A National PFAS Roadmap
Western Michigan University White Paper

Executive Summary

A Washington Post story on Jan. 2, 2019[1] entitled "Not a Problem You Can Run Away From: Communities Confront the threat of unregulated chemicals in their drinking water", focused on the discovery of PFAS in the drinking water in Parchment, Michigan, just 3 miles from the campus of Western Michigan University (WMU). This was not the first or most serious site in Michigan where PFAS has been found to contaminate the water supply. Michigan's early detection of at least 35 sites with 70 additional sites currently being tested provide a unique opportunity for applied research that will undoubtedly be important for other states and federal agencies in coming years.

Widespread contamination by per- and polyfluoroalkyl substances (PFAS), a diverse set of 3,000+ synthetic chemicals with at least one fully fluorinated carbon, is the most critical environmental contamination crisis in communities across the nation. The chemicals, found in firefighting foam, water-repellant clothing and footwear, non-stick pans and other household items, and used in many industrial processes is an emerging groundwater and human health threat.

Significant gaps in knowledge on detection, impact, spread and cleanup are frustrating communities and challenging regulators. This class of contaminants is toxic in parts per trillion concentration (lower than any other known contaminant), highly mobile in surface water and groundwater systems, resistant to degradation, and render most conventional remedial technologies ineffective. On February 14, 2019, the U.S. EPA (EPA) released the "PFAS Action Plan" as a first step toward setting a maximum contaminant level (MCL) in drinking that would be enforceable under the Safe Drinking Water Act. The plan also acknowledges that significant research is needed and identified multiple focal areas.

In this white paper, WMU proposes the development of a research consortium, The PFAS Analysis and Research Center (PAARC) with the express purpose of addressing many of the critical research areas using best science practices, state-of-the-art technology, and high impact dissemination of research findings and challenges.

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[1] https://www.washingtonpost.com/national/health-science/not-a-problem-you-can-run-away-from-communities-confront-the-threat-of-unregulated-chemicals-in-their-drinking-water/2019/01/01/a9be8f72-dd4b-11e8-b732-3c72cbf131f2_story.html?utm_term=.9a6bd82bf384

The research focus would include:

1. Identifying and Quantifying PFAS compounds
   PFAS is a complex class of contaminants with an estimated 3,000+ compounds. The detection and quantification of these chemicals are restricted to a very small subset of compounds using accepted analytical methods. Only two PFAS compounds – PFOS and PFOA – have established advisory or enforceable levels. Many other PFAS compounds may be present in soil, groundwater and/or surface water across the nation.

2. Characterization of PFAS-containing Foams in Surface Waters
   Michigan is the only state with documented formation of foams on surface water near known PFAS contamination sites. Preliminary sampling has confirmed these foams hold much higher concentrations than found in the water itself. Visible and accessible PFAS-rich foams create significant public health concerns. Proper identification, containment and cleanup of these foams are critical.

3. Improved Technologies for PFAS Stabilization And Immobility Within Landfills
   The extent of PFAS contamination and risks to human health associated with PFAS in landfills and leachates are poorly understood. In Michigan alone, there are 78 active and 60 inactive permitted landfills and at least 1,650 un-permitted and legacy dump sites. Methods must be developed to stabilize, solidify or otherwise immobilize PFAS compounds in liquid wastes and biosolids so they can be safely landfilled. Preliminary experiments by the WMU research team show great promise in reducing water solubility of these materials.

4. Development of PFAS Fate and Transport Data
   One of the largest and most significant knowledge gaps and perhaps the most critical for identifying and quantifying exposure risks and pathways. The WMU research team has already developed a plan to generate the data for PAARC collaborators to quickly valuate exposure and extrapolate risks for human health at one of the largest contamination sites in Michigan.

5. Development and Utilization of Environmental Forensic Techniques
   Understanding past, current, and future PFAS releases to streams and waterways is vitally important to future remediation and cleanup. Wastewater treatment plants around the nation have unknowingly received PFAS laden waste and discharged this to waterways at the end of the treatment process. Plants have been known to uptake PFAS which can bioaccumulate in plant tissue. Coring of trees and testing plants located down gradient of waste water treatment plants provides a way to forensically reconstruct historical PFAS exposure.

