JULY 9, 2024

PFAS CHARACTERIZATION AND ARGONNE'S PFAS R&D EFFORTS

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U.S. DEPARTMENT OF ENERGY
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World-class expertise, facilities, and tools for water S&T breakthroughs

ALCF, APS, CNM

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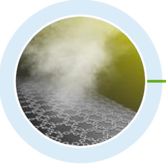
Materials discovery, synthesis, characterization, and scale-up

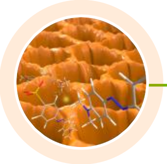
New process technologies for systems that sense, treat, and handle water

AI/ML, data science, modeling, and simulation

MERF, PicoProbe

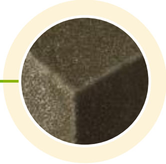


Solar Steam Generation

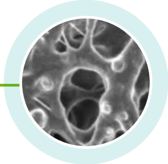


Advanced Oxidation Processes

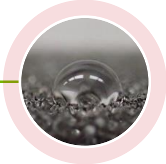
Dating of Groundwater



Advanced Sorbents for Pollution Remediation

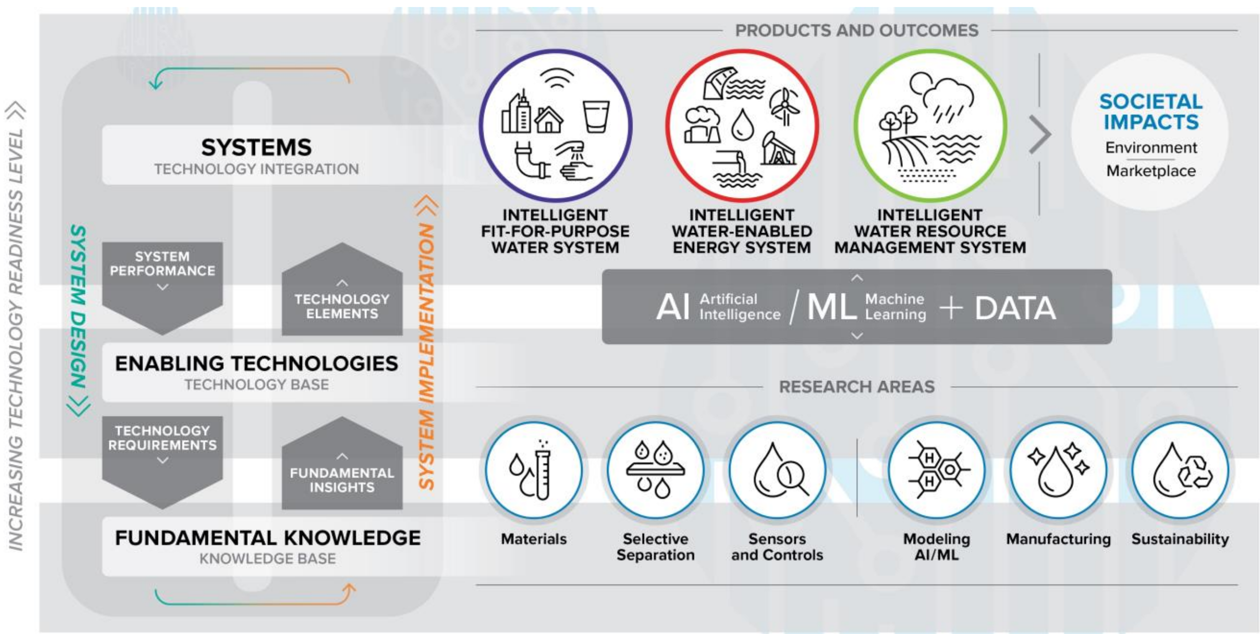


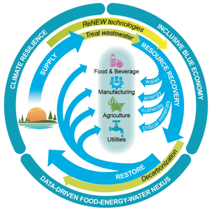
Selective Membrane Technologies



Functional Surfaces and Coatings

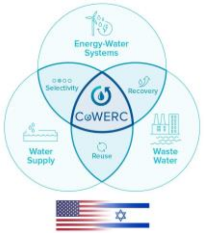
ARGONNE'S WATER + AI STRATEGY





SYSTEM GAPS

- ☐ Cost-effective
- ☐ Reliable
- ☐ Socially responsible systems

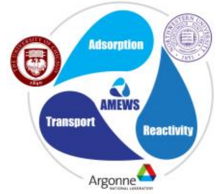


TECHNOLOGY GAPS

- ☐ Low-cost / scalable design
- ☐ Materials
- ☐ Sensors
- ☐ Algorithms
- ☐ Tools

