DEPARTMENT OF DEFENSE
UNITED STATES OF AMERICA

CHIEF OF ENGINEERS
ENVIRONMENTAL ADVISORY BOARD
WASHINGTON, DC 20314-1000 (CECW-P)

December 31, 2019

SUBJECT: Proposed Research and Development Areas to Advance Site Characterization and Remediation of Per- and Poly-Fluorinated Substances

Lieutenant General Todd T. Semonite
U.S. Army Corps of Engineers
441 G Street NW
Washington, DC 20314-1000

Dear LTG Semonite;

In your memorandum of 05 SEP 2019, you requested that the Environmental Advisory Board (EAB) conduct a study to aid in the advancement of site characterization and/or remediation of per- and poly-fluorinated substances (PFAS) in the environment. Furthermore, you requested that the EAB provide you with an assessment that both identifies actionable gaps in current methods and technologies and recommends research and development (R&D) initiatives to help address those gaps.

EAB members have consulted with the scientific leads at the USACE Engineer Research and Development Center (ERDC) Environmental Laboratory (EL) and have reviewed information available from the scientific literature, as well as a number of publicly available resources.

The EAB has identified two broad areas of need in addressing PFAS contamination and impacts on USACE missions. Within each of the broad need areas, we have identified actionable gaps to be addressed and recommendations to address those gaps. A summary of supporting background information on broad needs, knowledge gaps, and provided recommendations are presented in the enclosures.

a. NEED 1: Assessing the Extent of PFAS Contamination

- Gap 1.1 – Efficient and effective sampling designs needed
    - Recommendation 1.1.1 – R&D for “plug and play” sampling and modeling software for sample locations and “heat map” development

- Gap 1.2 – Technical difficulties with sampling and analytical methods (e.g. limited number of competent laboratories)
    - Recommendation 1.2.1 – Pursue R&D for PFAS analyses emphasizing simplicity and speed.
    - Recommendation 1.2.2 – Target R&D to methods that use commonly available equipment.
    - Recommendation 1.2.3 – Produce analytical kits and training modules that expand analytical capabilities.
    - Recommendation 1.2.4 – Pursue R&D for concentration of PFAS from environmental matrices, e.g. use of nucleic acid and amino acid aptamers.
    - Recommendation 1.2.5 – Pursue R&D for nanoscale, real-time PFAS detection arrays.

- Gap 1.3 – High costs per sample analyzed, and the large number of analyses needed.
    - Recommendation 1.3.1 – Establish or expand partnerships with other federal, state and/or university labs to expand PFAS analytical network.
- Gap 1.4 – The large number of PFAS that may be present.
    - Recommendation 1.4.1 – Develop a quantal test for fluoroalkly compounds.

b. NEED 2: Remediation Technologies

- Gap 2.1 – Sequestration technologies are non-destructive and require long-term surveillance and maintenance.
    - Recommendation 2.1.1 – Sequestration should be used as a temporary measure while starting/continuing R&D on destructive technologies.

- Gap 2.2 – Recovery technologies are susceptible to non-specific binding, and have potential problems with both regeneration and disposal.
    - Recommendation 2.2.1 – Pursue R&D for aptamer-based PFAS binding media to reduce non-specific binding and simplify regeneration and disposal.

- Gap 2.3 – Demonstrated destructive technologies are currently limited to incineration; in-situ destructive technologies are needed.
    - Recommendation 2.3.1 – Continue R&D into membrane-based, electrochemical degradation.
    - Recommendation 2.3.2 – Pursue R&D for biotic and abiotic reductive dehalogenation and dehalorespiration with various electron donors.
    - Recommendation 2.3.3 – Pursue R&D for in situ immobilization in humic fraction of soils.

While working on this topic, EAB members recognized additional actionable gaps in ecological risk assessment that are outside of the scope of the 05 SEP 2019 memorandum. Those gaps are in the ecotoxicology of PFAS and next-gen fluoroalkyl compounds, the design and testing of replacement chemicals, and the long-term risks to personnel from occupational PFAS exposure.

