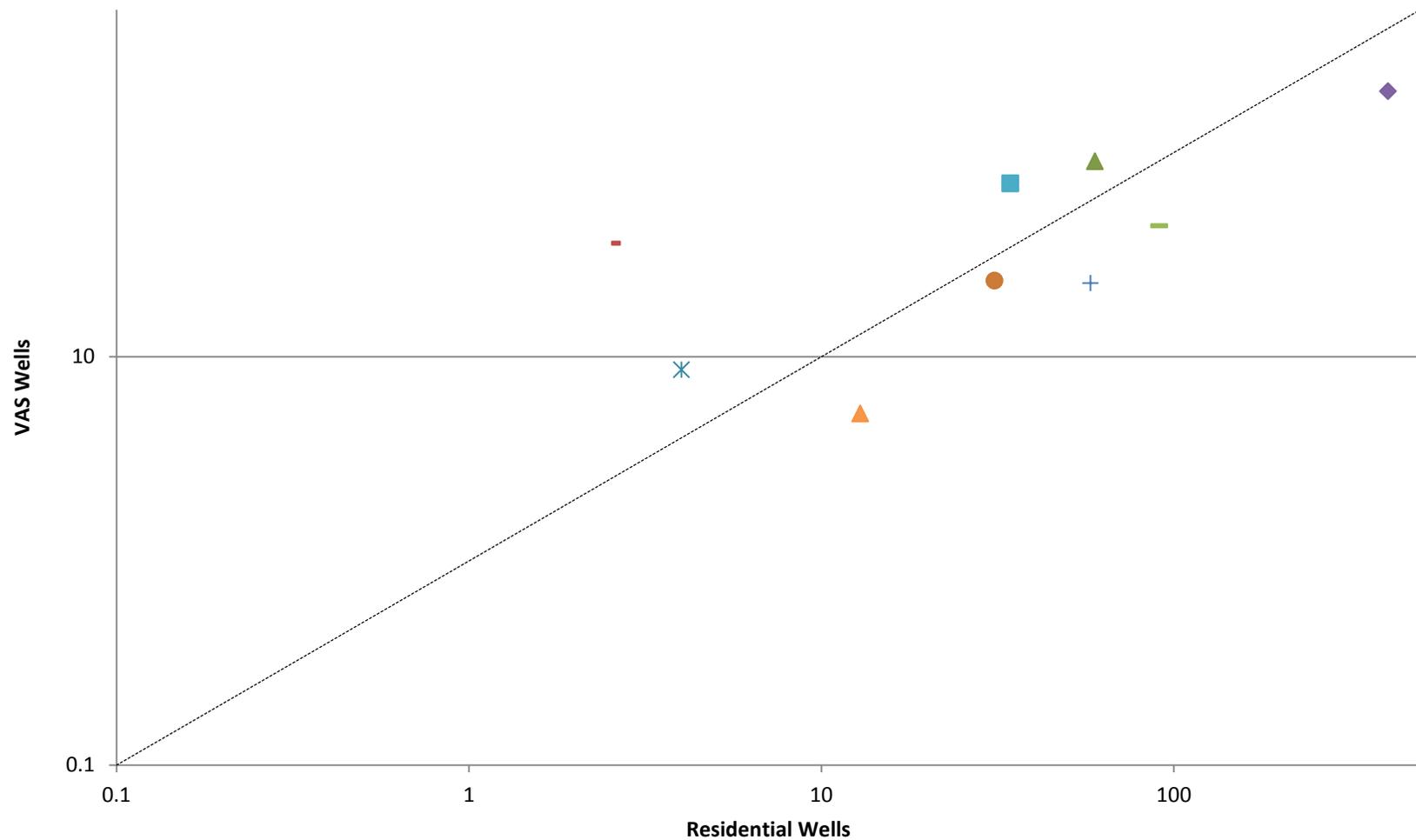
# Grayling Study Area

## Average Detected PFOA + PFOS (ng/L)



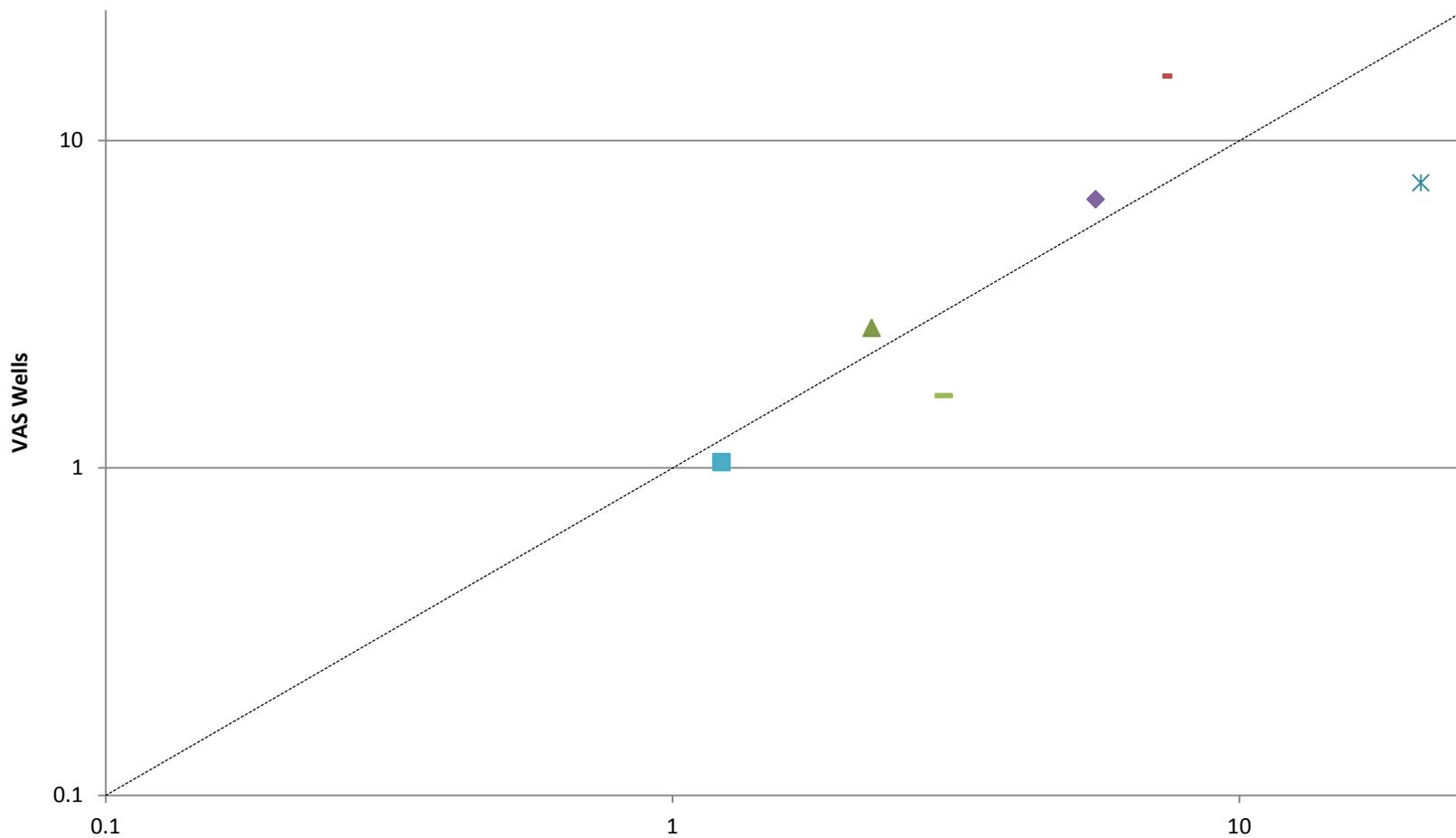
- ▲ Group 3
- Group 4
- ✱ Group 5
- Group 6
- + Group 7
- Group 8
- Group 9
- ◆ Group 10
- Group 11
- ▲ Group 12
- ✱ Group 13
- ✱ Group 14
- Group 15
- 1-1 Line

# Grayling Study Area Average Detected PFHxS (ng/L)



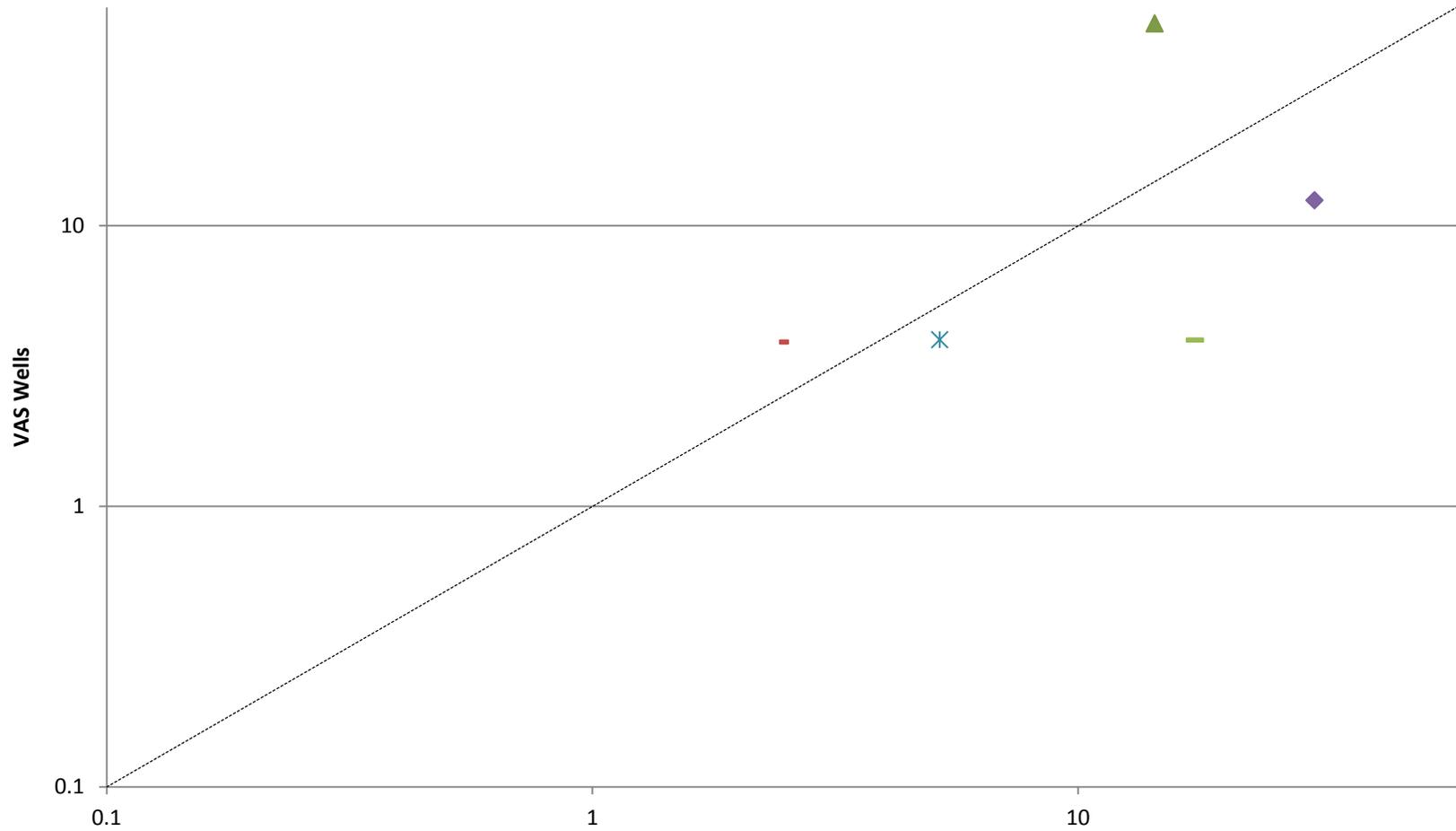
- ▲ Group 3
- Group 4
- ✕ Group 5
- Group 6
- + Group 7
- Group 8
- Group 9
- ◆ Group 10
- Group 11
- ▲ Group 12
- ✕ Group 13
- ✕ Group 14
- Group 15
- 1-1 Line