KNOWLEDGE GAPS

- ☐ High-throughput design
- ☐ Synthesis
- ☐ Characterization
- ☐ Manufacturing
- ☐ Decision making



Subscribe to Argonne's Water + AI Newsletter at www.anl.gov/water

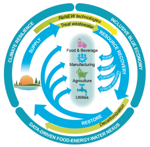
AMEWS ADVANCED MATERIALS FOR ENERGY-WATER SYSTEMS

FUNDAMENTAL SCIENTIFIC GAPS (TRL=1–2)

Fundamental Knowledge
Knowledge Base

GAPS / BARRIERS
- High-throughput design
- Synthesis
- Characterization
- Manufacturing
- Decision-making

	Materials (BES)	Sensors and Control (BES)	Selective Separation (BES)	Modeling (ASCR, BER)	Manufacturing and Processing (AMO)	Techno-economic-environmental (EM/LM, EERE)
GAP 1	High throughput water materials design/discovery	Novel sensing modalities and materials	Water science for adsorption/ separation	Multiscale and Multiphysics modeling	Scale-up materials manufacturing and processing	Resilience evaluation of extreme events
GAP 2	Material surface/interface design/discovery	Sensing mechanisms	Surface reactivity	New AI algorithms, particularly with sparse data sets	Additive manufacturing and fabrication	Impact and risk analysis
GAP 3	Selective molecular probe design/discovery	Analyte-probe interactions	Transport phenomena in confined space	Models for integration of different sectors	Data-enabled cybermanufacturing	Techno-economic analysis and Life cycle analysis

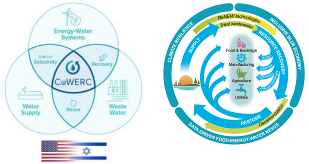


ENABLING TECHNOLOGIES GAPS (TRL=3–5)

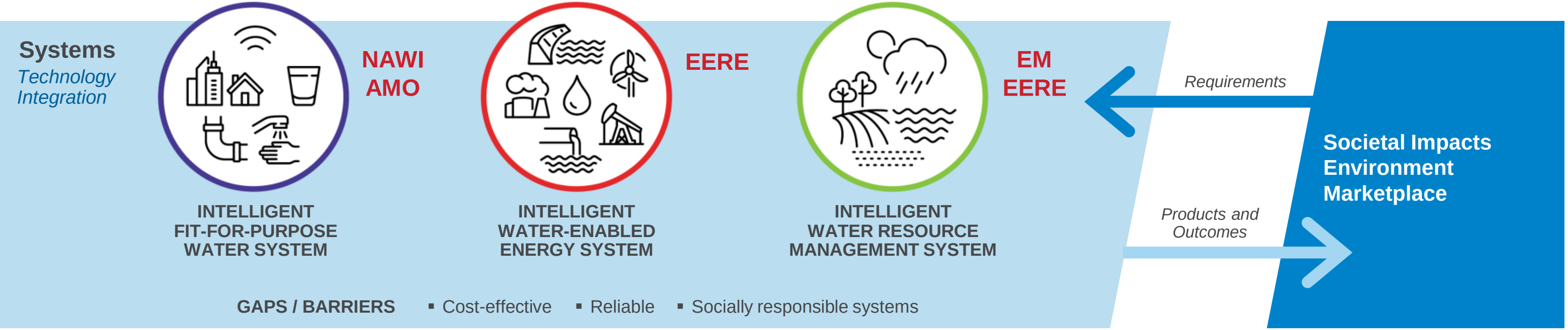
Enabling Technologies
Technology Base

GAPS / BARRIERS
- Low-cost and scalable design
- Materials
- Sensors
- Algorithms
- Tools

