EXECUTIVE SUMMARY

A Framework for Assessing Bioaccumulation and Exposure Risks of Per- and Polyfluoroalkyl Substances in Threatened and Endangered Species on Aqueous Film Forming Foam (AFFF)-Impacted Sites

SERDP Project ER18-1502

JANUARY 2020

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ACRONYMS AND ABBREVIATIONS

AC50	concentration at 50% maximum activity for in vitro assays
AFB	Air Force Base
AFFF	aqueous film forming foam
DoD	U.S. Department of Defense
EC50	concentration causing sublethal effects in 50% of the test organisms
EPA	United States Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
HC5	hazardous concentration corresponding to 5% of affected species
LC50	concentration causing 50% mortality in the test organisms
LD50	dose causing 50% mortality in the test organisms
LOC	level of concern
N-Et-FOSA	N-ethyl per- fluorooctanesulfonamide
PFAA	perfluoroalkyl acid
PFAS	per- and polyfluoroalkyl substance
PFNA	Perfluorononanoic acid
PFHxS	perfluorohexanesulfonic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PFOSA	N-alkyl perfluorooctanesulfonamide
RQ	risk quotient
SERDP	Strategic Environmental Research and Development Program
SSD	species-sensitivity distribution
T&E	threatened and endangered
TRV	toxicity reference value

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1.0 INTRODUCTION

For several decades, the U.S. Department of Defense (DoD) widely used aqueous film forming foams (AFFF) formulations for training and operations involving fire suppression. These AFFF formulations contained relative high quantities of perfluorooctane sulfonate (PFOS), as well a range of other of per- and poly-fluoroalkyl substances (PFASs).

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2.0 OBJECTIVES

The objective of the present study was to develop a framework for conducting scientifically sound risk assessments for PFAS in Threatened and Endangered (T&E) species at these sites. The study involved the following:

- A comprehensive literature review of physical-chemical properties, bioaccumulation metrics, and environmental concentrations.

- Development of a risk assessment framework for assessing PFAS bioaccumulation and exposure risks in T&E species at AFFF-impacted DoD sites.

- Application of the proposed framework to several DoD sites for which existing PFAS monitoring data are available. The study aims to help guide future research efforts and risk assessment initiatives related to exposure of legacy PFASs in T&E species at AFFF-impacted DoD sites.

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3.0 TECHNICAL APPROACH

The proposed approach generally follows conventional methods employed for ecological risk assessment, including exposure characterization, effects characterization and risk estimation. In particular, the proposed approach utilizes a combination of field-based measurements and bioaccumulation modeling to evaluate exposure in T&E species. Toxicity reference values (TRVs) are derived using the available toxicity data, along with species-sensitivity distributions (SSDs) and resulting 5th percentile of the hazardous concentration levels (HC5s) or application of uncertainty factors to the lowest observed toxicity values.

In the proposed framework, a chemical activity-based risk assessment approach is used. The chemical activity of a contaminant (*a*, unitless) in a given medium is the ratio of the concentration (*C*, mol/m^3) of the contaminant in the medium and the chemical's apparent solubility (*S*, mol/m^3) in the medium (i.e., $a = C/S$). The approach involves three key steps: (i) determining chemical activities of PFAS in external environmental media (e.g., water, soil, prey items), (ii) determining internal chemical activities of PFAS in T&E species, and (iii) comparing those estimated activities to activities related to biological effects observed in vivo and/or in vitro. The merits of this approach are that monitoring data from several or diverse environmental media and sampling devices can be included in a risk assessment and monitoring data of multiple PFAS contaminants can be interpreted in terms of toxicity. This approach increases the weight of evidence in risk evaluations and facilitates coordination of research efforts by different research groups by expressing available information (i.e., from monitoring, modelling and toxicity assays) in terms of a common metric.

The chemical activity-based risk assessment approach also can incorporate ToxCast AC50 and other in vitro assay data in a risk assessment, which is particularly useful for T&E species which can often not be used in in-vivo toxicity studies. This approach is consistent with the goal of minimizing animal studies in toxicity testing, highlighted in the National Research Council's vision and strategy for exposure and toxicity testing in the 21st Century. While the chemical activity-based approach can increase the information that is used in a risk assessment, the risk assessment remains primarily focused and reliant on ecologically relevant metrics (e.g., growth, development, reproduction) in wildlife.

Evaluation of the available ToxCast data for individual PFASs indicates that commonly detected perfluoroalkyl acids (PFAA) (e.g., PFOS, PFHxS, PFOA, PFNA, PFDA) exhibit specific mode of toxic action, in the chemical activity range of between 10-6 to 10-3, generally below levels related to narcosis ($a = 0.01$). Chemical activities of PFAA associated with effects in vitro (i.e., ToxCast AC50 values) are generally similar to those associated with toxic effects in vivo. ToxCast data for PFAA precursors (N-Et-FOSA and PFOSA) suggests these neutral hydrophobic compounds tend to exhibit baseline toxicity behavior, with effect levels occurring in the range known to be associated with nonpolar narcosis ($a = 0.01$). As PFAAs exhibit toxic effects in the same chemical activity range, a simple additivity approach may be adopted to incorporate mixture effects. However, as PFOS is typically the predominant PFAA (> 95%), contribution of other PFAAs to the toxicity of PFAA is often negligible. Risk assessments based solely on PFOS may adequately represent the overall PFAS risk at a given site, especially if PFAAs are the main PFAS class of concern.