# Grayling Study Area Average Detected PFBS (ng/L)



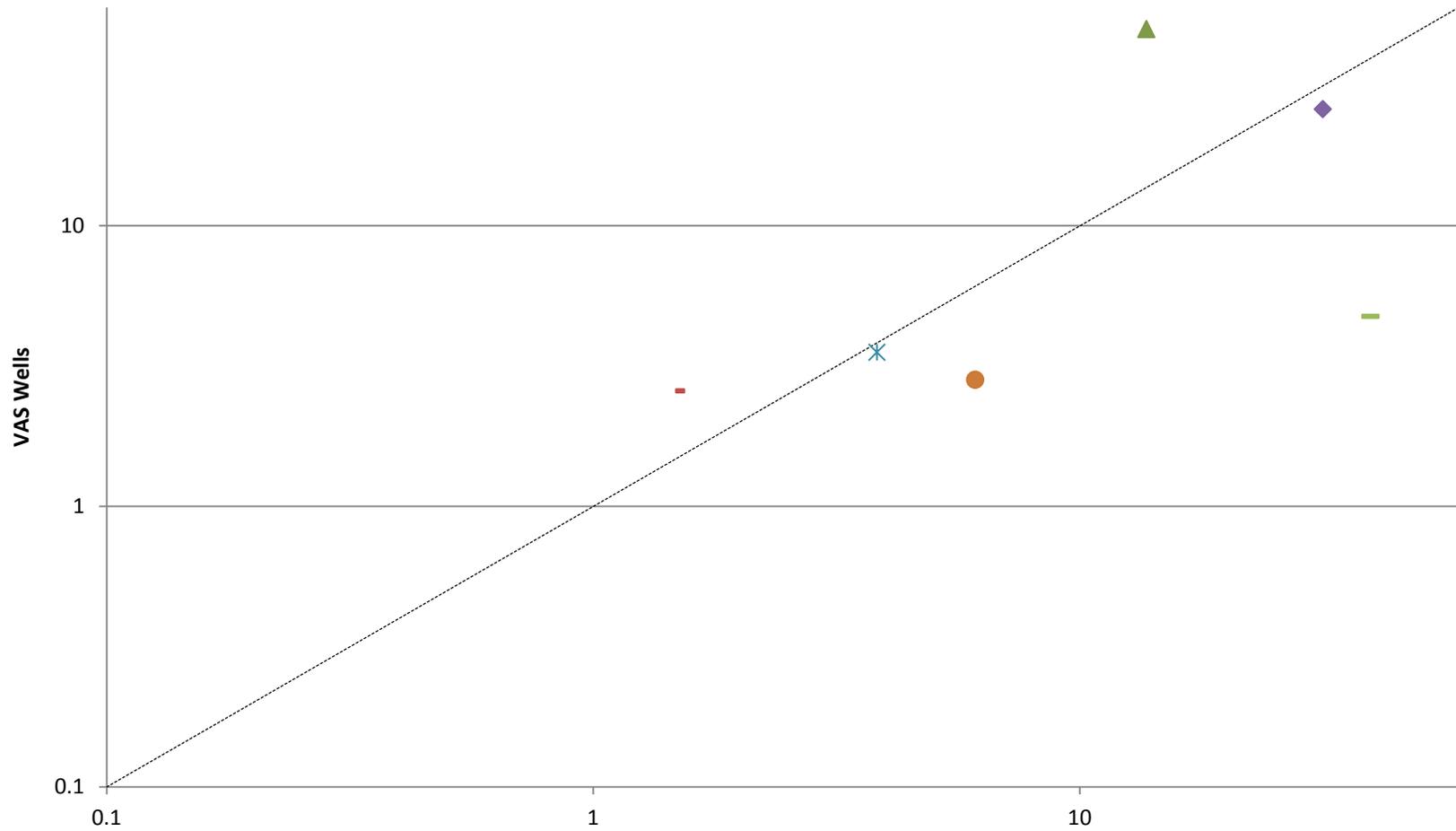
- ▲ Group 3    × Group 4    × Group 5    ● Group 6    + Group 7    - Group 8    - Group 9  
◆ Group 10    ■ Group 11    ▲ Group 12    × Group 13    × Group 14    ● Group 15    ..... 1-1 Line

# Grayling Study Area Average Detected PFBA (ng/L)



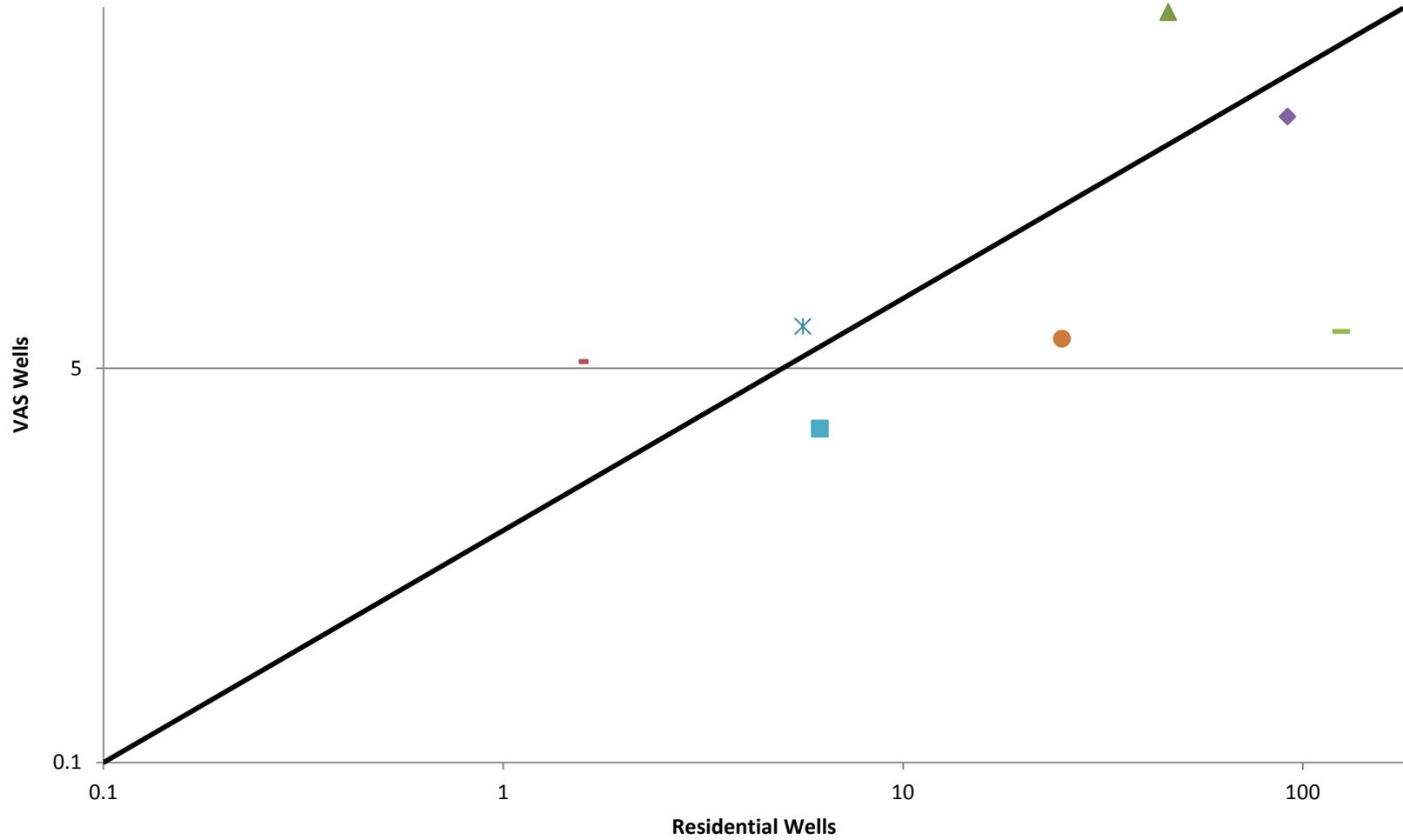
- ▲ Group 3
- ✕ Group 4
- ✕ Group 5
- Group 6
- ⊕ Group 7
- Group 8
- Group 9
- ◆ Group 10
- Group 11
- ▲ Group 12
- ✕ Group 13
- ✕ Group 14
- Group 15
- 1-1 Line