	Materials (AMO, BETO)	Sensors and Control (AMO, BETO)	Selective Separation (AMO, BETO)	Modeling (ASCR, AMO, BETO, WPTO)	Manufacturing and Processing (AMO)	Techno-economic-environmental (AMO, EM/LM, EERE)
GAP 1	Membranes	Chemical sensors	Selective membranes	Physics-based models	Manufacturing tools	Life cycle assessment (LCA) tools
GAP 2	Sorbents	Biosensors	Selective sorbents	New AI/ML algorithms	Manufacturing infrastructure	Techno-economic analysis (TEA) tools
GAP 3	Catalysts	Data and control	Selective catalysts	Software for simulation	Cybermanufacturing	Risk analysis tools



SYSTEM-LEVEL TESTBEDS (TRL=6–9)



EXAMPLE TARGETS

Emerging Contaminants	PFAS (per- and polyfluoroalkyl substances)	Microplastics	Fracking HCs
Resilience	Infrastructure	Emergency situations e.g., COVID-19	Extreme conditions

PFAS FOREVER CHEMICALS IN WATER

TOXICITY OF PFAS

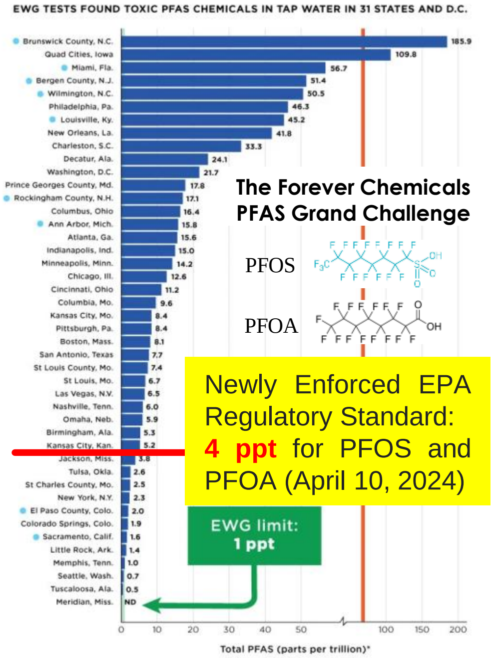
Compromised immune system

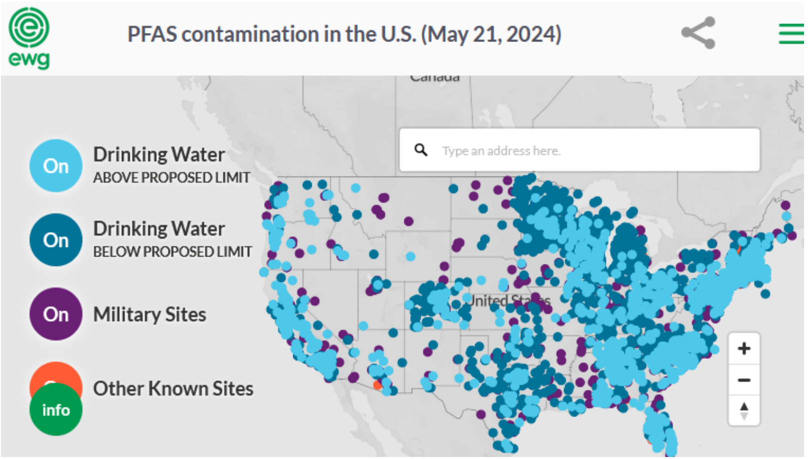
Thyroid disease

Liver damage

Reproductive and developmental defects

Cancers





www.cdc.gov/healthywater/drinking/public/water_quality.html

ARGONNE PFAS R&D ACTIVITIES

Detect, Adsorb, Destroy (DAD)

Cost-Effective, Cutting-Edge Solutions for PFAS Cleanup

Ecological-Risk – National Screening Level Values

Current Air Force Funded Project -

Development of PFAS Ecological Screening Level values for future remediation activities, (Air Force, Army, Navy, EPA)

Kurt Picel (PI), Ihor Hlohowskyj, David Gartman (PM, EVS)

Develop AI Framework to Predict PFASToxicity

Current Opportunity (submitted proposal 4/20) AI LDRD

Alvaro Vazquez, Kurt Picel, Ben Blaiszik, Ian Foster, Margaret MacDonell, Lynda Soderholm,, Junhong Chen, Eugene Yan, David Gartman

Remediation

In Discussions – Remediation Investigations at Various Air Force Installations 7/2020