- Toxicology of PFAS and Next-Generation Fluorinated Substances. There are many gaps in the ecotoxicology of fluoroalkyl compounds, and particularly with respect to those compounds that have recently, or will soon, come online to replace PFOS, PFOA and aqueous film-forming foams (AFFF). There is little reason to believe that they will be safe or, as long as they retain the -[CnF2n]- moiety, significantly less recalcitrant to degradation. EAB members strongly recommend that approval for USACE use of new fluoroalkyl compounds be limited to the greatest extent practicable until toxicological assessments have been completed on vertebrate models.

- Design and Testing of New Firefighting Chemicals. Although EAB members are deeply concerned about the continued use of toxic and recalcitrant chemicals in both military and civilian applications, we also understand that the efficacy of PFAS, particularly firefighting foams, means that they may not be phased out until functional substitutes are identified. We recommend R&D activities in the design and testing of new firefighting foams that are not as toxic or persistent as the PFAS-based AFFF, such as new formulations of protein based foams and fluorine-free foams. Research in this area is critical to protection of personnel and the environment.

- Lack of Robust Data on Long-Term Health Effects of PFAS Exposure. We also believe that USACE, in fact DoD as a whole, has a unique opportunity to contribute to the body of knowledge on the human health impacts of acute and/or chronic exposure to PFAS. This opportunity arises due to documentation of duty station, work assignments and health records that may be available for DoD personnel, and can be used to construct retrospective longitudinal databases for the assessment of exposure outcomes. To be clear, we are not suggesting that USACE undertake clinical research. Rather, we recommend the development and analyses of data bases that could help more clearly define the human health outcomes of PFAS exposure and, thus, be critical in safely managing PFAS use and remediation.

The EAB hopes that this assessment and our comments on additional actionable gaps prove to be useful in USACE efforts to address existing PFAS contamination and avoid future contamination and exposure. We are prepared to continue work in this area as requested.

Sincerely,

Mary C B

Mary C. Barber, PhD
Chair, Environmental Advisory Board
Subcommittee,
Army Science Board

Enclosures.

cc:
Chief, Planning and Policy Division
Chief, Environmental Division
Chief, Engineering and Construction Division
Chief, Operations and Regulatory Division
Director, ERDC, Environmental Laboratory

Enclosure 1

ENVIRONMENTAL ADVISORY BOARD
Proposed Research and Development Areas to Advance Site Characterization and Remediation of Per- and Polyfluoroalkyl Substance (PFAS) in the Environment.
December 31, 2019

Overview of Per- and Polyfluoroaklyl Substances

Per- and poly-fluoroalkyl substances, collectively referred to as PFAS, are members of a class of more than 4,000 manmade chemicals that have been commercially manufactured and used since the 1940's (1,2). PFAS are thermostable surfactants with both hydrophilic and hydrophobic domains. When used as metal coatings, they reduce surface friction. When used as textile, film and paper additives, they impart stain and water resistance. Their surfactant nature and themostability have made them valuable as firefighting foams, and they have been used extensively in that application since the 1960's (2).

The broad use of PFAS in industrial applications and fire-fighting has led to their wide distribution in the environment, where they are both highly persistent and mobile. PFAS are known to bioaccumulate, and probable links have been reported between PFAS and human health impacts, including liver disease, developmental disorders, kidney cancer, thyroid cancer, high cholesterol, pre-eclampsia, and ulcerative colitis (3).

There are multiple areas of research that could help address the PFAS threat. Herein we identify two broad areas of response to environmental contamination with PFAS – assessing the extent of contamination, and advances in site remediation. For each broad area, we identify "actionable gaps in methodologies and/or technologies" and suggest research and development opportunities that we believe are both relevant to USACE expertise and can help address the identified gaps.

I. ASSESSING THE EXTENT OF PFAS CONTAMINATION

Though PFAS are known to be widely distributed in the environment, and have been found in locations that are well-removed from sites of manufacture or commercial use, their presence in the environment is not homogeneous or universal. For example, the state of Michigan has the most aggressive program in the country for identifying PFAS contamination in drinking water, groundwater, lakes, rivers, streams, soils, sediments, and wastewater. At the time of this writing, Michigan lists 67 PFAS sites (i.e. sites with 70 parts-per-trillion or greater concentrations of PFOA plus PFOS), but only about 10% of samples from community water supplies to date have had detectable levels of PFAS (4). Therefore, it should not be assumed *a priori* that an environmental compartment (i.e. soil, water, sediment, atmosphere, or tissue) is contaminated unless it is known to have had historical contamination or PFAS release. It is, therefore, necessary to have reliable methods for the assessment of PFAS distribution, including detection in a variety of environmental matrices. Significant progress has been made in terms of analytical methods (5,6), but knowledge of the distribution of PFAS in the environment is far from complete and is a critical element of managing the environmental and public health risks of PFAS.

