Polymeric electrospun nanofiber mats (ENMs) as fast-equilibrium passive samplers for organic pollutants

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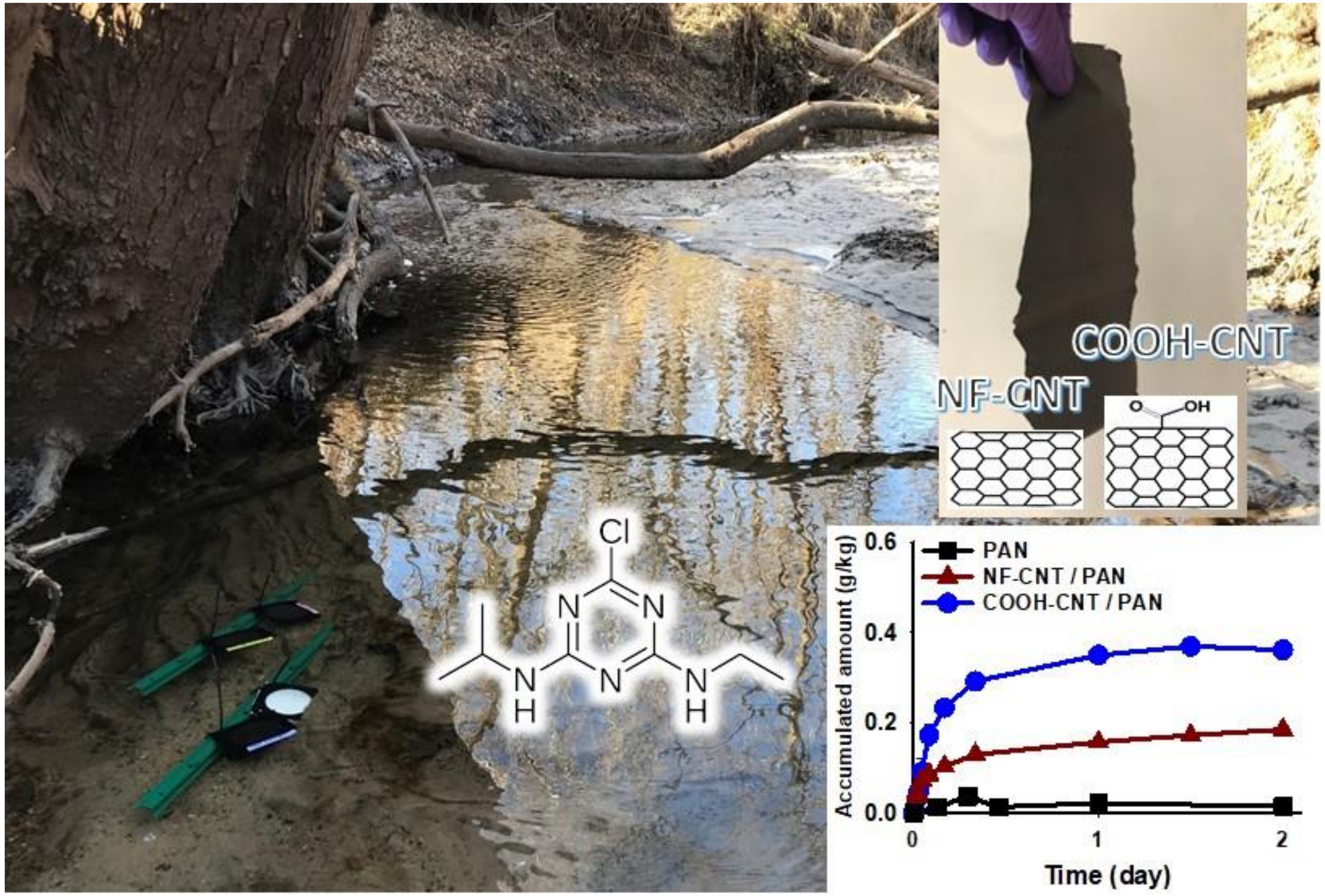


Background Information

- Determine presence & occurrence of pollutants (temporal & spatial) in the environment.

- Field measurements (air, water & sediment pore water):
  - Hydrophobic (legacy contaminants: PCBs, dioxins)
  - Hydrophilic (emerging contaminants: pesticides, personal care products)
  - Not trivial (↓ concentrations, fluctuations, $$)
  - Freely dissolved vs. total concentration
  - Active vs. passive methods
  - Integrative vs. equilibrium passive samplers (fast?)
  - Multi-target passive sampler?

- Assess risk and exposure, remediation alternatives.

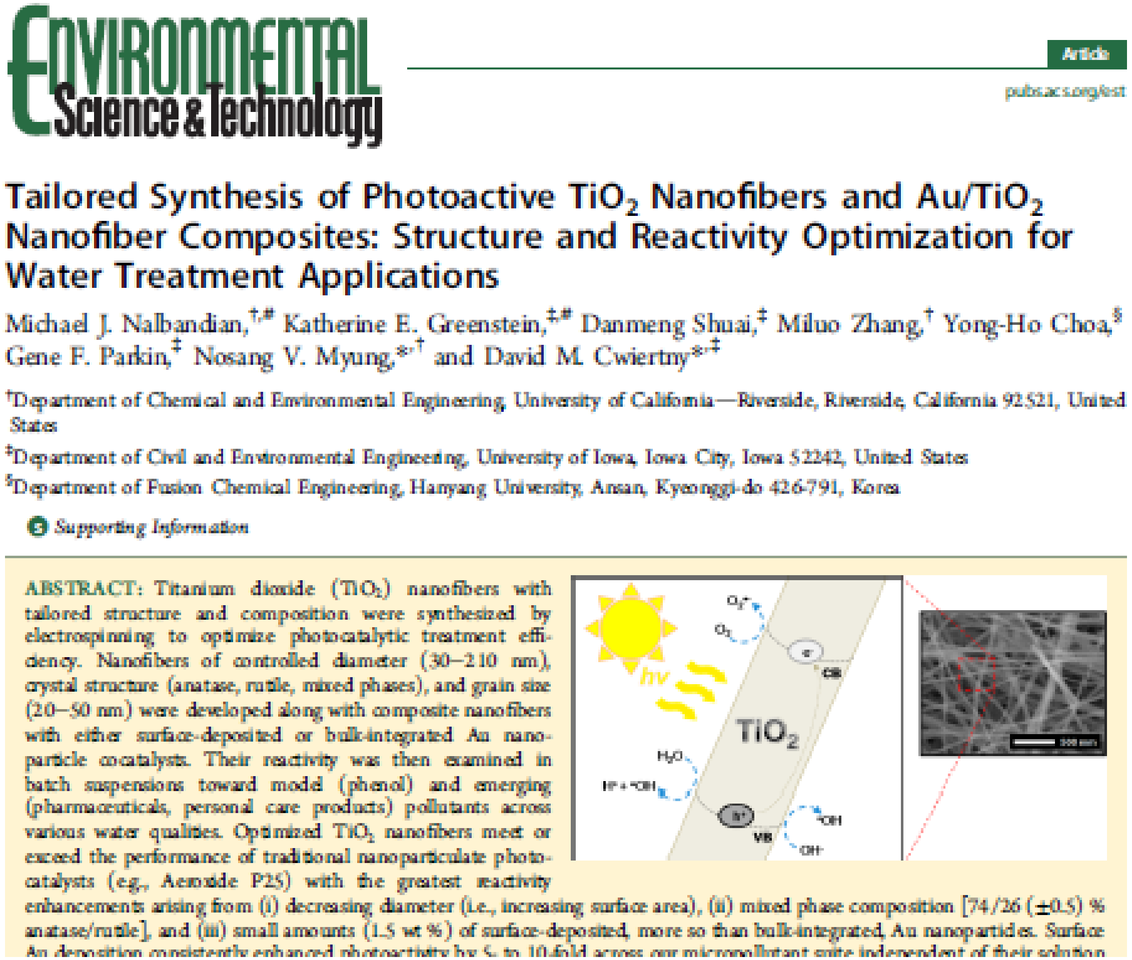
POCIS

PUF-PAS

Our approach: Development of a fast-equilibrium passive sampler for organic pollutants

Polymeric electrospun nanofiber mats (ENMs) initially used for water treatment applications: reactive/sorption water filtration.

But, can we utilize ENMs as a passive sampler media?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Tailored Synthesis of Photoactive TiO_2 Nanofibers and Au/TiO_2 Nanofiber Composites: Structure and Reactivity Optimization for Water Treatment Applications

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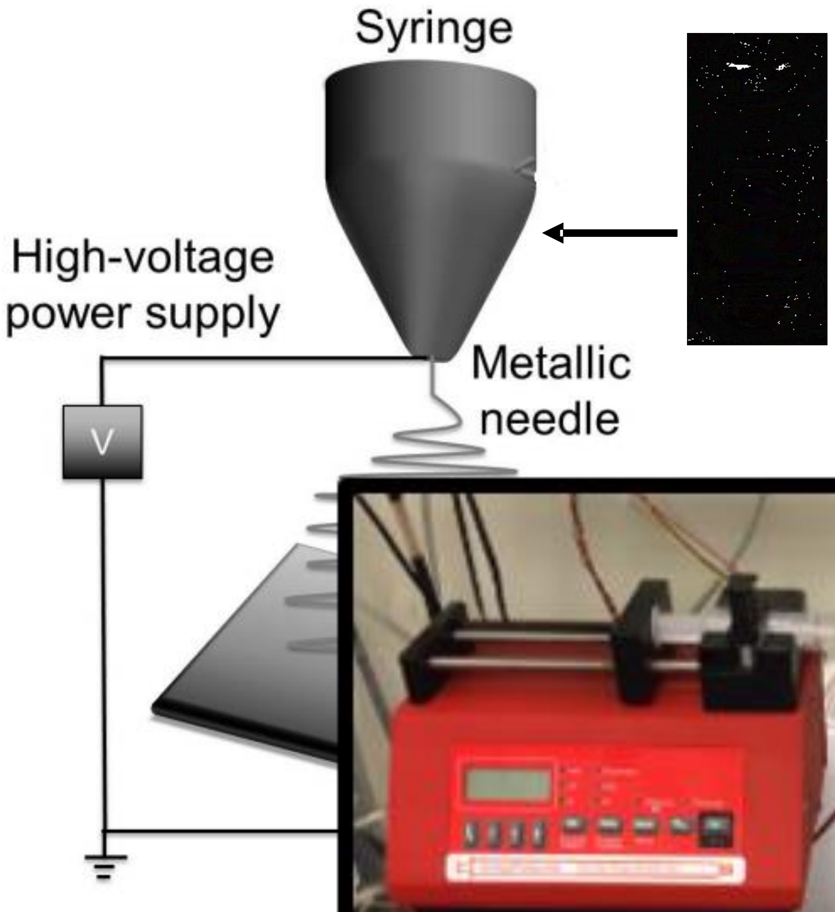
Supporting Information

ABSTRACT: Titanium dioxide (TiO_2) nanofibers with tailored structure and composition were synthesized by electrospinning to optimize photocatalytic treatment efficiency. Nanofibers of controlled diameter (30–210 nm), crystal structure (anatase, rutile, mixed phases), and grain size (20–50 nm) were developed along with composite nanofibers with either surface-deposited or bulk-integrated Au nanoparticle cocatalysts. Their reactivity was then examined in batch suspensions toward model (phenol) and emerging (pharmaceuticals, personal care products) pollutants across various water qualities. Optimized TiO_2 nanofibers meet or exceed the performance of traditional nanoparticulate photocatalysts (e.g., Aeroxide P25) with the greatest reactivity enhancements arising from (i) decreasing diameter (i.e., increasing surface area), (ii) mixed phase composition [74/26 (±0.5) % anatase/rutile], and (iii) small amounts (1.5 wt %) of surface-deposited, more so than bulk-integrated, Au nanoparticles. Surface Au deposition consistently enhanced photoactivity by 5- to 10-fold across our micropollutant suite independent of their solution