In Discussions – PFAS Liability Assessments – DOE-EM

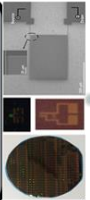
David Gartman, Eugene Yan (EVS)

Detect (Sensors)

Molecular engr. of field-effect transistor for rapid ultrasensitive detection of PFAS in water

Current Opportunity – Funded Swift LDRD

Stuart Rowan (CSE), Junhong Chen (PSE)
Cristina Negri, Eugene Yan, David Gartman (EVS)



Long-Term Site Monitoring

Utilize Deep Learning to Screen for PFAS Adsorption Materials

Current Opportunity (submitted proposal 4/20) AI LDRD

Ed Barry, Junhong Chen, Alvaro Vasquez, Seth Darling, David Gartman, Eugene Yan

Adsorb (Gel, Sponge)

PFAS adsorption strategies using platforms based on OleoSponge and EZSelect technologies

Current Opportunity – Funded Swift LDRD

Ed Barry, Jeff Elam (AMD), John Quinn, David Gartman, Eugene Yan, Cristina Negri (EVS)

Destroy (Plasma-low energy)

Low-Energy Microwave Plasma Technology to destroy carbon-fluorine bond - improves cost effectiveness of using plasma microwave. Multiphysics model, utilize AI/ML for scale up.

Current Opportunity – Will submit proposal for 2021 LDRD 4/2020

Santanu Chaudhuri (EGS), Cristina Negri, Eugene Yan, David Gartman (EVS), Keith Bradley (EGS, NSP)

EPA PFAS ANALYSIS METHODS

Recent Accomplishments

AIR

OTM-45 (air emissions; 2021)
OTM-50 (air w/ canister; 2024)

LAND / WATER

EPA Method 533 (drinking water; 2019)
EPA Method 537.1 (drinking water; 2018/2020)
SW-846: Method 8327 (wastewater, groundwater, surface water; 2021)
EPA Method 1633 (water, solids, tissue; 2021/2024)
EPA Method 1621 (wastewater; 2022/2024)
Adsorbable organofluorine (AOF/CIC)

Current & Ongoing Efforts

AIR

Develop and test methods for additional PFAS in air emissions

LAND / WATER

3512/8327 updates
Aqueous leaching methods (LEAF)
Direct injection for drinking water
Semi-volatile PFAS

OTHER METHODS: “TOTAL” PFAS

Non-targeted analysis (NTA)
Extractable organofluorine (EOF/CIC)
Total Oxidizable Precursor (TOP) **Assay**

Credit: EPA ORD

TARGETED VS. NON-TARGETED ANALYSIS

TARGETED

Methods applicable to a specific defined set of known analytes

Analytical standards must exist for quantitation

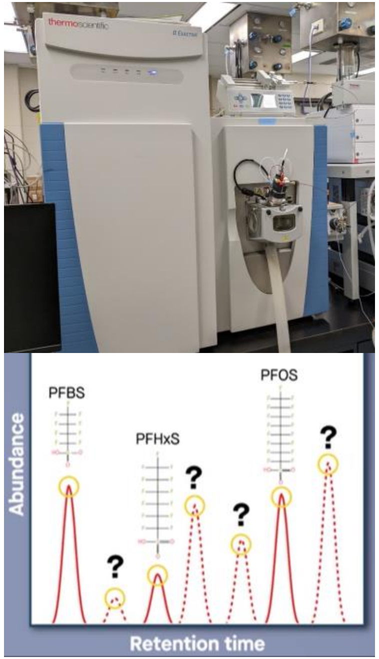
Methods only measure for analytes on the targeted list; once the analysis is complete, you can't look for other analytes

NTA

Methods use high resolution mass spectrometry (HRMS) capable of identifying all known & unknown analytes in that chemical space

Can screen for lists of known suspects & can discover new or unknown analytes providing a tentative ID

HRMS data can be stored and analyzed later for newly identified analytes



Introduction to NTA (from EPA) video at nontargetedanalysis.org

EVALUATION OF METHOD 533

for Analysis of Non-potable Aqueous Samples

Method 533 performed acceptably for the tested matrices as defined by the criteria in the method

