Naval Facilities Engineering Systems Command

EXWC Engineering and Expeditionary Warfare Center

Incorporating Ecological Risks into PFAS Investigations

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FRTR Fall 2024 General Meeting

October 29, 2024

Speaker Introduction

Jason Conder, PhD
Principal
Geosyntec Consultants

- PhD Environmental Toxicologist and Chemist
- Environmental risk assessor certified by the International Board of Environmental Risk Assessors
- Working with the Navy as a consultant for over 15 years
- Professional focus on PFAS site investigation and risk assessment
- Various PFAS projects since ~2005
  - 14 peer-reviewed papers on PFAS (chemistry, ecotoxicology, risk assessment)
  - US DoD Frequently Asked Questions PFAS
  - US DoD Guidance for PFAS ERA
  - Several ongoing risk assessments for PFAS
  - Working with DoD on several PFAS ecorisk, ecotoxicology, and passive sampling research projects (SERDP, ESTCP)

PhD: Doctor of Philosophy

Presentation Overview

- ERA for PFAS: *Preface*
- PFAS CSM Considerations and Planning
- Planning for Tier 1 SERA and Tier 2 BERA PFAS ERAs
- PFAS Exposure and Effects Estimation
- PFAS Exposure and Effects Estimation Case Study
- Conclusions

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PFAS Risk Assessment: What We Know So Far

- Off-site issues are often most important
- Concentrations of PFAS at many sites can trigger concerns
- Quantifying the risk of PFAS background exposures is challenging
- There is much left to learn about PFAS—a lot of uncertainties and unanswered questions
  - Most current knowledge is based on select PFCAs and PFSAs, like PFOA and PFOS

Short-chain PFCAs				Long-chain PFCAs				
PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFUnS	PFDoS
Short-chain PFSAs		Long-chain PFSAs						

(Conder n.d.)

- Site-specific risk assessment and decision-making criteria are ongoing now and still being developed
  - In many cases, there is no time to wait for a perfect understanding or final regulatory directives

PFCA: perfluoroalkyl carboxylic acid
PFOA: perfluorooctanoic acid
PFSA: perfluorosulfonic acid
PFOS: perfluorooctanesulfonic acid

Risk-based Decisions Work for PFAS

- PFAS obey the laws of physics
- "The dose makes the poison" (don't forget Paracelsus)
- We don't have to reinvent the wheel
- We still can (and should) use risk assessment to make decisions

Paracelsus
(1493-1541)
Founder of Toxicology
Portrait by Quentin Matsys

PFAS ERA Resources

- Ecological risk of PFAS is a rapidly growing research area, and there are many resources available
- Critical resources for ERAs for PFAS
  1. SERDP Projects on Ecotoxicity of PFAS
     - Specific projects, workshops, tools and trainings are available
     - Conder et al. (2020), Devine et al. (2020) are important references for Tier 1 SERAs
  2. Ecological Risk Assessment for Per- and Polyfluorinated Alkyl Substances (PFAS)
     - Special Issue in Integrated Environmental Assessment and Management in 2021
  3. ITRC PFAS Guidance Chapter 9 - Site Risk Assessment
  4. Navy EWC Issue Papers on PFAS ESVs (available internally)

ESV: ecological screening value
EWC: electronic warfare center

ITRC: Interstate Technology Regulatory Council

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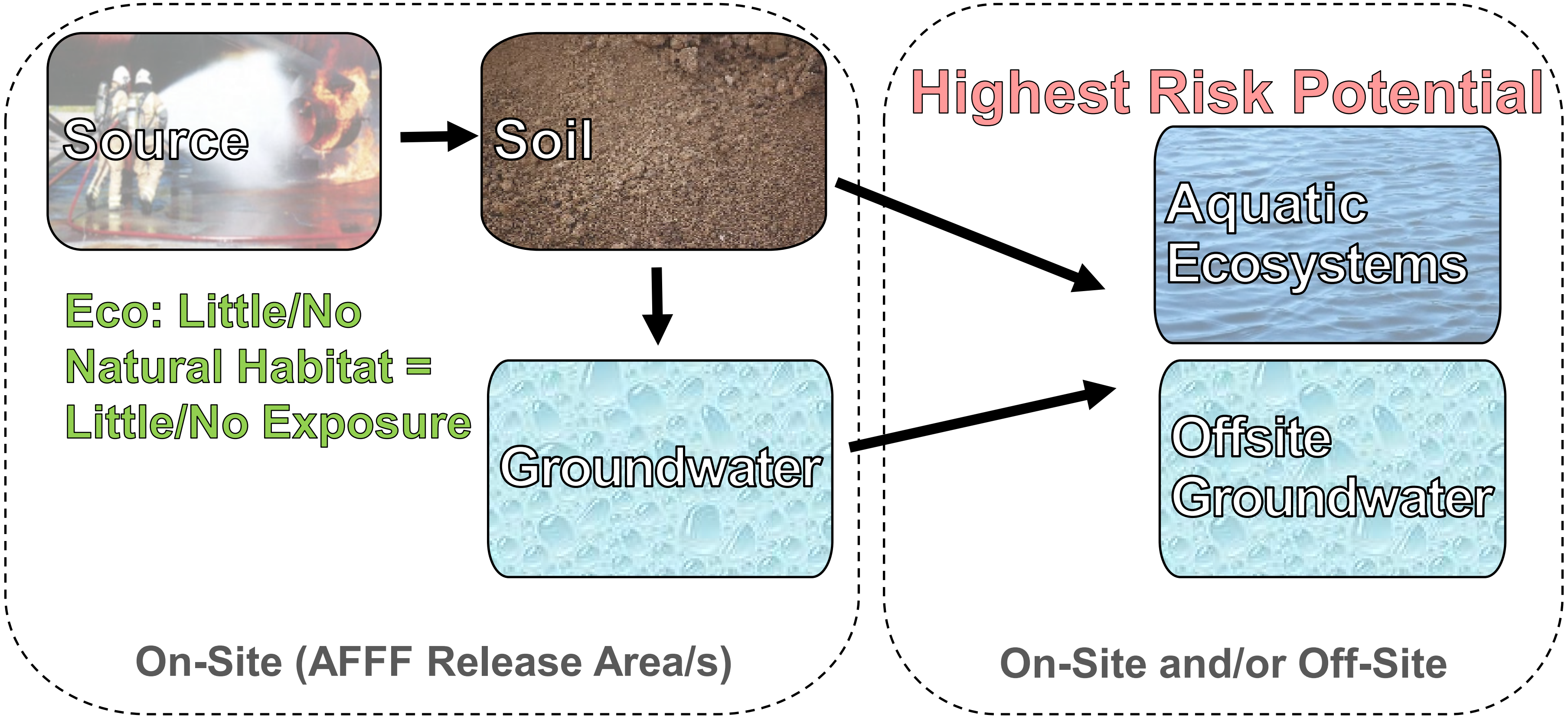
Considerations for PFAS Ecological CSMs