# Grayling Study Area Average Detected PFHpA (ng/L)



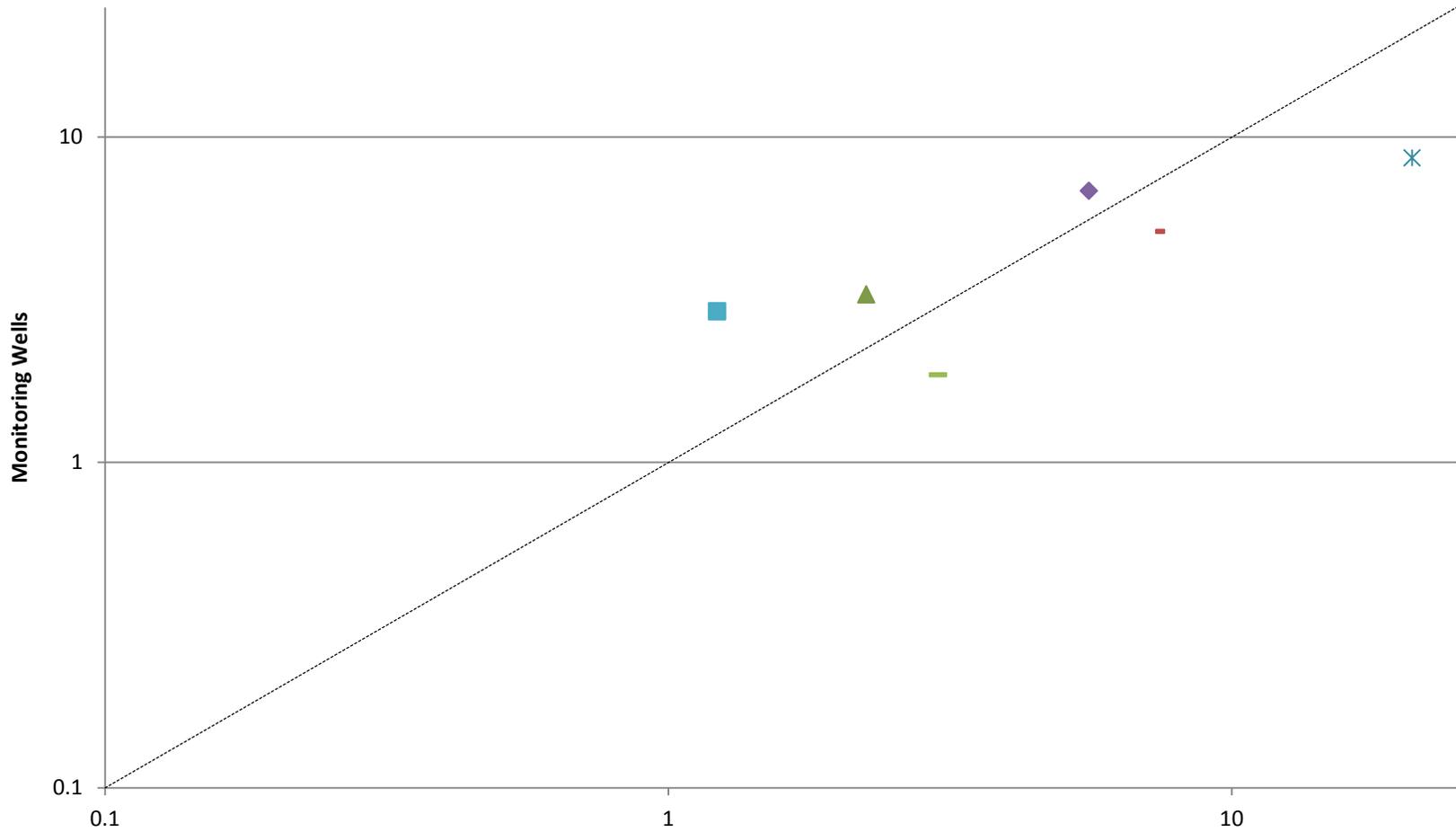
- Residential Wells
- ▲ Group 3
  - ✕ Group 4
  - ✕ Group 5
  - Group 6
  - + Group 7
  - Group 8
  - Group 9
  - ◆ Group 10
  - Group 11
  - ▲ Group 12
  - ✕ Group 13
  - ✕ Group 14
  - Group 15
  - ..... 1-1 Line

# Grayling Study Area Average Detected PFPeA (ng/L)



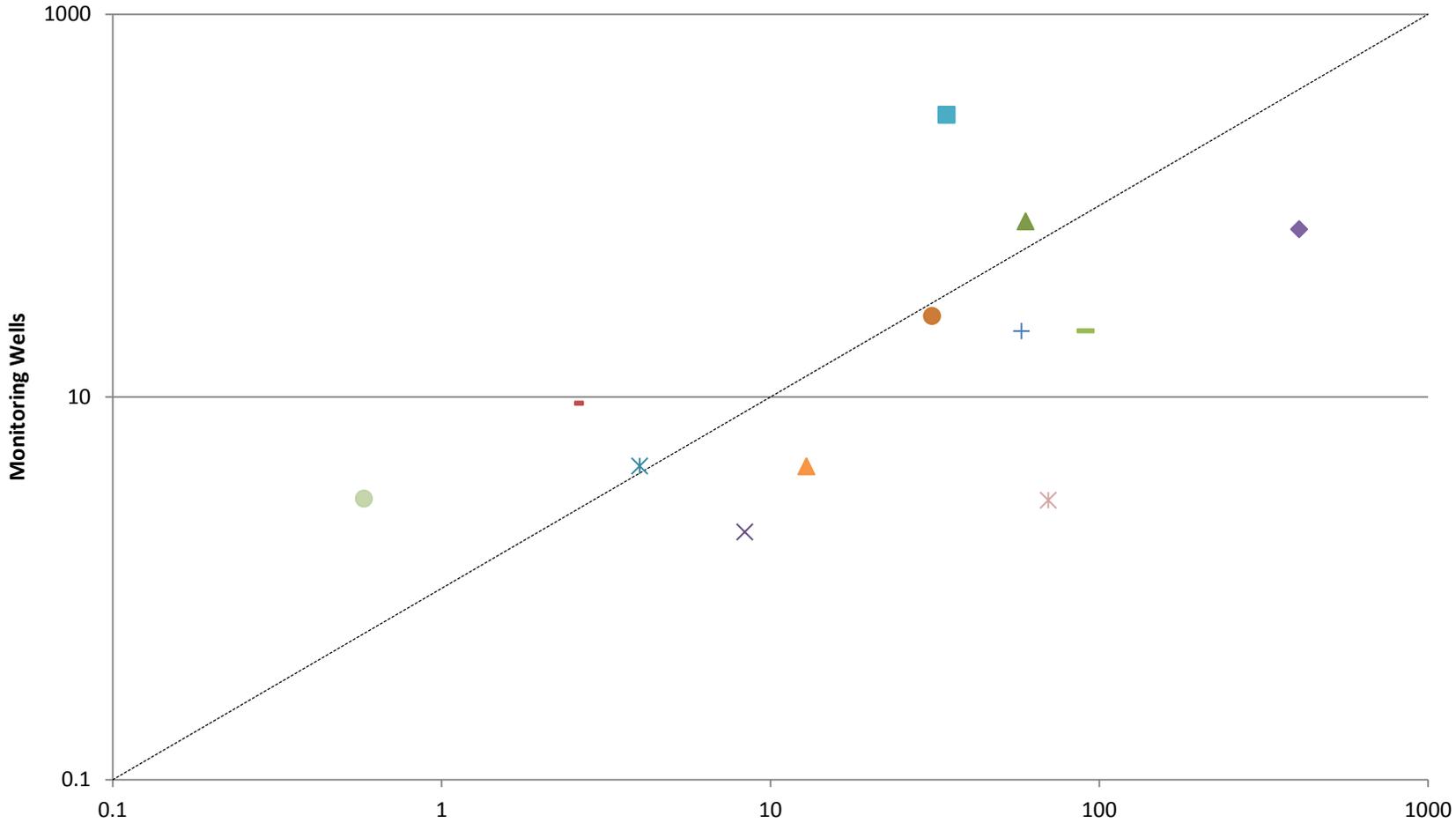
- ◆ Group 1
- Group 2
- ▲ Group 3
- × Group 4
- ✖ Group 5
- Group 6
- + Group 7
- Group 8
- Group 9
- ◆ Group 10
- Group 11
- ▲ Group 12
- × Group 13
- ✖ Group 14
- Group 15
- 1-1 Line

# Grayling Study Area Average Detected PFBS (ng/L)



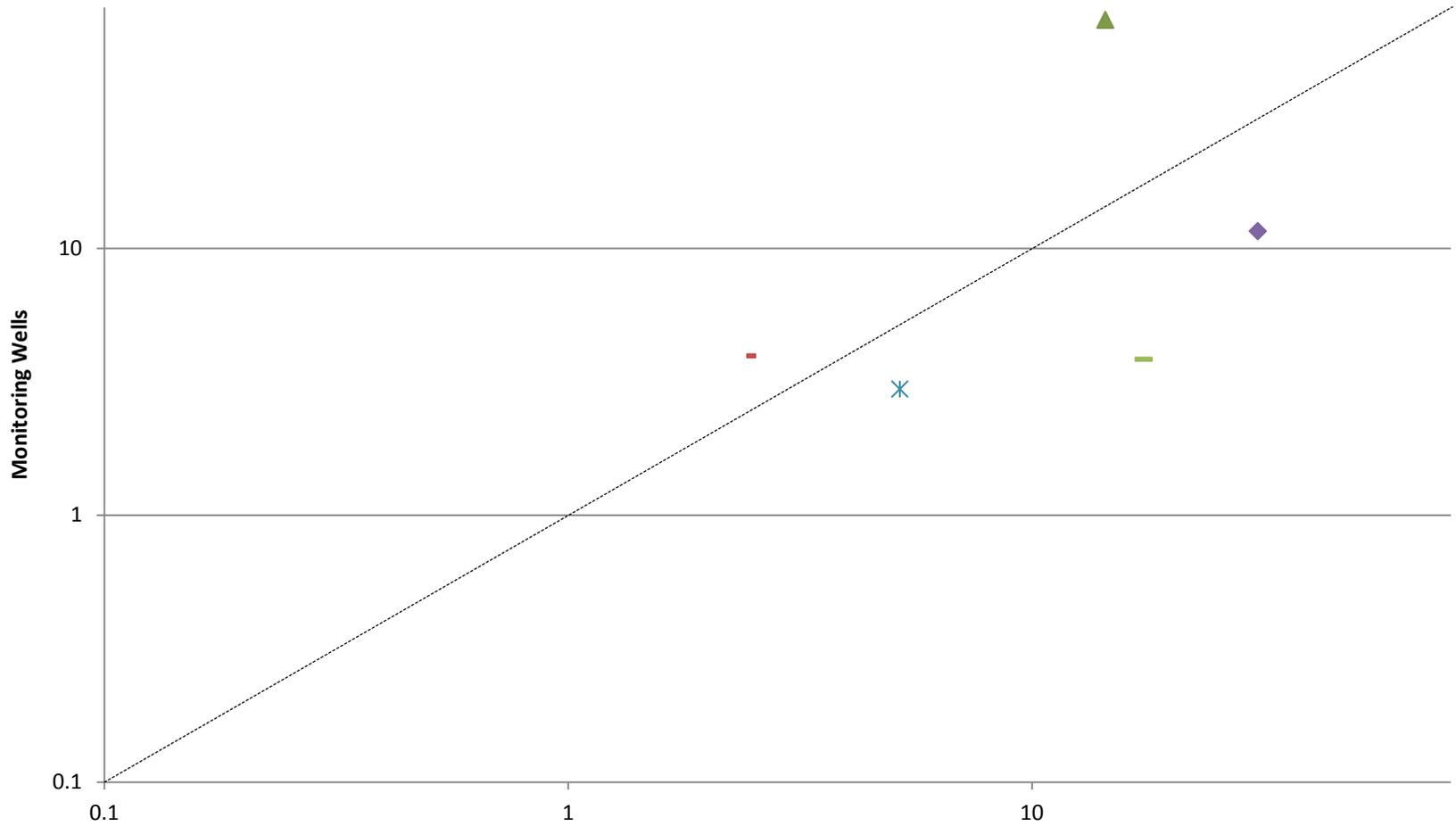
- Residential Wells
- ▲ Group 3
  - ✕ Group 4
  - ✕ Group 5
  - Group 6
  - + Group 7
  - Group 8
  - Group 9
  - ◆ Group 10
  - Group 11
  - ▲ Group 12
  - ✕ Group 13
  - ✕ Group 14
  - Group 15
  - ..... 1-1 Line