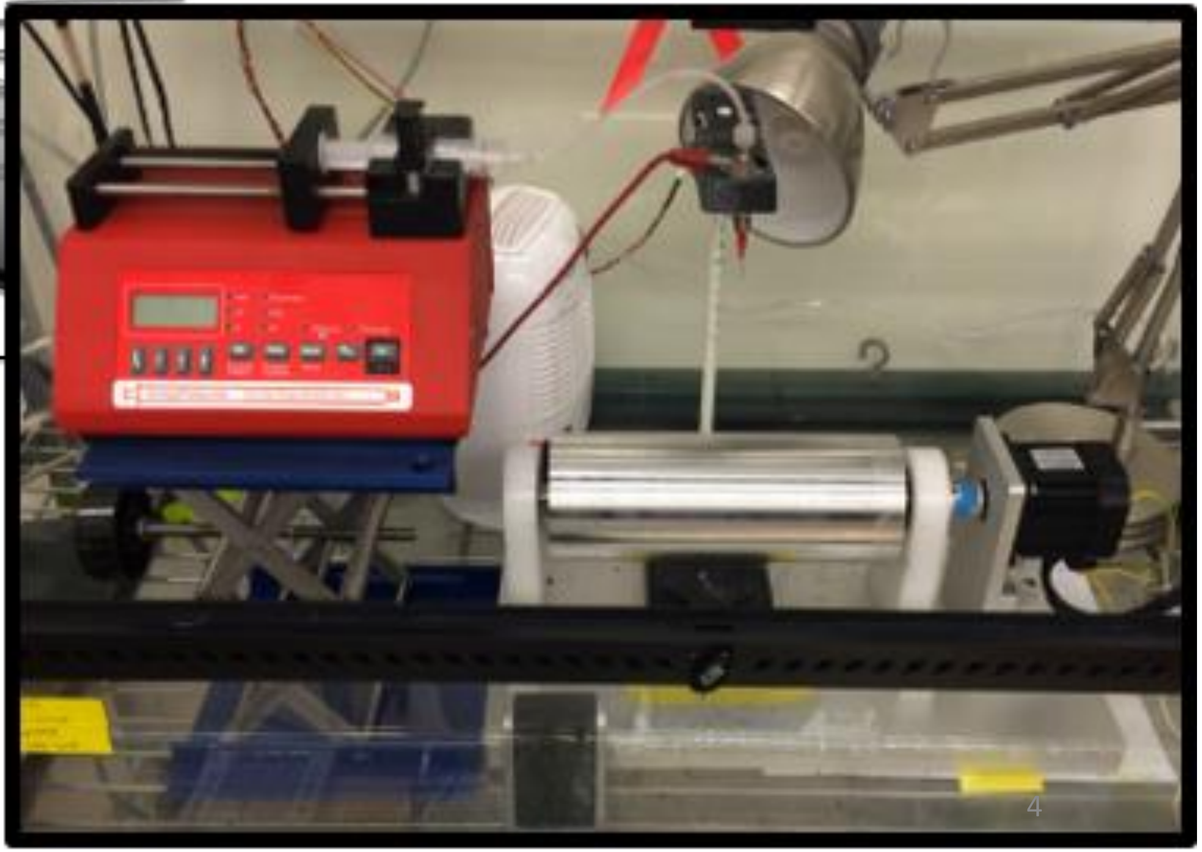
ENMs fabrication

Benefits of electrospinning:

- Ease of nanomaterial fabrication
- Tunable synthesis for tailoring diameter (i.e., surface area), thus high surface area to volume (↑ S/V) platform
- Variable composition from precursor solution (e.g., composite production)
- Industrially viable

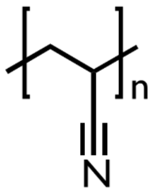


Polymer Precursor Solution

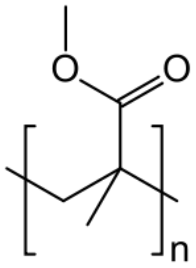


Synthesis ENMs using electrospinning

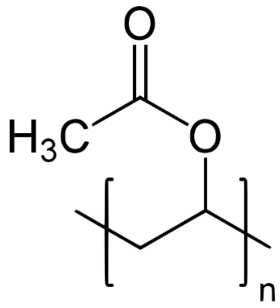
Hydrophilic Polymers



PAN
Polyacrylonitrile

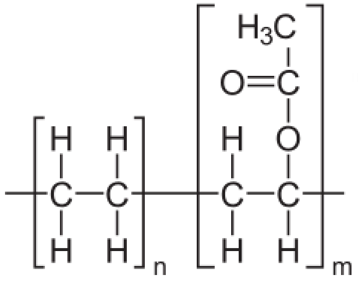


PMMA
Polymethylmethacrylate



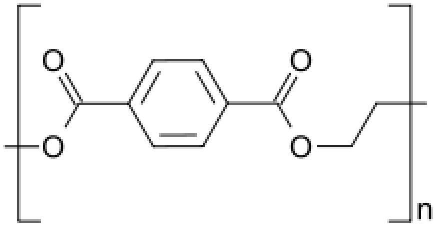
PVAc
Poly(vinyl acetate)