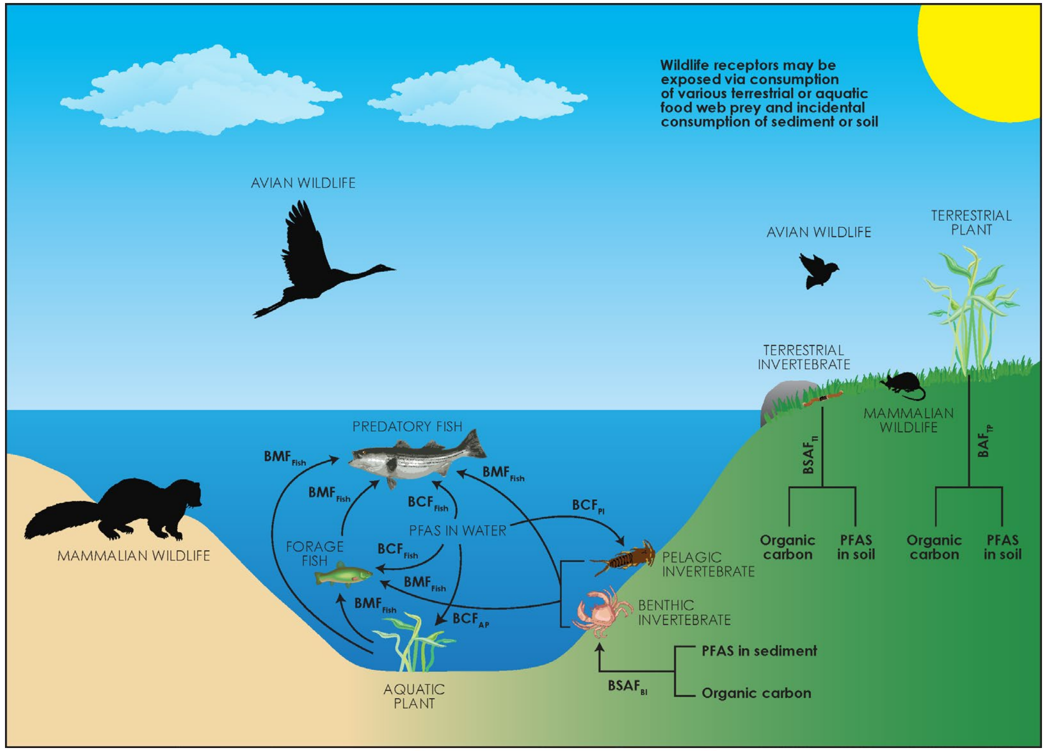


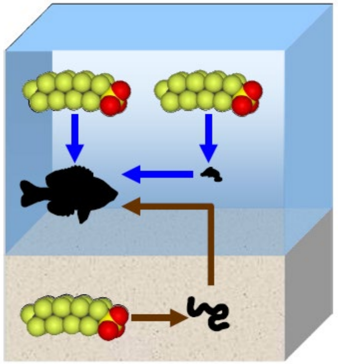
AFFF: aqueous film forming foam

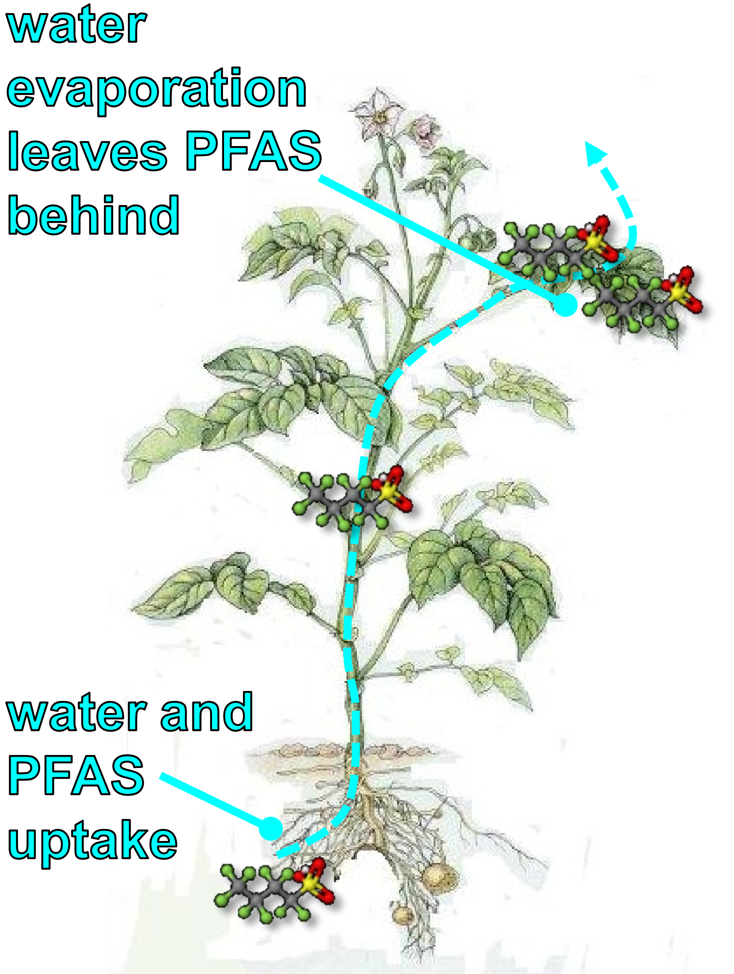
(Conder n.d.)

Bioaccumulation Exposures Are Important for Ecological Risks

- PFAS bioaccumulate into ecological food webs
    - Aquatic life (e.g., fish and invertebrates)
    - Soil life (e.g., earthworms, insects, plants)
- PFAS tends to bind to proteins, not lipids, so models we often rely upon to predict bioaccumulation are not useful for PFAS