# Grayling Study Area Average Detected PFHxS (ng/L)



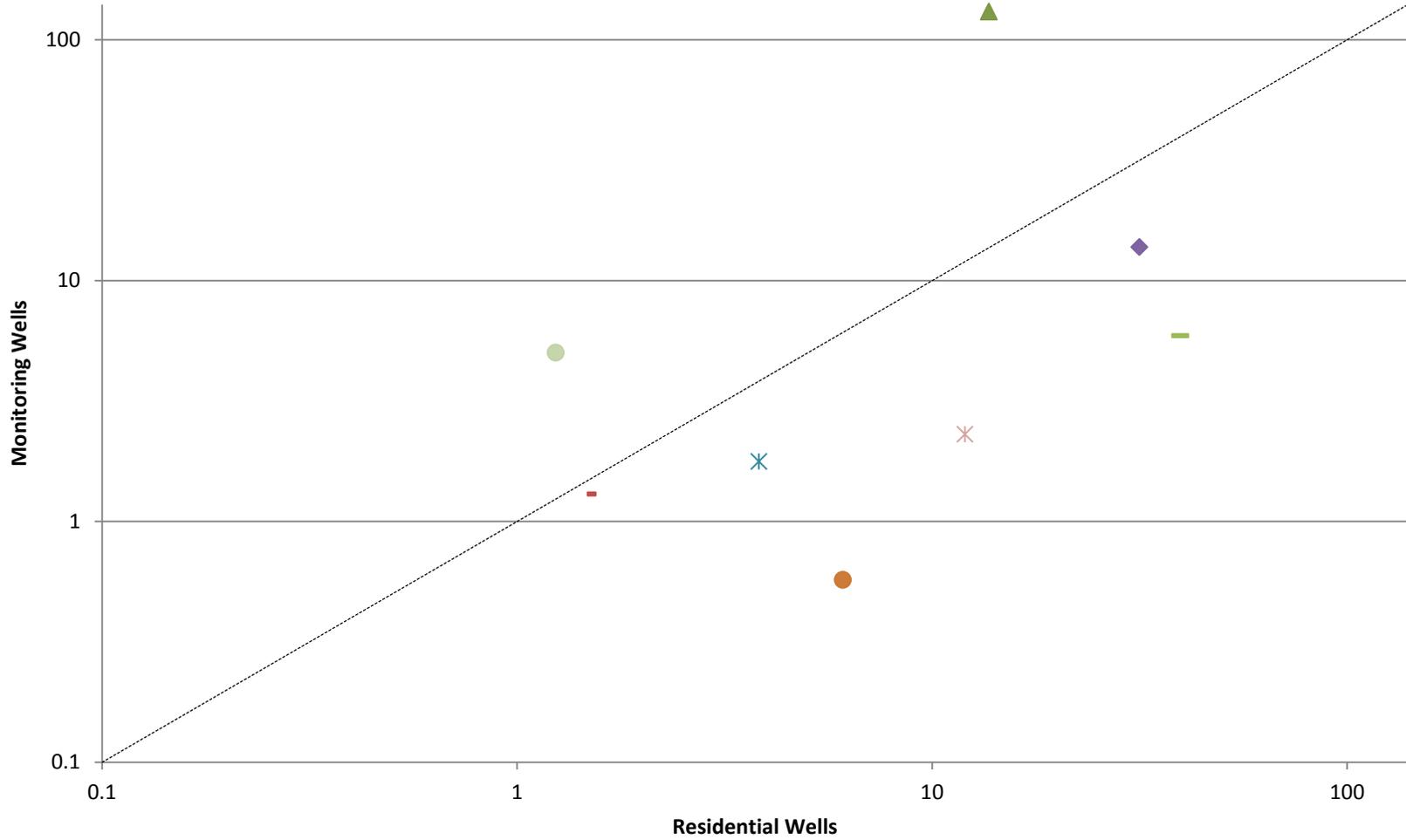
- Residential Wells
- ▲ Group 3
  - ✕ Group 4
  - ✕ Group 5
  - Group 6
  - + Group 7
  - Group 8
  - Group 9
  - ◆ Group 10
  - Group 11
  - ▲ Group 12
  - ✕ Group 13
  - ✕ Group 14
  - Group 15
  - ..... 1-1 Line

# Grayling Study Area Average Detected PFBA (ng/L)



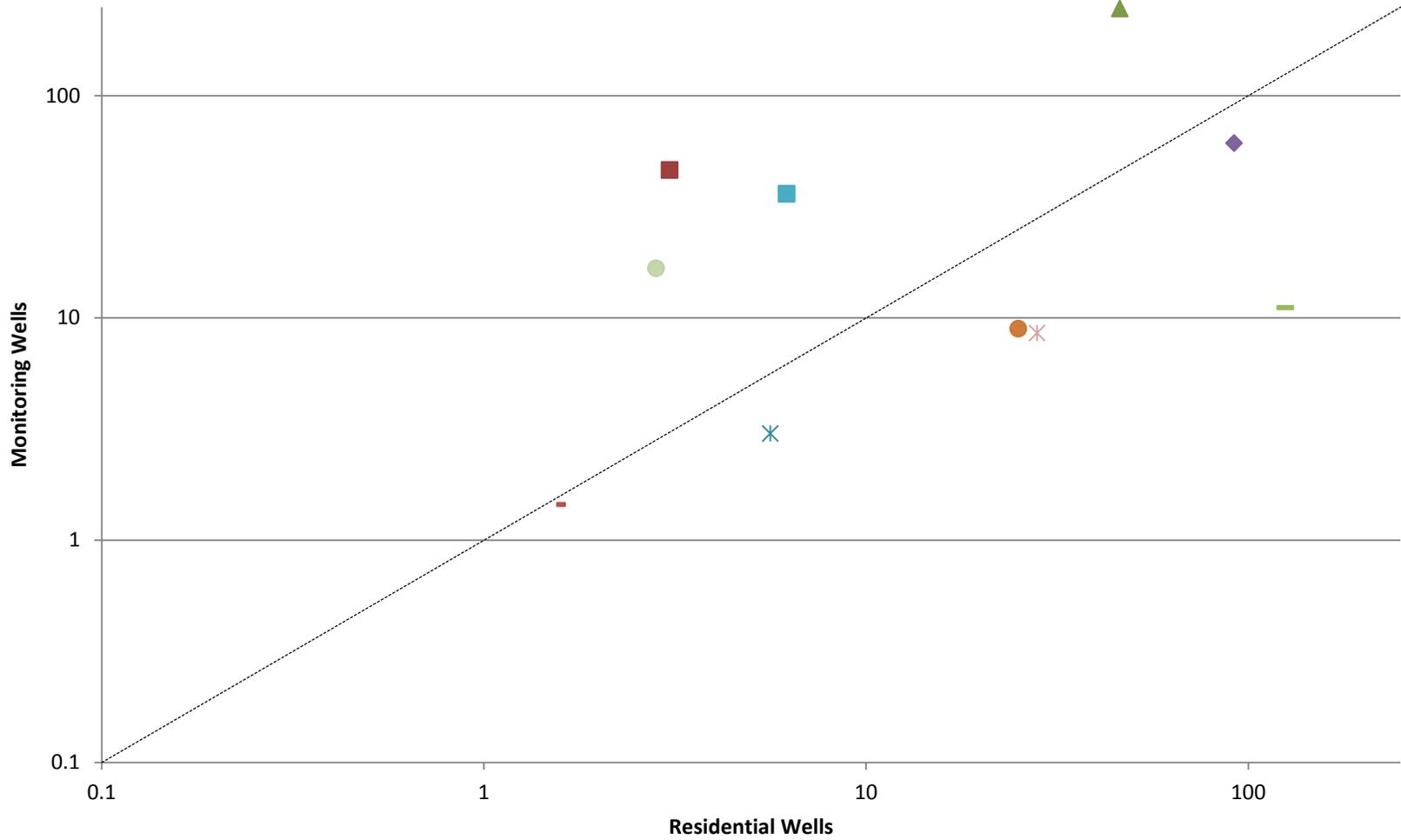
- Residential Wells**
- ▲ Group 3
  - ✕ Group 4
  - ✕ Group 5
  - Group 6
  - + Group 7
  - Group 8
  - Group 9
  - ◆ Group 10
  - Group 11
  - ▲ Group 12
  - ✕ Group 13
  - ✕ Group 14
  - Group 15
  - ..... 1-1 Line

# Grayling Study Area Average Detected PFHpA (ng/L)



- |            |            |            |            |            |            |                |
|------------|------------|------------|------------|------------|------------|----------------|
| ▲ Group 3  | × Group 4  | × Group 5  | ● Group 6  | + Group 7  | - Group 8  | - Group 9      |
| ◆ Group 10 | ■ Group 11 | ▲ Group 12 | × Group 13 | × Group 14 | ● Group 15 | ..... 1-1 Line |

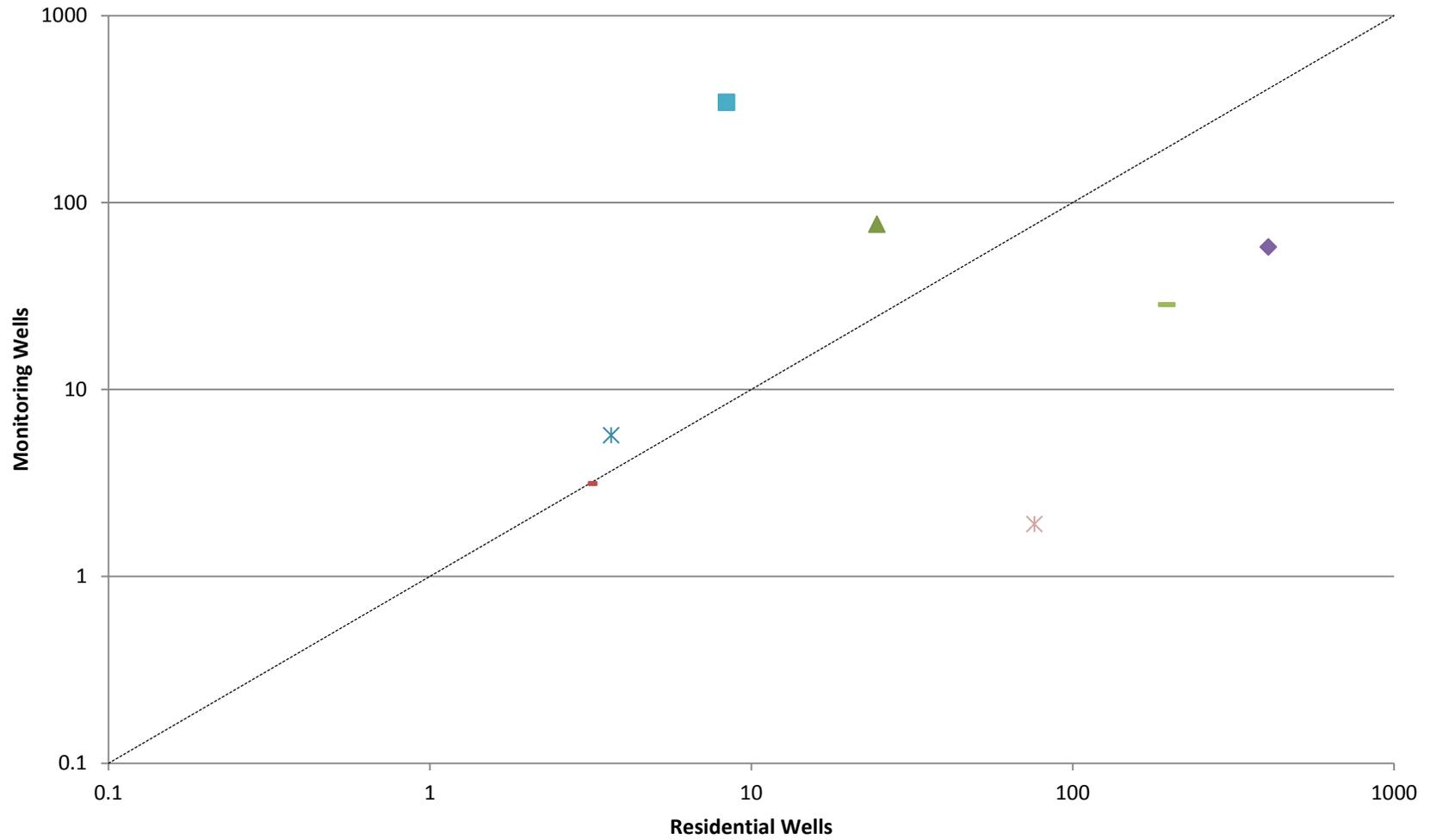
## Grayling Study Area Average Detected PFPeA (ng/L)