Co-Polymers

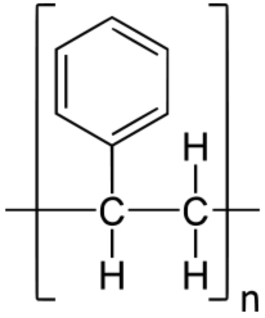


EVA
Ethylene-vinyl acetate

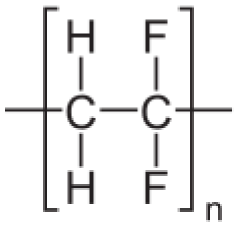
Hydrophobic Polymers



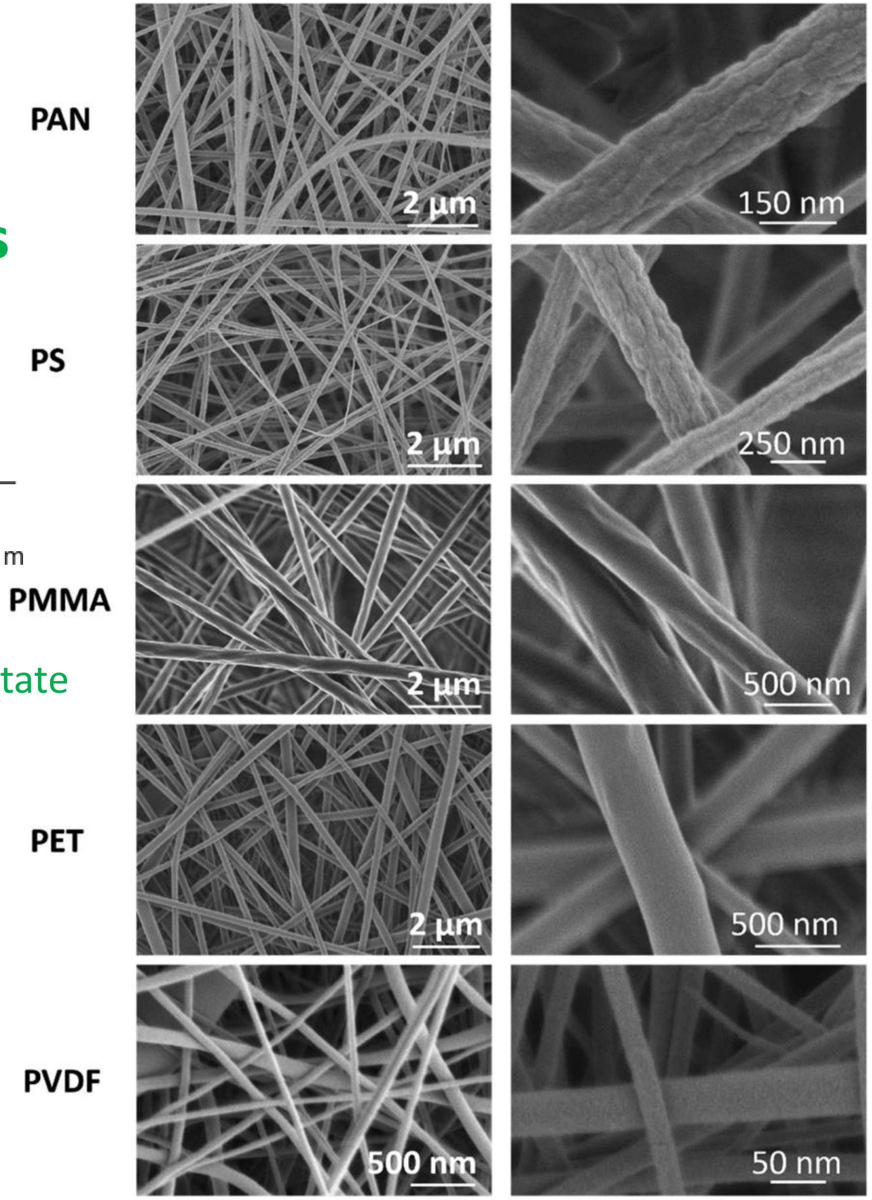
PET
Polyethylene terephthalate

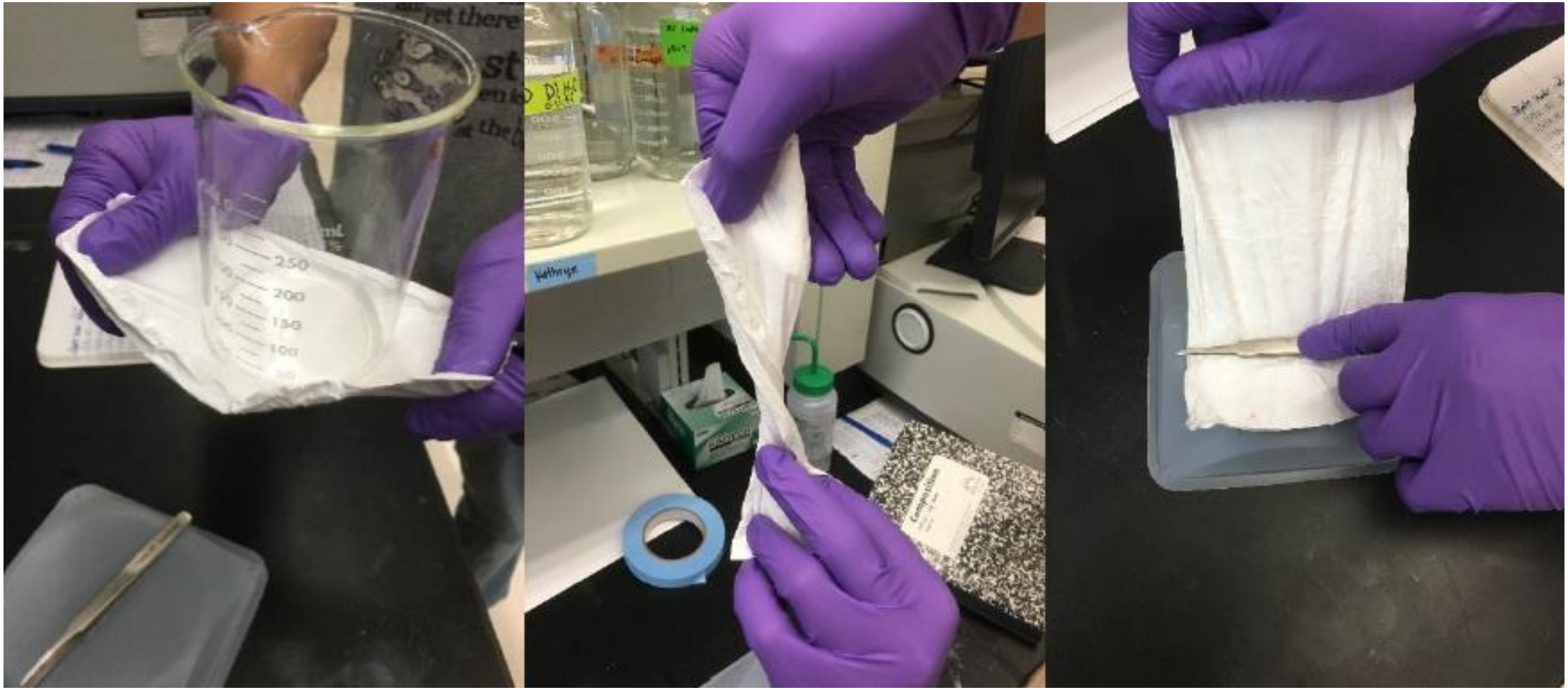


PS
Polystyrene



PVDF
Polyvinylidene fluoride




250
200
150
100

ENMs characterization & stability testing

Results: Electrospinning provides *reproducible* and tunable synthesis of various ENMs.

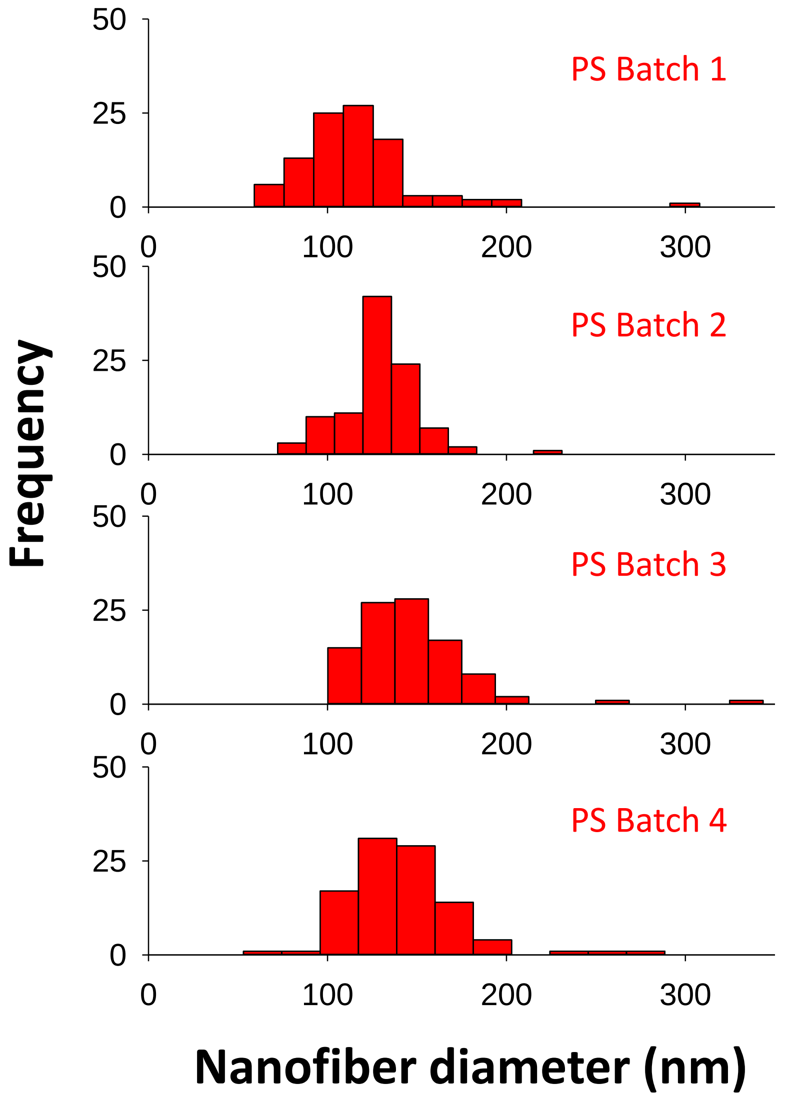
ENM nanofiber diameters:

- **PS = 130 ±30 nm (n = 4)**
- PET = 70 ± 23 nm (n = 3)
- PAN = 160 ±60 nm (n = 8)
- PMMA = 360 ± 60 nm (n= 7)

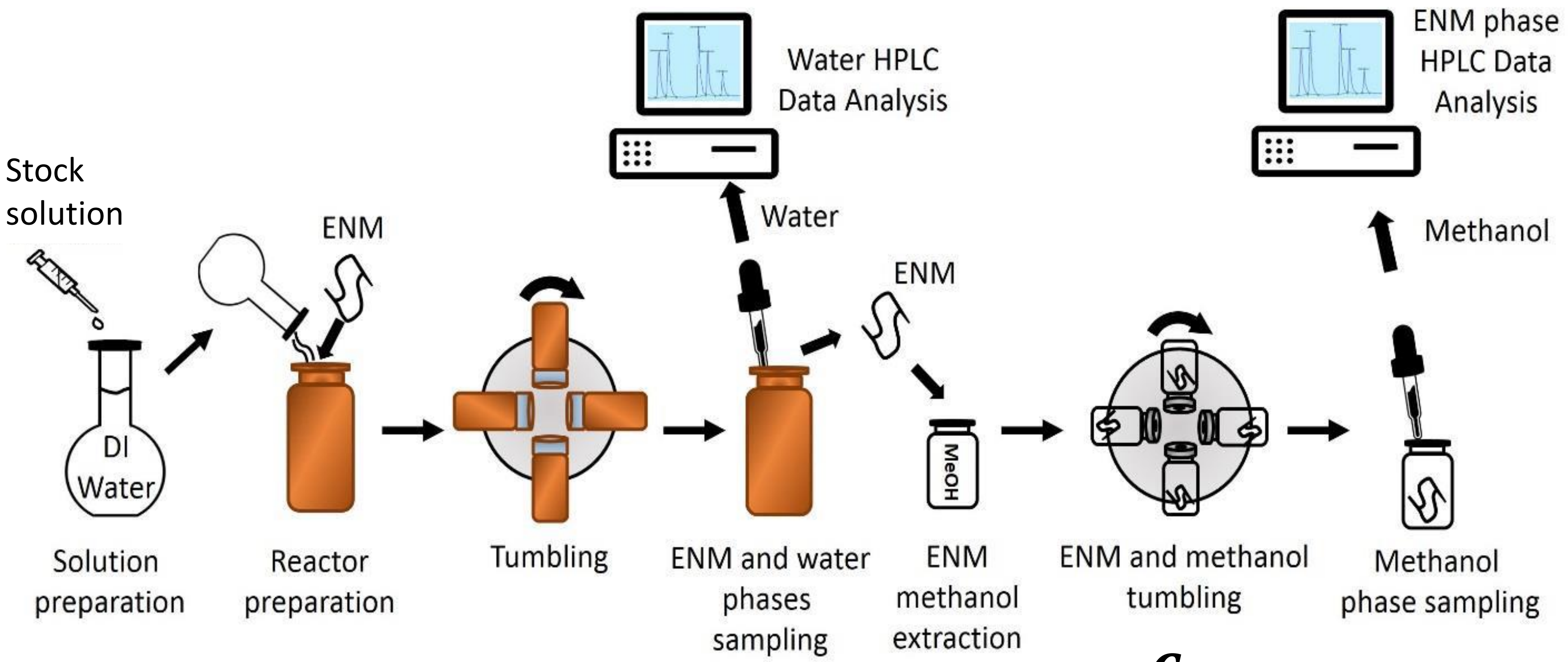
Diameter Tuning of PAN-ENM:

- 5% RH = 100 ± 20 nm
- 20% RH = 160 ± 60 nm
- 40% RH = 290 ± 90 nm

Surface area, water contact angle, porosity.



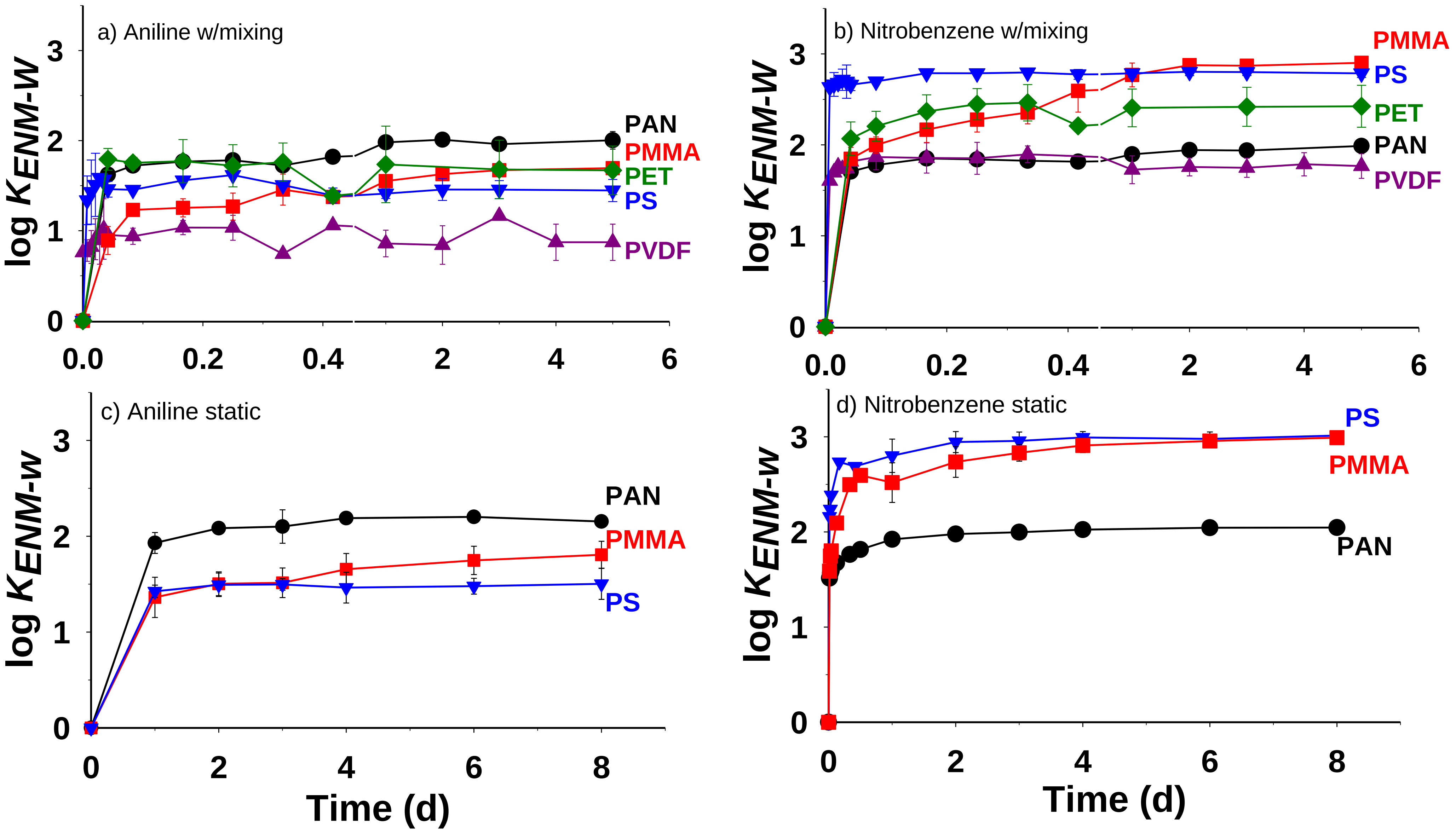
Batch uptake experiments of organic pollutants