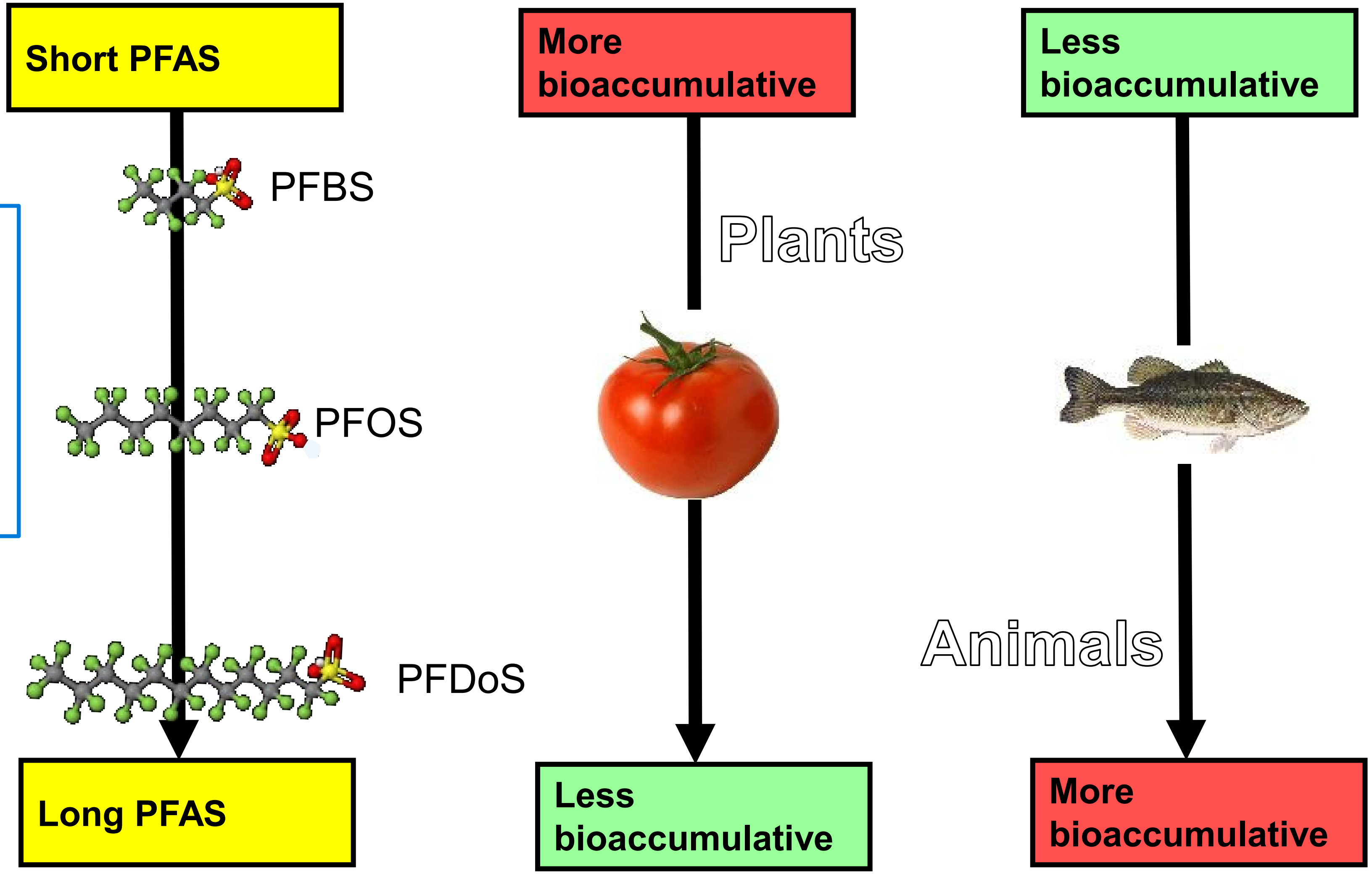


(Conder n.d.)

Chemical Size Affects Bioaccumulation

KEY POINT

Short-chain PFAAs accumulate in plants more. Long-chain PFAAs accumulate in animals more.



PFAA: perfluoroalkyl acid
PFBS: perfluorobutanesulfonic acid
PFDoS: perfluorododecane sulfonic acid

(Conder n.d.)

Chemical Type Affects Bioaccumulation

Carboxylates PFCAs (e.g., PFOA, PFNA)

Carboxylate "head"

Sulfonate "head"

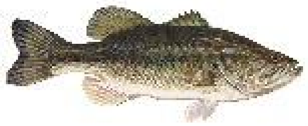
Sulfonate PFSAs (e.g., PFOS, PFDS)

More bioaccumulative

Plants

Less bioaccumulative

Less bioaccumulative



Animals

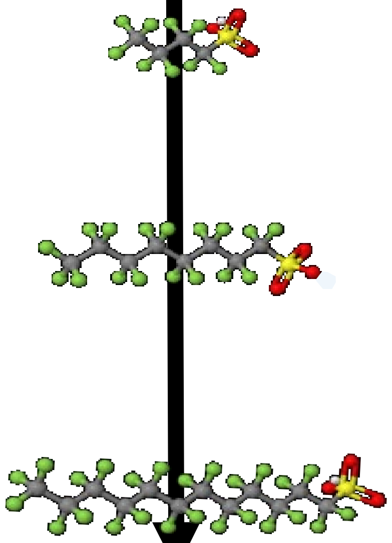
More bioaccumulative

PFDS: perfluorodecane sulfonate
PFNA: perfluorononanoate

(Conder n.d.)

Chemical Type Affects Bioaccumulation

Short PFAS



Long PFAS

Carboxylates PFCAs (e.g., PFOA, PFNA)

Carboxylate "head"

Sulfonate "head"

Sulfonate PFSAs (e.g., PFOS, PFDS)

More bioaccumulative

Plants

Less bioaccumulative

Less bioaccumulative

Animals

More bioaccumulative

KEY POINT

Long-chain PFSA = most bioaccumulative in animals
Short chain PFCAs = most bioaccumulative in plants

(Conder n.d.)

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Planning for ERAs during the RI

- Beware of science projects
  - PFAS are still relatively new to many regulators and consultants
  - Beware of extra questions/bloated investigations because of natural curiosity
  - Stick to clear DQOs within the regulatory-driven risk assessment
- Consider which PFAS to include
  - ERAs not possible for full PFAS list for 1633; focus on PFSAs, PFCAs, and select PFAS with ecotox information
  - Remember data gaps for PFAS are frequently updated (e.g., marine toxicity, toxicity data for more PFAS); include areas of potential data gaps to reduce uncertainties

KEY POINT

Data gaps are unavoidable but should not prevent risk assessment.

RI: remedial investigation

Sampling for ERAs for Tier 1 SERA / Tier 2 BERA

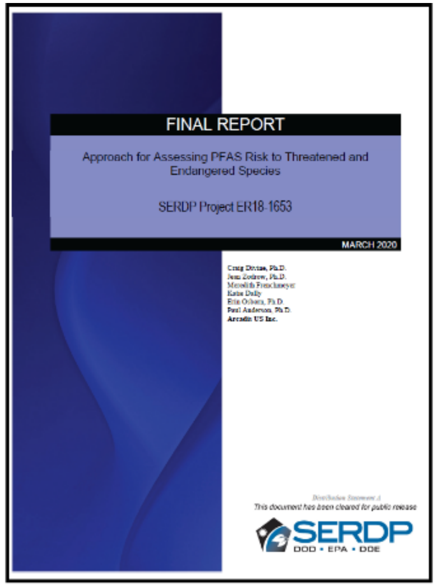
Consider data needed for all aspects of RI

- Recommendations for PFAS sampling
  - Terrestrial
    - Definitely: soil (measure organic carbon too)
    - Possibly: soil invertebrates, plants, and other biota (usually latter stages of BERA)
    - Usually not: groundwater, soil gas, air
  - Aquatic
    - Definitely: sediment (measure organic carbon too), surface water
    - Possibly: sediment porewater; benthic and pelagic invertebrates, plants, fish, and other biota (usually latter stages of BERA)
- Consider background sampling in a reference area
    - Important Reminder: CERCLA does not allow clean up below background
- Avoid the developing PFAS chemistry methods (e.g., total organofluorine methods, TOP assay, PIGE)
    - These methods do not have a clear DQOs for evaluating risk
    - These methods are considered screening methods with potential use in identifying areas to collect definitive data or as sensitivity analyses around ERA results on definitive data

PIGE: particle-induced gamma ray emission
TOP: total oxidizable precursor

PFAS Ecological Screening Values (ESVs)

- Sources of screening values for abiotic environmental media
  - Zodrow et al. 2021; Devine et al. 2020 (SERDP Project ER18-1653)
  - Conder et al. 2020 (SERDP Project ER18-1614)
  - Grippo et al. 2024 (Argonne National Laboratory under agreement with AFCEC)
    - Focused on eight PFAS commonly found in AFFF
    - Soil and surface water ecological screening values (ESVs) only
    - Grippo et al. (2024) involved review by USEPA’s Office of Water and Ecological Risk Assessment Team
  - Amphibians: Sepulveda 2023 (SERDP Project ER-2626); Pandelides et al. 2023 (ET&C)