- |           |            |            |            |            |            |            |                |
|-----------|------------|------------|------------|------------|------------|------------|----------------|
| ◆ Group 1 | ■ Group 2  | ▲ Group 3  | × Group 4  | × Group 5  | ● Group 6  | + Group 7  | - Group 8      |
| - Group 9 | ◆ Group 10 | ■ Group 11 | ▲ Group 12 | × Group 13 | × Group 14 | ● Group 15 | ----- 1-1 Line |

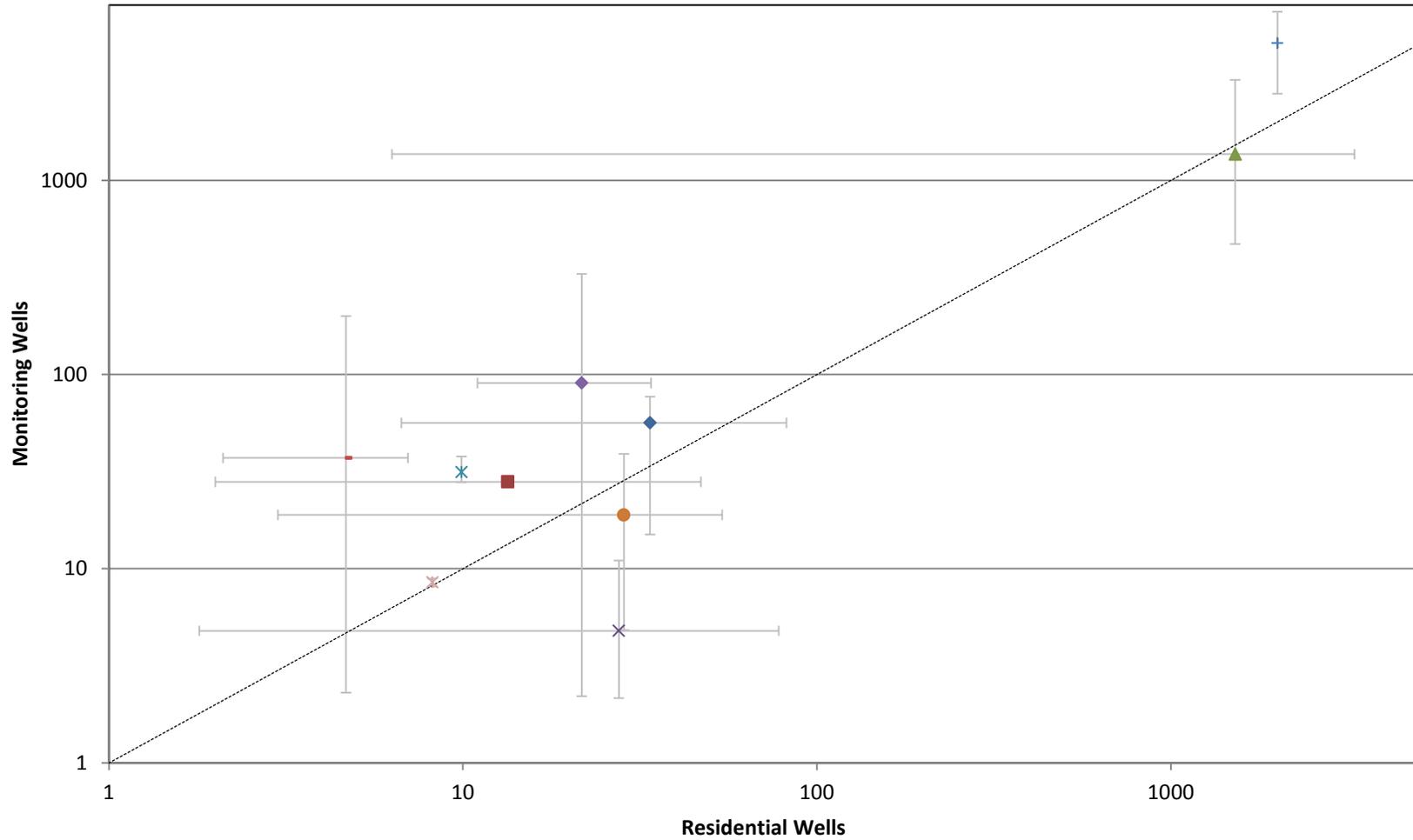
# Gryaling Study Area

## Average Detected PFOA + PFOS (ng/L)



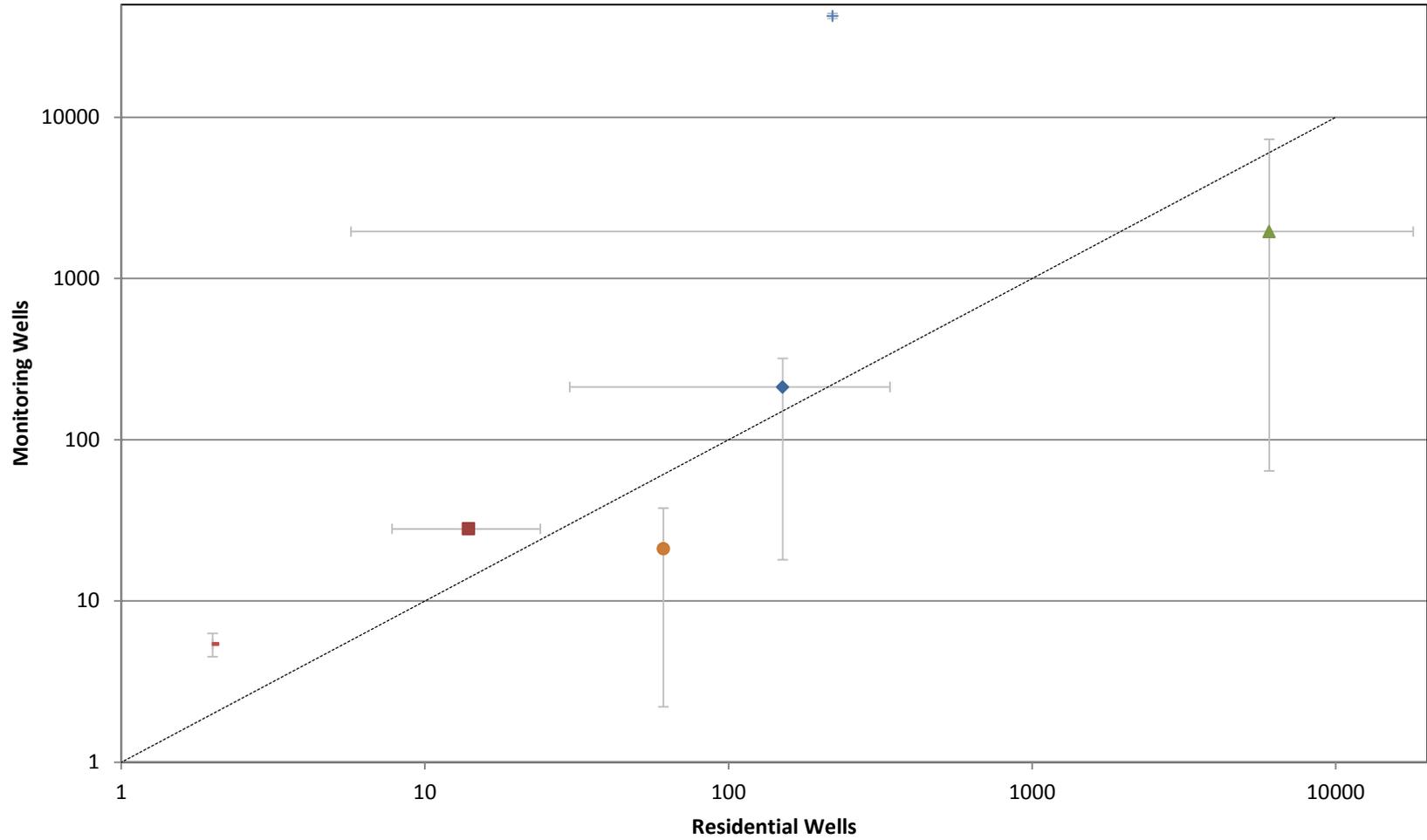
- ▲ Group 3
- ✕ Group 4
- ✕ Group 5
- Group 6
- + Group 7
- Group 8
- Group 9
- ◆ Group 10
- Group 11
- ▲ Group 12
- ✕ Group 13
- ✕ Group 14
- Group 15
- 1-1 Line

