Pilot scale removal of pathogens and emerging contaminants from graywater: Overcoming the barriers to reuse

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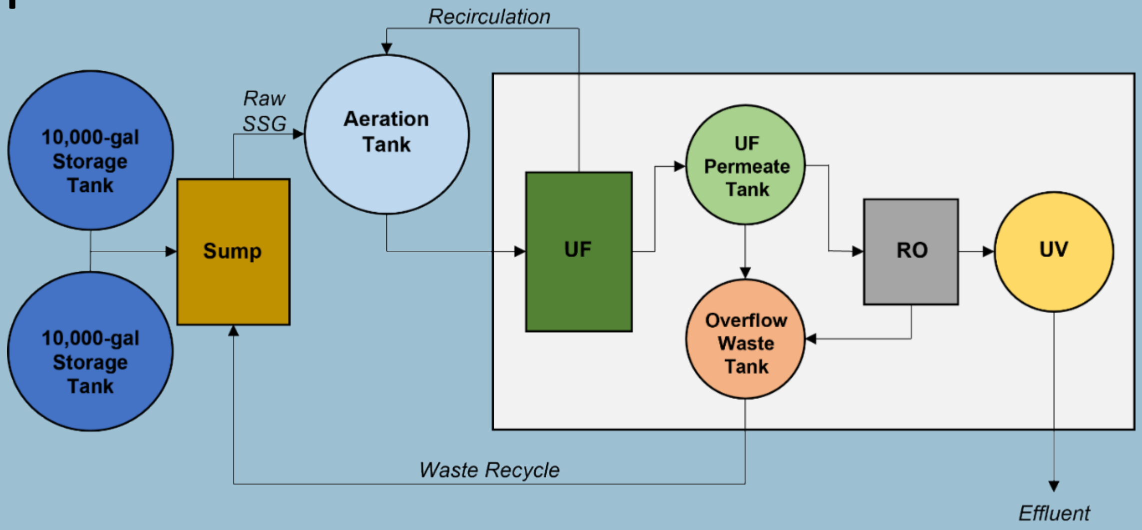
Unclassified

Water Scarcity

- 4 billion people experience water scarcity at least 1 month per year, with 2 billion people living in countries without adequate water supply
- Water reuse MUST be considered to help address the water supply issue
    - Graywater reuse
- Distributed systems can target specific opportunities for reuse to offset costly modifications to infrastructure
    - UF/RO/UV



Lalley *et al.*; *J Water Proc Engineering* (2023); 53, 103736

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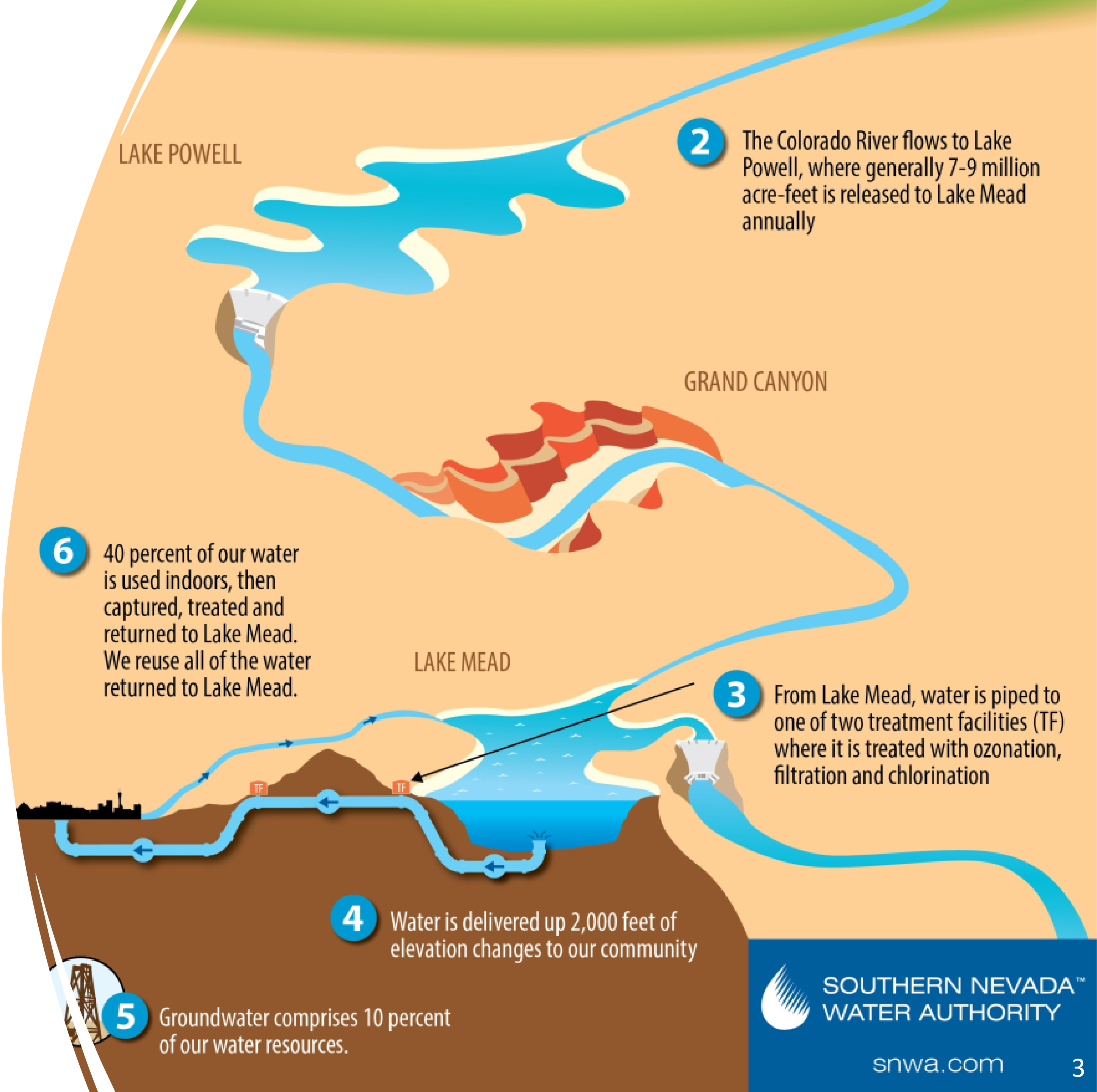
Large Scale Graywater Reuse: Las Vegas

- 100% of showers and faucets recycled through Las Vegas Wash back into Lake Mead.(pop. 5K to 2M)



Pilot Scale Decentralized Treatment

- Why Graywater?
- Navigating the Regulatory Criteria for Re-use
- Chemistry of Source Separated Graywater (SSG)
- Unit Operations for Source Separated Graywater (SSG)
- Challenges of Micropollutants and Emerging Contaminants