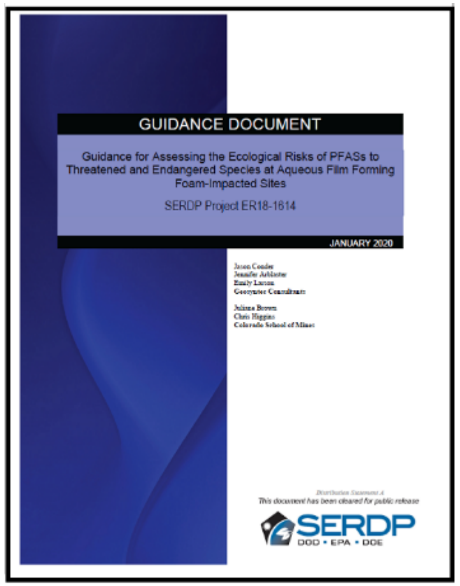

FINAL REPORT

Approach for Assessing PFAS Risk to Threatened and Endangered Species

SERDP Project ER18-1653

MARCH 2020

SERDP

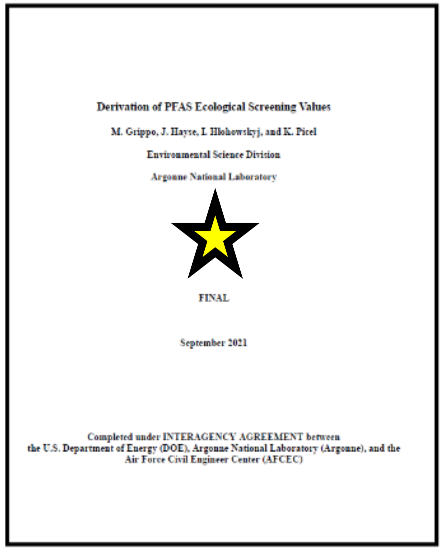

GUIDANCE DOCUMENT

Guidance for Assessing the Ecological Risks of PFASs to Threatened and Endangered Species at Aqueous Film Forming Foam-Impacted Sites

SERDP Project ER18-1614

JANUARY 2020

SERDP


Derivation of PFAS Ecological Screening Values

M. Grippo, J. Hayse, I. Hlohowskyj, and K. Picel

Environmental Science Division

Argonne National Laboratory

FINAL

September 2021

Completed under INTERAGENCY AGREEMENT between the U.S. Department of Energy (DOE), Argonne National Laboratory (Argonne), and the Air Force Civil Engineer Center (AFCEC)

AFCEC: Air Force Civil Engineer Center
ET&C: Environmental Toxicology and Chemistry

PFAS ESVs, Continued

- Grippo et al. for screening of soil and surface water (USEPA collaboration)
- Zodrow et al. and Conder et al. to supplement Grippo et al.
- USEPA published AWQC for PFOA and PFOS for protection of aquatic life in September 2024:
  - Consider these values in Tier 1 SERA
    - Freshwater chronic values:
      - PFOS: 250 ng/L
      - PFOA: 100,000 ng/L
  - USEPA also published marine acute values (PFOA and PFOS) and acute freshwater values for PFBA, PFHxA, PFNA, PFDA, PFBS, PFHxS, 8:2 FTUCA, and 7:3 FTCA
    - These may be useful, but are less technically supported
- Also Navy Ecological Screening Values Issue Paper – interim final as of Jan 2024 (Navy Emerging Chemicals WG); available from Navy

TABLE ES-3 Summary of Results and Data Gaps for PFAS Soil and Surface Water ESVs

	Soil ESVs (mg/kg)				Surface Water ESVs (µg/L)[d]			
					Freshwater			Marine
PFAS	Terrestrial Plants	Terrestrial Invertebrates	Terrestrial Mammals[e]	Terrestrial Birds[e]	Aquatic Life[b]	Aquatic-Dependent Mammals[c,e]	Aquatic-Dependent Birds[e]	Aquatic Life[b]
PFBA	—[a]	—	2.98	—	75.7	119	—	
PFHxA	—	—	6.20	—	33.8	544	—	
PFOA	101	77.8	3.84	—	**109**	47.6	—	3.16
PFNA	—	10	0.0242	—	16.9	0.116	—	
PFDA	—	—	0.0677	—	3.44	0.0937	—	
PFBS	—	100	0.817	15.8	446	209	2,783	
PFHxS	—	10	0.145	—	94.2	14.1	—	
PFOS	17.3	57.6	0.0040	0.0386	**4.85**	0.0167	0.487	1.44

[a] Dash (—) indicates a data gap – data not available.
[b] Chronic ESV values; PFOA and PFOS are Tier I ESVs (bold); the remaining are Tier II ESVs.
[c] The lower of the aquatic-dependent mammal or bird value is selected as the Aquatic-Dependent Wildlife ESV.
[d] The surface water values should only be used when the water column is relatively quiescent and sediments at the site are relatively undisturbed: the derived ESVs do not consider the antagonistic, additive or synergistic effects of other PFAS or other aquatic contaminants in combination with individual PFAS chemicals.
[e] Interspecies uncertainty factors were used to derive screening levels; see Sections 3.6.2 and 3.6.4.

Screening Values Soil and SW
(Grippo et al. 2024)

ANL: Argonne National Laboratory
ARAR: applicable or relevant and appropriate requirements
ng/L: nanograms per liter
SW: surface water

KEY POINT

Ecological screening levels are available for many PFAS and receptors, but use wisely.

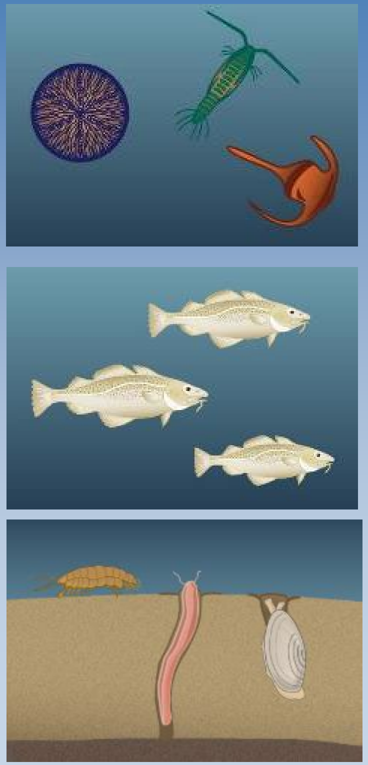
Saltwater Aquatic Life Screening Values

- Not many studies on saltwater organisms
- Limited available data (USEPA review in PFOA and PFOS aquatic life documents) suggests PFAS toxicity to saltwater aquatic life is different
- SERDP and the Navy (NESDI) recognized data gaps and have funded several research efforts to generate raw saltwater data for generation of marine aquatic life ambient water quality criteria

SERDP Statement of need for PFAS in the marine environment: https://serdp-estcp.mil/page/f7ad705d-e8ef-11ec-9685-026db1cbe810