6. <u>Evaluation of Remediation Technology Efficacies</u>
   Through predictive computer model simulations, laboratory and pilot-scale field projects, the research team can evaluate remediation techniques. This will ensure proven technologies are helping communities across the country respond to PFAS contamination.

These activities seamlessly align with the identified research in EPA's Action Plan. Through successful funding, critical research activities can rapidly commence. WMU will lead the establishment of a multi-disciplinary team of internal and external partners to fulfill the PAARC research mission. This multi-collaborative approach will accelerate high quality scientific investigations urgently needed for assessment and mitigation of human health exposure and risks associated with the legacy of PFAS use in a center located in the epicenter of this emerging contamination threat. WMU is uniquely qualified to develop this critical state and national recourse with multidisciplinary faculty innovation in aviation, environmental biology, chemistry, computational science, environmental engineering, geophysics, and hydrogeology; its applied scientific focus; existing collaborations with Michigan DEQ, MGREE geologic core laboratory, Michigan Geological Survey, and U.S. Geological Survey.

These assets, combined with collaboration of leading experts, will facilitate knowledge, tools and expedite remediation at PFAS contaminated sites across the country._WMU will work with state and federal agency partners, private testing labs, community stakeholders and experts from other institutions to build this important knowledge data base. Working together, we can swiftly and scientifically help communities impacted by the most significant emerging environmental crises in a generation.

<u>Michigan's National Significance</u>

There are currently 35 announced sites in Michigan with confirmed PFAS contamination in the soil, groundwater and/or surface water, and the list is rapidly growing with the advancement of the State testing program for PFAS. Approximately 70 more sites are under investigation by the Michigan Department of Quality (MDEQ) for suspected PFAS contamination. Many of the announced and suspected PFAS-contaminated sites are either municipal landfills or legacy dumps that received PFAS-laden waste generated by industrial processes and consumer products such as cosmetics, food containers and wrappers, non-stick cookware, and outdoor clothing as well as airports and military sites.

Michigan's early detection of PFAS sites provide a unique opportunity for applied research directed towards environmental fate and transport of PFAS that will undoubtedly be important for other states and federal agencies in coming years. These reasons include:

1. Michigan is one of the most industrialized states in the Nation, with a legacy of industries utilizing PFAS including auto manufacturing, metal plating and impregnation, carpet and fabric coating, leather tanneries, paper mill sludge, plus airports and military bases that have used aqueous film-forming foams for fire training and accidents;
2. Michigan has the most aggressive PFAS sampling plan in the nation that will test approximately 75% of the state citizen's drinking water, including private wells, and 100% of all drinking water to public schools;
3. The Michigan DEQ is investigating industrial processes utilizing PFAS to identify potential contaminated sites and mitigate risks to human health;
4. Michigan is the only state experiencing PFAS-concentrated foams in lakes and waterways, e.g., Huron River, Lake Huron and Van Etten Lake; and
5. The Clark's Marsh plume at the former Wurtsmith Air Force Base and the Wolverine Worldwide sludge dump rank among the most data-rich PFAS contaminated sites in the United States, yet the fate and transport and risks of exposure to human health remain to be determined for these sites.

The vision and leadership of a Michigan-based partnership will implement cutting edge research directed towards addressing critical knowledge gaps through intensive integration, synthesis, and interpretation of proactively generated data over a diverse set of PFAS contaminated sites throughout the state. Impacts of this research are intended to drive and improve the federal and state responses needed over the next decade.

Proposed Research Focus

This White Paper outlines needed research activities where Western Michigan University is uniquely qualified to assist public and private stakeholders and the communities impacted by PFAS contamination. Specific details for each of these research areas are identified below:

<u>Environmental Fate and Transport</u>

Of the many knowledge gaps with regards to PFAS, environmental fate and transport is perhaps the largest and most critical for assessing exposure and risks to human health. Environmental fate and transport is a very large umbrella category and includes: sampling and quantifying PFAS concentrations in surface water, ground water, soils and biota; characterization of local and regional subsurface geology and ground water flow systems; laboratory testing of PFAS retention mechanisms; development of site conceptual models of PFAS transport and mobility;

and development, calibration, and execution of cutting edge numerical models to estimate PFAS transport within the subsurface to derive mass loading rates to high exposure pathways such as municipal, community and private wells and surface waterways.