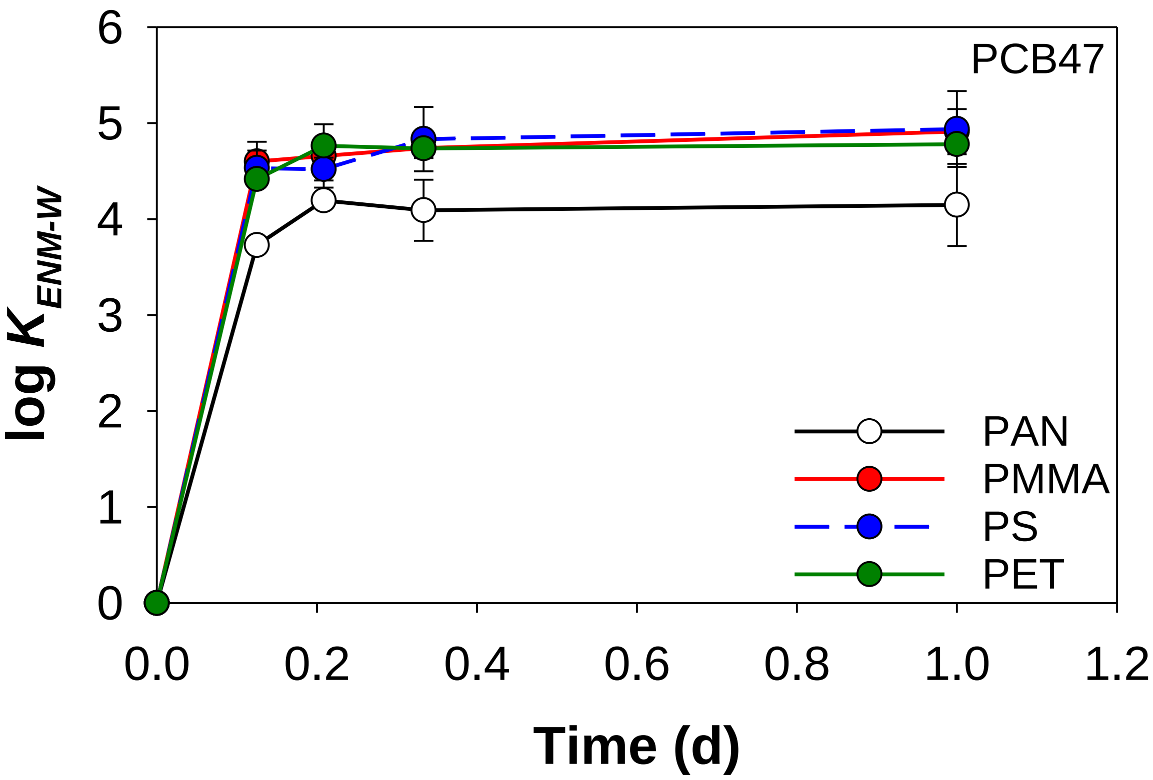
ENM-water partition coefficient: $$K_{ENM-w} = \frac{C_{ENM}}{C_W}$$

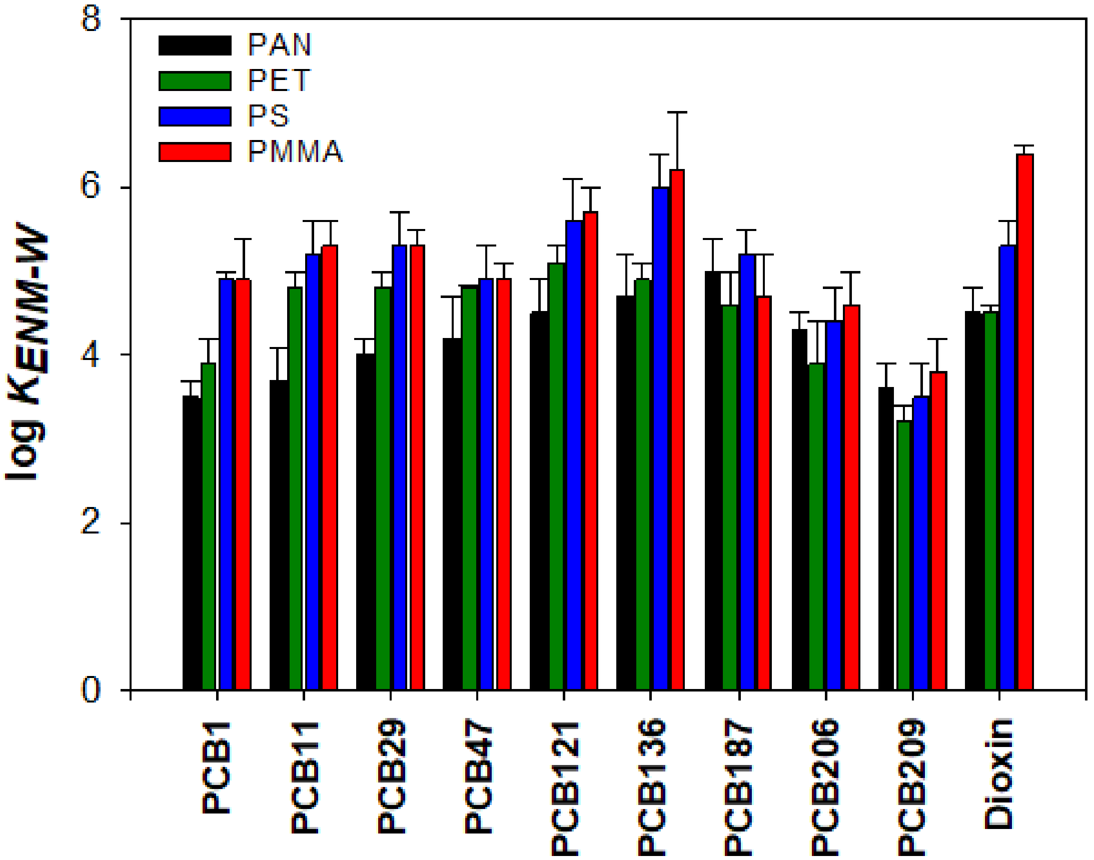
C_{ENM} and C_w are the measured concentration of the chemical in the ENM and aqueous phase, respectively

ENMs uptake results (aniline & nitrobenzene)



ENMs uptake and $K_{ENM\text{-}W}$ results (PCBs & dioxin)





Nitrobenzene uptake into PS as function of nanofiber diameter

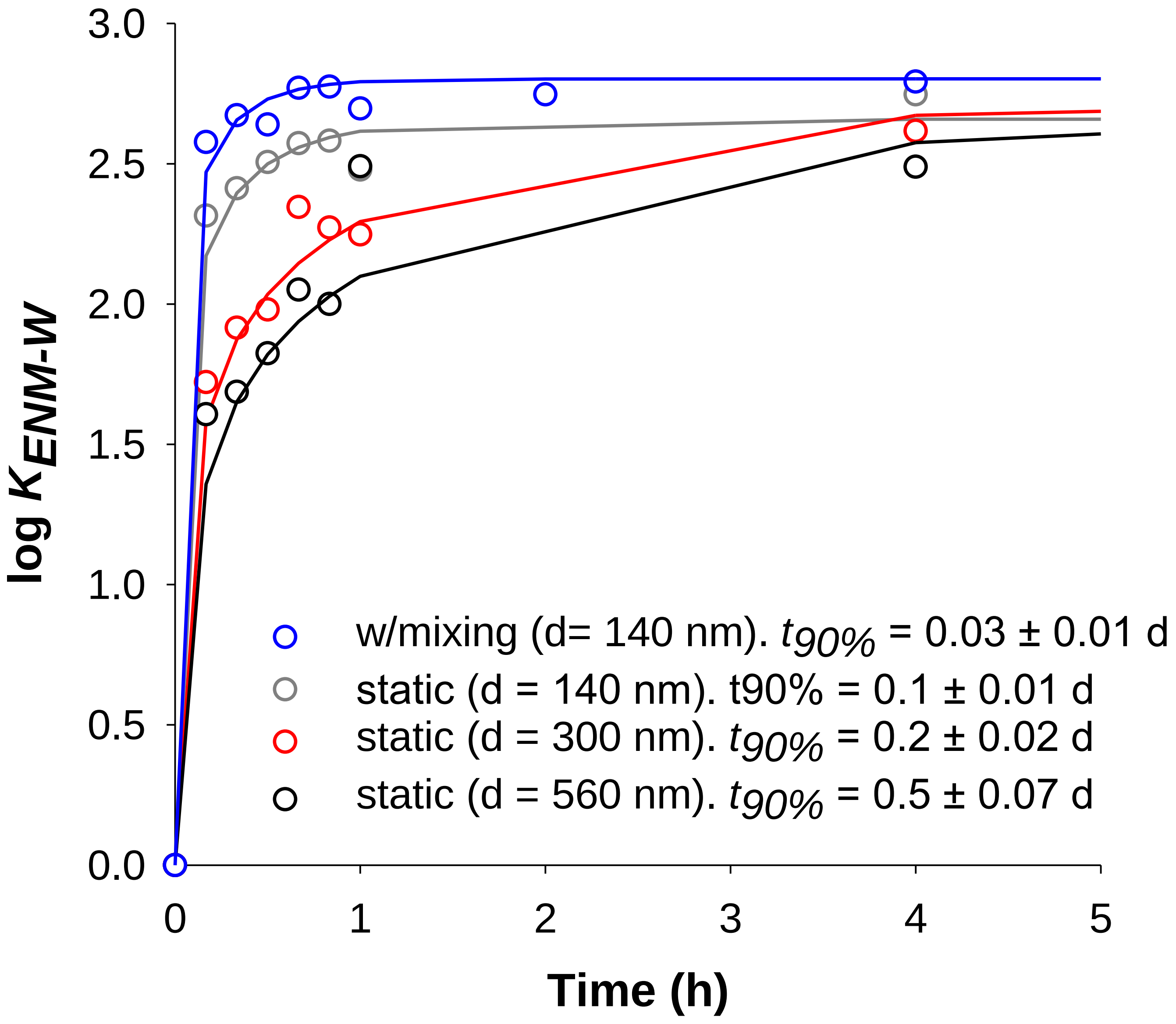
Uptake rate = f(S/V)

Interesting, S/V = 2/r (or 4/d)