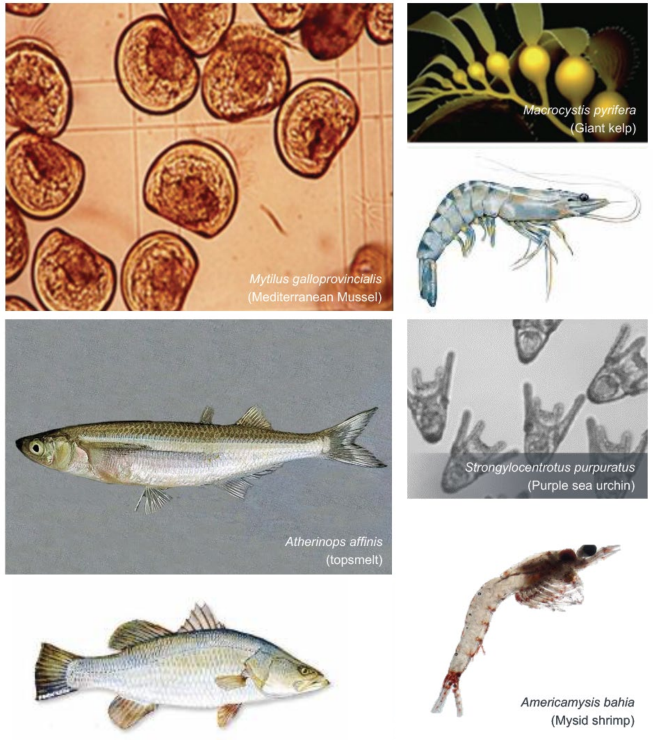
Marine Aquatic Life

- Pelagic invertebrates
- Algae / phytoplankton
- Fish
- Benthic invertebrates



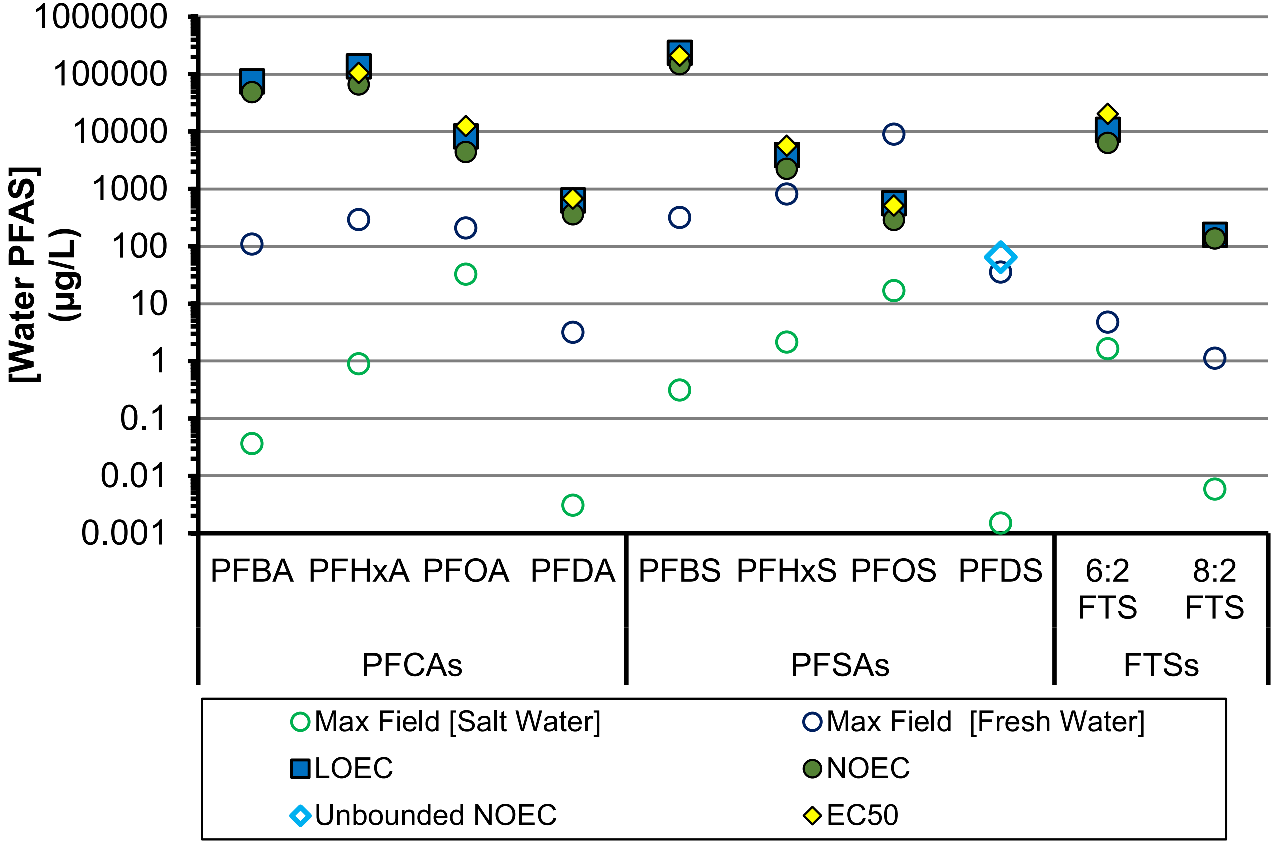
Saltwater Aquatic Life Screening Values

- SERDP Project ER22-3214 / NESDI Project #601 (Geosyntec, US Navy NIWC, CSIRO)
  - 3-year laboratory toxicity testing project
  - 10 target PFAS
  - 163 laboratory toxicity tests
  - 10 marine aquatic life species
- Additional project by US Army Corps of Engineers (ER22-3392)
- Both projects together will provide data on more than 10 marine species
- Both projects also evaluating PFAS bioavailability and toxicity in marine sediment



Saltwater Aquatic Life Screening Values

- General initial observations (water)
  - Marine aquatic life not as sensitive as freshwater species
  - Invertebrates (mussels, shrimp, copepods) tend to be most sensitive
  - PFOS most toxic
  - Longer chained PFAS more toxic
  - PFSAs more toxic than PFCAs or FTSs
  - Adverse chronic effect thresholds ≥ 0.1 to 1 mg/L, and generally much higher than maximum concentrations observed at AFFF sites



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PFAS Ecotoxicology Overview

- Demonstrated effects of PFAS in laboratory studies (mostly from study of PFCAs and PFSAs like PFOA and PFOS)
  - Animals
    - Mortality and growth effects
    - Reproductive effects (decreased reproductive output)
    - Organ-specific effects (e.g., changes in liver, kidney)
    - Immunological effects
    - Endocrine system effects (e.g., thyroid)
    - Tumors (e.g., liver, testicular, pancreatic)
  - Plants
    - Mortality and growth effects
- Field studies at AFFF sites that document a clear cause-and-effect link to PFAS exposures and effects remain elusive (need for more study)

Animal PFAS mode of toxic action for apical endpoints used in ecological risk assessments (i.e., mortality, growth, reproduction) currently under study

- Aquatic life: could be narcosis (effects biological membranes)
- Mammals: general narcosis, effects on fatty acids, other biochemical pathways in liver

Effects and Exposure of PFAS: Soil and Aquatic Life (Non-Wildlife Receptors)

- Aquatic toxicity data (fish, invertebrates) for some compounds
  - Most direct toxic effects occur at concentrations much higher than other concerns (e.g., drinking water)
- Plants and soil invertebrates relatively insensitive to PFAS
  - Effects occur in the milligram per kilogram (mg/kg) range (higher than other concerns)
- In both Tier 1 and Tier 2, use EPCs in soil, water, and sediment with these screening levels (i.e., use as TRVs) to calculate HQs

(Pixabay n.d.)

$$Hazard\ Quotient = \frac{EPC}{TRV}$$

Effects and Exposure of PFAS: Wildlife (Birds and Mammals)

- Wildlife tend to be most sensitive ecological receptors (especially for PFOS)
  - Focus on small animals (high site fidelity, high dietary exposure)
    - Tend to drive decisions for most bioaccumulative chemicals
  - Modeling exposure to carnivorous and wider-ranging wildlife is more complicated, but is not expected to drive risk
- Field studies have shown mixed results
  - Custer et al. (2012, 2014) note decreased hatching success in a wild population of tree swallows,
    - Other chemicals complicate the direct casual link to PFAS (see Custer [2021] additional analysis)
  - Other studies have found minimal or no reproductive effects in birds, including under much higher PFAS exposures

(Pixabay n.d.)