The WMU technical team has already developed a detailed plan using state-of-the-art equipment and techniques to generate the necessary data for external PAARC collaborators to valuate exposure and extrapolate risks to human health for the PFAS plume originating from the House Street sludge dump, located near Belmont, MI. This plume is arguably the highest profile site in Michigan in terms of potential exposure, total PFAS mass and near complete lack of understanding with regards to human health and risk. The other proposed research areas and facilities in the WMU PAARC will support this overarching research focal area.

Identifying and Quantification of PFAS Compounds

PFAS is a complex class of emerging contaminants with an estimated 3,000+ compounds. Of this total, the two most commonly accepted analytical standard methods, U.S. EPA method 537.1 and ASTM D7979-17, only provide concentrations for only 18 and 24 PFAS compounds, respectively. Furthermore, only two PFAS compounds – PFOS and PFOA – have established advisory and/or state-enforceable concentration levels. Many other PFAS compounds excluded from the 18 or 24 PFAS sampling suite (depending on analysis method), including many of the widely used GenX compounds (industrial replacements for PFOA and PFOS), may be present in soil, groundwater and/or surface water across the nation and pose significant health risks, yet remain undetected. At known contaminated sites, unknown PFAS compounds may include precusors and/or degradation products of known PFAS compounds. Better characterization of PFAS excluded from standard methods will provide critical insight into the potential for physical and chemical weathering at decadal scales, and perhaps evidence of microbially facilitate degradation.

The lack of information regarding PFAS compounds provides the need for state-of-the-art laboratory equipment for rapid identification, characterization, and quantification of a broader range of PFAS than currently available at the very few PFAS certified laboratories available in the nation.

Characterization of PFAS-containing foams in surface waters

Michigan is the only state with documented formation of foams on the top of the water surface near sites of known PFAS contamination. These foams result from the unique physical and chemical properties of PFAS and have been discovered on the water surface and at the water-land interface for rivers and streams, inland lakes, and in some of the Great Lakes. Preliminary sampling by MDEQ has confirmed that these foams concentrate PFAS to much higher concentrations than are found in the water body itself. Unlike dissolved PFAS, the PFAS-rich foams are highly visible and accessible which draws public health concerns. The first step is to develop precise sampling methods specific to these foams, followed by analyses of the samples for PFAS identification and concentrations. The conditions that generate these foams must also be monitored so their formation can be predicted. Finally, remediation methods must be developed to skim or otherwise collect these PFAS-rich foams from the surfaces of Michigan waters.

Proper characterization, control and cleanup of these foams are critical. The research from these initial Michigan sites could directly impact public health if more foam formations appear in other communities.

PFAS stabilization and immobilization of wastes in Landfills

Some of the most significant PFAS contamination in Michigan is associated with landfill generated leachates. Many landfills in the state are no longer receiving certain PFAS-contaminated waste as a result, and certain generators of PFAS- contaminated wastes are experiencing critical storage problems. Specific examples include aqueous film-forming foams (AFFFs) used at airports and military bases for fire suppression, and PFAS-laden biosolids generated at wastewater treatment plants. Methods must be developed to stabilize, solidify, or otherwise immobilize (i.e., reduce the water solubility of) PFAS compounds in liquid AFFF wastes and in biosolids so that they can be safely landfilled. Such stabilization methods have been developed for other contaminants, but PFAS have unique chemical and physical properties requiring additional research. Some preliminary experiments have already been conducted by members of this research team on PFAS-contaminated biosolids and liquid AFFFs, and show great promise in reducing the water solubility of PFAS in these waste materials.