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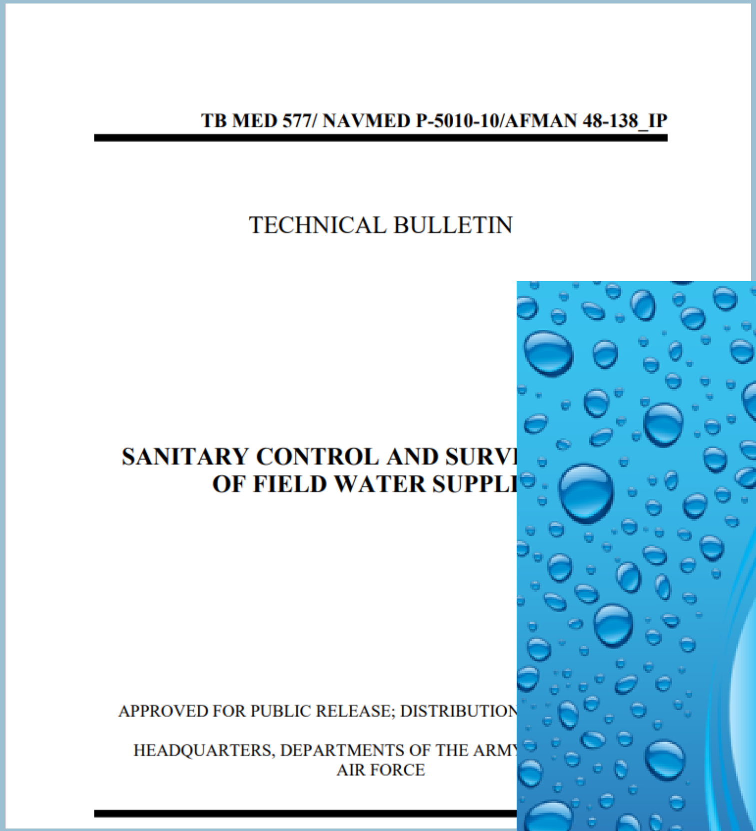
“Tapping” into Graywater

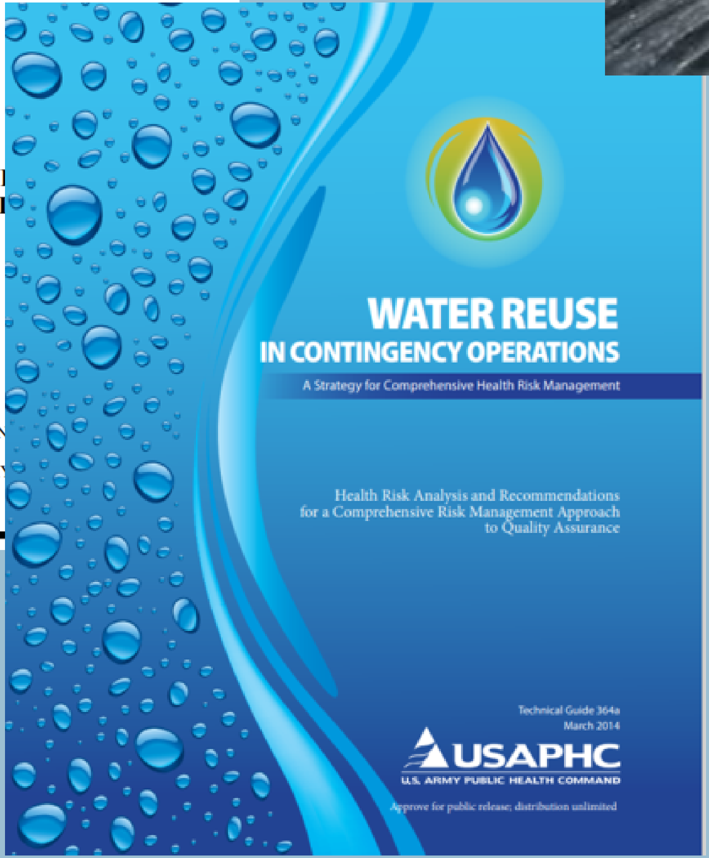

TB MED 577/ NAVMED P-5010-10/AFMAN 48-138_IP

TECHNICAL BULLETIN

SANITARY CONTROL AND SURV
OF FIELD WATER SUPPL

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION

HEADQUARTERS, DEPARTMENTS OF THE ARMY
AIR FORCE


WATER REUSE
IN CONTINGENCY OPERATIONS

A Strategy for Comprehensive Health Risk Management

Health Risk Analysis and Recommendations
for a Comprehensive Risk Management Approach
to Quality Assurance

Technical Guide 364a
March 2014

USAPHC
U.S. ARMY PUBLIC HEALTH COMMAND

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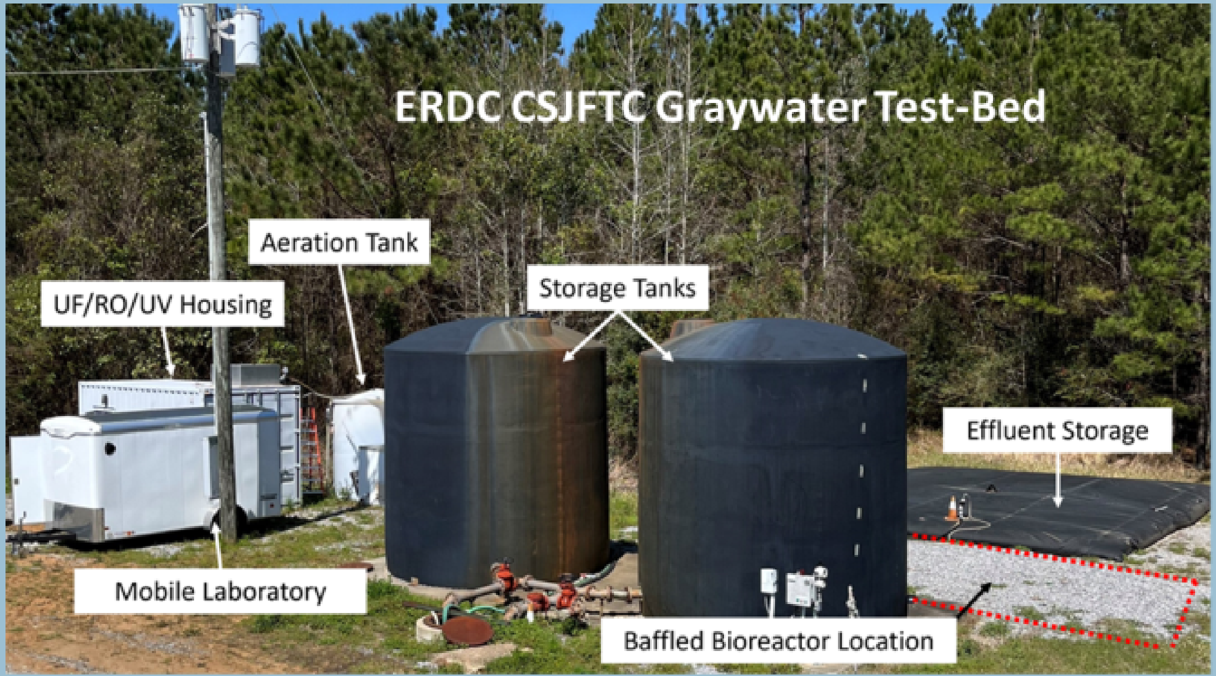

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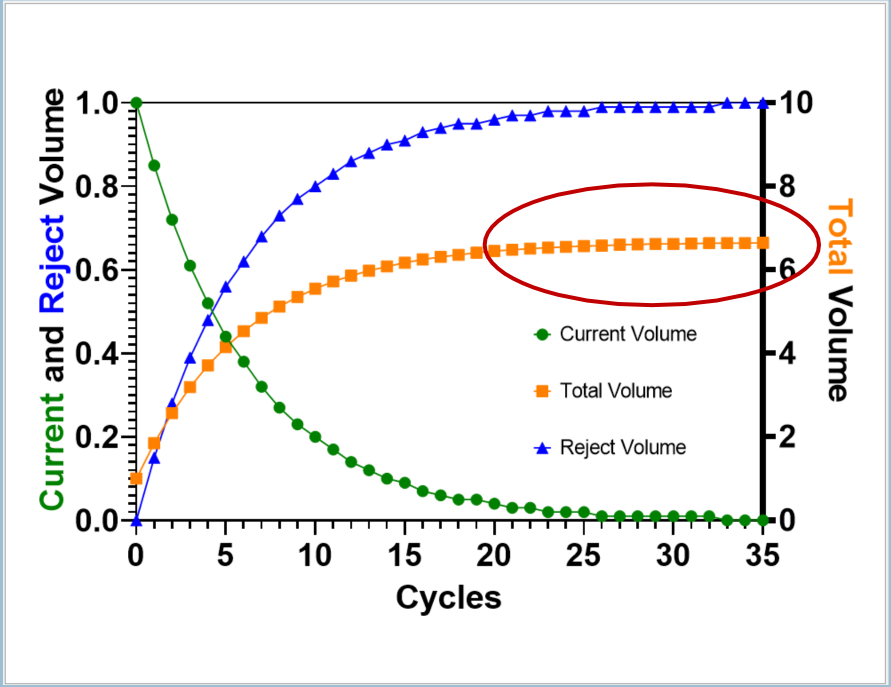
Membranes as a technology requirement for graywater reuse