The lack of comprehensive environmental characterization stems from at least four actionable knowledge gaps: a) the need for efficient and effective sampling designs, b) the difficulty in sampling and analysis for PFAS at toxicologically relevant concentrations, which limits the number of laboratories that are equipped and staffed to perform PFAS analyses; c) the high cost of commercial PFAS analyses for organizations/communities that cannot perform analyses in house; and d) the large number of PFAS that have been used and new compounds that are in use/production, many of which do not have approved analytical methods. These four identified gaps have been targeted for specific recommendations to improve the scope and speed of site characterization.

Need for efficient and effective sampling designs. There are a number of factors that have a direct impact on the determination of PFAS distribution; perhaps none more critical than the need to create an efficient and effective sampling design. Sampling methodologies and analytical methods are addressed below. Here we recommend that the locations at which initial samples are taken, and the environmental matrices sampled, should be determined through the use of a probabilistic sampling design. The ideal outcome of the initial round of sampling is a georeferenced "heat map" of known contaminants, which can then be used to inform further sampling, geared toward the detailed identification of sources. Because not all organizations will have the ability to design an ideal sampling regimen and create spatial models of the results, we recommend research and development (R&D) activities to produce "plug and play" design and modeling programs for broad use. A design and modeling tool when paired with a rapid, quantal analytical method (described below) would provide for both efficient and effective characterization of PFAS contamination at sites of concern.

Limited number of labs equipped for PFAS analyses. Where analytical capacity is an issue, addressing that issue can be done by enhancing the throughput efficiency of the analytical processes, expanding the number of laboratories that are capable of performing the analyses, or both. In this case, we recommend both, and specifically that R&D activities emphasize simplicity and speed – understanding that the low analytical thresholds required for effective assessment of PFAS contamination (e.g. the low part-per-trillion range in water) will make this difficult. However, the development of methods that use highly sophisticated and expensive equipment will only serve to maintain existing bottlenecks. Those laboratories with the capability of sophisticated analyses will not be able to handle the throughput required for comprehensive surveillance. Our recommendation in this regard is two-fold: i) keep the capacity issue in mind during new methods development by targeting methods to analytical equipment that is widely available, and ii) include R&D for analytical kits and training modules that can be used to expand analytical capacity. As an example, these methods may require R&D around the elution and concentration of PFAS from various sample matrices, so that low part-per-trillion (ppt) PFAS concentrations can be detected without requiring the most sophisticated analytical instruments. With respect to analyte concentration, we recommend

R&D on the use of nucleic acid and/or amino acid aptamers for the specific binding of PFAS in water, or as they are eluted from soil, sediment, or tissue matrices. Longer-term R&D could be directed toward immobilization of specific binding aptamers on nano-scale scaffolds, which have the potential to lead to simultaneous, real-time detection systems for a suite of PFAS compounds.

High Cost of PFAS analyses. To some extent, the cost of PFAS analyses will be addressed by the development of methods for simplicity, speed, and the use of widely available equipment. More widely accessible methods will create market forces that should drive down the costs of commercial analyses. It may also be prudent to establish partnerships with federal, state, and university laboratories that could be certified not only to conduct PFAS analyses, but to train additional laboratory personnel and certify additional laboratory equipment for the performance of these procedures.

Large Number of PFAS. As mentioned above, there are over 4,000 chemicals that are collectively referred to as PFAS. That means, that even an aggressive sampling and analysis plan will only provide data on a small fraction of the potential parent compounds present, and may provide no useful information on transformation products or co-contaminants. In order to address this problem, we recommend the development of a rapid and inexpensive quantal test for the presence/absence of fluorinated alkyls. Ideally, the test would detect fluorinated alkyls of various chain lengths, and would be agnostic to the chemical nature of the hydrophilic (polar) head group. Such a test, if sufficiently sensitive, would be most useful as a rapid screening tool to eliminate costly and time-consuming analyses performed on samples that contain no PFAS – saving the full analyses for sites that have screened positive for PFAS. In addition, a positive quantal test could lead to the recognition of new transformation products under environmental conditions and would be helpful in tracking PFAS transport through food webs.