- Groundwater
- Surface water
- Wastewater influent
- Wastewater effluent

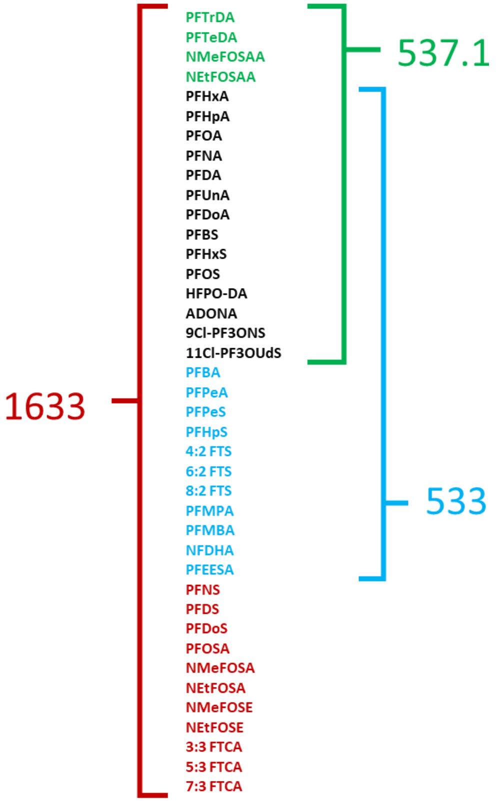
Failures of the method were related to complete clogging of SPE cartridges by wastewater influent, but recoveries were acceptable even in cases when SPE cartridges were nearly clogged but flow was still possible

Possible modifications requiring further evaluation:

- Centrifugation prior to SPE
- Filtration prior to SPE
- SPE cartridges with a sorbent of larger particle size

This study did not determine whether PFAS associated with solids are recovered

Credit: Jim Voit and Jean Van Buren (EPA ORD), Adrian Hanley (EPA OW)

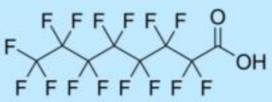


PFAS ANALYSIS VIA HIGH SENSITIVITY MASS SPECTROMETRY

PI: Dr. Pietro Papa Lopes (ESCG-MSD); Collaborator: Dr. Ronnie Emmons (Postdoc)

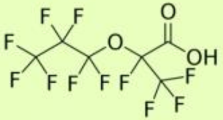
LC-MS/MS

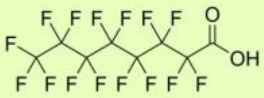
- Electrospray ionization (ESI) coupled to triple quadrupole mass spectrometry permits great sensitivity for PFAS
  - Low part-per-trillion for short to long PFAS, part-per-quadrillion possible with preconcentration
- Chromatography is necessary, the use of a delay column allows the removal of interferences from the instrument flow path.



LC/Q-TOF

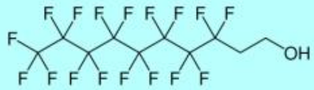
- High-resolution mass spectrometry enables structural elucidation of unknown PFAS and its degradation products
  - Low to mid-part-per-trillion sensitivity
- Use of data analytics such as Kendrick Mass Defect Analysis facilitates a holistic approach toward the characterization of chemical constituents with repeating unit structure (e.g., CF_2).

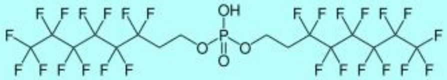




GC-MS/MS

- Enables the analysis of PFAS fluorotelomer precursors
  - Low part-per-billion to part-per-trillion sensitivity
  - Most PFAS require derivatization



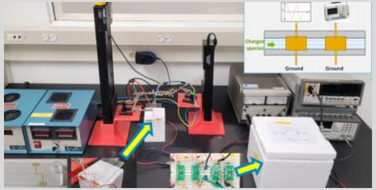


CONTACTLESS CONDUCTIVE SENSOR

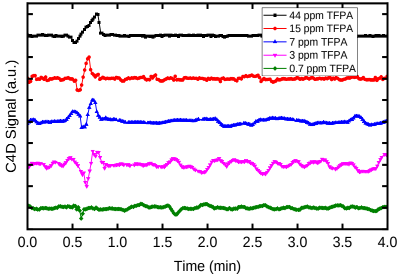
for Short-/Long-Chain PFAS Detection in (Waste)water