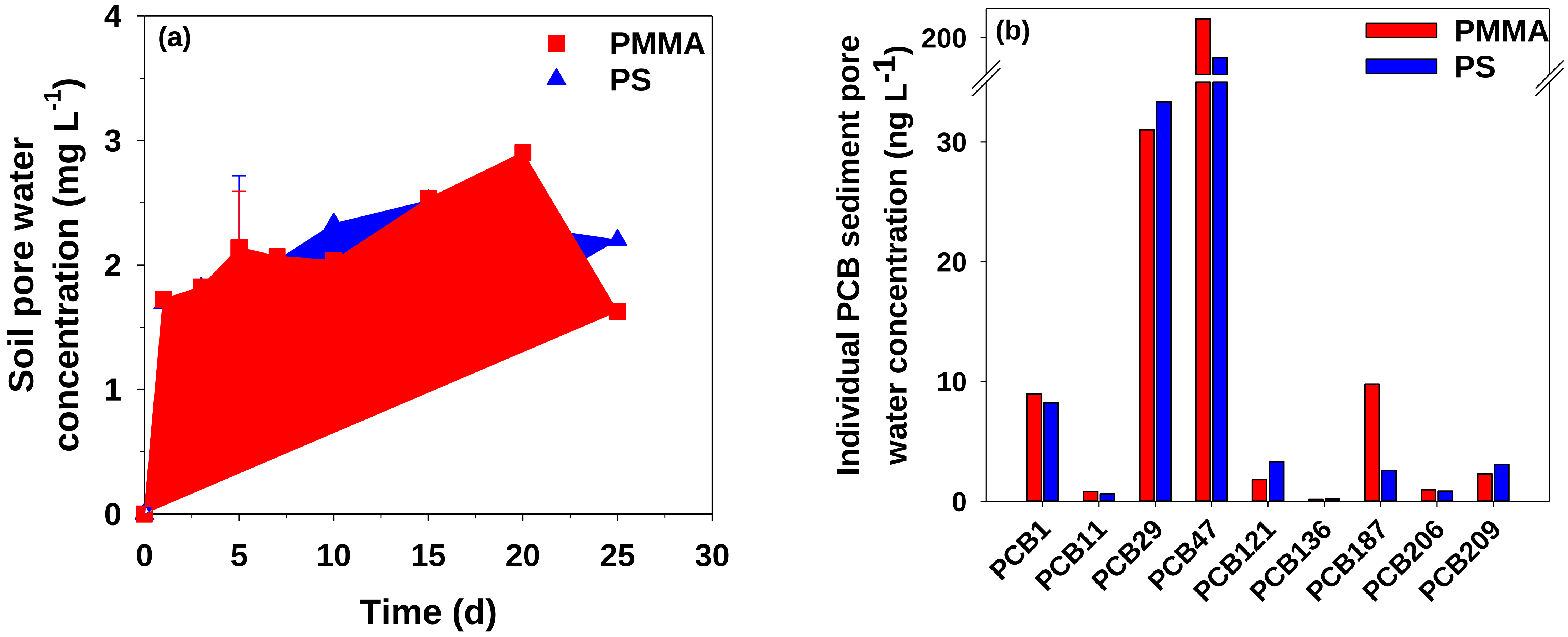
Thus, ↓ d means ↑ uptake (↓ $t_{90\%}$)

$$C_{ENM} = C_w \frac{k_1}{k_2}\left(1 - e^{(-k_2 t)}\right)$$

$$t_{90\%} = \frac{\ln 10}{k_2}$$



Nitrobenzene spike soil and PCB sediment pore water measurements



Summary of average $K_{ENM\text{-}W}$ and $t_{90\%}$ for 12 hydrophilic and moderately hydrophobic compounds

	PAN			PS		
	log $K_{ENM\text{-}W}$ (L kg^{-1})		$t_{90\%}$	log $K_{ENM\text{-}W}$ (L kg^{-1})		$t_{90\%}$
Analytes	Measured	Model	(Day)	Measured	Model	(Day)
Aniline ($n = 10$)	1.9 ± 0.06	1.9 ± 0.04	2.2 ± 0.4	1.5 ± 0.03	1.5 ± 0.01	0.01 ± 0.01
Anisole ($n = 6$)	1.9 ± 0.04	1.9 ± 0.01	0.4 ± 0.12	3.1 ± 0.05	3.0 ± 0.02	0.1 ± 0.1
Atrazine ($n = 4$)	1.2 ± 0.1[a]	1.1 ± 0.01	0.01 ± 0.01	1.6 ± 0.01	1.6 ± 0.01	4.2 ± 0.3
Benzylamine ($n = 6$)	2.0 ± 0.03	2.0 ± 0.01	0.01 ± 0.01	1.3 ± 0.06	1.3 ± 0.01	0.1 ± 0.02
17β-Estradiol ($n = 6$)	3.2 ± 0.2	3.4 ± 0.02	1.1 ± 0.1	3.2 ± 0.1	3.2 ± 0.01	0.2 ± 0.1
Caffeine ($n = 6$)	1.3 ± 0.05[a]	1.3 ± 0.02	0.1 ± 0.03	1.3 ± 0.07[a]	1.2 ± 0.02	0.11 ± 0.13
Diuron ($n = 6$)	1.4 ± 0.02[a]	1.4 ± 0.01	0.01 ± 0.01	1.3 ± 0.1[a]	1.4 ± 0.1	3.1 ± 1.8
Nitrobenzene ($n = 10$)	1.9 ± 0.1	1.9 ± 0.01	0.1 ± 0.03	2.8 ± 0.01	2.8 ± 0.01	0.03 ± 0.01
Phenol ($n = 6$)	1.7 ± 0.02[a]	1.6 ± 0.01	0.2 ± 0.07	1.7 ± 0.03[a]	1.7 ± 0.01	0.1 ± 0.05
p-Nitrophenol ($n = 6$)	1.7 ± 0.06	1.8 ± 0.01	0.1 ± 0.1	1.6 ± 0.1	1.7 ± 0.1	2.5 ± 1.3
RDX ($n = 6$)	1.8 ± 0.03[a]	1.9 ± 0.01	0.1 ± 0.01	1.8 ± 0.1[a]	1.8 ± 0.01	0.2 ± 0.04
TNT ($n = 6$)	1.9 ± 0.03	1.9 ± 0.01	0.2 ± 0.1	2.8 ± 0.01	2.7 ± 0.02	1.5 ± 0.2

[a] Less than 5% of the total aqueous mass was sorbed into the ENM.

ENMs fast equilibrium passive sampler, but sorption capacity?

Our goal: Produce novel nanocomposites of ENMs with addition of carbon nanotubes (CNTs) to improve pollutant sorption uptake.

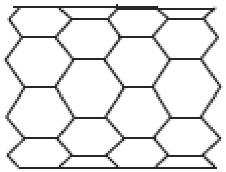
Why CNTs?:

- Recognized high capacity nanosorbents
- Tunable surface chemistry to control pollutant interactions
- Very high mechanical strength
- Antimicrobial activity

Multi-walled CNTs

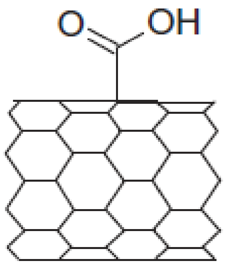
Results: Properties of ENM-CNT composites

Non-functionalized CNT



NF-CNT (10-40%)