As mentioned above, R&D projects with libraries of nucleic acid or amino acid oligomers have the potential to identify and isolate aptamers with specific PFAS binding capabilities. In addition to the development of a quantal test for fluorinated alkyls, we recommend R&D toward the development of addressable nanoarrays with individual PFAS binding aptamers at indexed locations. The end goal of this research would be array-based sensors for real-time, single molecule detection of a broad array of PFAS, transformation products, and synthons.

II. REMEDIATION TECHNOLOGIES

For the purposes of this discussion, we have placed remediation technologies for PFAS contaminated sites into three broad categories: sequestration, recovery, and destruction.

Sequestration refers to actions that are intended to isolate PFAS exposure routes and prohibit further migration away from a contaminated site without an attempt to recover them from the contaminated material – typically soil. Sequestration may involve capping at the original contaminated site, or removal of contaminated materials to a secondary site (e.g. a landfill) where sequestration can be maintained using standard liner and cap technology. Mature, field-tested and commercialized technologies exist for this remediation category (7), and we are not recommending R&D work in this area. However, it should be noted that although sequestration can be protective of human and environmental health, PFAS parent compounds and transformation products continue to pose a risk of mobilization, and long-term monitoring and maintenance are, therefore, required. For these reasons, sequestration is recommended only as an interim step in environmental protection and restoration.

Recovery refers to remediation technologies that separate contaminants from the environmental matrix by some mechanism of elution and capture. Recovery processes create relatively high concentrations of target chemicals on a capture medium, and require additional steps to either regenerate usable capture media or provide for safe storage of the contaminated media. For both contaminated solids and contaminated liquids, sorption on modified carbon, modified mineral sorbants, activated charcoal, and anion exchange resins are the most mature recovery technologies (7). Because mature, field tested and commercialized technologies exist for the recovery of PFAS from environmental samples, R&D in this area is likely to be incremental. We do, however, recommend R&D in the area of aptamer-based capture systems. The projected advantages of aptamer-based systems are their selectivity and potential for their relative ease of regeneration through manipulation of temperature and/or pH.

Selectivity is important because PFAS are often present at very low concentrations - far below the levels of other anthropogenic or naturally-occurring chemicals at the same sites. Those co-located chemicals can quickly overwhelm the capacity of non-specific binding media; increasing the costs of recovery-based cleanup actions. Highly selective binding media, such as nucleic acid oligomer or peptide aptamers, could reduce non-specific binding and, therefore, the amount of binding media required to complete site remediation.

Ease of regeneration is also an important element of containing the costs of remediation. In the most extreme cases, when regeneration is either very difficult or inefficient, the capture media becomes long-term hazardous waste, which must be properly stored, or discarded in a way that may lead to long-term monitoring requirements. Nucleic acid oligomer and peptide aptamers should be re-generable through relatively modest changes in temperature and/or pH. If R&D work in this area confirms the potential for high selectivity and low-cost regeneration, it could lead to significant reductions in the final volume of wastes accumulated during remediation.

Research and development in aptamer-based, specific binding technologies has at least one additional advantage, and that is that such research can inform the development of both assessment (e.g. concentration and real-time detection arrays), and remediation technologies.

Destruction technologies are those methods that permanently change the chemical structure of target chemicals, with the most effective destructive technologies being those that result in the complete mineralization of the parent compound. Destruction of PFAS, either *in situ* or in conjunction with a recovery technology is preferable to either sequestration or recovery alone because it provides final remediation without the need for long-term storage or monitoring. However, one must be mindful that destructive technologies can produce intermediates or end-products that are not fully mineralized, and can be as toxic or more toxic than the parent chemical. To date, incineration of contaminated solids, or the transfer of PFAS to a recovery medium followed by incineration, is the only mature, field-tested and commercialized technology for the destruction of PFAS (7). However, ongoing research with novel membrane systems that are designed to mineralize PFAS through electrochemical degradation (8) is promising. The EAB recommends further work with these *in situ*, membrane-based, degradative technologies.