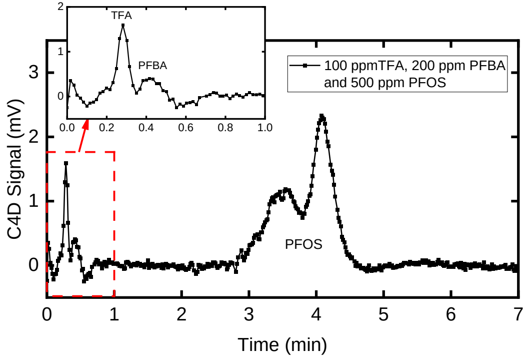
Yuepeng Zhang in collaboration with 3M

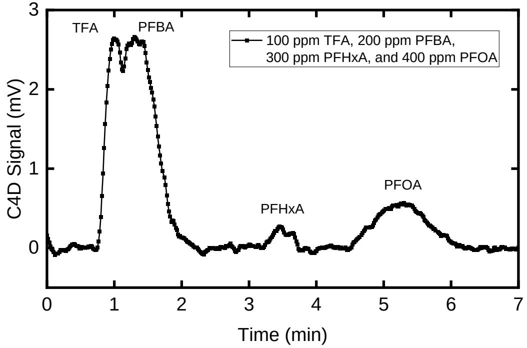
- Label-free determination
- Measure the inductance current induced by the movement of ionized PFAS species
- Contactless - no corrosion or fouling issues
- Can be made lab-on-chip and portable
- Completed feasibility study using in-house designed electronic circuit and measurement system
  - Detected PFAS with 2-8 carbon chain length
  - Demonstrated 7 ppm detectability of TFPA
- Opportunity to further improve detectability to ppb with PCB and noise canceling strategy



PFAS	FORMULA
TFA	CF_3COOH
TFPA	C_2HF_4COOH
PFBA	C_3F_7COOH
PFHxA	$C_5F_{11}COOH$
PFOA	$C_7F_{15}COOH$
PFOS	$C_8HF_{17}O_3S$