Recovery Rate	Volume Multiplier
50%	2.0
60%	2.5
70%	3.33
75%	4.0
80%	5.0
85%	6.65

The estimated concentration of rejected compounds can be calculated using Equation 1.

$$C_r = \frac{C_i - C_p}{1 - R}$$

C_r = concentration in the reject stream
C_i = concentration in the influent
C_p = concentration in the permeate stream
R = water recovery rate



Water volume multiplier for 85% = 6.65!

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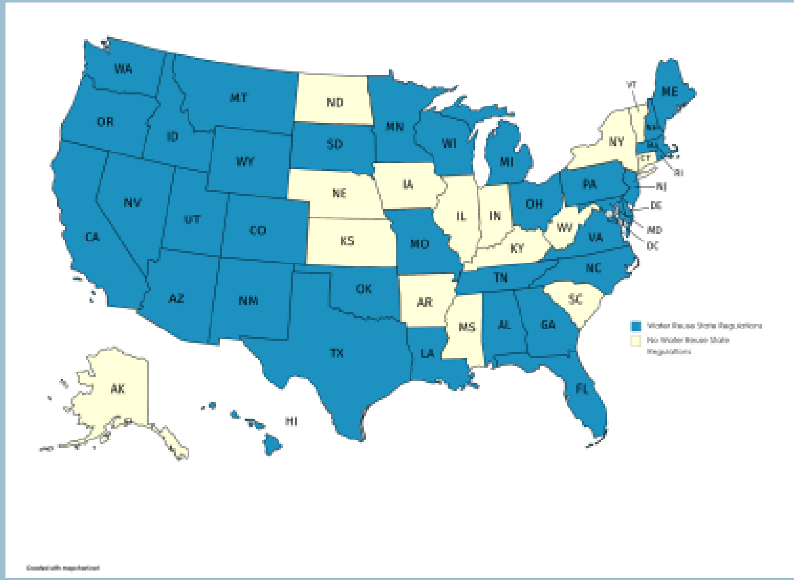
Lalley, J. *et al.* Source separated graywater: Chemistry, unit operations, and criteria towards re-use. *Journal of Water Process Engineering* **53** (2023).

Navigating the Regulatory Criteria for Re-use

Criteria	Value	Units
Total Coliform	< 2.2	CFU/100 mL
Fecal Coliform	< 2.2	CFU/100 mL
E. Coli	< 1	CFU/100 mL
Total Nitrogen	< 10[a]	mg-N/L
TSS	<5	mg/L
Turbidity	<1[b]	NTU
BOD	<2	mg/L
Free Residual Chlorine	1-4	mg/L
Chlorine Disinfection Contact Time	>15	Min
UV Transmittance	>90	% at 254 nm
pH	6.5-8.5	



- Values proposed based on CONUS standards for: toilet flushing, laundry, fire fighting, vehicle washing, dust suppression, and industrial uses
- Proposed treatment goals used for system evaluation based on published non potable reuse standards from 35 states
- Comprehensive data analysis of the 35 states with published reuse standards

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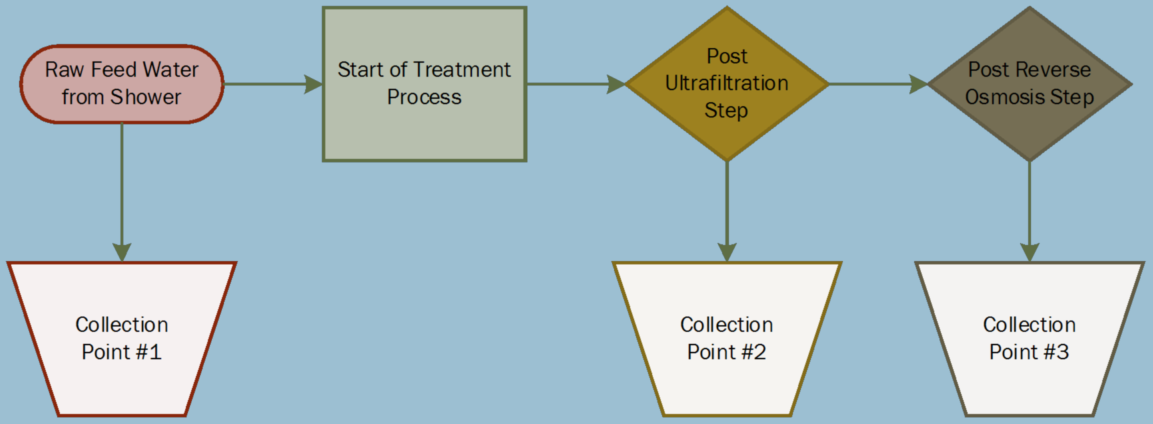
Chemistry of Source Separated Graywater (SSG)

	Parameter	Reference Method
Metals (Total) by EPA 200 Series Methods	Hardness as $CaCO_3$	SM22 2340B-2011
Wet Chemistry Analysis	Alkalinity	SM22 2330B-2011
	Ammonia as N	EPA350.1 R2.0
	BOD	SM22 5210B-2011
	COD	SM22 5220D-2011
	Nutrients	EPA300.0 R2.1
	MBAS	SM22 5540C-2011
	Phosphorus, Total	SM 4500-PE
	Specific Conductance	SM22 2510B-2011
	TDS	SM22 2540C-2011
	TKN as N	EPA351.2 R2.0
	TOC	SM22 5310C-2011
	Turbidity	EPA180.1
Microbiological Analysis	E. Coli (MPN)	Colilert 18 QT
USGS National Water Quality Laboratory	Micropollutants	TMR book 5, chap B4 (Zaugg, Smith and Schroeder 2007)



ERDC CSJFTC 1)Raw, 2) Primary Effluent 3) Final Product Water

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Chemistry of (SSG): WW Strength

Raw graywater chemistry during the two Battalion Training events (post human contact)

ANALYTE	Average	Std Dev	Min	Max
COD (mg/L)	102	79.8	17.6	273
BOD (mg/L)	49.6	33.9	11.3	134
MBAS (mg/L)	0.74	0.77	< 0.10	2.50
TOC (mg/L)	22.2	16.7	6.3	54.5
NH_3 (mg-N/L)	9.94	5.78	1.92	22.6
Nitrate (mg-N/L)	0.58	0.81	< 0.10	2.89
PO_4 (mg/L)	5.64	2.55	2.34	10.9
TDS (mg/L)	645	251	351	1230
Turbidity (NTU)	19.1	14.2	1.18	45.2
E. coli (MPN/100mL)	1259*	1145	5	2420*

* These values are skewed low due to the upper limit of the analytical method being reached.