The persistence of PFAS in the environment suggests that these chemicals are highly recalcitrant to both biotic and abiotic degradation *in situ*, but we believe that further R&D in this area is warranted. A recent report on the microbial-mediated defluorination of PFOS and PFOA (9) suggests that PFAS may be co-metabolically reductively dehalogenated in the presence of iron reducing bacteria using ammonia or hydrogen as the electron donor. Although this study was conducted in pure and enrichment cultures, the conditions under which defluorination occurred can be used to design and test *in situ* remediation conditions that select for similar outcomes.

The EAB recommends two broad areas for research in the biological/chemical remediation of PFAS with an emphasis on the eventual design of methods for use *in situ*. The first area encompasses studies of the potential for biotic and abiotic reductive dehalogenation and dehalorespiration under highly anaerobic conditions with a variety of electron donors. The second area for recommended research is in the biologically- or chemically-mediated immobilization of PFAS in humic acids *via* the reactivity of their polar head groups. Reductive dehalogenation (whether biotic or abiotic) has the potential to produce intermediate chemicals that are readily mineralized through well-known metabolic pathways. Furthermore, because mineralization of the products of PFAS defluorination would produce energy, the processes should be sustainable under environmental conditions. The second area for study would essentially determine the potential for the immobilization of PFAS in the humic fraction of soils. Although sequestration has been identified as a less-than-ideal approach to remediation, the use of humic acid binding could allow the process to occur *in situ* and, if determined to be permanent, could essentially eliminate mobilization and obviate the need for long-term monitoring.

SUMMARY

Table 1 summarizes the needs associated with managing PFAS releases, the actionable gaps in current methods and technologies, and the specific recommendations made to address the identified gaps.

ACKNOWLEDGEMENTS

The Environmental Advisory Board (EAB) wishes to thank Ms. Sheri Moore for her leadership role in coordinating multiple efforts associated with the PFAS task, Ms. Jeannette Gallihugh for support on this and multiple other EAB tasks, Ms. Mindy Simmons for her continuing support and guidance as the EAB Designated Federal Officer, and Dr. David Moore at the USACE Engineer Research & Development Center (ERDC) for helpful discussions regarding ERDC expertise in PFAS-related research. In particular, we wish to thank Dr. Al Cofrancesco, the Technical Director of the Environmental Engineering and Sciences Laboratory at ERDC – we have gained much from his help and guidance over several years as the ERDC liaison to the EAB. As Al retires, we are certain that the EAB will continue to be ably assited by ERDC, but no one will take his place.

CITATIONS

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Enclosure 2

Table 1. Summary of EAB research and development recommendations.

Need Category	**Gaps**	**Recommendations**	
1.	**Assessment of PFAS Distribution**		
	1.	Need for efficient and effective sampling designs	
		1.	R&D for "plug and play" sampling and modeling software for sample locations and "heat map" development
	2.	Technical difficulties with sampling and analytical methods; limited number of competent laboratories	
		1.	R&D for PFAS analyses emphasizing simplicity and speed
		2.	Target R&D to methods that use commonly available equipment
		3.	Produce analytical kits and training modules that expand analytical capabilities
		4.	R&D for concentration of PFAS from environmental matrices. e.g. use of nucleic acid and amino acid aptamers
		5.	R&D for nanoscale, real-time PFAS detection arrays
	3.	High costs per analysis, and large number of analyses needed	
		1.	Establish/expand partnerships with other federal, state, university labs to expand PFAS analytical network
	4.	Large number of PFAS chemicals	
		1.	Develop a quantal (presence/absence) test for fluoroalkyl chemicals
2.	**Remediation Technologies**		
	1.	Sequestration technologies are non-destructive, and require long-term surveillance and maintenance	
		1.	Sequestration should be used as a temporary measure; continue R&D on destructive technologies
	2.	Recovery technologies are susceptible to non-specific binding and have potential problems with regeneration	
		1.	R&D for aptamer-based PFAS binding media to reduce non-specific binding and simplify regeneration
	3.	Destructive technologies currently limited to incineration. *In situ* technologies needed	
		1.	Continue R&D using membrane-based, electrochemical degradation
		2.	R&D for biotic and abiotic reductive dehalogenation and dehalorespiration with various electron donors.
		3.	R&D for in situ sequestration of PFAS in humic fraction of soils