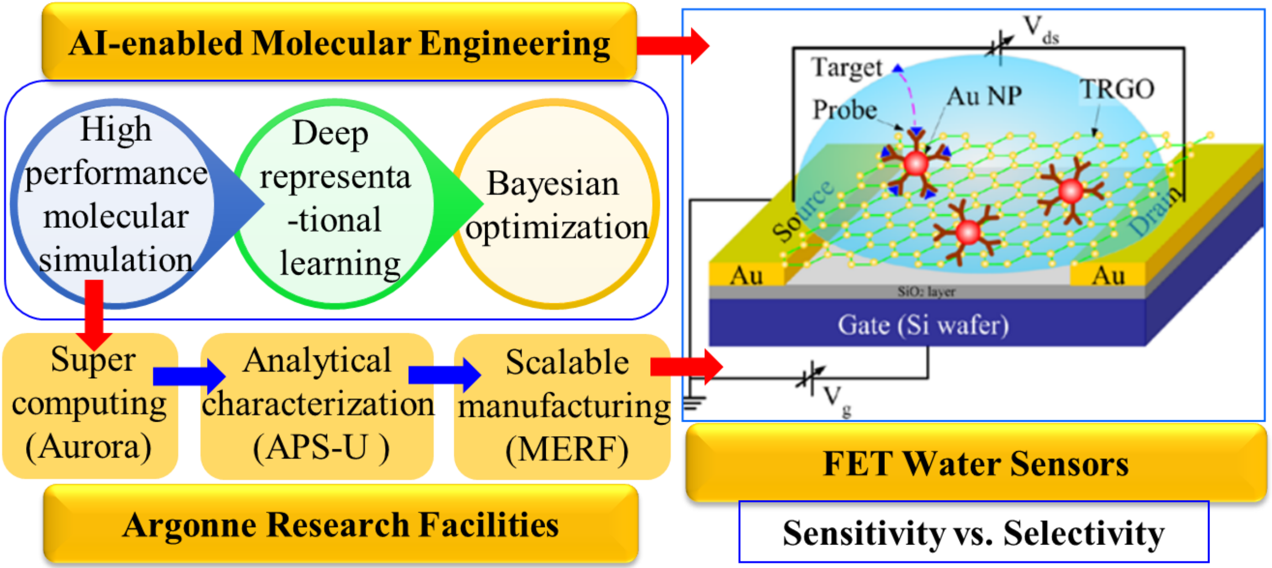




AI-ENABLED MOLECULAR PROBE DESIGN

Funded by UChicago CDAC on PFAS detection

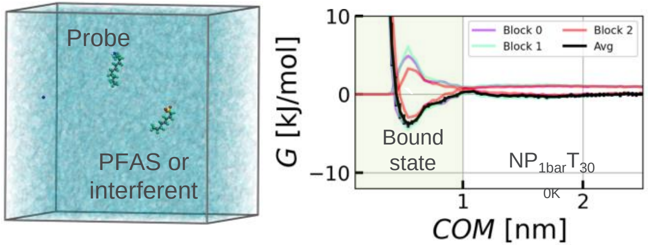
Rich opportunity in design of molecular probes for detection of a wide range of water contaminants (PFAS detection in collaboration with Seth Darling, Sang Soo Lee, Chris Benmore, Andy Ferguson, Stuart Rowan, Becca Willett, and Eric Jonas).

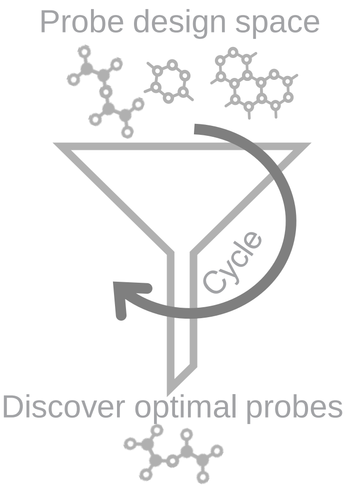


ACTIVE LEARNING OF MOLECULAR PROBES

Ground truth evaluation of objectives

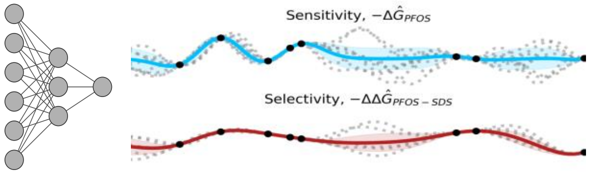
Evaluate probe **sensitivity ΔG_{PFAS}** and **selectivity $\Delta G_{PFAS} - \Delta G_{Interferent}$** using molecular dynamics simulations





Surrogate model training to predict objectives

Deep representational learning of probes using SELFIES, surrogate model training and Bayesian optimization