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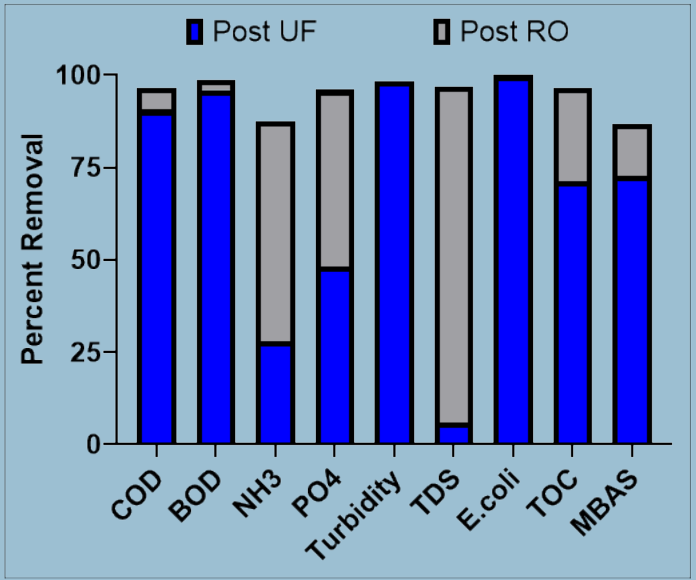
Griggs et. al "Employing Reverse Osmosis and Ultrafiltration Treatment Systems for Treatment of Source Separated Graywater." 2024. *ESTCP ER-201632*

Unit Operations for (SSG): UF-RO

Reverse Osmosis Results from both Battalion Events

Analyte	Canadian Average	NMCB Average	Combined Average
COD (mg/L)	< 10.0	< 10.0	< 10.0
BOD_5 (mg/L)	< 0.2	< 0.2	< 0.2
MBAS (mg/L)	< 0.10	< 0.10	< 0.10
TOC (mg/L)	< 1.0	< 1.0	< 1.0
NH_3 (mg-N/L)	1.04	1.23	1.15
Nitrate (mg-N/L)	0.12	0.12	0.12
PO_4 (mg/L)	0.05	0.50	0.31
TDS (mg/L)	15	21	19
Turbidity (NTU)	< 0.50	< 0.50	< 0.50
E. coli (MPN/100mL)	0	0	0

Removal Efficiencies of UF/RO from both Battalion Events



- The combined treatment train of UF and RO met all compliance metrics for all analytes of interest except ammonia in two samples and for phosphate in five samples.
- However, since ammonia and phosphate are not included in any published re-use criteria, all the water treated met standards for un-restricted reuse where guidelines are established.

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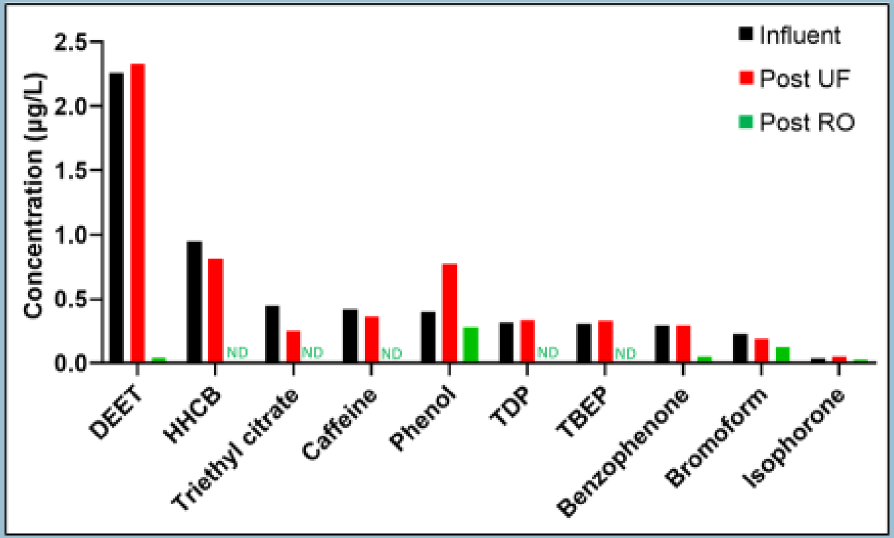
Micropollutants

- Personal care and pharmaceutical products (PCPP)
- Can get through current treatment technologies



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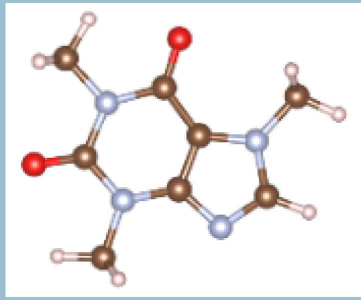
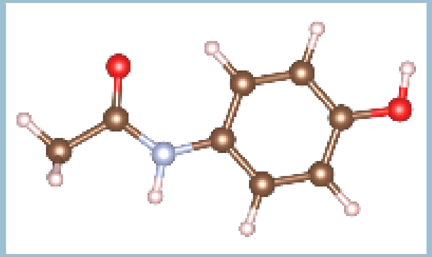
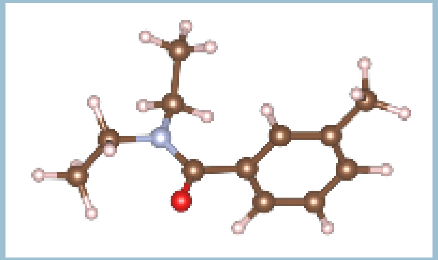
- Looking at 4 common micropollutants found in graywater



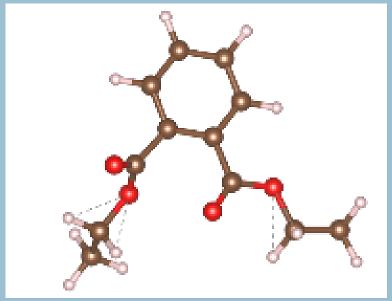
Caffeine



Acetaminophen (APAP)



N,N-diethyl-m-toluamide (DEET)



Diethyl phthalate (DEP)

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Potential Adsorbents: Graphene Nanoplatelets (GnPs) and Granular Activated Carbon (GAC)

XG Sciences C-750 Graphene

Applied Membranes Coconut shell GAC

- Graphene (G) is a 2D honeycomb network of sp^2 hybridized carbon
- Affordable and scalable material for water treatment applications
- GAC is a porous amorphous carbon and is a water treatment industry standard

Material	Total Pore Volume (cc/g)	Avg Pore Diameter (nm)	Mesopore Volume (cc/g)	Micropore Volume (cc/g)	BET Surface Area (m/g)
GnP	0.9602	1.341	0.698	0.166	646.0
GAC	0.3968	1.764	0.026	0.371	826.7