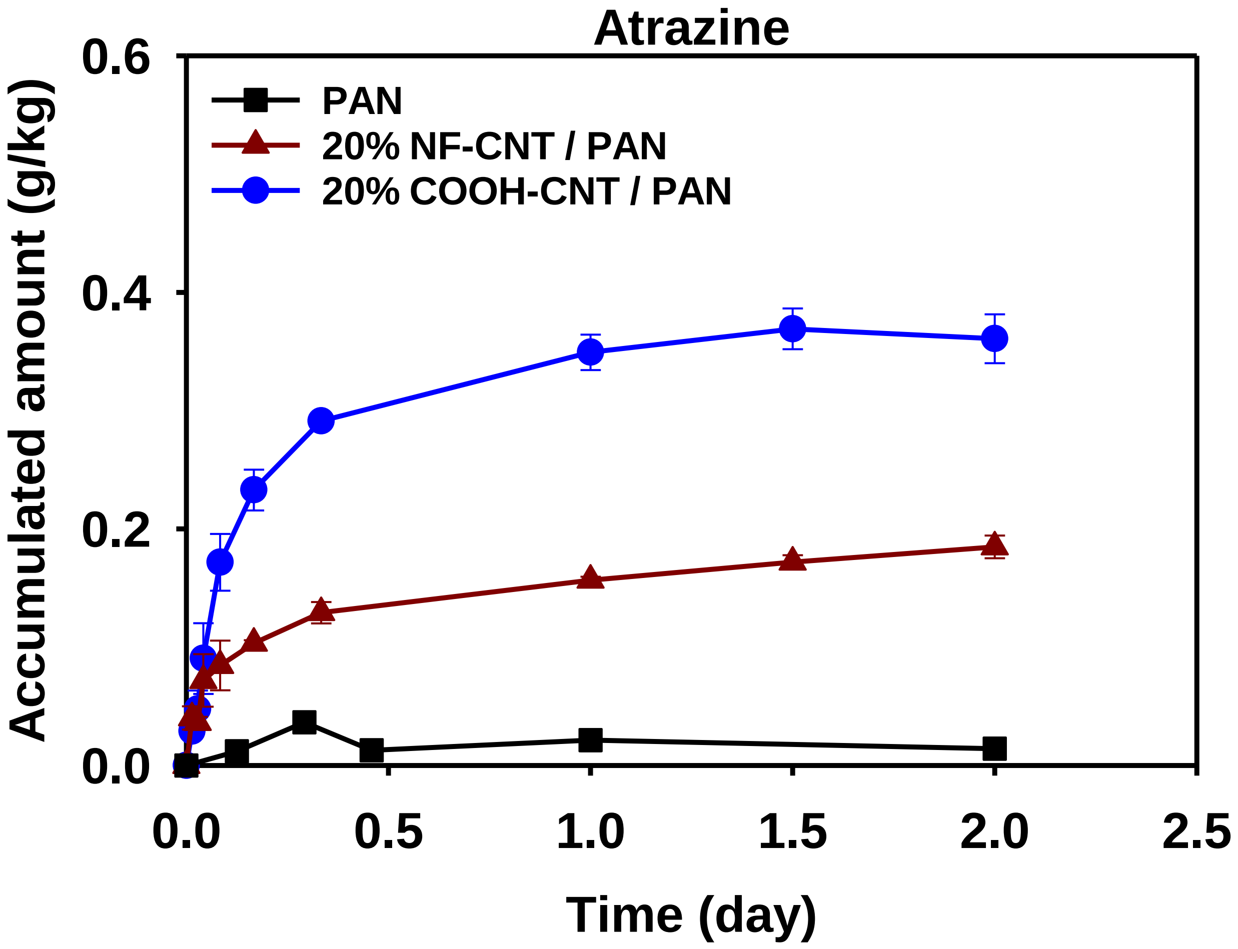
Functionalized CNT

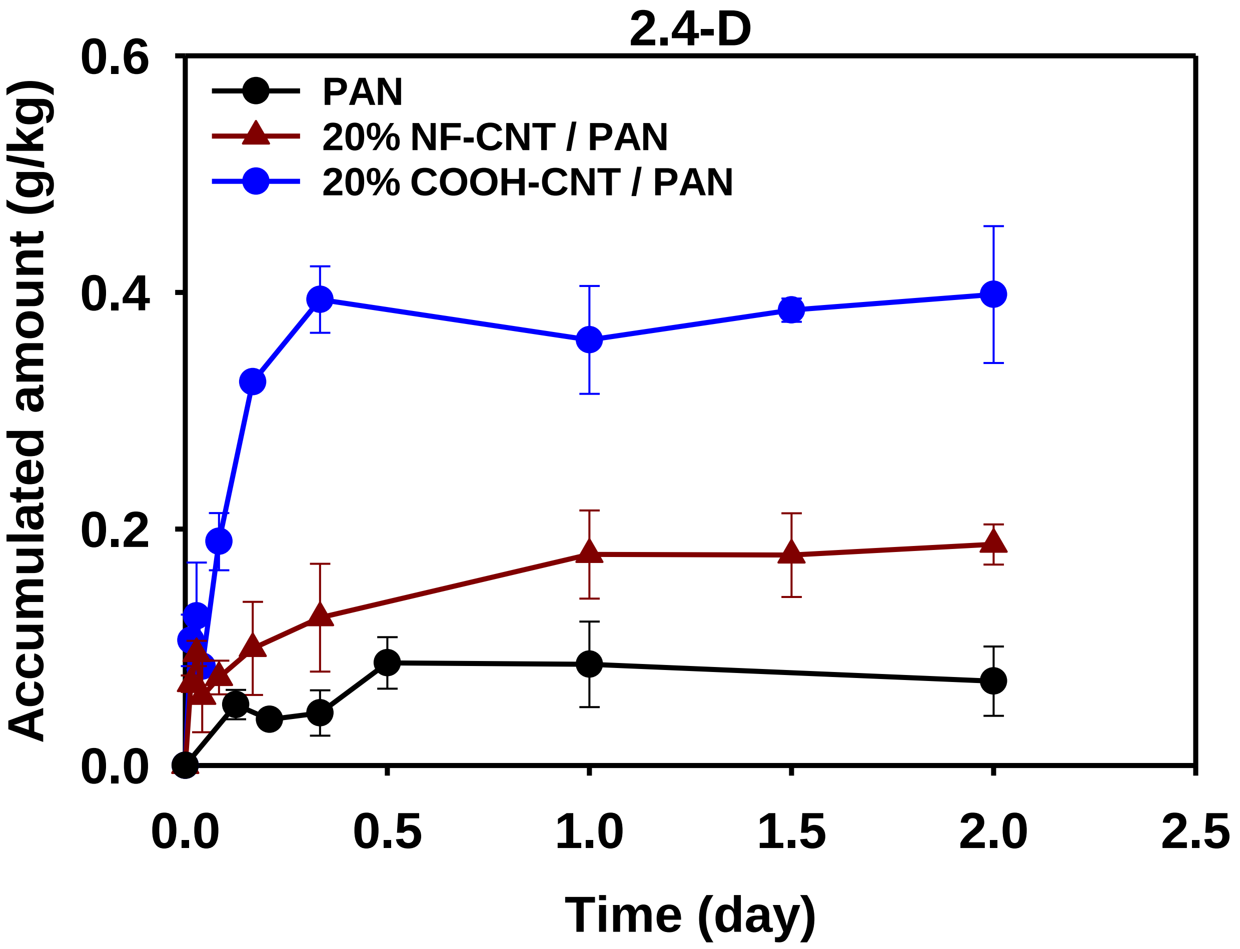


COOH-CNT (10-25%)

	Surface area (m^2/g)	Pore volume ($10^{-3}mL/g$)	Water contact angle (°)	Diameter (nm)
PAN	12 ± 0.5	23 ± 1.7	44 ± 6.2	160 ± 30
10%NF-PAN	15 ± 1.0	35 ± 2.2	43 ± 5.0	230 ± 60
20%NF-PAN	14 ± 3.0	37 ± 8.0	47 ± 2.0	210 ± 50
30%NF-PAN	15 ± 0.4	48 ± 3.0	51 ± 1.0	250 ± 70
40%NF-PAN	22 ± 1.6	78 ± 3.0	49 ± 4.0	210 ± 50
10%F-PAN	14 ± 0.6	38 ± 1.0	45 ± 2.0	220 ± 40
15%F-PAN	15 ± 0.3	37 ± 1.0	50 ± 2.0	240 ± 50
20%F-PAN	16 ± 2.0	43 ± 6.0	43 ± 3.0	200 ± 40
25%F-PAN	17 ± 0.5	52 ± 2.0	48 ± 1.0	250 ± 50
PS	27 ± 3.5	76 ± 3.0	109±9.9	140 ± 30
20%NF-PS	48 ± 2.0	168 ± 3.0	123±6.0	150 ± 20
20%F-PS	43 ± 2.0	140 ± 3.0	130±5.0	150 ± 30

Results: CNT integration generally increases pollutant uptake capacity





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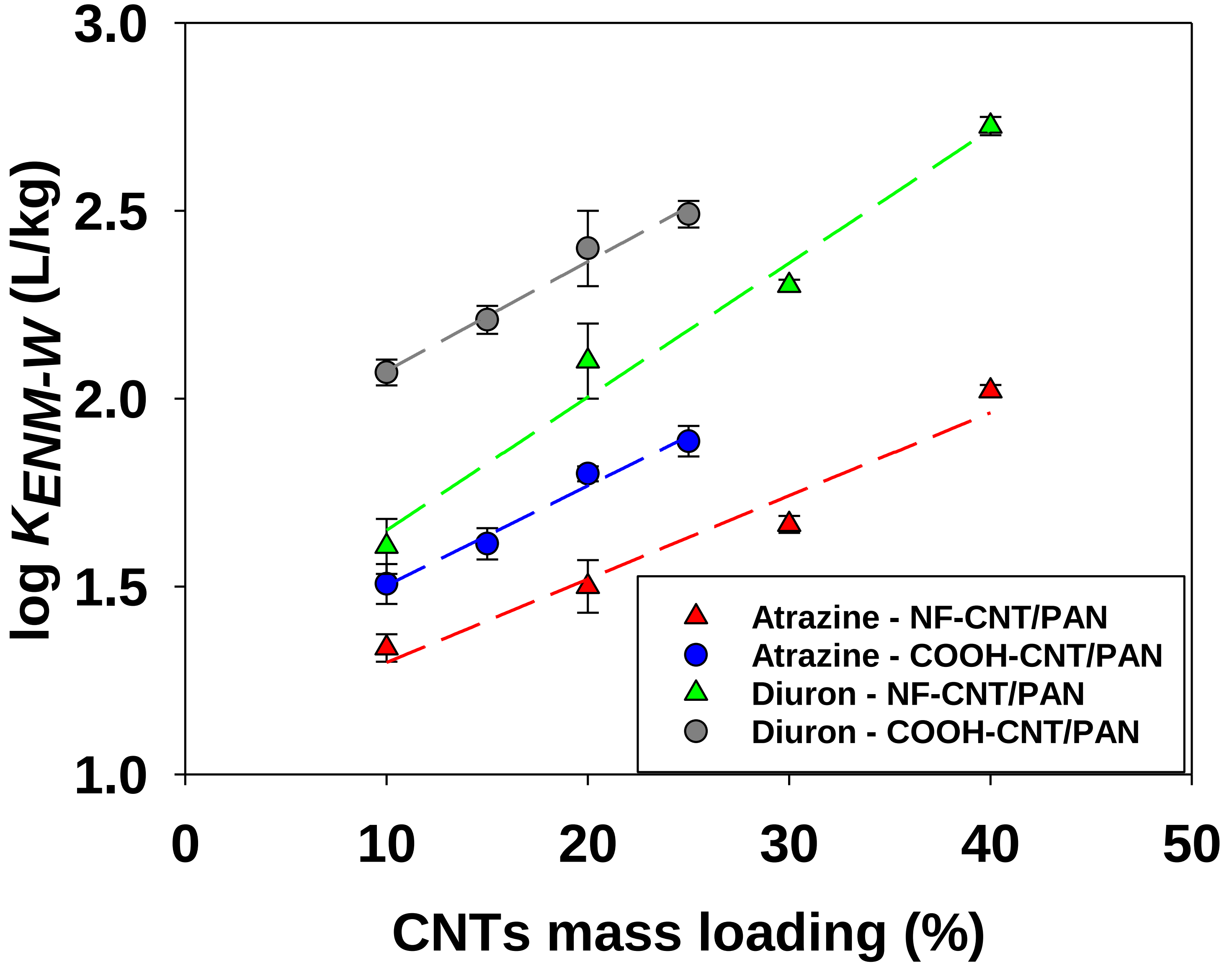
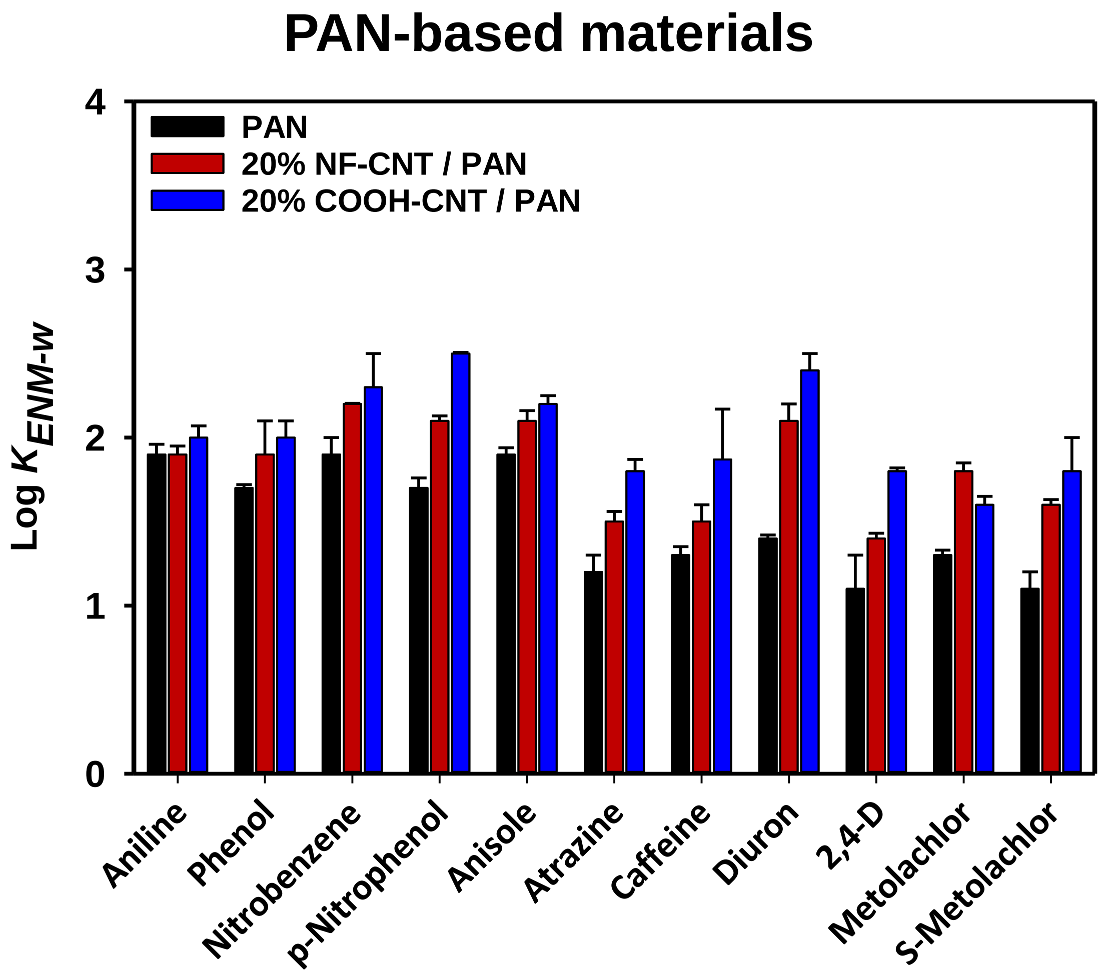
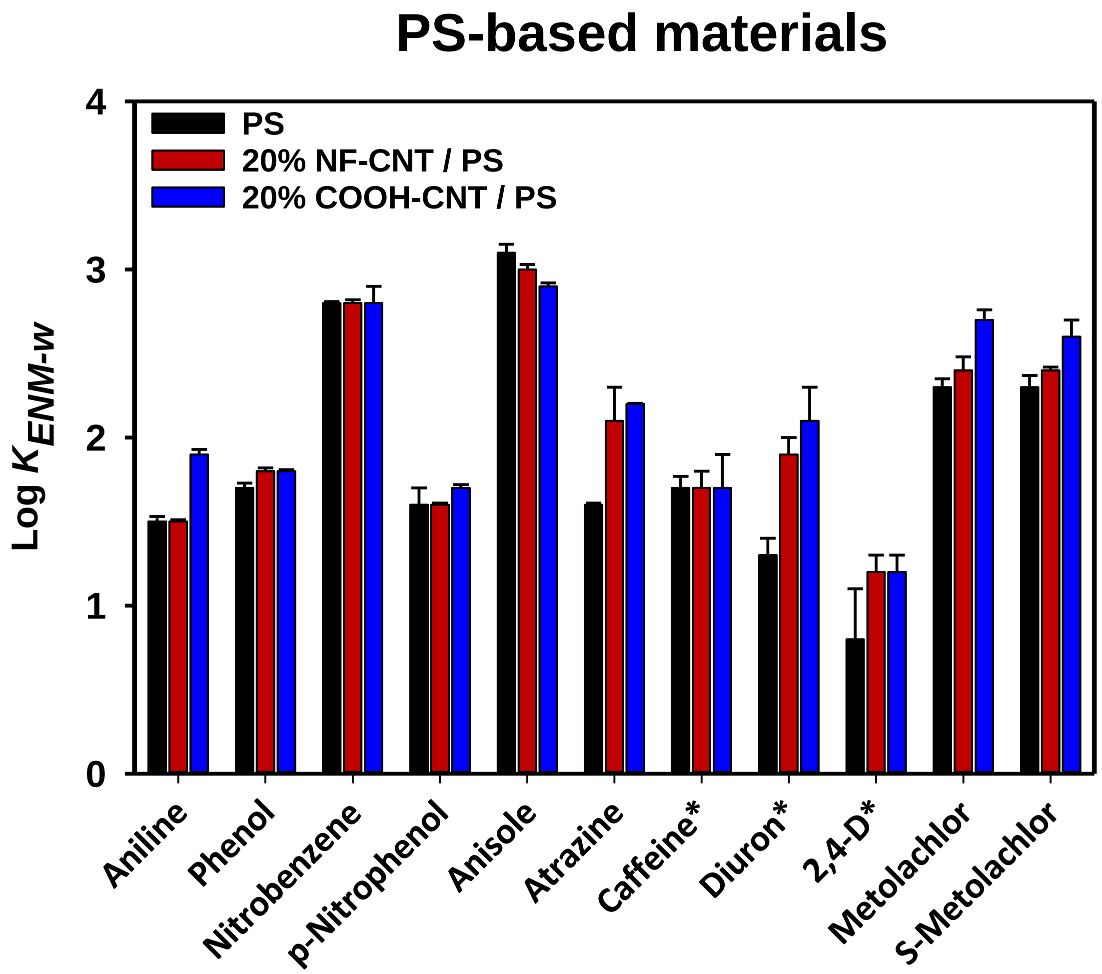