## North Kent Study Area Average Detected PFOA (ng/L)



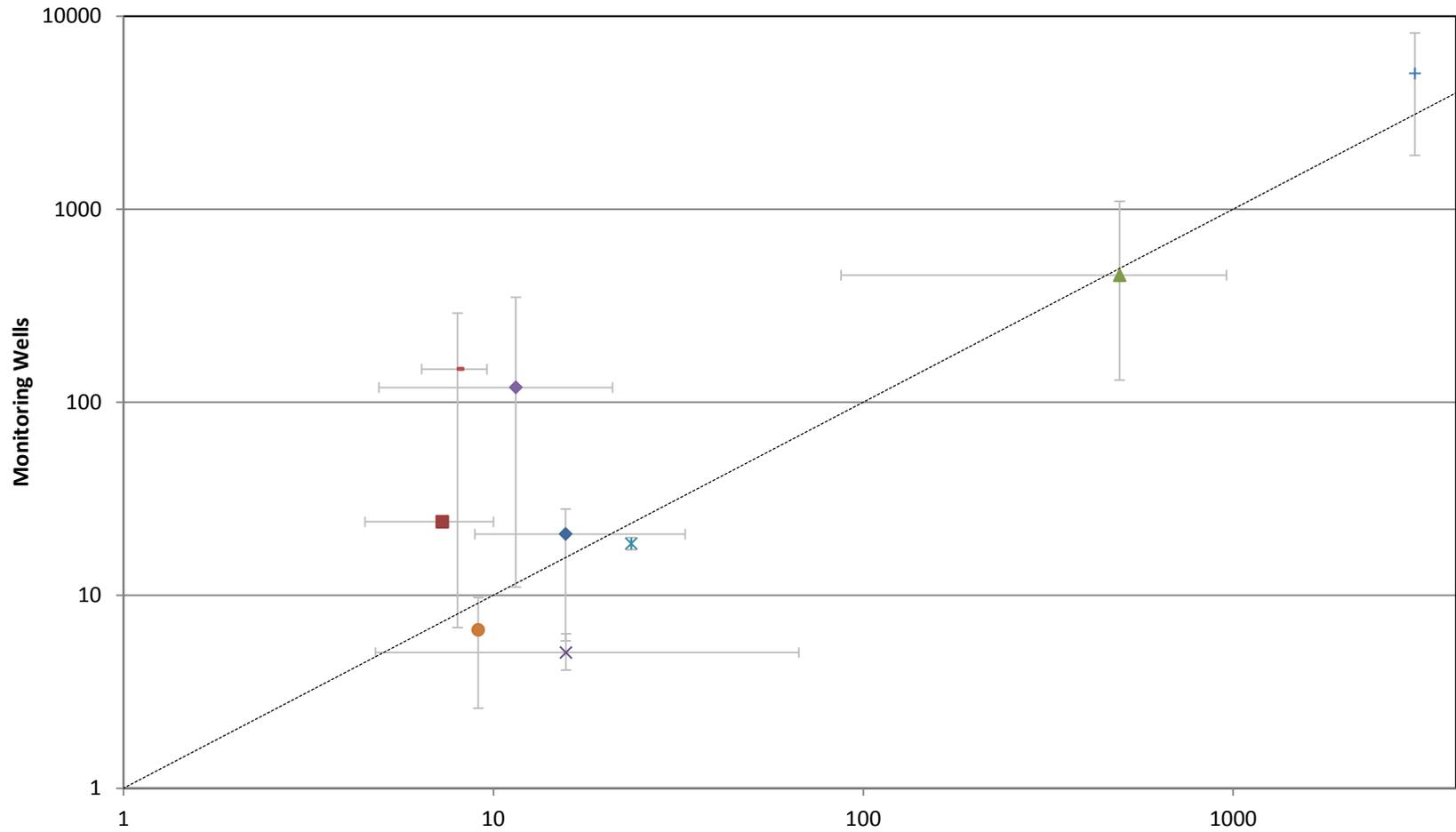
- |            |            |            |            |                |
|------------|------------|------------|------------|----------------|
| ◆ Group 1  | ■ Group 2  | ▲ Group 3  | × Group 4  | × Group 5      |
| ● Group 6  | + Group 7  | - Group 8  | - Group 9  | ◆ Group 10     |
| ■ Group 13 | ▲ Group 15 | × Group 17 | × Group 19 | ----- 1-1 Line |

## North Kent Study Area Average Detected PFOS (ng/L)



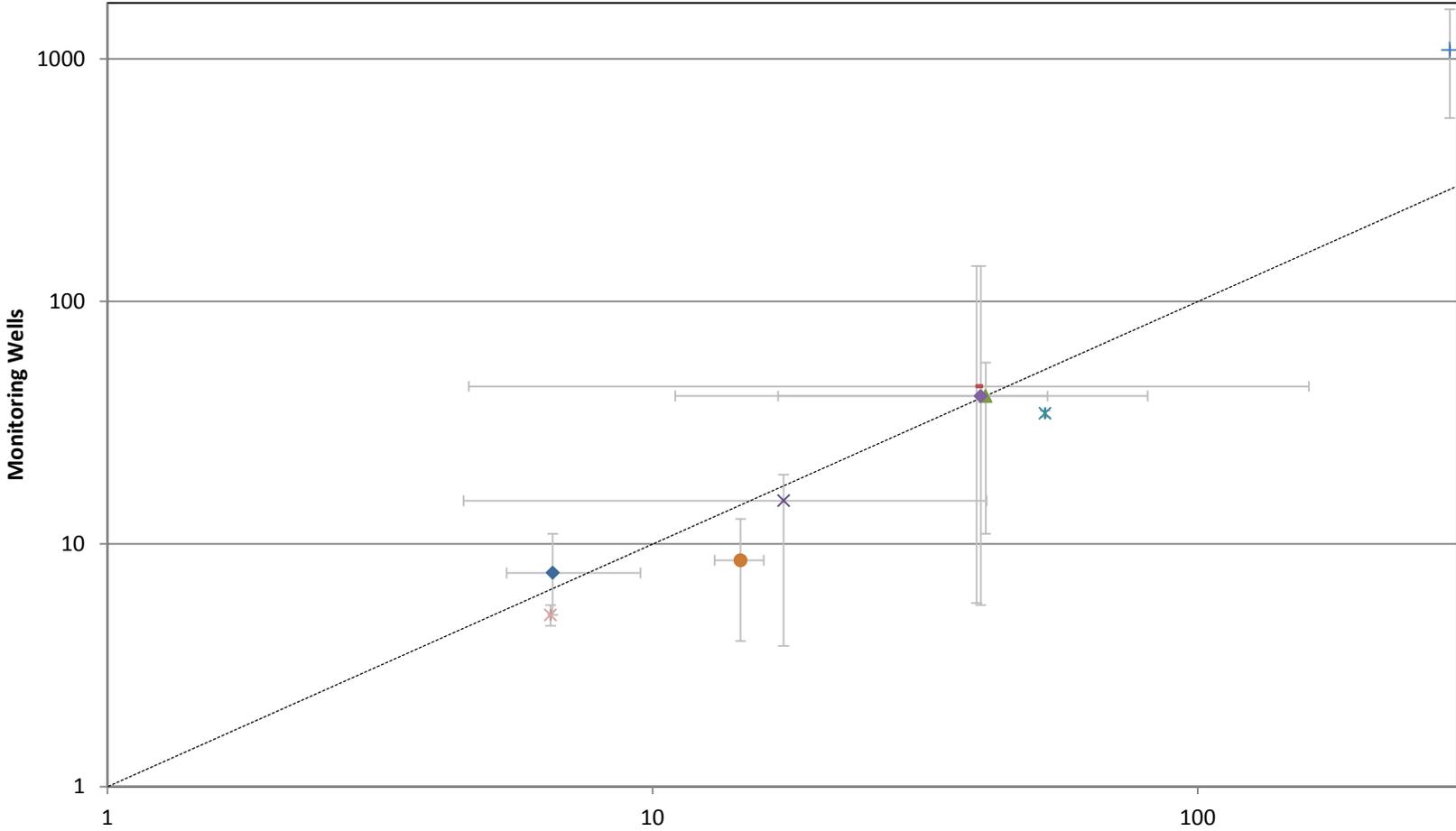
- |            |            |            |            |                |
|------------|------------|------------|------------|----------------|
| ◆ Group 1  | ■ Group 2  | ▲ Group 3  | × Group 4  | × Group 5      |
| ● Group 6  | + Group 7  | - Group 8  | - Group 9  | ◆ Group 10     |
| ■ Group 13 | ▲ Group 15 | × Group 17 | × Group 19 | ----- 1-1 Line |

## North Kent Study Area Average Detected PFHxS (ng/L)



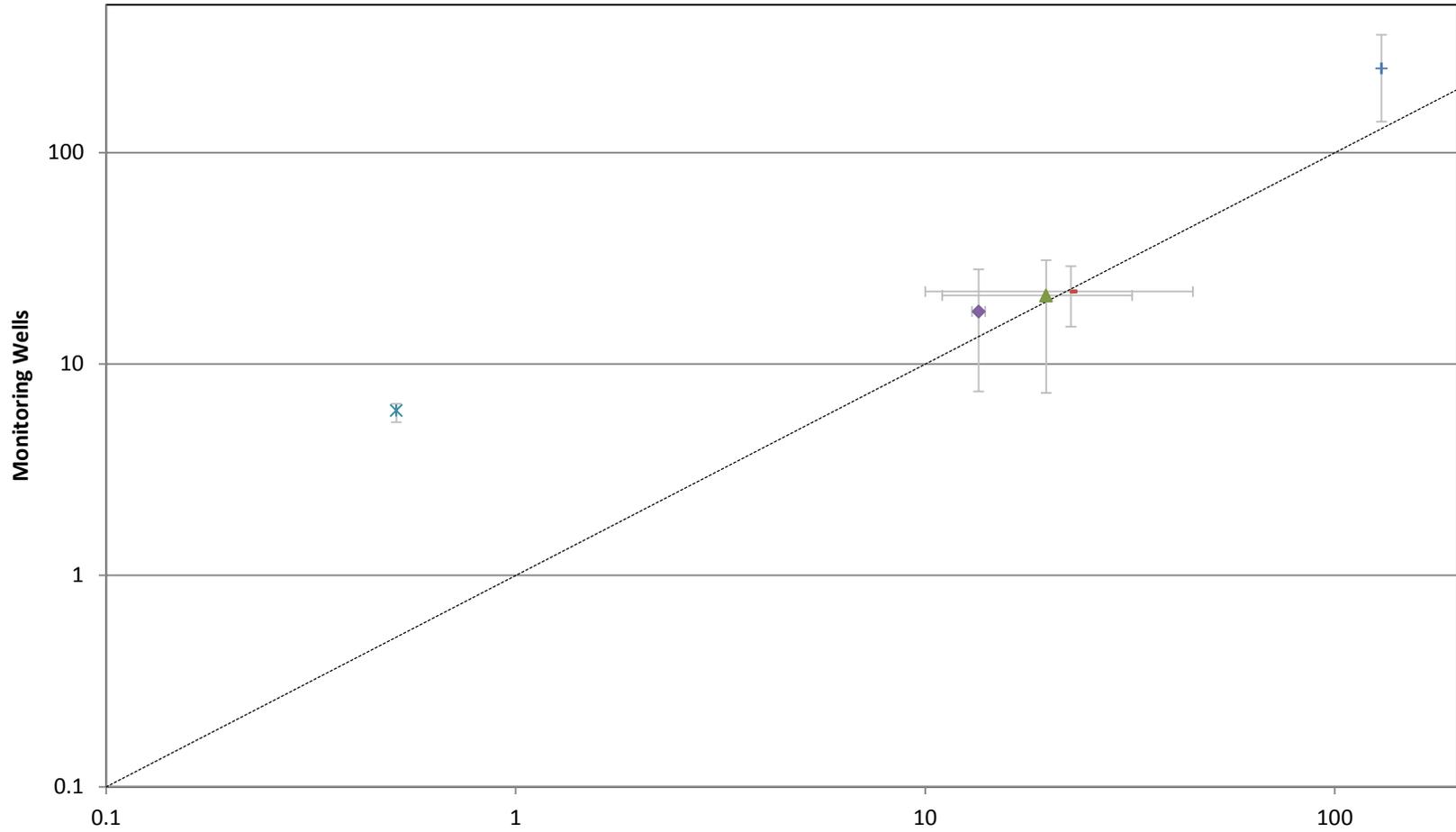
- Residential Wells**
- |            |            |            |            |                |
|------------|------------|------------|------------|----------------|
| ◆ Group 1  | ■ Group 2  | ▲ Group 3  | × Group 4  | ✕ Group 5      |
| ● Group 6  | + Group 7  | - Group 8  | - Group 9  | ◆ Group 10     |
| ■ Group 13 | ▲ Group 15 | × Group 17 | × Group 19 | ----- 1-1 Line |