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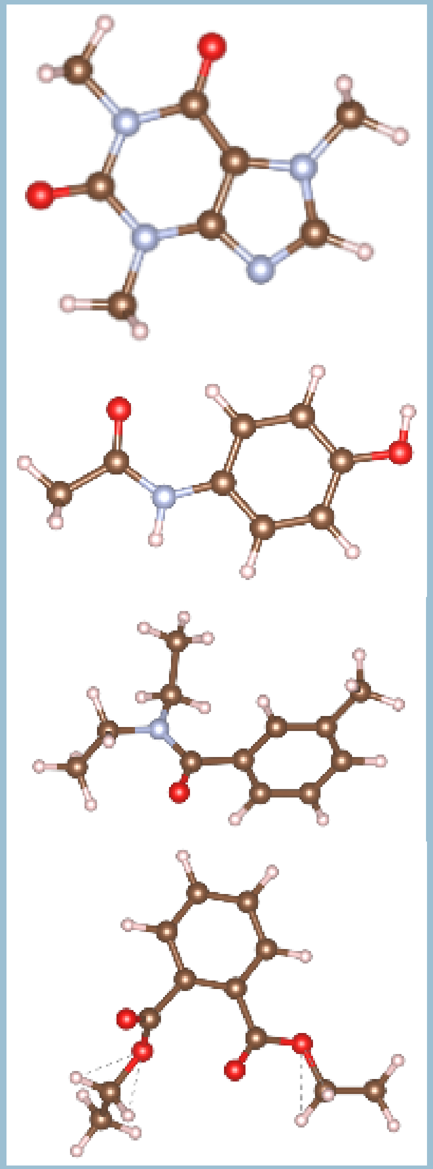
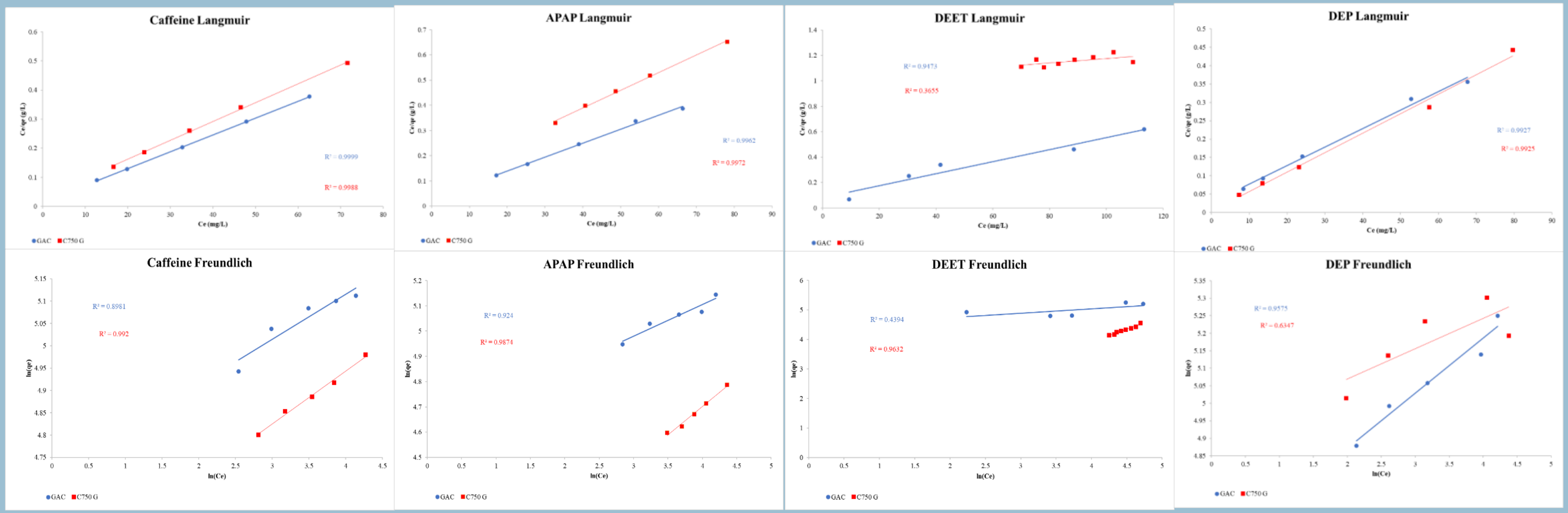
Roberts *et al.; J Haz Materials* (2023); 458,131737

Experimental Design

1. **Determine Micropollutant Adsorption Parameters**
   - Isotherm Modeling
     - Langmuir vs. Freundlich
   - Kinetic Modeling
     - Pseudo First Order
     - Pseudo Second Order (PSO)
2. **Determine Adsorption Mechanism**
   - Intraparticle Diffusion Model (IPD)
   - Capacity vs K_{ow}
   - Computational results
   - NMR studies



Adsorption Isotherm Modeling



Micropollutant	Adsorbent	Capacity Results $q_{e,max,exp}$ (mg/g)
Caffeine	GAC	**169.8**
	GnP	147.1
Acetaminophen	GAC	**172.2**
	GnP	123.8
DEET	GAC	**187.5**
	GnP	104.9
DEP	GAC	186.7
	GnP	**187.0**

- Langmuir fit was best in almost all cases.
- DEP GnP had a higher capacity than GAC.
- GAC had a higher capacity in all other cases.

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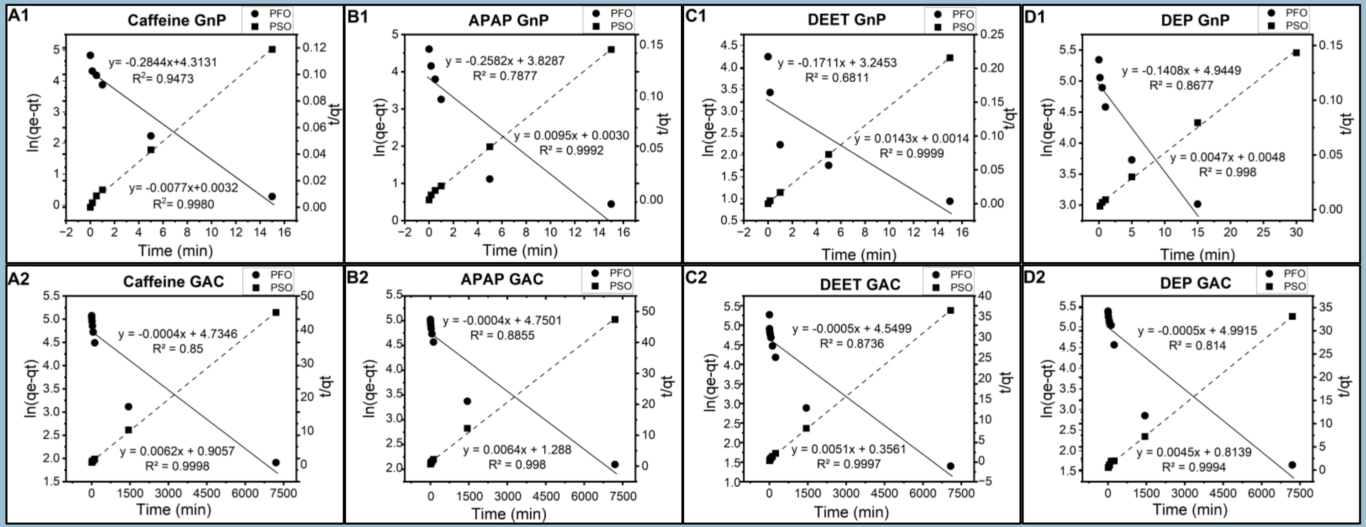
Kinetics Analysis



- PSO had the best fit.
- GnP rates were 2-4 orders of magnitude higher than for GAC.