Exposure Assessment for PFAS: Wildlife

- Typical Tier 1 SERA and Tier 2 BERA exposure model approach can be used to estimate **PFAS daily doses for wildlife**

Site Measurements (or Model Predictions)

Chemical in Soil (ng/g) → Accidental Soil Ingestion Rate (g/day)

Chemical in Food (ng/g) → Food Ingestion Rate (g/day)

Assumptions and Modeling

DI = [Σ(Ci x Fi x FIR) + (Cs x SIR)] x AUF x (1/BW)

Where:

DI = daily intake (dose) (mg/kg*day)
Ci = concentration in food item i (mg/kg; wet weight)
Fi = fraction of diet comprised of food item i (unitless)
FIR = food ingestion rate (kg/day; wet weight)
Cs = concentration in soil (or sediment) (mg/kg; dry weight)
SIR = soil (or sediment) ingestion rate (kg/day; dry weight)
AUF = area use factor (unitless, max of 1) = Home range ÷ Site Area
BW = body weight (kg)

Predicted daily chemical dose (ng/day)

- Food samples often hard to come by
  - Often start by predicting what's in the food using concentrations of chemicals in soil, sediment, and/or water (i.e., food web models)

g/day: gram per day
ng/day: nanogram per day
ng/g: nanogram per gram

Bioaccumulation Modeling Needs and Resources For PFAS

- Site-specific data needs are as follows
  - Concentration of PFAS in water and sediment (aquatic); soil (terrestrial)
  - Organic carbon content in sediment and soil
- Uptake factors to estimate PFAS concentrations in wildlife diet items are available using food web models
  - Conder et al. (2020)—SERDP Project ER18-1614 and modeling tool
  - Mechanistic models (similar to Gobas models for lipophilic organics) recently developed (Sun et al., 2022; Kelly et al., 2024)
- Food web modeling for PFAS also comes in handy for human health risk assessments

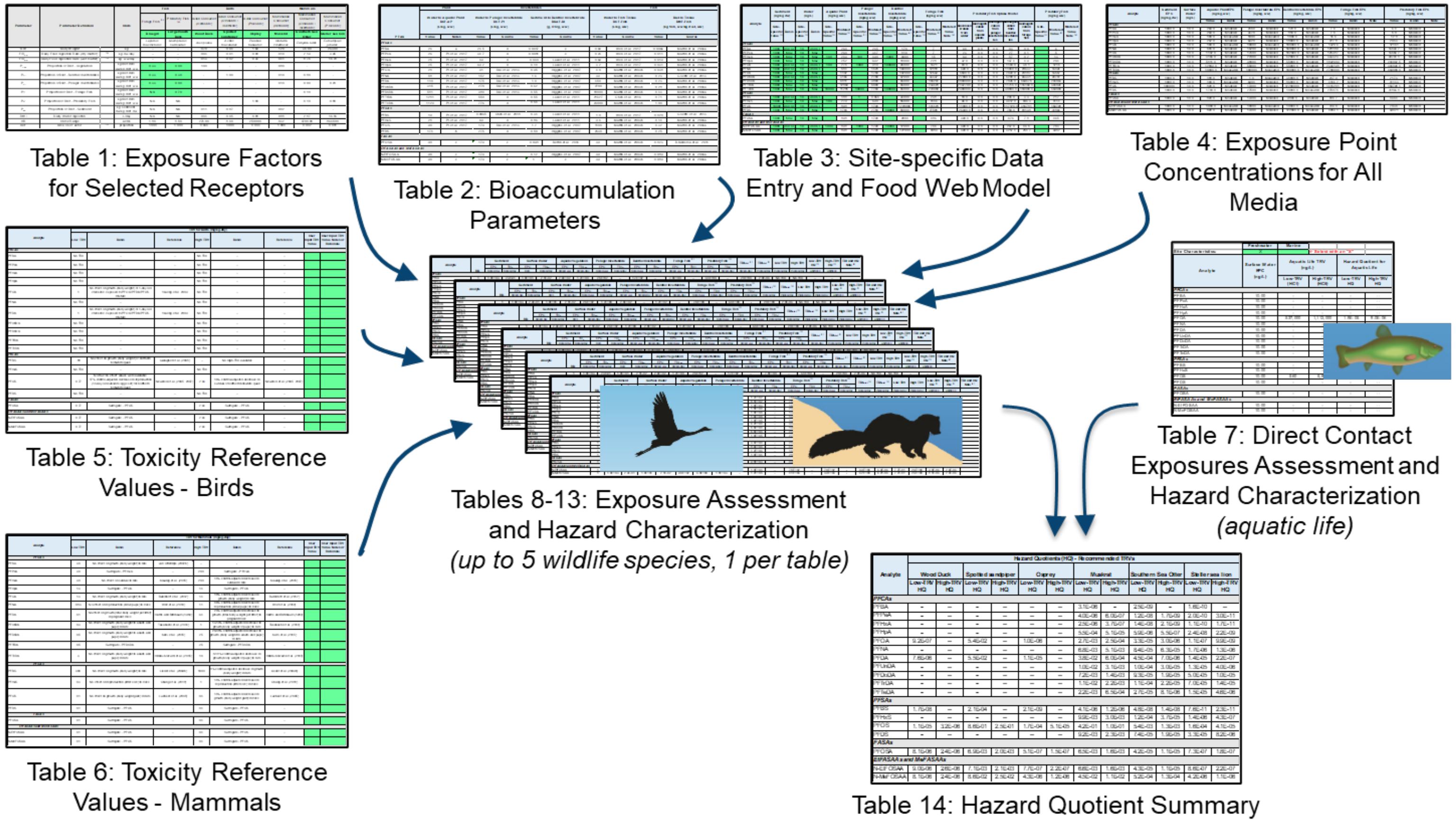
SERDP PFAS Food Web Modeling Tool for Excel

- Available as Excel files, with “how to” instructions and technical support for models
- Free PFAS ecorisk food web models (SERDP Project ER18-1614)

https://tinyurl.com/PFAS-Risk-Tools

- Not mandated by the Navy, but using/adapting these tools will save folks from re-inventing the wheel

Example: ERA Model Tool for Aquatic Ecosystems



PFAS Wildlife Toxicity Benchmarks

- PFAS mammalian laboratory toxicity studies primarily limited to a handful of the PFCAs and PFSAs
- PFAS avian laboratory toxicity studies even more limited
- Several resources for wildlife TRVs (i.e., SEVs in Navy terms) for PFAS
  - Conder et al. (2020)—SERDP Project ER18-1614 (included in SERDP PFAS food web modeling tool)
  - Grippo et al. (2024)—Argonne National Laboratory under agreement with AFCEC
  - Narizzano et al. (2022)—Mammalian TRVs basis
  - NAVFAC developed issue papers to support refinement TRVs for mammals (PFOS and PFHxS) and birds (PFOS)
    - Review and Summary Issue Paper Preparation funded by NAVFAC
      - Mammal TRV paper uses Narrizano et al. data for mammalian TRVs
    - Navy Emerging Chemicals Workgroup issued these as Interim Final May 2024 (available from Navy via Jason Speicher)

PFHxS: perfluorohexanesulfonic acid
SEV: screening ecotoxicity value

Tier 2 BERA, Step 3b: Advanced PFAS Investigations

- Many traditional advanced ERA methods are applicable to PFAS
  - Toxicity testing, passive sampling, benthic community assessment, tissue analysis, etc.
  - Refer to usual guidance for these tests
- Focus on the 'Eco' in the ERA
  - Consider how site communities compare to reference; are impacts indicated?
- Focus on specific DQOs that add risk management value and not on undertaking multiyear research projects without clear goals and objectives

Risk Characterization and Communication

- Follows bioaccumulation/exposure modeling and TRV selection for wildlife and standard ERA approaches
  - Hazard Quotient (HQ) = Predicted Dose ÷ TRV
- For Aquatic life/terrestrial plants or invertebrates
  - HQ = Exposure ÷ ESV
- HQ ≤ 1 indicates effects are unlikely to occur; HQ > 1 indicates additional evaluation and possible management could be needed
  - However, examine predicted doses relative to the effect and magnitude of the effect associated with the TRV

KEY POINT

Communicate risks specifically; focus on the level of potential impact and to which receptors.