# North Kent Study Area Average Detected PFBS (ng/L)



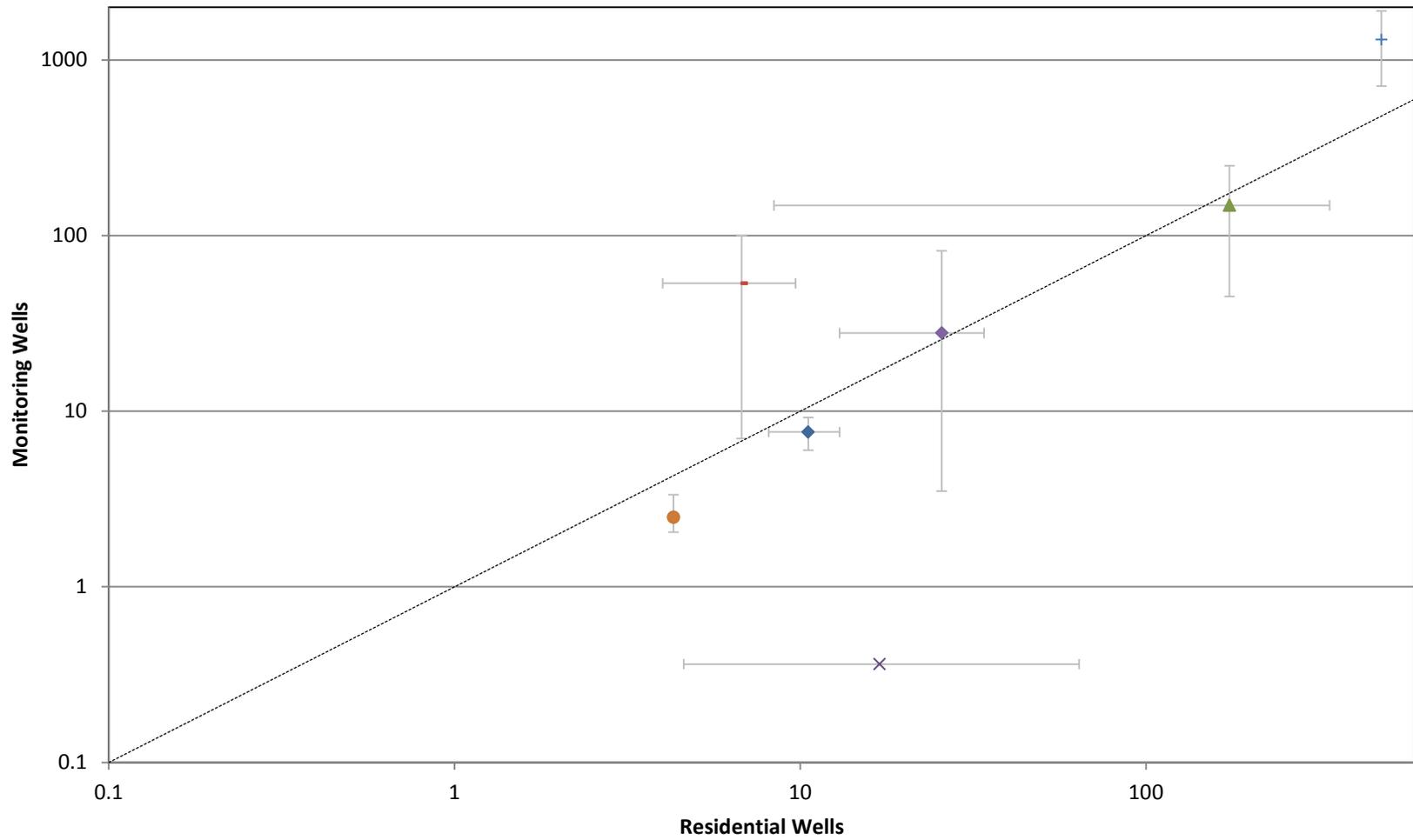
- ◆ Group 1
- Group 2
- ▲ Group 3
- × Group 4
- ✖ Group 5
- Group 6
- + Group 7
- Group 8
- Group 9
- ◆ Group 10
- Group 13
- ▲ Group 15
- × Group 17
- ✖ Group 19
- - - 1-1 Line

## North Kent Study Area Average Detected PFBA (ng/L)



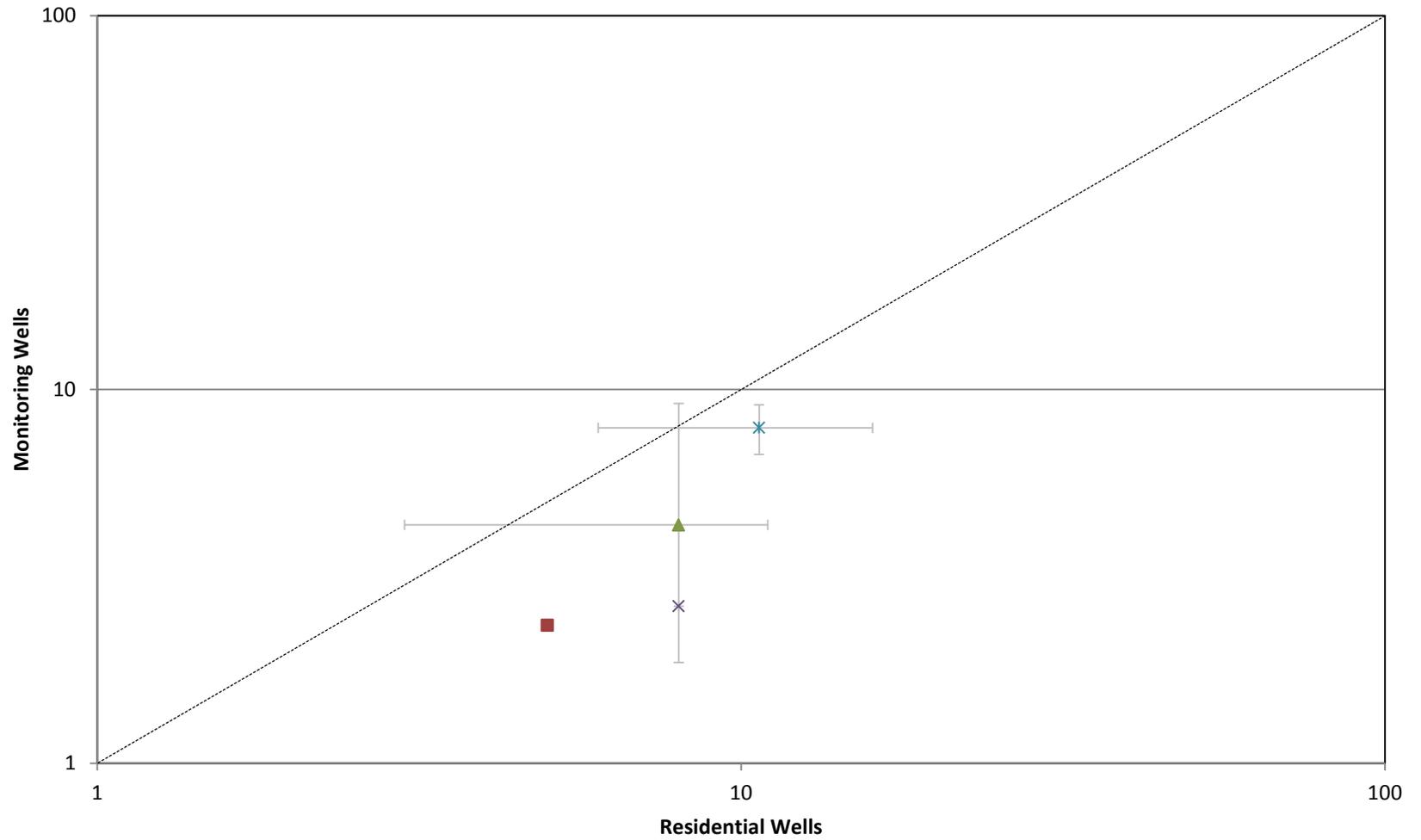
- Residential Wells**
- |           |            |            |            |            |            |                |           |
|-----------|------------|------------|------------|------------|------------|----------------|-----------|
| ◆ Group 1 | ■ Group 2  | ▲ Group 3  | × Group 4  | ✖ Group 5  | ● Group 6  | + Group 7      | - Group 8 |
| — Group 9 | ◆ Group 10 | ■ Group 13 | ▲ Group 15 | × Group 17 | ✖ Group 19 | ..... 1-1 Line |           |