Comparison of $K_{ENM\text{-}W}$ of 11 hydrophilic and moderately hydrophobic compounds

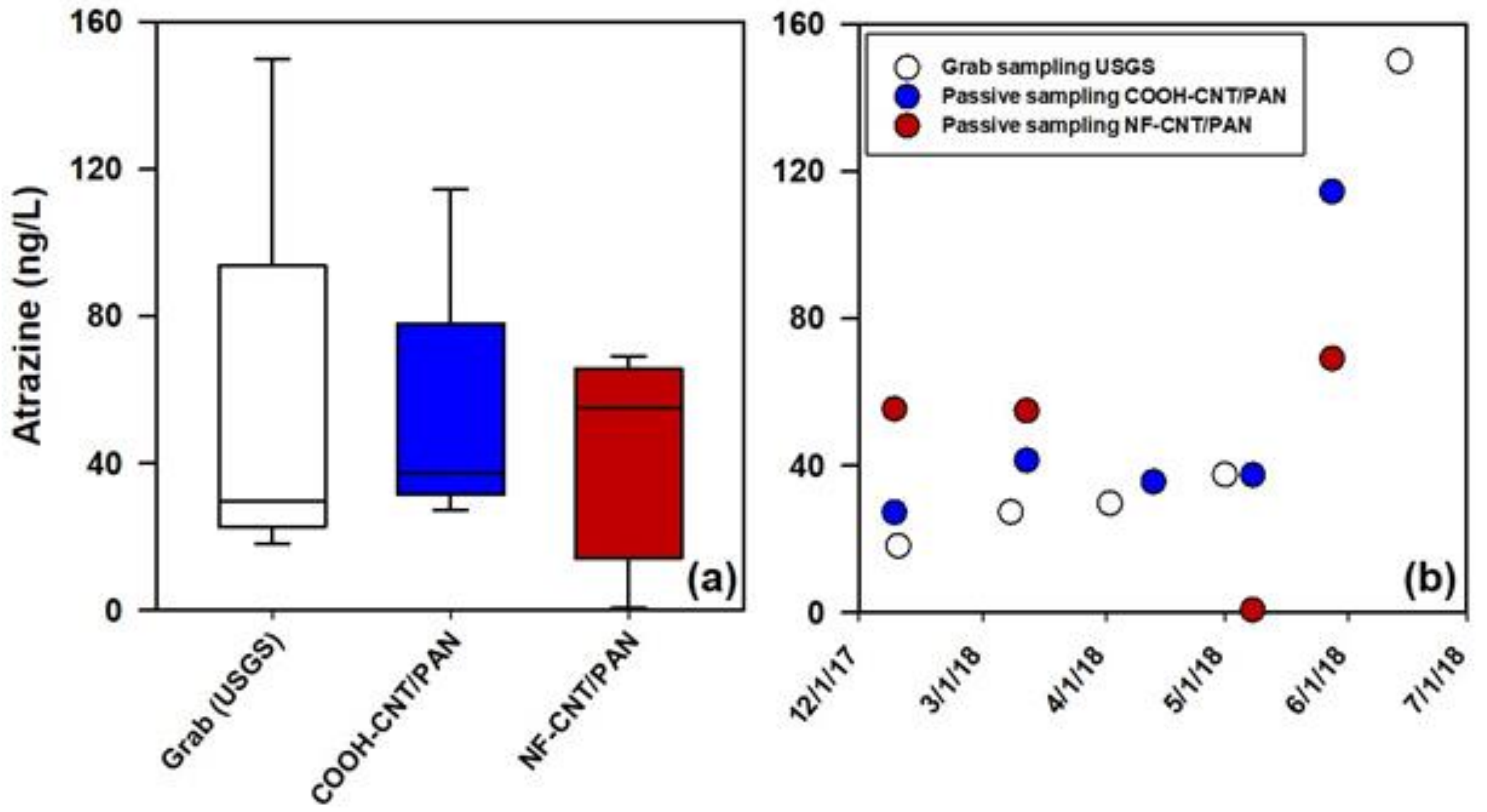




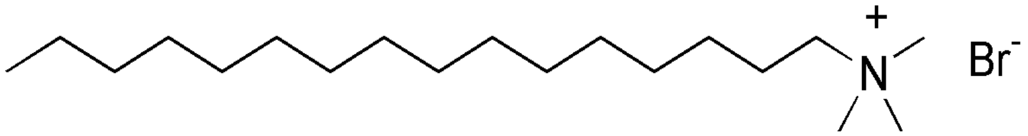
Field deployment and performance validation in effluent impacted stream

Water samples from USGS site (05454050) Muddy Creek at Coralville, IA

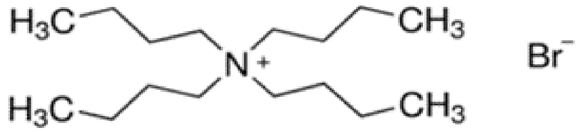
Atrazine concentration in Muddy Creek, IA measured by ENM-CNT composites and grab samples (12/2017-7/2018) - provides a “snapshot”.



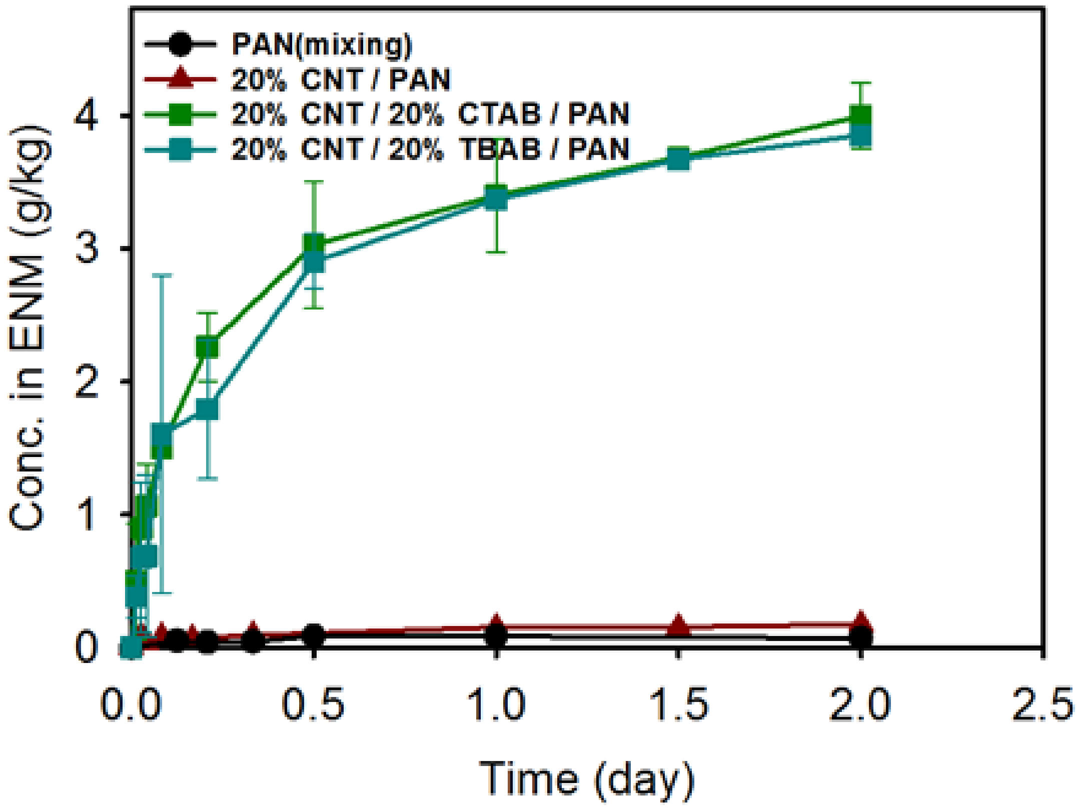
Ongoing work: Surfactant integration results in greater uptake of charged species (2,4-D)