PFAS-specific Ecological Risk Uncertainties

1. PFAS Mixtures
   - Multiple HQs for multiple PFAS
2. PFAS Detected at Site, but no ESVs/TRVs
   - Especially a challenge for many PFAS with marine aquatic life and birds
3. PFAS 'Dark Matter'
   - PFAS that may be present but cannot be detected
     - Like PAHs and other compounds that are beyond the 16 priority pollutant PAHs (and other petroleum analytical approaches)

Recommendations / Considerations

1. Mixtures?
   - Acknowledge as uncertainty
   - Modeling sensitivity analysis ideas
     - Could sum HQs (Hazard Index), but not yet supported
2. No TRVs?
   - Acknowledge as uncertainty
   - Modeling sensitivity analysis ideas
     - Still estimate exposure and qualitatively compare to PFOS or other PFAS with values
     - Develop surrogate PFAS by selecting similar chain-length and functional group where able
3. PFAS Dark Matter
   - Acknowledge as uncertainty
   - No good quantitative approach to estimate site concentrations, uptake factors, or TRVs
   - Resist overly conservative assumptions or arbitrary uncertainty factors
   - May need to support risk assessment modeling (conducted with measurable PFAS) with ecological investigations

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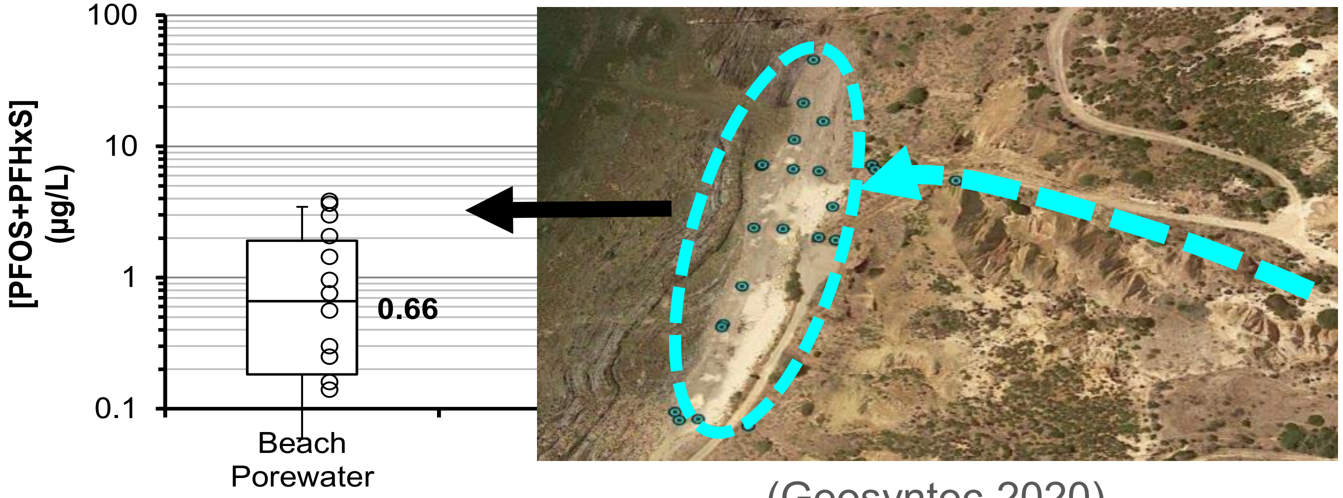
Australia Site

- Former industrial site with AFFF impacts from storm water discharge to a small beach area
- Not a US Navy Site, but great example of more advanced Tier 2 BERA work

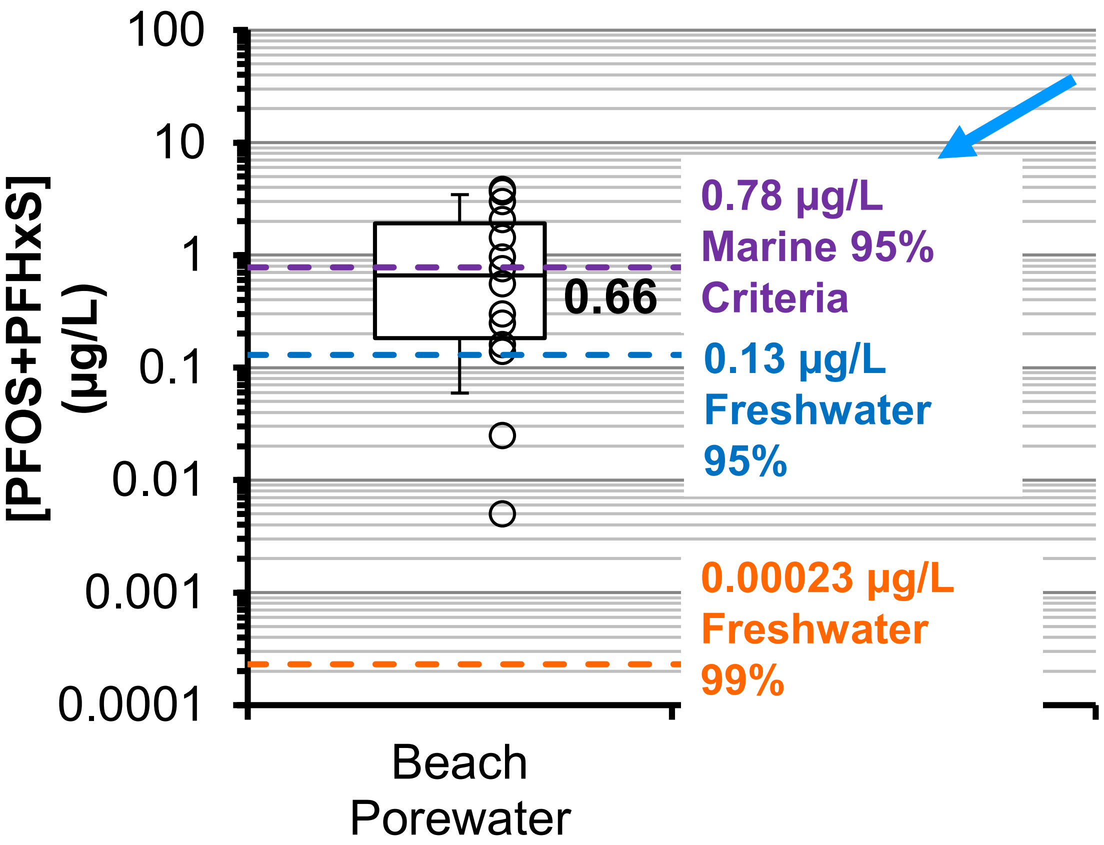
- Complete exposure pathways
  - Aquatic birds nesting or feeding on shore; food web models indicated minimal risks
  - On-shore benthic community



(Geosyntec 2020)

µg/L: microgram per liter

So Now What?