## North Kent Study Area Average Detected PFHpA (ng/L)



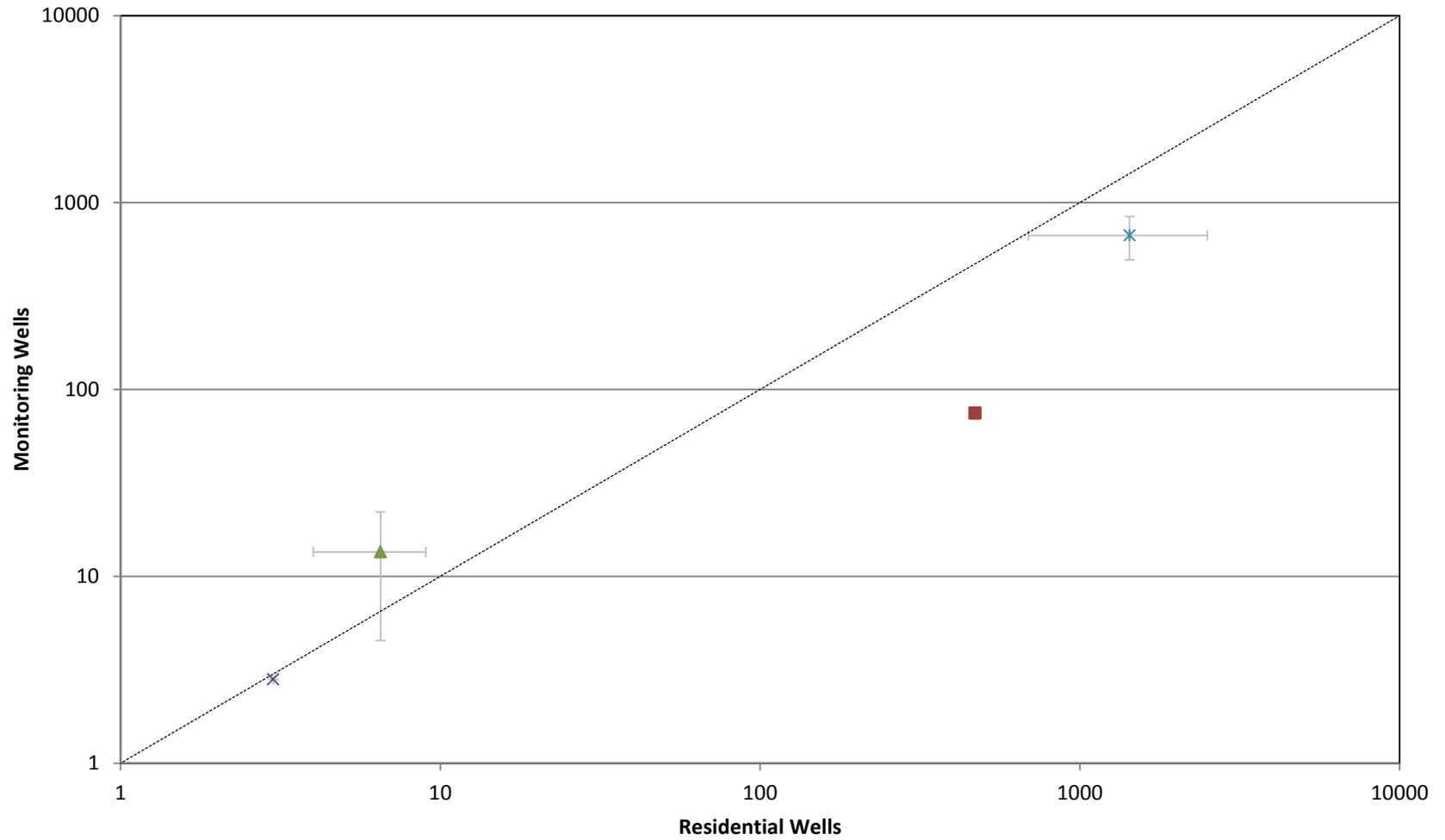
- ◆ Group 1
- Group 2
- ▲ Group 3
- × Group 4
- ✖ Group 5
- Group 6
- + Group 7
- Group 8
- Group 9
- ◆ Group 10
- Group 13
- ▲ Group 15
- × Group 17
- ✖ Group 19
- ..... 1-1 Line

# Richland Study Area Average Detected PFOA (ng/L)



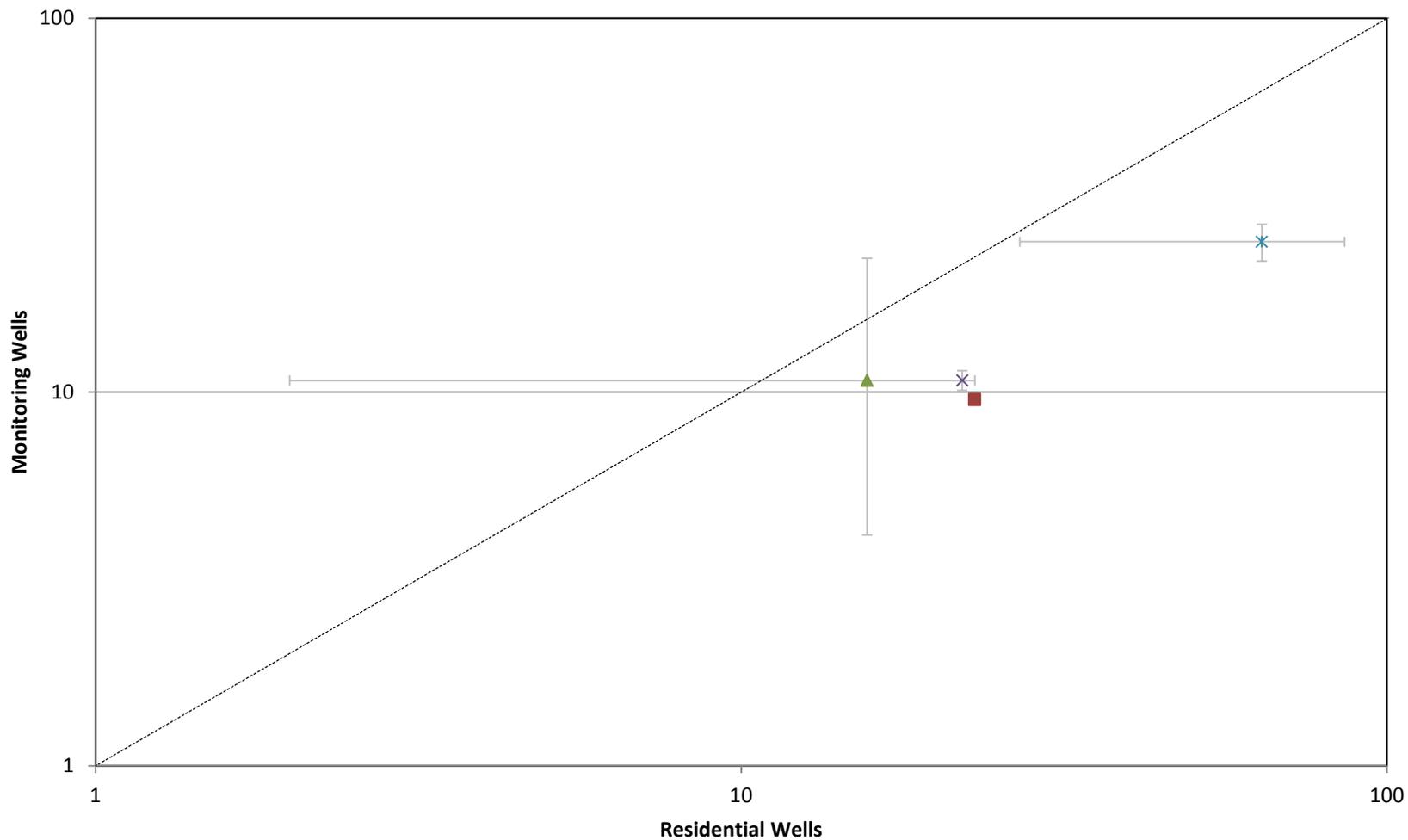
■ Group 2    ▲ Group 3    × Group 4    \* Group 5    ● Group 6    + Group 7    - - - - - 1-1 Line

# Richland Study Area Average Detected PFOS (ng/L)



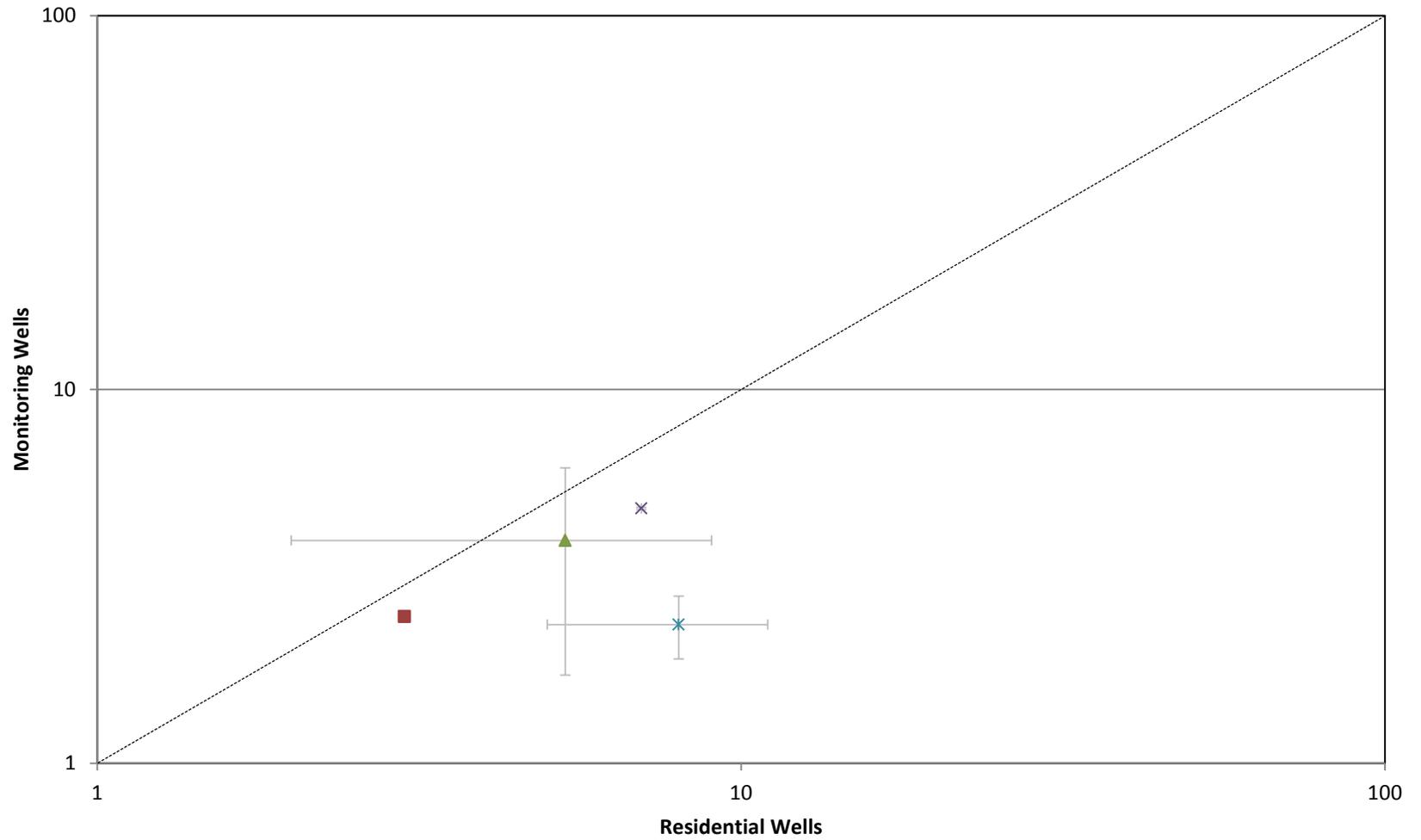
■ Group 2    ▲ Group 3    × Group 4    \* Group 5    ● Group 6    + Group 7    ..... 1-1 Line

# Richland Study Area Average Detected PFHxS (ng/L)



■ Group 2    ▲ Group 3    ✖ Group 4    ✖ Group 5    ● Group 6    + Group 7    ..... 1-1 Line

# Richland Study Area Average Detected PFBS (ng/L)



■ Group 2    ▲ Group 3    × Group 4    \* Group 5    ● Group 6    + Group 7    - - - - - 1-1 Line

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