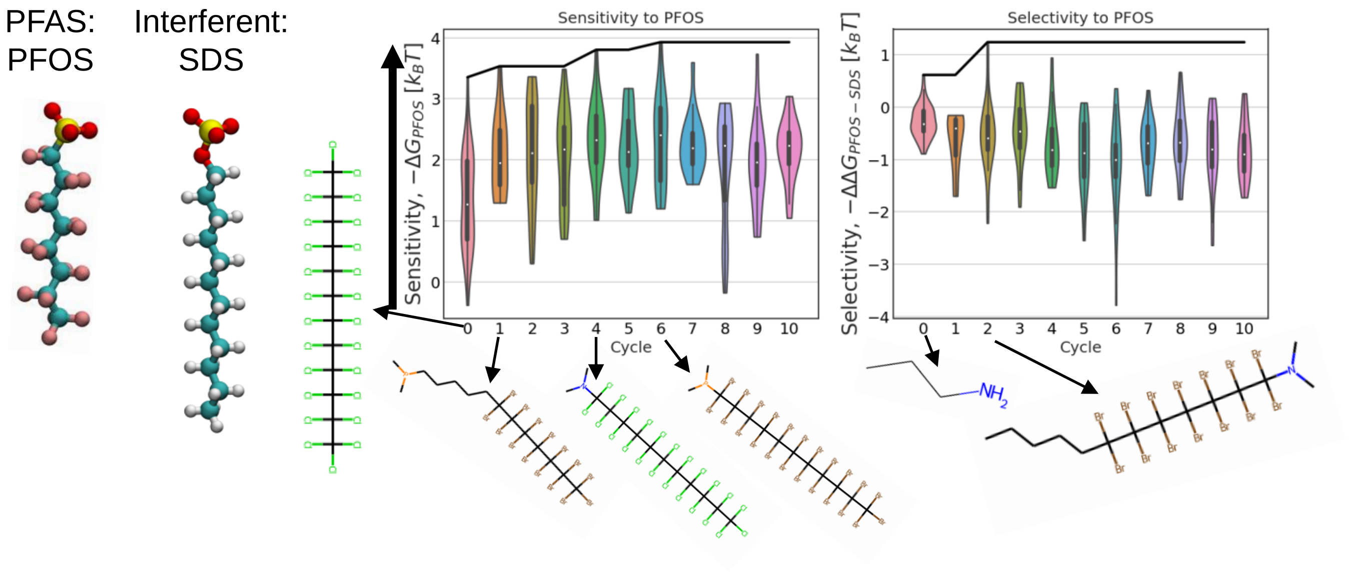


Using molecular dynamics simulations with enhanced sampling and machine learning, we develop a high-throughput screening approach to find optimal probes.

Dasetty et al., JCED 68 *(12), 3148-3161, 2023.*

DISCOVERED OPTIMAL PROBES

Longer probes are generally more sensitive but not necessarily selective. Halogenation and cationic head groups can improve selectivity of probes to PFOS relative to SDS.



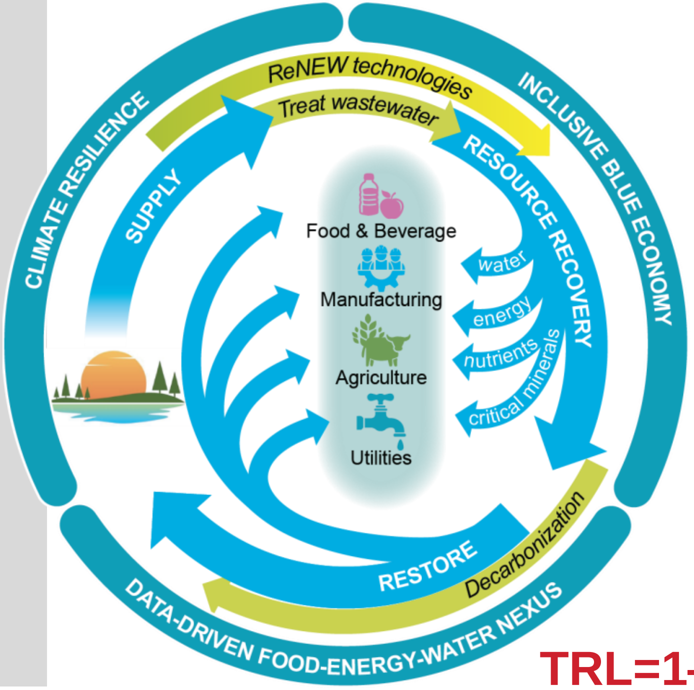
Dasetty et al., JCED 68 *(12), 3148-3161, 2023.*

NSF GREAT LAKES RENEW RIE

GREAT LAKES ReNEW

VISION

A circular water/ blue economy by converting waste into wealth through precision detection and separation of resources/ contaminants in wastewater.



TRL=1–9

ReNEW's INTEGRATED R&D AND TRANSLATION STRATEGY

Technology Integration

Testbeds: Intelligent Water Resource Recovery Systems

- Subsystem technology testbeds
- Scale up and manufacturing
- Systems analysis tools

Gaps/Barriers

- Scaleup of components
- Circularity
- Cost
- LC impact
- Policy and social

SCALABILITY SUPPORT

TECHNOLOGY ELEMENTS

Enabling Technologies

C1: Selective Separation

- High-throughput material design
- Selective design
- AI/ML and modeling

C2: Process technologies

- Selective process design
- Process simulation and mechanistic understanding
- Process optimization

C3: RT Sensors/Sensor Networks

- Sensing platform design
- Sensor selectivity and molecular probe design
- Real-time sensing, analytics, and control

Gaps/Barriers

- High throughput design
- Scaleable manufacturing
- Co-design
- Modular design
- AI and ML
- Modeling

REQUIREMENTS

PRODUCTS & OUTCOMES

ENVIRONMENT/ MARKETPLACE

Community

Utility

Industry

OUR TEAM

THANK YOU

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