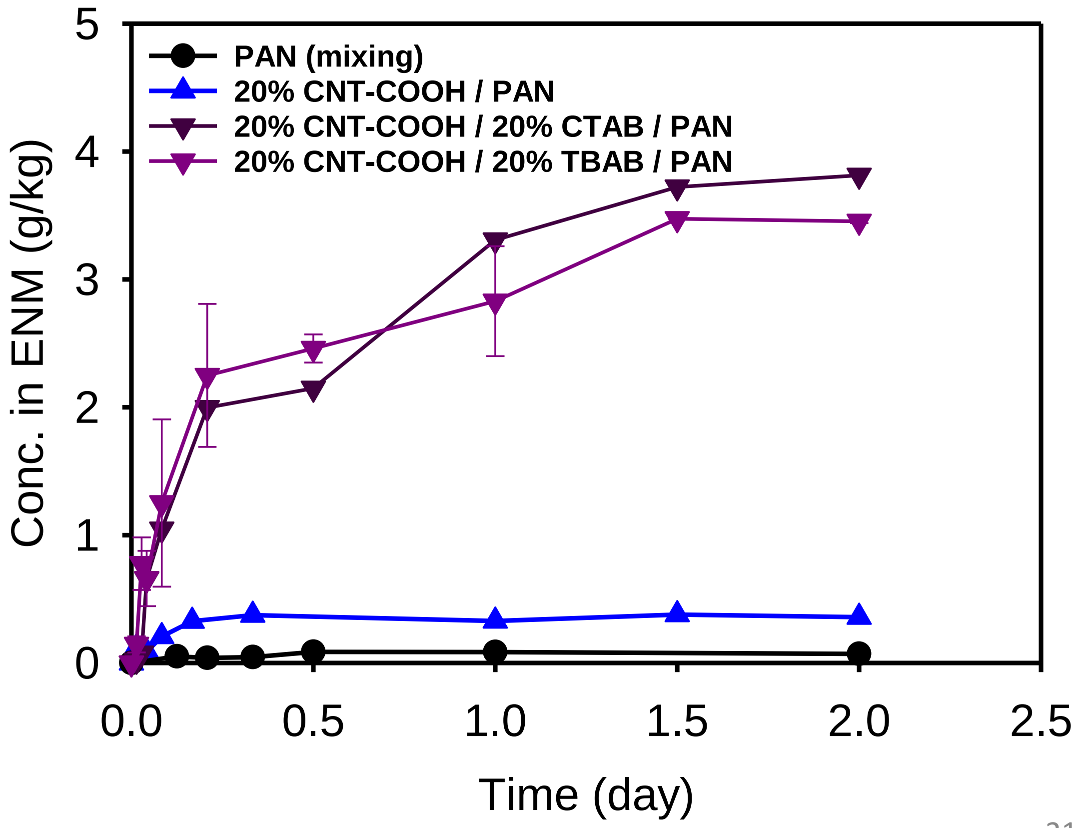


Cetrimonium bromide (CTAB)



Tetrabutylammonium bromide (TBAB)

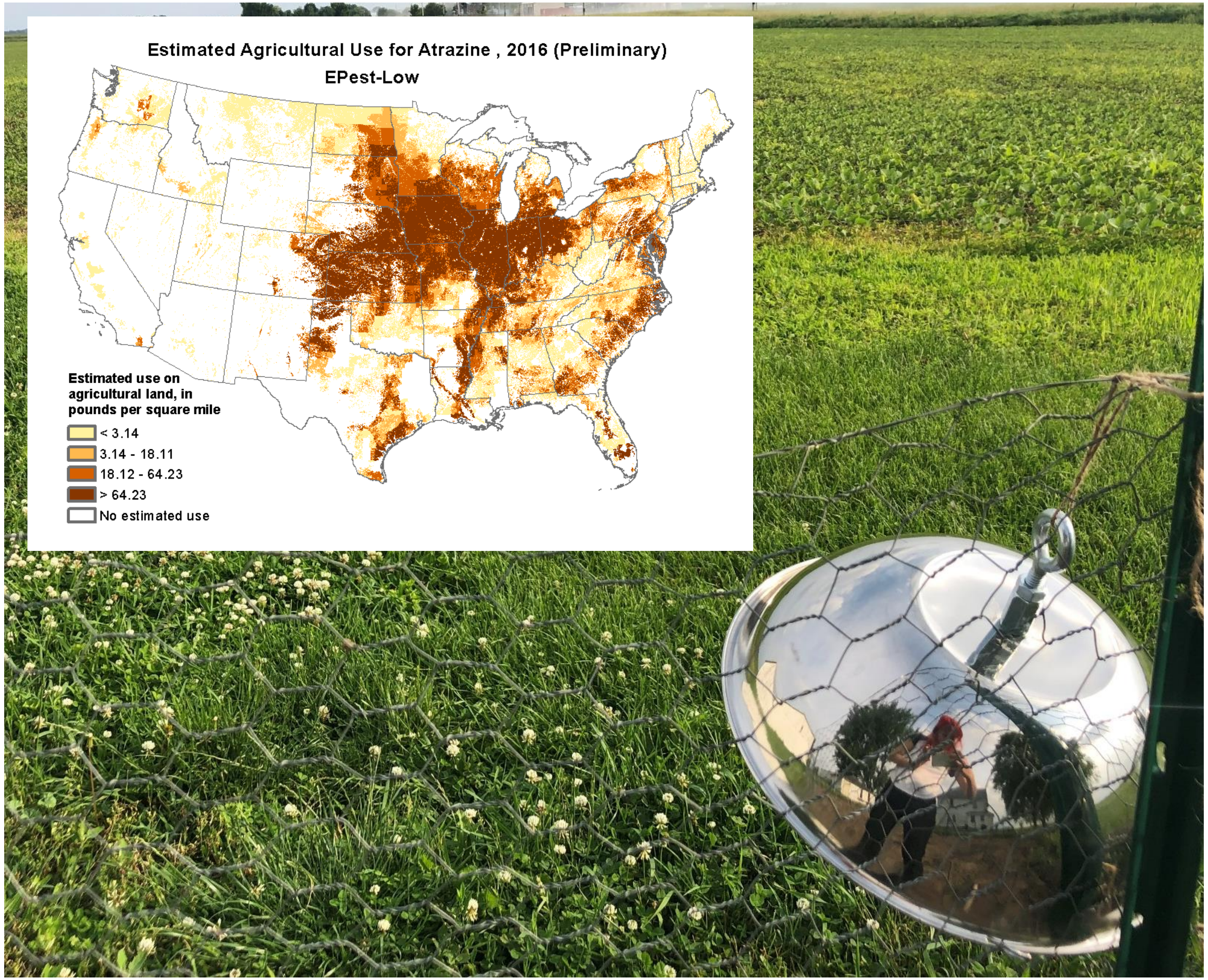


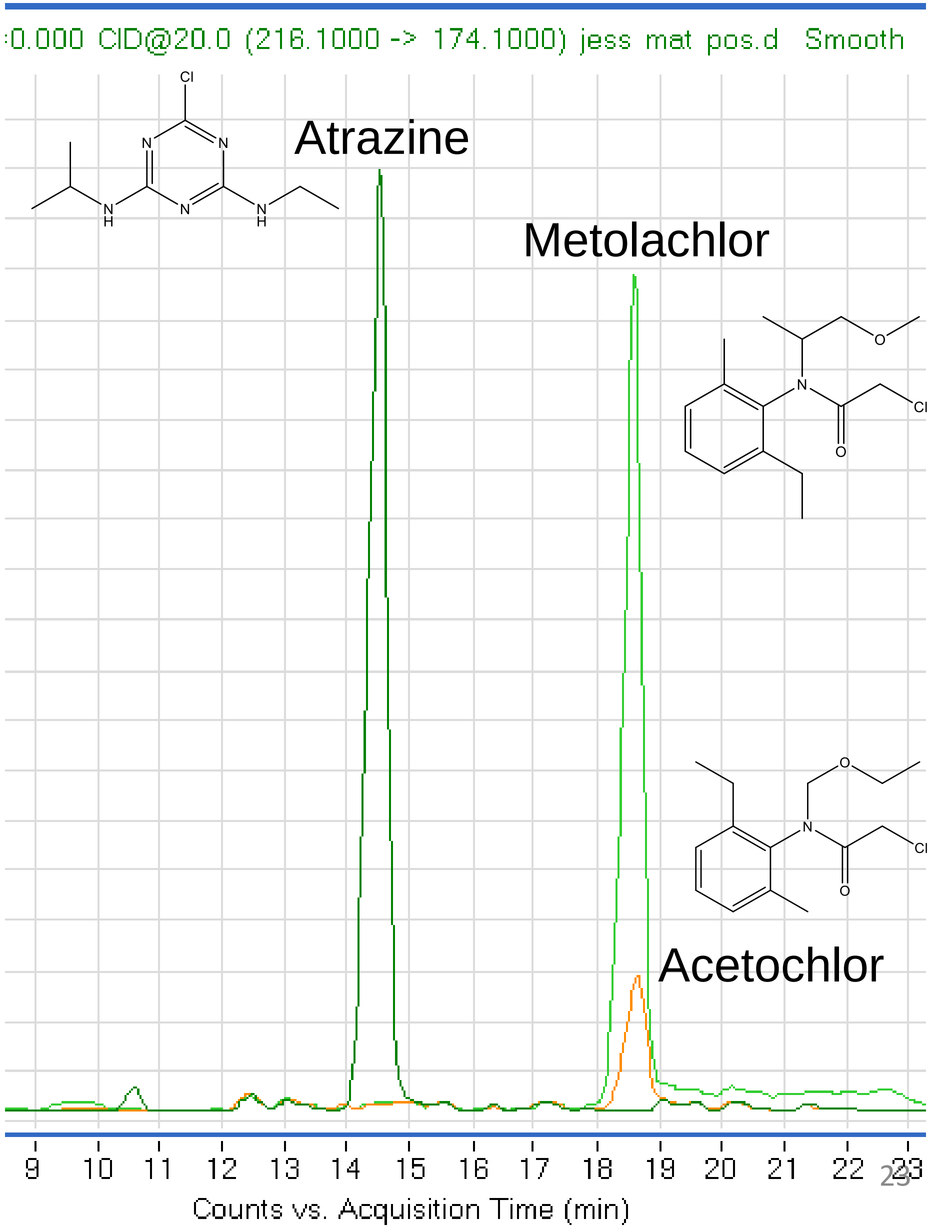


Ongoing work: ENM passive air sampler for pesticides

Evaluate ENM-CNT composites for equilibrium passive sampling of **semi-volatile pesticides in air**

Atrazine, metolachlor, and acetochlor were detected in all ENM samplers deployed





Conclusions/Implications

- Develop a passive sampling material (ENM) that shows a fast uptake for a wide ranged of organic pollutants.
- ENM can be tailored to improve organic pollutants uptake.
- ENM can be used as equilibrium passive samplers in air, water, soil and sediment.
- ENM complementary to integrative passive samplers (e.g., POCIS)
- More field validation is needed.

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- UI Graduate College

SERDP DOD ▪ EPA ▪ DOE

isrp iowa superfund research program

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ehsrc environmental health sciences research center