Micropollutant	Adsorbent	Pseudo-Second Order	
		k_2 (g/mg/min)	R^2
Caffeine	GAC	4.24E-05	0.9998
	GnP	0.0185	0.9980
APAP	GAC	3.18E-05	0.9980
	GnP	0.0300	0.9992
DEET	GAC	7.30E-05	0.9997
	GnP	0.1460	0.9999
DEP	GAC	2.88E-05	0.9988
	GnP	0.0046	0.9980

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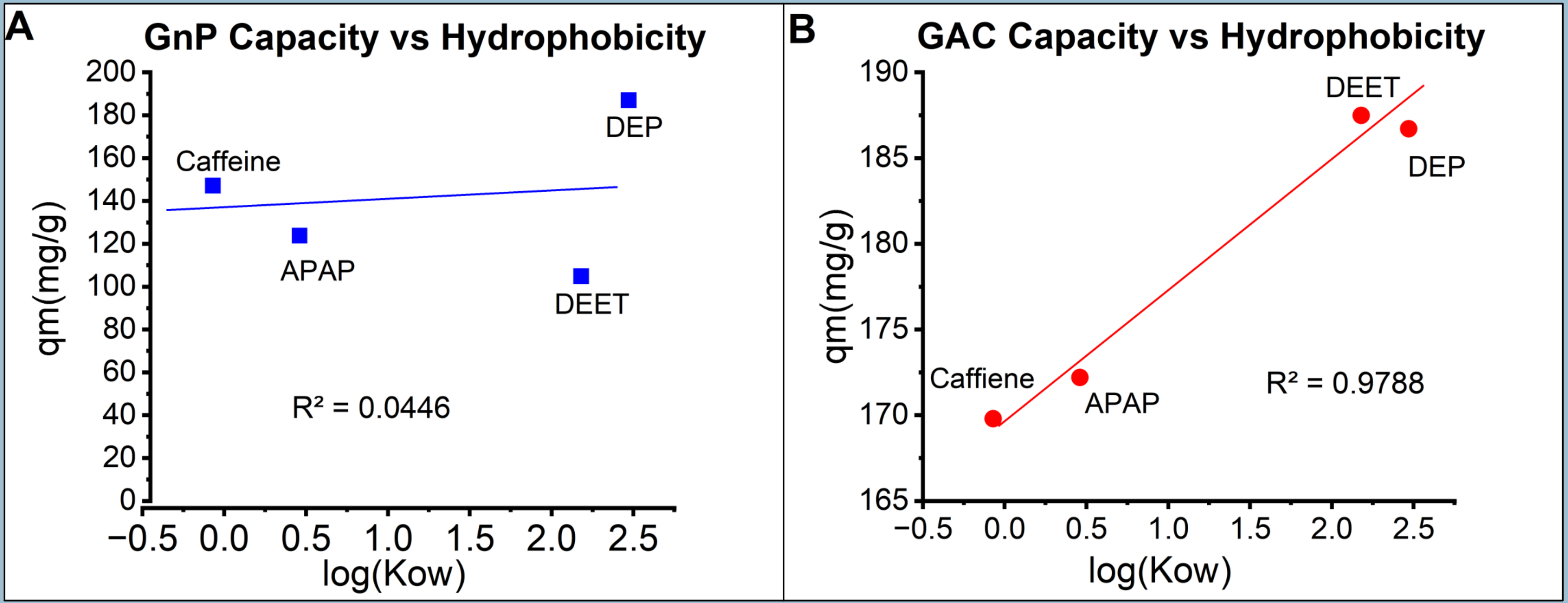
Mechanism Determination- K_{ow}



- No correlation between K_{ow} and capacity for GnP
- Positive correlation between K_{ow} and capacity for GAC

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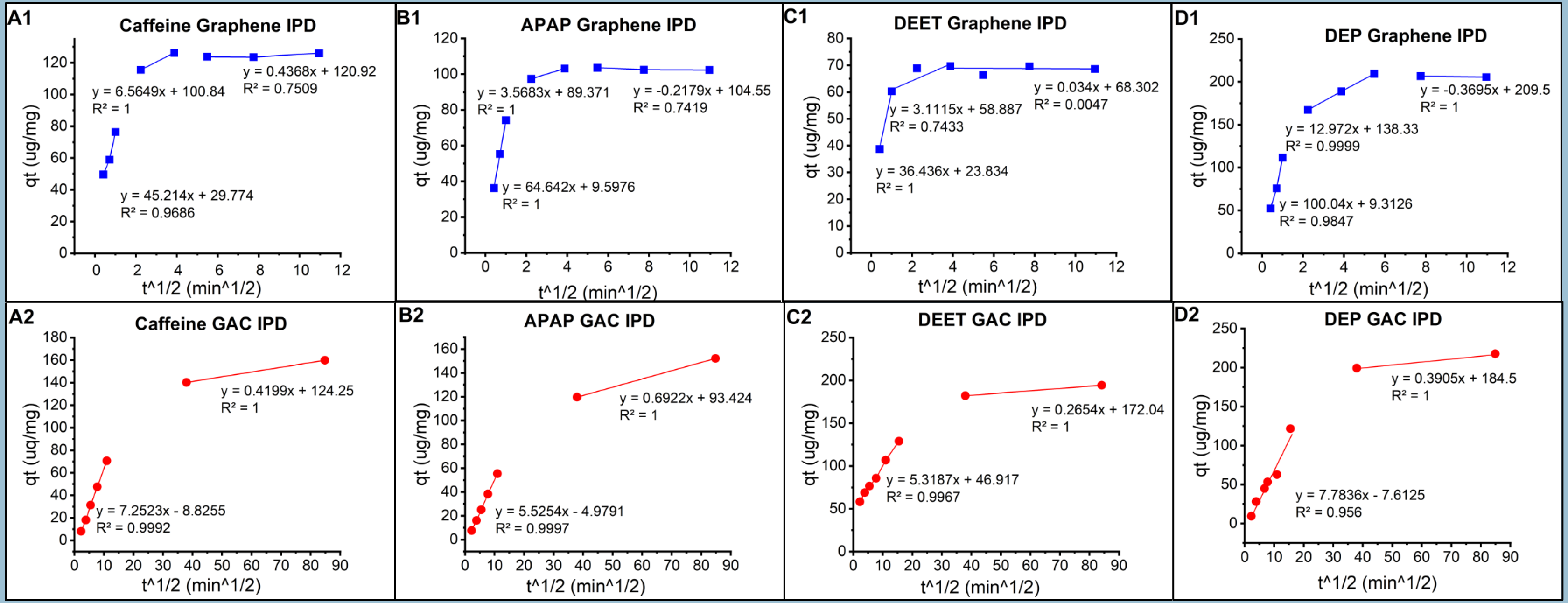
Mechanism Determination- IPD



Micropollutant	Adsorbent	$K_{p,1}$ (mg/g min$^{1/2}$)	R^2	$K_{p,2}$ (mg/g min$^{1/2}$)	R^2	$K_{p,3}$ (mg/g min$^{1/2}$)	R^2
Caffeine	GAC			7.25	0.9992	0.4199	1.00
	GnP	45.214	0.9686	6.56	1.00	0.4368	0.7509
Acetaminophen	GAC			5.525	0.9997	0.6922	1.00
	GnP	64.64	1.00	3.57	1.00	-0.218	0.7419
DEET	GAC			5.319	0.9967	0.2654	1.00
	GnP	36.44	1.00	3.112	0.7433	0.034	0.0047
DEP	GAC			7.783	0.956	0.3905	1.00
	GnP	100.04	0.9847	12.97	0.9999	-0.3695	1.00

Step 1 ($K_{p,1}$): Bulk Adsorption (interactions)