Environmental Forensics

PFAS has been used since the 1950s, yet is only recently recognized as an emerging contaminant. Previous contamination events to the nation's waterways are virtually unknown. For example, waste water treatment plants around the nation that have unknowingly received PFAS laden waste and discharged this waste to waterways at the end of the treatment process. Plants have been known to uptake PFAS which can bioaccumulate in plant tissue. Coring of trees located down gradient of waste water treatment plants provides a way to forensically reconstruct historical PFAS loading rates. Plants also serve as an additional, and not well characterized, accumulation reservoir and can be used as a non-invasive sampling method to sample for PFAS contamination within soil water accessible by plant roots. Numerical modeling can also be used to calculate the backward trajectories of known PFAS contaminant plumes. This is critical for identifying initial PFAS release regions which are often either unknown, due to the legacy of PFAS use or disperse source regions typically generated during training with PFAS fire suppression foams.

Facilities and Field Site Identification

State-of-the-Art PFAS Analytical Laboratory

To conduct the applied research outlined above, proper analytical equipment is critical. WMU already contains aqueous geochemistry laboratories and a high-resolution nuclear magnetic resonance spectrometer. The PAARC concept necessitates the establishment of a PFAS dedicated laboratory to serve as a key resource for internal and external investigators and promote collaboration with state and federal agencies and private laboratories. The key equipment acquisition for the laboratory is a Liquid Chromatograph (LC) and a high-resolution Linear Trap Quadrupole (LTQ) Orbitrap Velos mass spectrometer with tandem Mass Spectrometry (MS/MS). Liquid Chromatography coupled with tandem Mass Spectrometry (LC/MS/MS) is the analytical equipment required to quantify PFAS in samples of drinking water (EPA Method 537.1) and samples of water, sludge, influent, effluent and wastewater (ASTM Method D7979-17). The LC portion separates the individual PFAS compounds and the MS/MS portion quantifies the individual PFAS compounds thus separated. The LTQ capabilities of the proposed equipment will allow for significantly lower detection than both EPA Method 537.1 and ASTM Method D7979-17. Additionally, it will allow for Total Oxidized Precursor (TOP) and Time of Flight (TOF) assessments to identify the total mass and chemical structures of individual PFAS compounds present at contaminated sites, but not quantified by either the EPA and ASTM analytical methods.

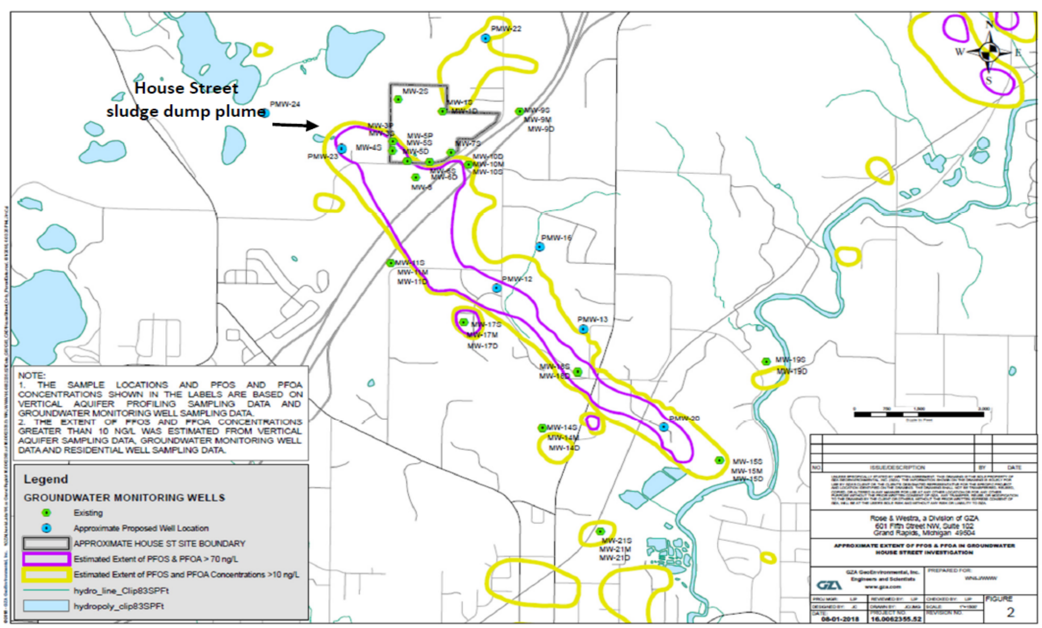
This laboratory will serve as the cornerstone for the PAARC concept and will serve as the central analytical hub for all projects. Beyond the advantages listed above, current fees from laboratories can be approximately $500/sample with a turn-around-time (TAT) of 2 to 3 weeks. PFAS analytical capabilities would create an immediate TAT when results are critical and is likely to significantly reduce the cost per sample. The WMU analytical laboratory would provide faster, less expensive, and more precise test results. Faster responses can be vitally important when public health is in question.