A preliminary mechanistic PFAS food web bioaccumulation model was developed to predict internal exposure levels (concentrations and activities) and external exposure (daily intake, µg/kg BW/d) of individual PFASs in various aquatic and terrestrial organisms that include T&E species and their prey items. The model was parameterized and applied to simulate PFAS bioaccumulation in T&E species at several DoD sites that have existing PFAS monitoring data. The model was shown to predict internal PFAS exposure levels in biota at DoD sites reasonably well, with model predicted values generally within a factor of three of the observed field data. The developed PFAS food web bioaccumulation model indicates this mechanistic modeling approach may be useful for future risk assessments of T&E species potentially exposed to PFAS at AFFF-impacted DoD sites. However, further development and testing of this modeling approach is still needed. In particular, information is needed on the partitioning properties of PFAS in biological media. This information is not only crucial to the development of a chemical activity-based risk assessment approach but also for other approaches.

4.0 RESULTS AND DISCUSSION

The present study provides a comprehensive literature review of physicochemical properties, bioaccumulation metrics and environmental concentrations. The proposed approach generally follows conventional methods employed for ecological risk assessment, including exposure characterization, effects characterization and risk estimation. The proposed risk assessment approach utilizes a combination of field-based measurements and bioaccumulation modeling to evaluate exposure in T&E species. TRVs are derived from available PFAS toxicity data. A chemical activity-based approach is presented which may aid exposure and effects characterization of PFASs. A mechanistic modeling approach is also presented for assessing PFAS bioaccumulation and exposure levels in aquatic and terrestrial food webs. The developed food web model was tested for several DoD sites where PFAS monitoring has been recently conducted.

T&E species with habitat ranges overlapping AFFF-impacted DoD sites included the bog turtle (*Clemmys muhlenbergii*), northern long-eared bat (*Myotis septentrionalis*), red-cockaded woodpecker (*Picoides borealis*), and eastern massasauga rattlesnake (*Sistrurus catenatus*). For sites with relatively high PFAS concentrations, risk quotients (RQs) related to PFOS exposure in T&E species often exceeded the level of concern (LOC) of 0.1. Omnivorous and carnivorous birds, mammals, and reptiles are shown to exhibit a relatively high degree of PFAS bioaccumulation and hence exposure risk, compared to aquatic organisms at a given site. Model predictions indicate that at some sites with elevated PFAS concentrations in sediments, concentrations in benthic invertebrates can attain levels similar to those expected to induce acute effects in aquatic organisms. Biomagnification of PFAS in aquatic insectivorous bird species (feeding on benthos) cause very high exposure levels and associated risks.

PFAS concentrations in soils were found to be very important for exposure risks in numerous T&E species within terrestrial food webs, such as Kirtland's warbler and terrestrial reptiles (e.g., eastern massasauga rattlesnake). PFAS exposure risks to upper trophic terrestrial wildlife were in many cases high. Risk quotients often exceed the LOC of 0.1. Sites exhibiting high PFAS concentrations in soils, such as those at several active United States Air Force sites, are expected to cause high levels of risks to terrestrial organisms. In some cases, the estimated dose in terrestrial wildlife exceeds the PFOS LD50 of 150 mg/kg BW/d. Our initial findings show that risks of PFAS to T&E species of terrestrial food-webs are of particular concern.

It is important to note that risk estimates for T&E species in the present study are based on scenarios that assume exposure occurs via concentrations at the studied DoD sites. The extent of interaction of T&E species and their prey with AFFF-impacted soils and surface waters is a major knowledge gap in the present assessment of PFAS exposure risks of these species at DoD sites. Other knowledge gaps include the frequency and duration of various T&E species at AFFF-impacted DoD sites. In particular, studies to determine PFAS concentrations in prey and relative prey consumption rates would be useful. Other important research needs include investigations to better understand the transfer of PFAS from to insect-consuming animals and upper trophic terrestrial wildlife.

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5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

Lastly, this study demonstrates the potential and merit of a chemical activity-based approach for assessing bioaccumulation and exposure risks of PFASs to T&E species of concern. A limitation of this approach is that the apparent solubility values used to estimate chemical activities are based on numerous assumptions regarding physicochemical properties, phase partitioning, protein-binding, and toxicokinetics. Currently, there is a need for further laboratory-based measurements of PFAS solubilities (S, mol/m^3) in different environmental and biological media, as well as media-water distribution coefficients for different transporter proteins and distribution coefficients for different transporter proteins ($D_{TP,W}$), structural proteins ($D_{SP,W}$), phospholipids ($D_{PL,W}$), neutral lipids ($D_{NL,W}$), carbohydrates (D_{CW}), and organic carbon (D_{OC}). Accurate estimates of solubility and distribution coefficient values will undoubtedly strengthen the reliability of the activity-based risk assessment approach. This will also aid PFAS bioaccumulation modelling efforts, as the various distribution coefficients are key parameters within the proposed mechanistic food web bioaccumulation model.