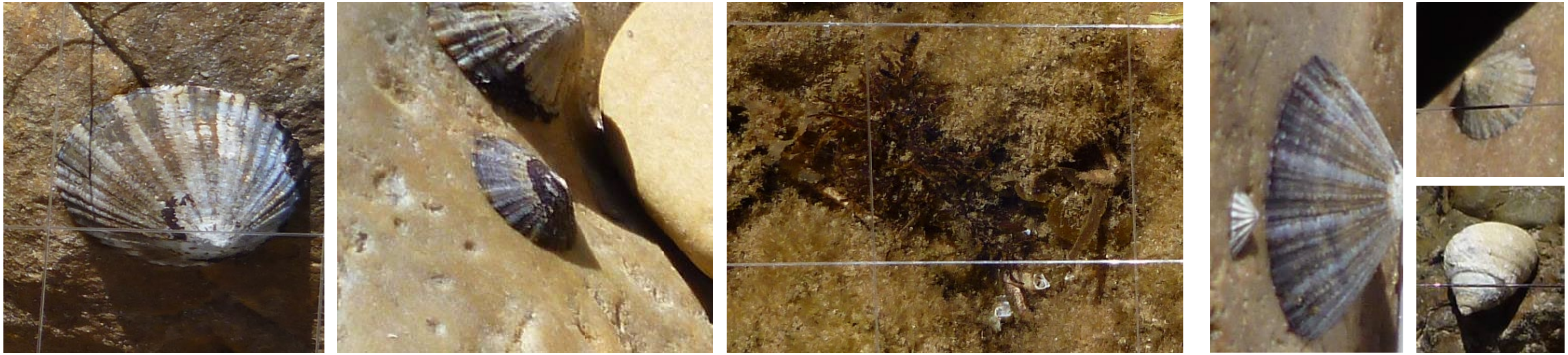
(Geosyntec 2020)

Concentrations in beach porewater that exceed screening criteria for aquatic life protection

- Could measure concentrations of PFAS in invertebrates, but no good criteria to compare to understand risk of adverse effects to aquatic life
- Could also do laboratory aquatic toxicity testing, but unclear what to test and species to use
- Other options?

Putting the Eco in the Ecological Risk Assessment

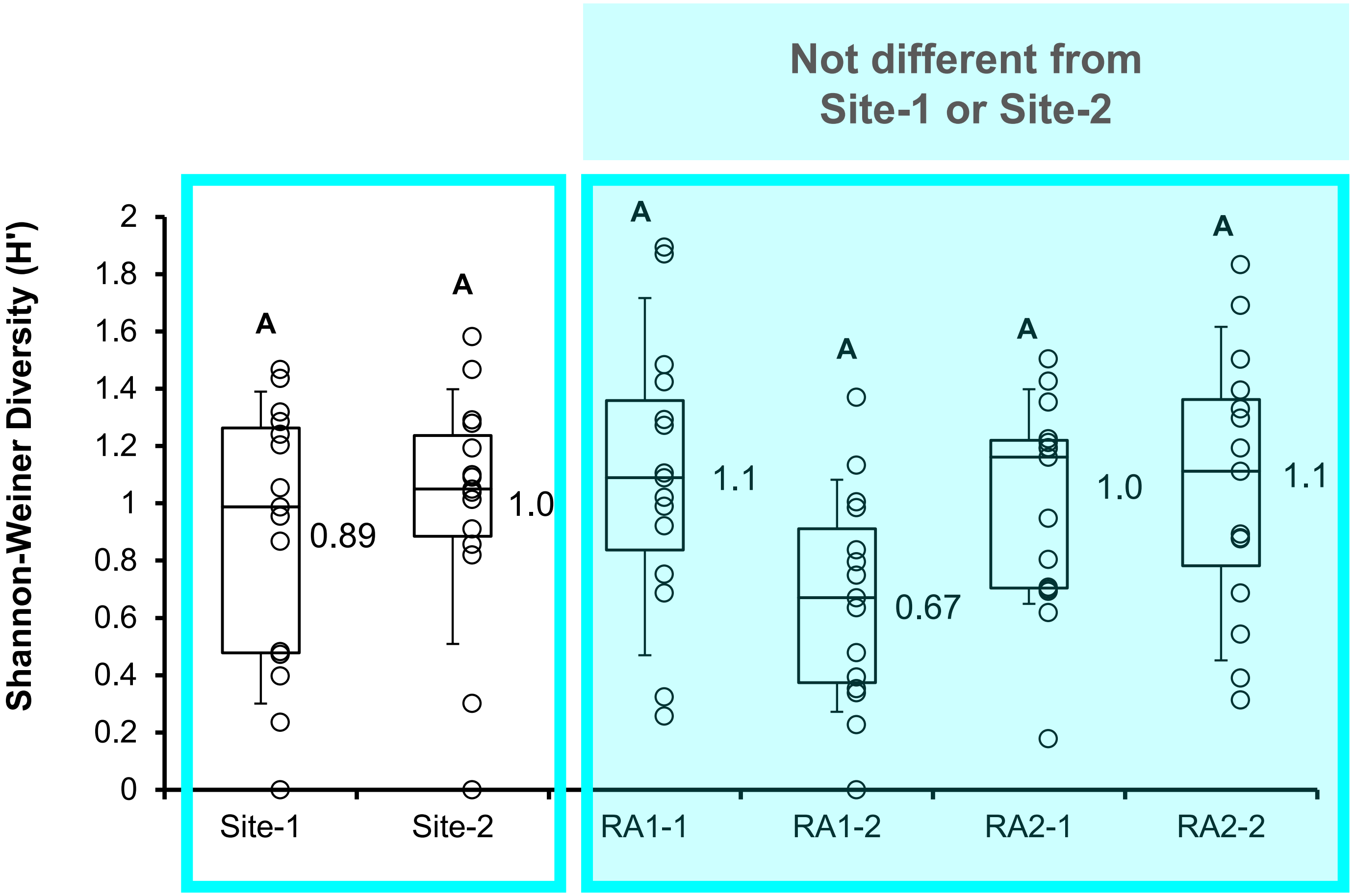
- Key ecological resource: intertidal invertebrate and algal community
  - Exposed to PFAS during storm events and from beach porewater
  - Important food source for wildlife
  - Can be evaluated through intertidal survey



(Geosyntec 2020)

Intertidal Survey: Community Results

- Diversity (site similar to all Reference Areas [RA1 and RA2])
- Other community census metrics indicated same conclusion: **Community at site not impacted**
  - Pielou's Evenness (J')
  - Species Richness
  - Swartz's Dominance Index (SDI)
- Uplands PFAS source managed, beach area left intact



Note: No statistical differences
(Geosyntec 2020)

Presentation Overview

- ERA for PFAS: Preface
- PFAS CSM Considerations and Planning
- Planning for Tier 1 SERA and Tier 2 BERA PFAS ERAs
- PFAS Exposure and Effects Estimation
- PFAS Exposure and Effects Estimation Case Study
- Conclusions

Conclusions (1 of 2)

- We have come a long way in terms of understanding PFAS ecological risk in the last 10-20 years
- A lot left to learn about PFAS ecological risk, but we know enough to make site-specific decisions using the best available data
  - We can do this using typical site investigation and ecological risk assessment tools that we use for other chemicals
- Uncertainties and data gaps abound, but, we can't necessarily wait for a perfect or complete understanding of PFAS

Conclusions (2 of 2)

- Focus on the decision-making process
  - Resist overly simplistic explanations and conclusions as much as possible
  - However, ultimately your ERA will result in a binary management action (“To dig or not to dig, that is the question”)
- Communicate effectively and clearly about your assessment, its assumptions, its sources of data, and model parameters
- Do what is right by the ecology
  - Protect from the adverse effects of chemicals
  - Protect from unnecessary remediation (“First, do no harm”)
- “Don’t do anything stupid” (Glenn Suter, USEPA (retired))

KEY POINT

An ERA is an ERA, whether its for PFAS or not.

Points of Contact and Acknowledgments

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Many thanks to my co-authors on this presentation

- Jason Speicher (NAVFAC Atlantic)
- Jenn Arblaster (Geosyntec)

And for the funding provided to Geosyntec for the Navy Remediation Innovative Technology Seminar (RITS) series, from which this presentation was derived

Naval Facilities Engineering Systems Command

EXWC Engineering and Expeditionary Warfare Center

Questions