Step 2 ($K_{p,2}$): Mesopore Diffusion

Step 3 ($K_{p,3}$): Micropore Diffusion

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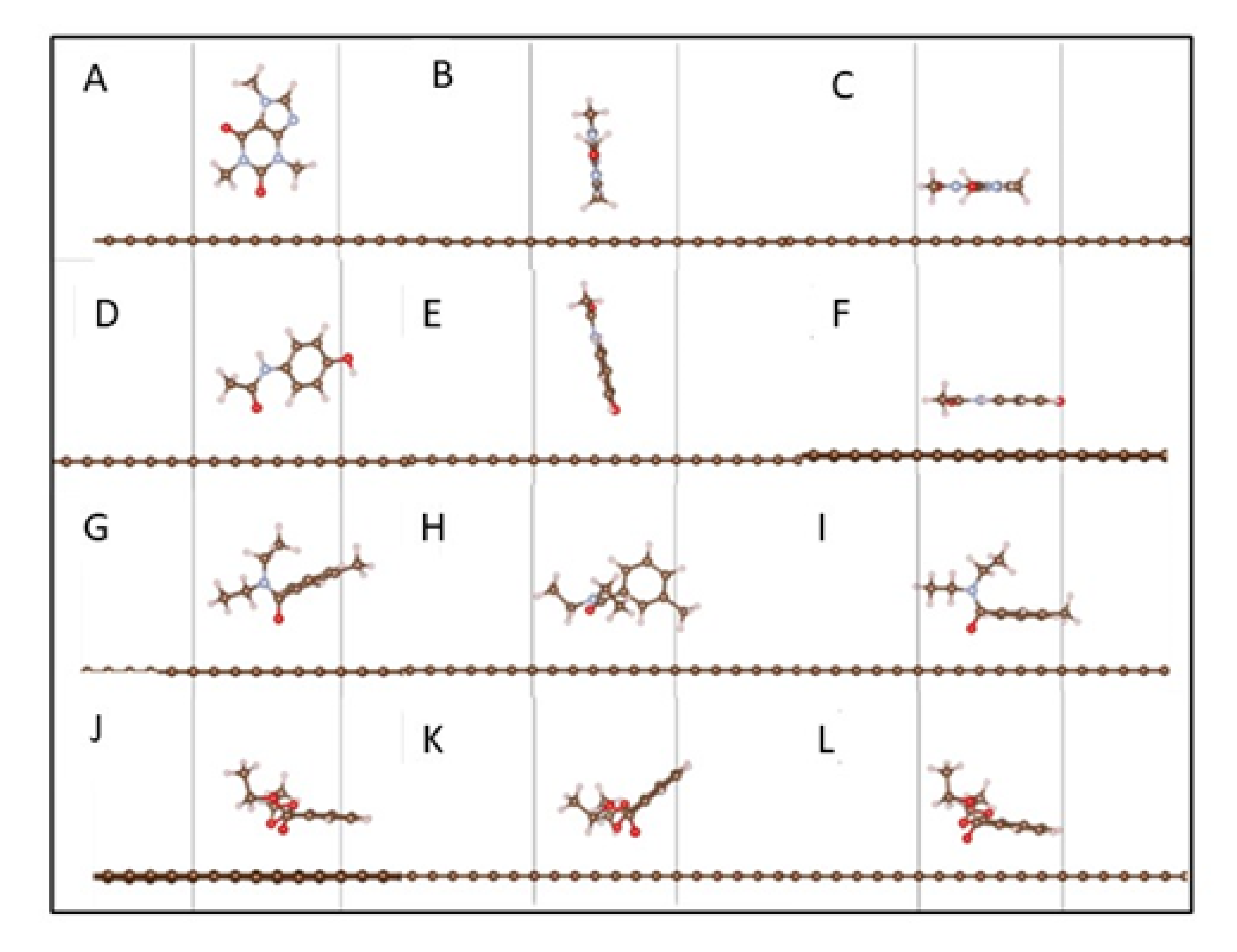
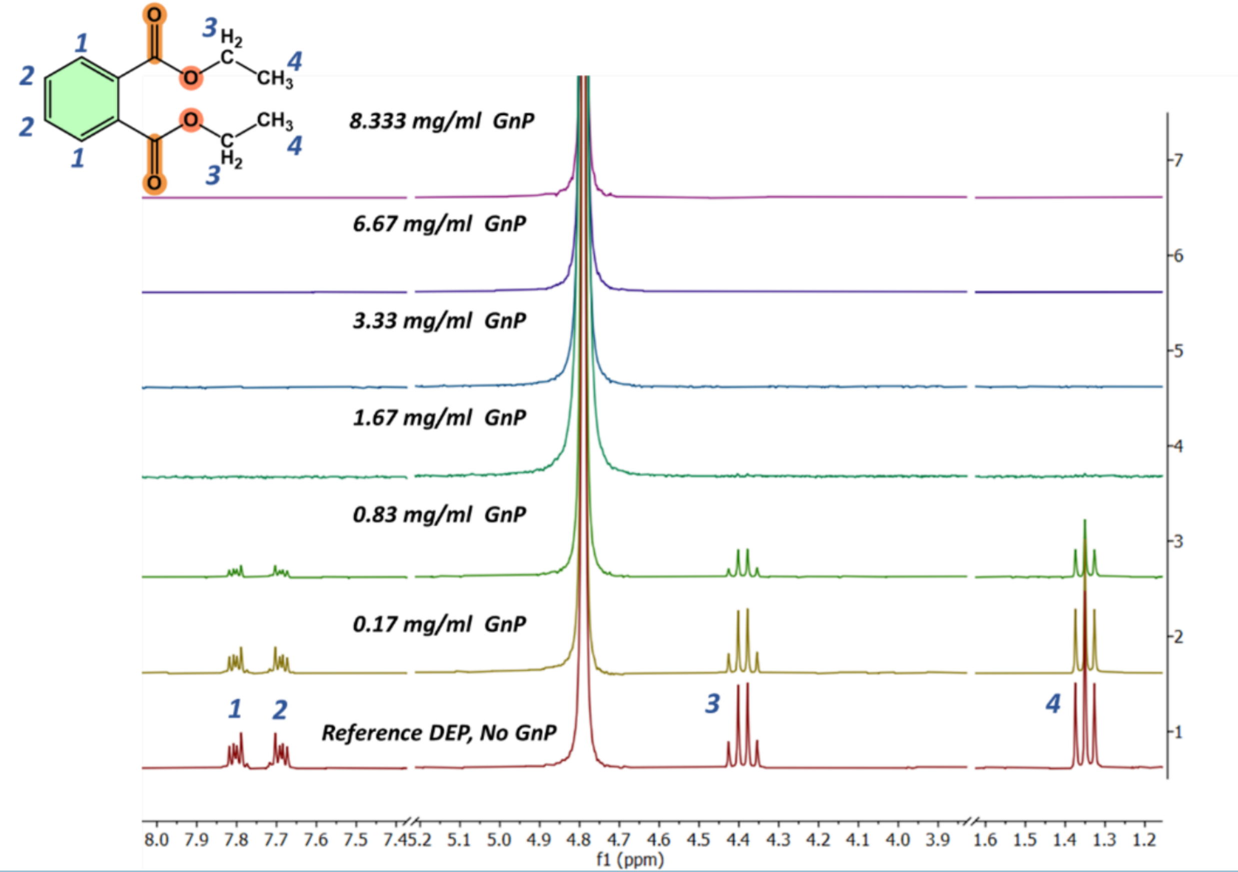
Mechanism Determination- Computational