Supercomputing Facility

Numerical models, developed and supported with physical data collected from field sites, represent the best science for predicting past, current and future movement and potential exposure pathways for PFAS plumes. The computer simulations include the dominant physical mechanisms and processes controlling PFAS fate and transport in the environment and require large amounts of detailed site information. Additionally, the natural environment is highly variable and leads to uncertainty in the flow and transport predictions that can be addressed using probabilistic assessment frameworks that require running large number of models to better understand impacts of natural environmental variability. These factors result in simulations that necessitate computational facilities beyond normal desktop computers due to computational, memory and storage demands. A supercomputing facility, comprised of either computational clusters at least 200 cores with high-speed connections for parallel simulations or a shared-memory supercomputer, is requested to run high-end numerical simulations and for post-processing subsurface geophysical data. The computational resources will be available to internal and external members of the PAARC.

<u>Field Site – House Street Sludge Dump PFAS Plume</u>

The field site identified for the majority of this research will be the House Street sludge dump in Belmont, MI. The sludge dump was a licensed and regulated 76-acre disposal facility located in a mixed rural and residential land use area that received tannery waste from the Wolverine Worldwide tannery from the mid-1960s until the 1970s. Remedial investigations over the dump site indicate total PFAS concentrations as high as 79,000,000 ppt in soil and borings and 280,000 ppt in ground water. Sampling of monitoring and private drinking water wells indicates the presence of a PFAS plume extending over 3 km from the dump that likely intersects the Rogue River. This is a very high profile site – perhaps the highest in the Nation – and the plume is very poorly characterized with little to no constraints or understanding of subsurface geology, total plume mass, plume geometry and historical PFAS concentrations, and most importantly, risks to human health exposure are completely unknown.



Delineated plumes in the Belmont and Rockford areas [Rose and Westra, 2018b]. The >3 km long House Street PFAS plume is in the center of the Figure (courtesy of GZA and MDEQ). The PFAS contamination associated with this site has affected many homeowners and resulted in, among other actions, the installation of a large number of in-home filtration systems. Groundwater analysis indicates the presence of volatile and semi-volatile organic compounds and inorganic compounds but are below regulatory limits except for a few instances in the source release area [Rose and Westra, 2018a,b].

Budget Summary

To execute the work described in this White Paper will require a diverse set of scientific expertise. Through successful funding, Western Michigan University will lead the establishment of a multi-disciplinary team of internal and external partners to fulfill the research mission. This multi-collaborative approach will accelerate high the assessment and mitigation of human health exposure and risks associated with the legacy of PFAS. WMU expertise, combined with collaboration of leading experts from state and federal agencies, private testing labs, community stakeholders and researchers at other institutions, will facilitate and expedite remediation at PFAS contaminated sites across the country.

The equipment identified in the budget justification includes analytical spectroscopic instruments that will aid in the detection of PFAS at low concentrations and identify molecular structures. Funding would support the faculty as well as three postdoctoral fellows. The plan would also support three graduate students. By specifically engaging graduate students, they can develop their expertise so they can continue to perform such tasks long into their careers in this important and emerging field.

Working together, we can swiftly and scientifically help communities impacted by the most significant emerging environmental crises in a generation.