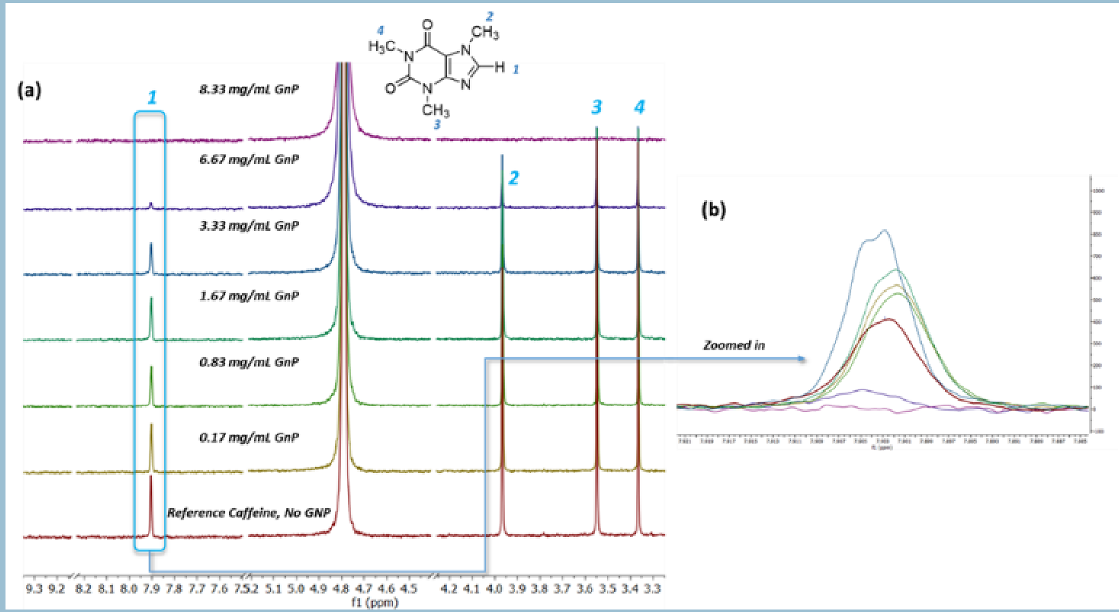
Micropollutants	Site	E_{ads}/eV
Caffeine	1-O	-0.38
	2-N	-0.35
	3-ring	-0.87
APAP	1-O1	-0.35
	2-O2	-0.29
	3-ring	-0.75
DEET	1-O	-0.41
	2-N	-0.65
	3-ring	-0.70
DEP	1-O1	-0.77
	2-O2	-0.65
	3-ring	-0.78



- Kinetics driven by π interactions
- Capacity driven by having multiple interaction sites

Mechanism Determination- NMR





- DEP is sequestered at low GnP concentrations- pore diffusion
- Caffeine requires much higher GnP concentrations to be removed

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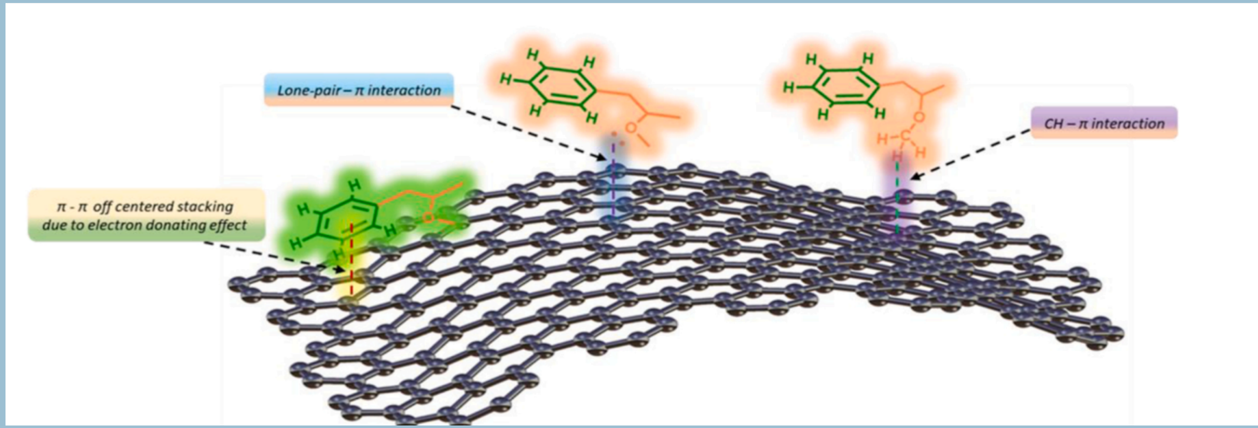
Conclusions



- **Overall Goal: Assess the efficacy of graphene nanoplatelets for micropollutant removal compared to GAC and gain insight to mechanism**
- GAC had a higher capacity in 3 out of 4 cases
- GnP was significantly faster in all cases
- π interactions are driving kinetics
- Ability to have other interactions and permeate the pores dictates capacity
- The Kow, IPD model, computational, and NMR results show that the performance is molecule- and structure-dependent.
- Using the selectivity afforded by GnP is a promising approach for tertiary treatment in a complex water matrices for next generation filtration media.

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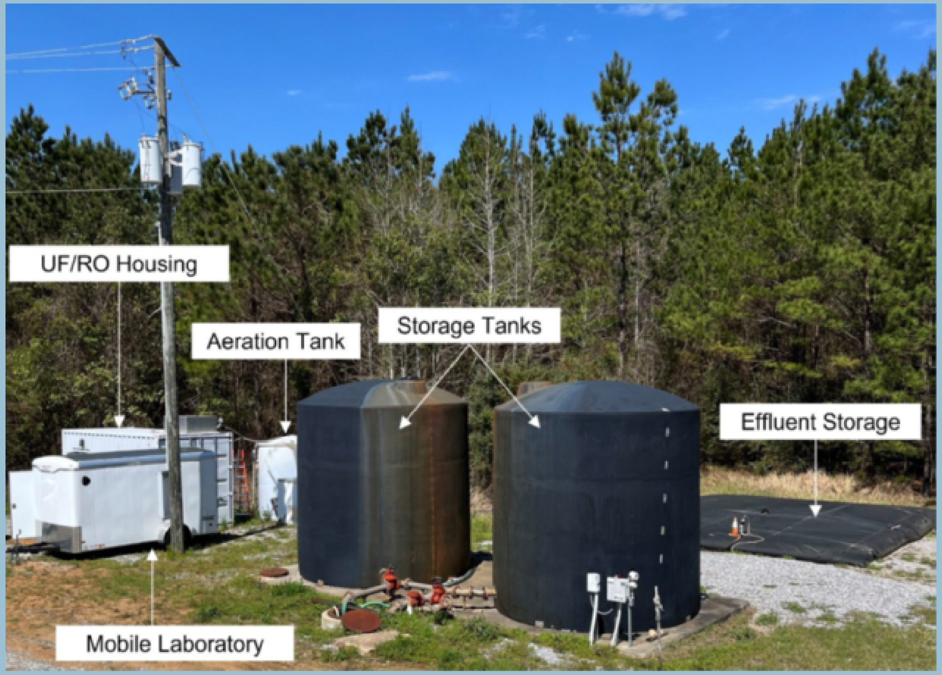
Future Directions

- ✓Use environmental water matrices and evaluate performance
- ✓Build prototype to implement in deployable treatment systems



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Questions?

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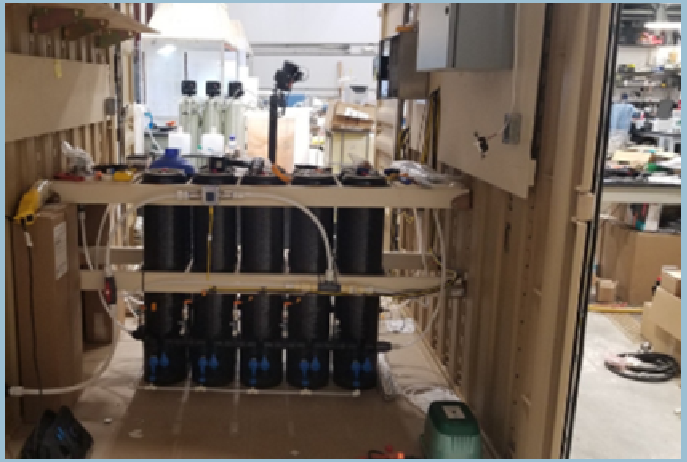
Matrix Considerations: Dilute Streams

- PFAS are emerging chemicals of environmental concern, which the Department of Defense (DoD) is investigating and responding to as appropriate.

- EEPA’s proposed rule identifies a maximum contaminant level (MCL) of 4 ppt or nanograms per liter (ng/L) for PFOA and PFOS.

- For drinking water and more dilute groundwater plumes media filtration will most likely be the solution. But ultimately spent media and solids will have to be managed as well.



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